TRANSFER REACTIONS IN CATIONIC POLYMERIZATION

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CONTENTS

		Page
Part 1	Introduction	1
Part 2	The Transfer and the Termination Reactions	14
Chapter 1	α-Methylstyrene	14
Section 1.1	The Effect of Solvent on the Degree of Polymerization of Poly-α-methylstyrene	14
Section 1.2	The Rate Constant Ratios of the Monomer Transfer Reaction and Unimolecular Termination Reaction	45
Chapter 2	Isobutene	77
Chapter 3	Ortho- and Para-methoxystyrene	109
Chapter 4	Ortho- and Para-chlorostyrene	152
Chapter 5	Methyl Vinyl Ether	192
Chapter 6	Isobutyl and Tertiarybutyl Vinyl Ether	219
Part 3	The Properties of Polymer	243
Chapter 7	Poly-α-methylstyrene	243
Section 7.1	Stereospecific Polymer	243
Section 7.2	The Molecular Weight	270

Chapter 8 The Molecular Weight and Molecular Weight Distribution of Polystyrene Obtained by Cationic Polymerization ... 291

Chapter 9 Poly-ortho- methoxystyrene and Poly-para-methoxystyrene ... 328

Part 4 The Reactivity of the Growing Ion in Ionic Polymerization ... 363

Chapter 10 Estimation of the Growing Ion Reactivity in Cationic Polymerization from the Chain Transfer Reaction ... 363

Section 10.1 Theoretical Considerations ... 363

Section 10.2 Ortho- and Para-chlorostyrene ... 386

Section 10.3 Styrene derivatives ... 405

Chapter 11 The Cross-transfer Reaction in the Copolymerization ... 433

Section 11.1 Lowering of Degree of Polymerization of Copolymer ... 433

Section 11.2 The Solvent Effect in Cationic Copolymerization of Isobutene with Styrene in Mixed Solvents ... 469

Part 5 Summary ... 509

Part I Introduction

Extensive investigations on the mechanism of cationic polymerization of vinyl monomers have recently been carried out[1], and in consequence, many differences between cationic polymerization and radical polymerization have emerged. Most of them are ascribed to the fact that in radical polymerization the growing radical formed by the addition of catalyst fragment to the double bond of monomer grows always acting as a free radical, while in cationic polymerization the growing cation is formed by addition of a proton or carbonium ion produced from a neutral catalyst molecule to the double bond of a monomer and associates with the anionic moiety of the catalyst molecule to give an ion-pair which acts as an active center of polymerization. Hence, in connection with the nature of the growing ion-pair, it is very important to study the elementary reactions in cationic polymerization.

Pepper stated in the recent review[2] that the following two facts regarding cationic polymerization remain to be explained:

(i) polymerization rate in cationic polymerization is in general larger than the radical polymerization, (ii) molecular weight of polymer in cationic polymerization

is in general lower than in radical polymerization. Here the significance of the second of these lies in that radical polymerization is usually carried out at room temperature or higher and polymers having the degree of polymerization of a few thousand or more can easily be produced if suitable polymerization conditions are employed, while in cationic polymerization, the degree of polymerization of the polymer is extremely low when polymerization is carried out at room temperature, and it is usual to effect polymerization at -78°C (dry ice temperature) or lower when polymer having a degree of polymerization of a few thousand is required. This means that in the cationic polymerization the transfer and the termination reactions, which determine the molecular weight of polymer, occur very easily and compete succesfully with the propagation reaction at higher temperature, but that at lower temperatures they are suppressed, and a high molecular weight polymer results.

Polyisobutene produced by cationic polymerization, has long been available industrially, and is an original synthetic rubber. Recently, cationic polymerization of aldehydes and cyclic ethers has been extensively studied and some aspects developed practically[3].

Though the product of cationic polymerization has practical value, there has been little study of the reactions which determine molecular weight, and there is scarcely anything known about how the nature of the growing ion-pair affects them.

Recently, basic research on the degree of polymerization of cationically polymerized polystyrene was reported from this laboratory[4], and it was established that monomer transfer reaction and unimolecular termination reaction are kinetically the molecular weight-determining ones. The monomer transfer constant ratio (k_{tm}/k_p) and the unimolecular termination constant ratio (k_t/k_p) were calculated by a suitable method, and the effect of the polymerization conditions on the rate constant ratios was discussed. It was found that the degree of polymerization of polystyrene is determined mainly by the monomer transfer reaction, and that k_{tm}/k_p is larger, the stronger the catalyst ($TiCl_4 > SnCl_4 > FeCl_3 > BF_3\ OEt_2$) and the less polar the solvent ($C_6H_6 > C_6H_6$ 40%-$(CH_2Cl)_2 > C_6H_6$ 20%-$(CH_2Cl)_2$). Hence it is to be predicted from the kinetic results that polymerization of styrene in a polar solvent using a mild catalyst will give a high molecular weight polymer,

and such was actually found to be the case. However, the paper went no further. It was left to explain how one could reconcile the apparently contradictory results that use of milder polymerizing catalyst or solvent giving a higher polymerization rate, gives a polymer of higher molecular weight. Thus, elucidation of the mechanism by which polymerization condition affects the transfer and the termination reactions was important and interesting, both theoretically and practically.

The present investigation deals primarily with three subjects: (i) determination of the transfer and the termination constant ratios for a series of monomers under various polymerization conditions, and deduction of the mechanisms of the transfer and termination reactions, (ii) relationship between polymerization kinetics and molecular weight distribution of the resultant polymer, and (iii) discussions of question such as reactivity of the growing ion and degree of polymerization of copolymer, utilizing information about the transfer reaction here obtained.

Firstly in Part 2, k_{tm}/k_p and k_t/k_p are determined for polymerization of nine kinds of monomers. The

values are discussed in relationship to polymerization conditions: mechanisms for the monomer transfer and unimolecular termination reactions are proposed.

In Chapter I, the solvent effect recognized in the polymerization of styrene[4] (stated above) was examined in the polymerization of α-methylstyrene by boron trifluoride etherate using a variety of polymerization solvents. On determining k_{tm}/k_p for a series of solvents of different dielectric constants, the same solvent effect as that observed in the polymerization of styrene (the larger the dielectric constant, the smaller k_{tm}/k_p.) was observed at dielectric constant below 6. This experimental fact suggests occurrence of a monomer transfer reaction with a mechanism other than observed in the styrene polymerization.

As the monomer structure of α-methylstyrene was considered to be intermediate between the structure of styrene and that of isobutene, transfer and termination reactions of isobutene were investigated. The experimental results are described in Chapter 2 and compare with those for styrene and α-methylstyrene.

k_{tm}/k_p for isobutene was found to be larger the milder the polymerization catalyst and the more polar the solvent. This is just reverse of what obtains in styrene polymerization, and it suggests that in isobutene polymerization the mechanism of the monomer transfer reaction is quite different to that for styrene or α-methylstyrene. Focussing attention on the monomer transfer reaction, since the structure of α-methylstyrene resembles that of isobutene or styrene, it is possible that both types of the monomer transfer reaction occur in polymerization of α-methylstyrene. Here, the monomer transfer reaction in the cationic polymerization of isobutene and styrene are respectively referred to as the isobutene-type and the styrene-type of monomer transfer reaction. Considering as a whole the experimental results reported by several workers for the cationic polymerization of isobutene, the mechanism of the isobutene-type monomer transfer reaction is proposed as the proton extraction by a monomer from the growing end. The effect of the nature of the growing ion-pair on this reaction is also discussed.

In Chapters 3 and 4, the mechanism of the styrene-type monomer transfer reaction is discussed. In

Chapter 3, the cationic polymerization of ortho- and para-methoxystyrene, which are the styrene derivatives with +M substituent on phenyl group of styrene, was carried out by boron trifluoride etherate, and the same relationship as in the cationic polymerization of styrene was observed for the effect of solvent dielectric constant on k_{tm}/k_p. The mechanism proposed for the styrene-type monomer transfer reaction is a Friedel-Crafts alkylation of phenyl group of monomer by the growing ion-pair.

In Chapter 4, the cationic polymerization of ortho- and para-chlorostyrene, which are the styrene derivatives with -I substituent on phenyl group of styrene, was carried out by stannic chloride--trichloroacetic acid as catalyst, to test the validity of the mechanism of the styrene-type monomer transfer reaction proposed in Chapter 3. The same effect of dielectric constant of solvent on k_{tm}/k_p as in the styrene polymerization and in the methoxystyrene polymerization was observed, and the validity of the mechanism of the styrene-type monomer transfer reaction proposed in Chapter 3 was confirmed.

In Chapters 5 and 6, the monomer transfer reaction

in the polymerization of alkyl vinyl ether, which is the third monomer group in the cationic polymerization and often serves as a standard research material, was studied. In Chapter 5, methyl vinyl ether, the lowest alkyl vinyl ether, was polymerized and the effects of the catalyst and the solvent on k_{tm}/k_p were studied. As consequence, k_{tm}/k_p in the methyl vinyl ether polymerization was found to increase with using a polar solvent and an active catalyst, which is a behavior different from either isobutene- or styrene-type. The suggested mechanism of the monomer transfer reaction in the methyl vinyl ether polymerization is based on the effect of polymerization conditions on k_{tm}/k_p and on end group analysis of polymer, and is cleavage of the ether bond of the monomer by the growing ion-pair.

In Chapter 6, cationic polymerizations of isobutyl and t-butyl vinyl ethers were carried out to investigate the electronic and the steric effect of the alkyl group on the vinyl ether-type monomer transfer reaction. It was found that with butyl vinyl ether the monomer transfer reaction is the same as with the methyl vinyl ether, and the validity of the mechanism of the vinyl

ether-type monomer transfer reaction was confirmed.

As is seen in the subsequent Chapters, the rate constant ratios were determined from the molecular weight of the polymer, and the following conditions must then be fulfilled: (i) The intrinsic viscosity—molecular weight equation is available for each polymer, (ii) The relationship between the degree of polymerization of polymer and the conversion is known, with special attention to possible chain branching during polymerization, and (iii) The relationship between the viscosity average molecular weight, which is in practise obtainable applying the intrinsic viscosity—molecular weight equation using the intrinsic viscosity of unfractionated polymer, and the number average molecular weight, which is required for the calculation of the true rate constant, must be known. In Part 3 the properties of polymer were investigated from these points of view.

In Chapter 7, the intrinsic viscosity—molecular weight equation of poly-α-methylstyrene was determined because it has not been reported anywhere and in this connection the properties of poly-α-methylstyrene in solution were compared with those of polystyrene.

Further, as benzene-insoluble polymer (partially crystalline polymer) was obtained, depending on the polymerization conditions, the steric configuration of the polymer was investigated.

In Chapter 8 the relationship between the degree of polymerization of polystyrene and conversion was investigated for various polymerization conditions. It was found that the degree of polymerization of polystyrene was constant or decreased with increasing conversion, depending on polymerization conditions. And in neither case was increase in molecular weight due to chain branching observed. But in an exceptional case, using nitrobenzene as the solvent, a slight increase in molecular weight of polymer with increase in conversion was observed, and this may indicate chain branching. The change of the molecular weight distribution as polymerization proceded was also studied.

In Chapter 9 the weight average ($\bar{\bar{M}}_w$), the number average ($\bar{\bar{M}}_w$), and the viscosity average ($\bar{\bar{M}}_v$) molecular weights and the molecular weight distribution of poly-p-methoxystyrene for a variety of polymerization conditions were determined. The actual $\bar{\bar{M}}_w$, $\bar{\bar{M}}_n$ and $\bar{\bar{M}}_v$ were compared with those calculated from the

rate constant ratios. Then how the broadening of the molecular weight distribution as polymerization proceeds affected calculation of the rate constant ratio was investigated.

Since some information about the transfer and termination reactions was obtained here, it was used to study unsolved problems in cationic polymerization, one of which is reactivity of carbonium ion. Before 1960, the reactivity of the growing ion had long been considered to be the same independent of the kind of monomer. But recently detailed investigations on cationic copolymerization have afforded evidence of a difference between reactivities of growing ions.[5] In Part 4, the reactivity of the growing ion was estimated making use of the transfer reaction, and some new information was obtained about reactivity of the growing ion.

In Chapter 10, the possibility of estimating reactivity of the growing ion was considered theoretically. Comparing the chain transfer constants of two or more cations for a certain transfer agent, the ratio of the reactivity of the different kinds of growing cations was determined, and with styrene derivatives

it was found that the more reactive monomer gave the less reactive cation.

In Chapter 11, lowering of the degree of polymerization of the copolymer especially in the cationic copolymerization of isobutene and styrene derivatives was studied. Comparing the transfer constant ratios to methanol, it was found that the isobutene cation, to which resonance stabilization makes a minor contribution, has a higher reactivity than the resonance-stabilized styrene derivative cations in the cross-transfer reaction leading to low molecular weight copolymer. Moreover, the special kind of solvent effect on the monomer reactivity ratio in the cationic copolymerization of isobutene and styrene, was explained in term of the lesser stability of the isobutene cation.

The present investigation, summarized above, deals with the mechanism of the transfer and termination reactions in cationic polymerization, and the experimental results will be explained in turn in the succeeding Chapters.

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Part 2 The Transfer and the Termination Reactions

Chapter 1 α-Methylstyrene

Section 1.1 The Effect of Solvent on the Degree of Polymerization of Poly-α-methylstyrene

1. Introduction

The experimental results on the cationic polymerization of styrene carried out in our laboratory establish that high molecular weight polystyrene is obtainable in a polar solvent.[1] The solvent effect in the cationic polymerization of α-methylstyrene has so far not been completely investigated though α-methylstyrene is relatively highly reactive in cationic polymerization.

On the other hand, Schildknecht[2] has found that alkyl vinyl ethers, which are highly reactive, can give a crystalline polymer in low temperature polyphase polymerization by boron trifluoride etherate. Of these, methyl vinyl ether, which has a relatively low reactivity, cannot polymerize in n-hexane but is polymerized on addition of a small amount of chloroform[3] or toluene[4], that is, by activated polymerization. The mechanism of the activation, however, has not been explained.

In this Section, the intrinsic viscosity of poly-

α-methylstyrene obtained by low temperature cationic polymerization in the mixed solvent is discussed.

2. Experimental

2.1 Procedure

The polymerization vessel was four-necked round-bottled flask equipped with a mercury sealed stirrer , as shown in Fig. 1-1. Solvent and monomer were introduced into the flask under a stream of dry air and

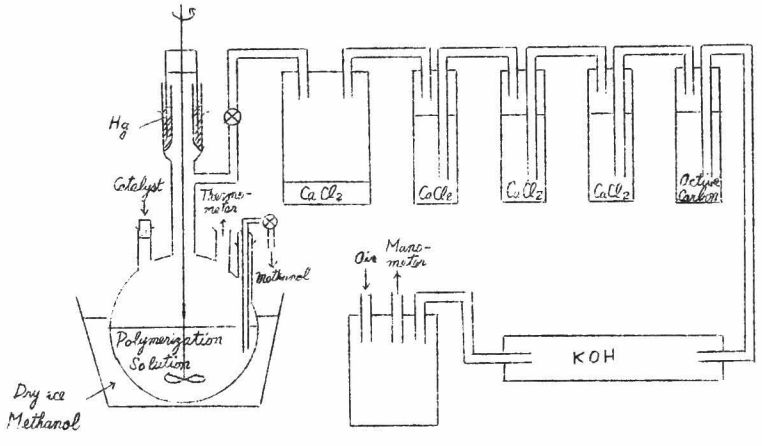

Fig. 1-1 The apparatus for polymerization

cooled with dry ice-methanol. A given amount of catalyst (boron trifluoride etherate) was added, through the catalyst inlet, to the precooled solution, and the polymerization started with agitation under a slight pressure of dry air. After a given time the polymerization solution was expelled, by pressure of dry air, into an excess of ammoniacal methanol. Conversion was calculated from the weights of the polymerization solution expelled and polymer precipitated. The polymer was repeatedly washed with methanol and dried in a vacuum. When it was required, polymer was dissolved in benzene and reprecipitated by methanol. Polymerizations at -50° and -20°C were carried out in a thermostatted bath cooled with Freon gas, the temperature of the bath being kept constant to ± 1°C. Polymer was dissolved in hot benzene and the intrinsic viscosity was measured at 30°C.

2.2 Reagent

α-Methylstyrene (Dow Chemical Co.) was washed with 10% aqueous sodium hydroxide solution and water, dried over K_2CO_3, and distilled in vacuum twice. (b.p. 52°C/10mmHg, $n_D^{20°C}$ = 1.5378).

n-Hexane (Guaranteed Reagent) was washed with concentrated sulfuric acid, water, 10% aqueous sodium hydroxide solution, an aqueous alkaline solution of potassium permangnate, and finally water, dried over calcium chloride, and distilled from sodium metal. (b.p. 65.5-66.1°C).

Chloroform (Guaranteed Reagent) was washed with concentrated sulfuric acid, water, 10% aqueous sodium hydroxide solution, and water, dried over phosphorus pentoxide, and twice distilled from phosphorus pentoxide just before use. (b.p. 60.4-61.0°C).

Methylene chloride (Guaranteed Reagent) was washed with water, 10% aqueous potassium carbonate solution, and finally water, dried over phosphorus pentoxide, and twice distilled from phosphorus pentoxide just before use. (b.p. 39.5-40°C).

Toluene (Guarantted Reagent) was washed with concentrated sulfuric acid, water, 10% aqueous sodium hydroxide solution, and water, dried over calcium chloride, and distilled from sodium metal. (b.p. 108°C).

Boron triflurodide etherate (Extra Pure) was distilled into a small ampoule. (b.p. 125°C/760mmHg).

3. Results

Unless otherwise stated, toluene, chloroform and methylene chloride which are good solvents for polymer and catalyst, and n-hexane, in which polymer and catalyst are insoluble were used as the polymerization solvent, boron trifluoride etherate being catalyst.

3.1 Relationship between solvent composition and intrinsic viscosity of the polymer

In order to determine the relationship between solvent composition and intrinsic viscosity of the polymer, polymerizations were carried out at -78°C in a good solvent—non-solvent mixed solvent system, the monomer concentration being 20 vol.% (1.54 mole/l). The relationship between the intrinsic viscosity of polymer, the appearence of the polymerization system and the solvent composition is shown in Fig. 1-2.

When n-hexane alone was used as the polymerization solvent, the added catalyst precipitated immediately. Polymerization took place at the interface between the n-hexane and the drops of boron trifluoride etherate, but the catalyst was soon covered with polymer insoluble in n-hexane. Hence the polymerization rate and intrinsic viscosity of the polymer were relatively low in this system.

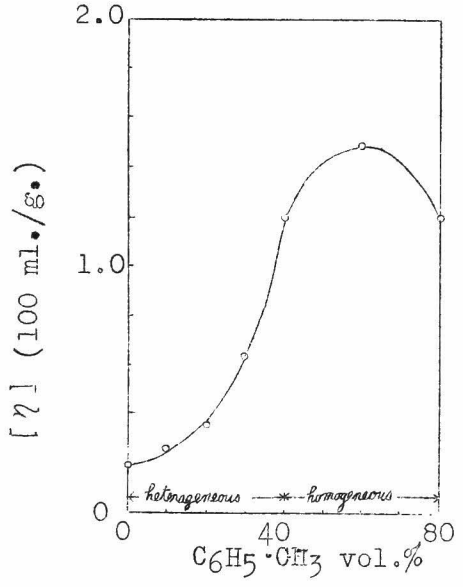

Fig.1-2a

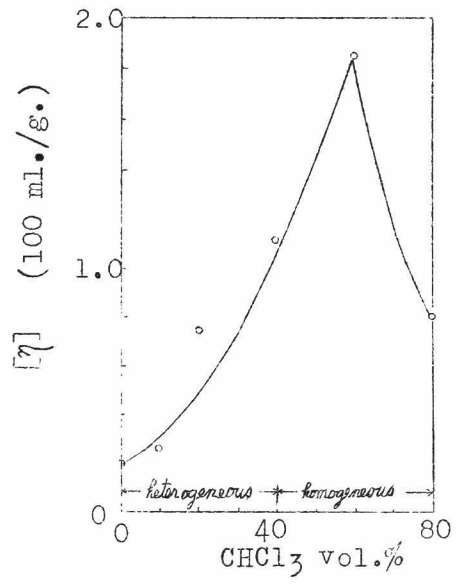

Fig.1-2b

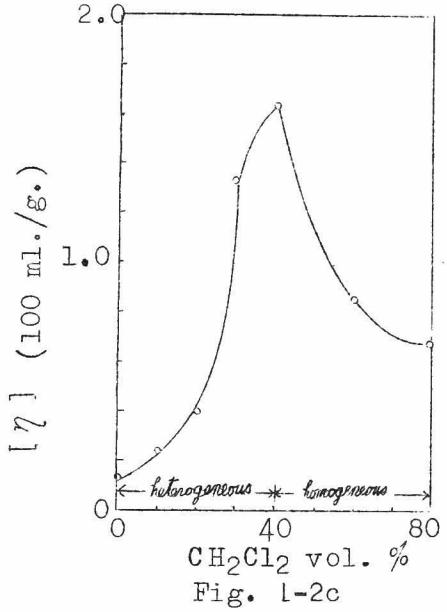

Fig. 1-2c

Fig.1-2 The relationship between the solvent composition and [η] of poly-α-methylstyrene [M] =1.54 mole/l.(=20 vol.%), -78°C, $BF_3 \cdot O(C_2H_5)_2$ a: Toluene—n-hexane mixture, [C]=0.05 mole/l.
b: Chloroform—n-hexane mixture, [C]=0.03 mole/l.
c: Methylene chloride—n-hexane mixture, [C]=0.02 mole/l.

On increasing the ratio good solvent/non-solvent, polymerization was initiated either by precipitated or dissolved catalyst, and polymerization rate and polymer intrinsic viscosity gradually increased. When the content of good solvent in the mixed solvent was very large, all of the added catalyst dissolved homogeneously and polymerization proceded without precipitation of polymer. The intrinsic viscosity of the polymer and the polymerization rate increased greatly, and the former had the maximum value at a certain solvent composition. (When toluene was used as the solvent in the combination with n-hexane, the change of intrinsic viscosity in the homogeneous system was small.) The solvent composition at which the intrinsic viscosity of the polymer became as maximum varied a little with polymerization batch, but in general was 40-60 vol.% of good solvent.

When the polymerization took place in two different phases, the intrinsic viscosity of the polymer obtained in the solution part was larger than that obtained in the precipitation part, as is seen from Table 1-1. This means that the polymer in the precipitation part is not a fraction of higher molecular weight from the solution part, but the polymer grown on the surface of precipitated

catalyst.

Table 1-1 The comparison of $[\eta]$ of polymer obtained in a homogeneous phase with that obtained in a heterogeneous phase ($-78^{\circ}C$)

	Composition of solvent				
	Toluene		Chloroform		Methylene chloride
	40 vol.%	60 vol.%	20 vol%	30 vol.%	20 vol.%
Polymer from solution part	2.065	2.760	0.825	2.040	0.550
Polymer from precipitation part	1.960	1.810	0.740	1.560	0.370

3.2 Polymerization rate

The most interesting thing about the solvent effect was appearence of a maximum intrinsic viscosity at a certain solvent composition. In an attempt to clarify this phenomenon, the polymerization rate was measured in three kinds of solvent, viz. mixed solvent containing 40, 60, and 80% by volume of good solvents (80 vol.% good solvent means the solvent without n-hexane, the rest

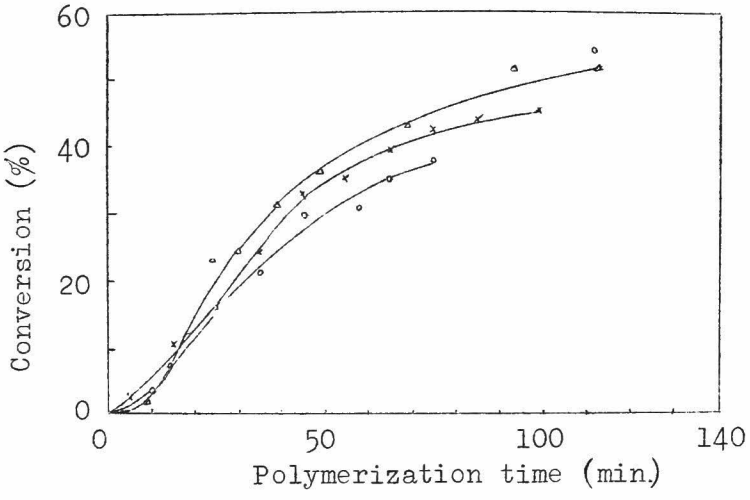

Fig.1-3a

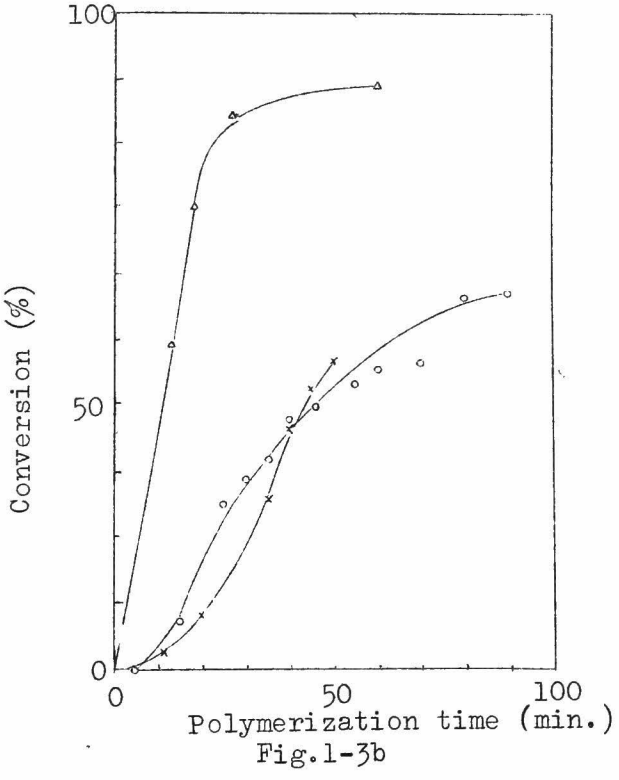

Fig.1-3b

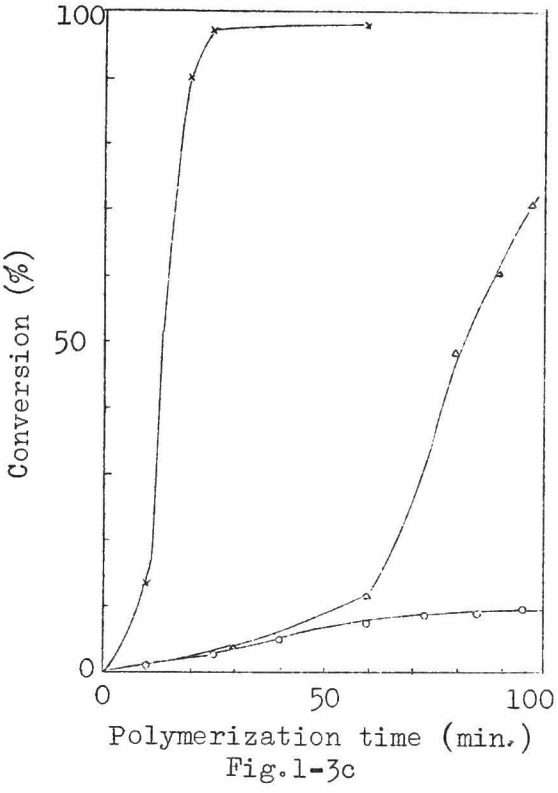

Fig.1-3c

Fig.1-3 The relationship between polymerization rate and the solvent composition (-78°C)
(○): solvent ($C_6H_5 \cdot CH_3$, $CHCl_3$, CH_2Cl_2) 40 vol. %
(△): solvent 60 vol. %, (×): solvent 80 vol. %
a : Toluene — n-hexane mixture [C] = 0.048 mole/l.
b : Chloroform — n-hexane mixture [C] = 0.024 mole/l.
c : Methylene chloride — n-hexane mixture
[c] = 0.020 mole/l.

(20 vol.%) being monomer.). In these solvents polymerization proceeded homogeneously or at least almostly homogeneously, which is convenient for studying the polymerization rate.

Fig. 1-3 a, b, c show the time--conversion curve obtained with the mixed solvents methylene chloride--n-hexane, chloroform--n-hexane, and toluene--n-hexane. When methylene chloride or toluene were used as the good solvent, the polymerization rate reached a maximum at 60 vol.% good solvent. When a polar solvent such as methylene chloride and chloroform was combinated with n-hexane, the polymerization rate and the effect of the solvent composition on the polymerization rate were larger than when toluene was used as the good solvent in the combination with n-hexane.

The effect of the catalyst concentration on the polymerization rate was investigated in a certain solvent. The experimental results are shown in Fig.1-4, and it was found that at a catalyst concentration above 0.024 mole/l, the initial rate of polymerization increased with increasing catalyst concentration, but when the catalyst concentration was less than 0.024 mole/l, the initial rate greatly decreased. This may

be due to existence of a critical catalyst concentration due to catalyst inactivation by adventitious water.

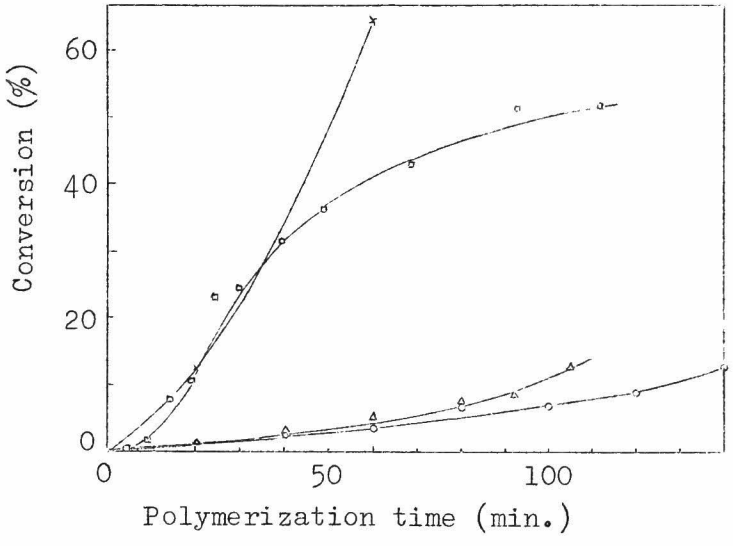

Fig.1-4 The dependence of the polymerization rate on catalyst concentration
Toluene 60%, -78°C [M]=1.54 mole/l.
[$BF_3 \cdot O(C_2H_5)_2$] = (○): 0.024 mole/l.
(△): 0.040 mole/l. (□): 0.048 mole/l.
(×): 0.059 mole/l.

The effect of monomer concentration on the polymerization rate is shown in Fig. 1-5. It can be said that the polymerization rate is roughly proportional to the monomer concentration.

The induction period has a low degree of reproducibility.

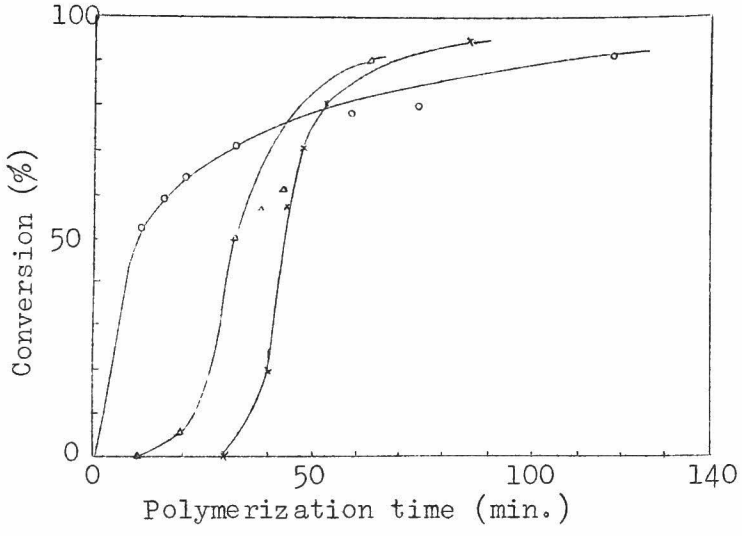

Fig.1-5 The effect of monomer concentration on the polymerization rate
Chloroform 60 vol.%, -78°C, [C] = 0.024 mole/l.
(○): [M] = 0.77 mole/l.(△): [M] = 1.54 mole/l.
(×): [M] = 2.31 mole/l.

3.3 Intrinsic viscosity of the polymer

In order to make clear the above-stated relationship between polymer intrinsic viscosity and solvent composition, the dependence of intrinsic viscosity on conversion was measured in a few kinds of mixed solvent. The results are shown in Fig. 1-6 a,b,c. When the conversion was less than 40%, the intrinsic viscosity of the polymer increased with increasing conversion, but when conversion reached 40-50%, the intrinsic viscosity of the polymer remained constant or sometimes

decreased with increasing conversion.

Fig. 1-6 b shows the reproducibility of the intrinsic viscosity. Though the intrinsic viscosity changed a little with polymerization batch, the reproducibility was fairly good apropos the present discussion. As is seen in Fig. 1-6, the polymer intrinsic viscosity unaffected by solvent composition in the initial stage of polymerization. But at a later stage differences between solvent compositions were reflected in the polymer intrinsic viscosity and this obtained for all the good solvents.

The experimental results shown in Figs. 1-2, 1-3 and 1-6 were compared with one other in relation to the solvent composition. As seen from Table 1-2, the absolute values of the polymerization rate and intrinsic viscosity vary in different polymerization batches, but the trends of their relationships to solvent composition are always the same. When toluene or chloroform was used as a good solvent, the dependence of polymerization rate on solvent composition resembled that of intrinsic viscosity on solvent composition.

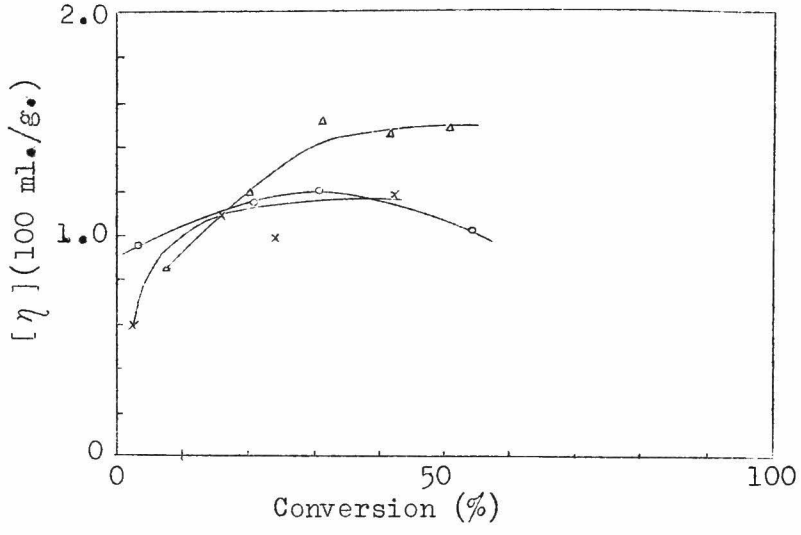

Fig.1-6a

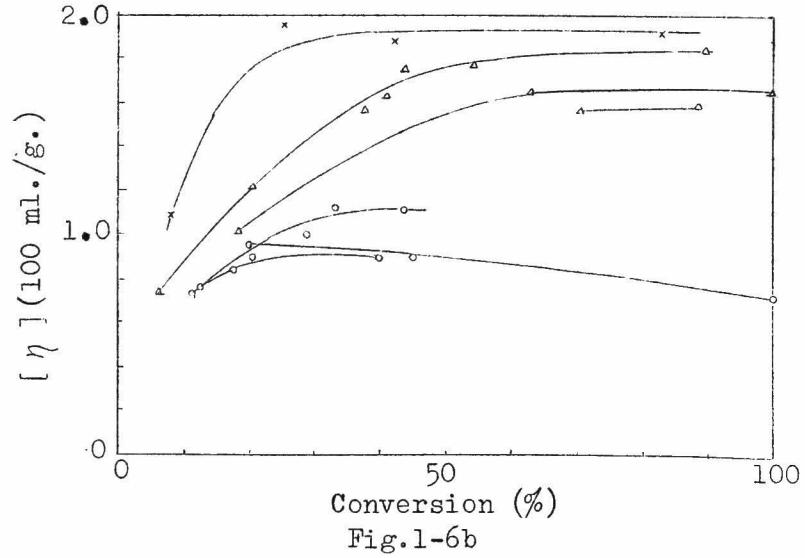

Fig.1-6b

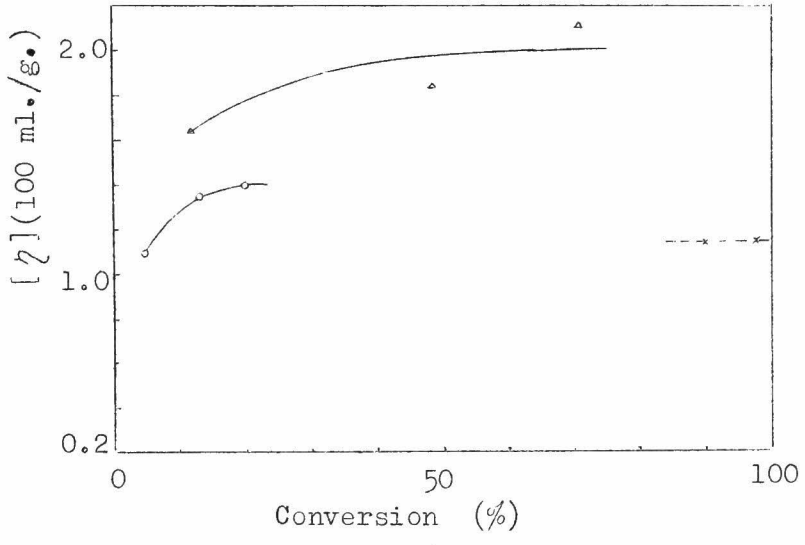

Fig. 1-6c

Fig. 1-6 The relationship between $[\eta]$ of polymer and conversion, -78°C

(○): solvent (toluene, chloroform, methylene chloride) 40 vol. %
(△): solvent 60 vol. %, (×): solvent 80 vol.%

a: Toluene—n-hexane mixture
b: Chloroform—n-hexane mixture
c: Methylene chloride—n-hexane mixture

Table 1-2 The dependencies of the polymerization rate and $[\eta]$ of polymer on the solvent composition, -78°C.

Good solvent	Catalyst concentration (mole/l.)	Solvent composition (good solvent vol.%)					
		40		60		80	
		Rp(%/min)	$[\eta]$	Rp(%/min)	$[\eta]$	Rp(%/min)	$[\eta]$
Toluene	0.024			0.25	1.52		
	0.040			0.32	0.78		
	0.048			1.4	1.51		
	0.059			1.6	1.20		
Chloroform	0.016			2	1.85	0.1	0.80
	0.024	0.2	1.12	10	1.70	2	1.87
		1.5	1.13				
	0.032	8	0.95	10	1.76	3	1.28
Methylene Chloride	0.020	0.12	1.41	3.3	2.12	7.7	1.14
	0.026		1.63		0.85		0.67

On the other hand, the intrinsic viscosity of the polymer did not vary regularly with changing monomer concentration. However, this might be due to complications such as increase of the polymer concentration and of viscosity of the polymerization solution as the polymerizationproceededsince polymerization was carried out at relatively high monomer concentration ranging from 10 vol.% to 30 vol.%. Consequently, the effect of monomer concentration has to be studied at monomer concentrations below 10 vol.%.

3.4 The molecular weight distribution of the polymer

As shown in Fig. 1-6, polymer intrinsic viscosity sometimes increased with increasing conversion. To find the reason for this, the resulting polymer was fractionated, and the polymer molecular weight distribution determined on polymer from polymerization where the intrinsic viscosity increased with increasing conversion. The sample was prepared by polymerizing monomer 20 ml. in chloroform 80 ml. using 0.4 ml. of boron trifluoride etherate catalyst at -78°C. The relationship between the intrinsic viscosity and the conversion was as follows:

Conversion:	31.1 %	48.3 %	71.6%
Intrinsic viscosity:	0.75	0.96	1.38

2.298g. of polymer obtained at 71.6 % conversion were dissolved in 300ml. of a mixture of equal volume of toluene and benzene, and fractionated into ten fractions by precipitation fractionation using methanol as the precipitating agent. The intrinsic viscosity of each fraction was measured in benzene at 30°C, from which the molecular weight was calculated using equation (7-3) of Chapter 7.

$$[\eta] = 2.49 \times 10^{-4} \times \bar{M}_n^{0.647} \qquad (1\text{-}1)$$

The molecular weight distribution curve is shown in Fig.1-7.

3.5 The effect of the polymerization temperature

Polymerizations of solution containing 20 vol.% of monomer were carried out at -50° and -20°C using toluene—n-hexane and chloroform—n-hexane as solvent. The experimental results are shown in Fig. 1-8. With increase in polymerization temperature, polymerization rate increased and intrinsic viscosity of the polymer decreased, which generally obtains in cationic polymerization.

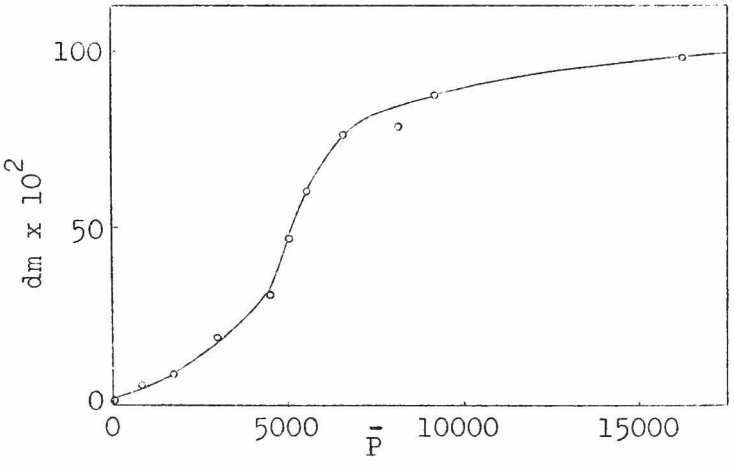

Fig.1-7 The molecular weight distribution of poly-α-methylstyrene

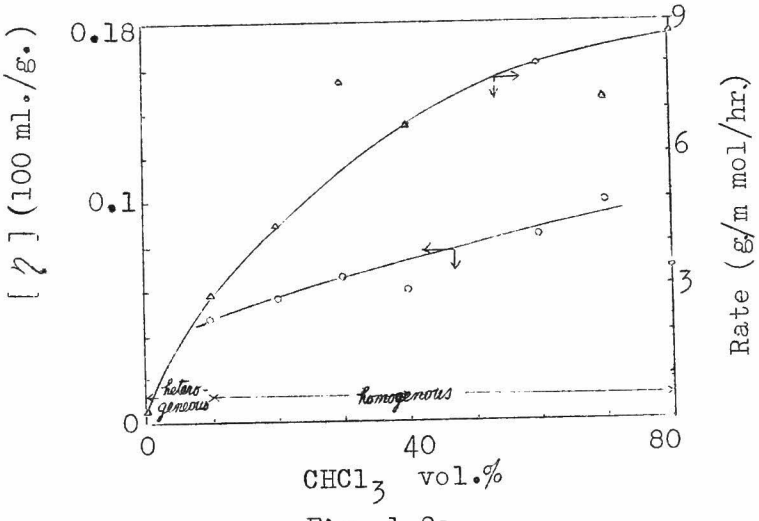

Fig. 1-8a

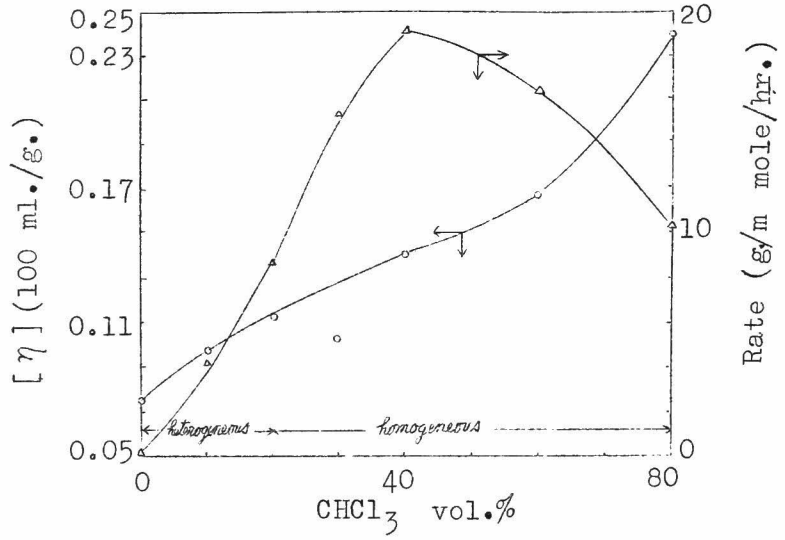

Fig. 1-8b

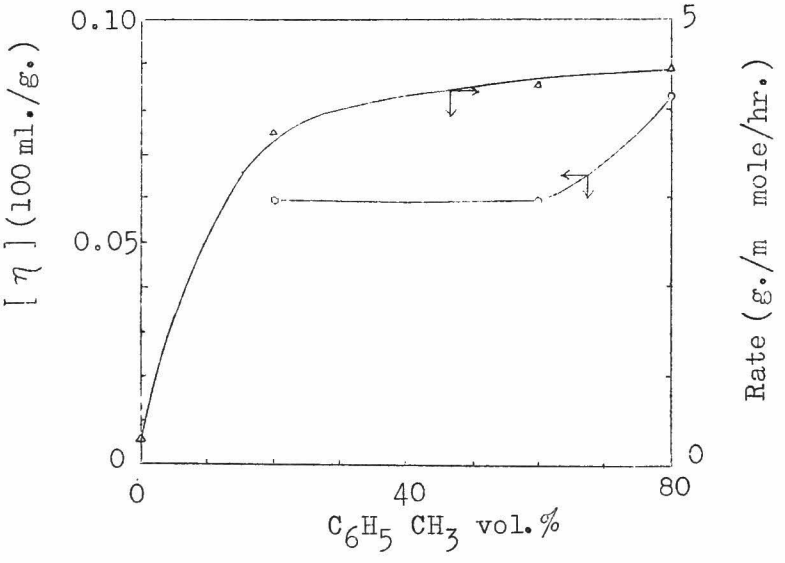

Fig.1-8c

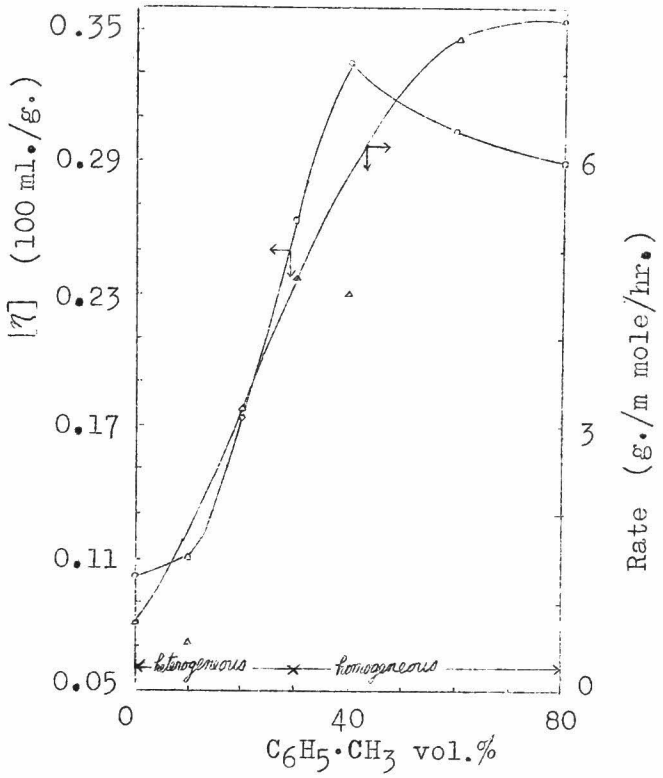

Fig.1-8d

Fig.1-8 The polymerization of α-methylstyrene at higher temperatures, [M] = 1.54 mole/l.
(○): Dependence of [η] of polymer on the solvent composition
(△): Dependence of the polymerization rate on the solvent composition
The polymerization rate was expressed as the yield of polymer g. per one mili mole of catalyst per one hour.
a: Chloroform—n-hexane mixture, -20°C
[C] = 0.035-0.105 mole/l.
b: Chloroform—n-hexane mixture, -50°C
[C] = 0.035-0.070 mole/l.
c: Toluene—n-hexane mixture, -20°C
[C] = 0.032 mole/l.
d: Toluene—n-hexane mixture, -50°C
[C] = 0.070 mole/l.

3.6 Solubility of the polymer

Polymers obtained in n-hexane--chloroform mixed solvent with over 50% chloroform were insoluble in benzene at room temperature, while polymers obtained under other polymerization conditions were soluble in it. This behavior of the polymer will be discussed in Chapter 7.

4. Discussion

The experimental results can be summarized into two parts: (1) The intrinsic viscosity of polymer can be varied widely by changing only the solvent composition. (2) When polymerization is carried out at low temperature, polymerization rate and intrinsic viscosity have maxima at certain solvent compositions.

Regarding the first of these, it has been recognized that the molecular weight of polymer can be changed moderately by changing the dielectric constant of the solvent. But here a wide change in intrinsic viscosity accompanied change of solvent composition. Furthermore, the intrinsic viscosity of polymer obtained under the optimum polymerization condition was higher than anything so far reported for polymerization at -78°C. In order to

bring about this point, the results obtained by Heiligmann et al.[5] are shown for comparison in Fig. 1-9.

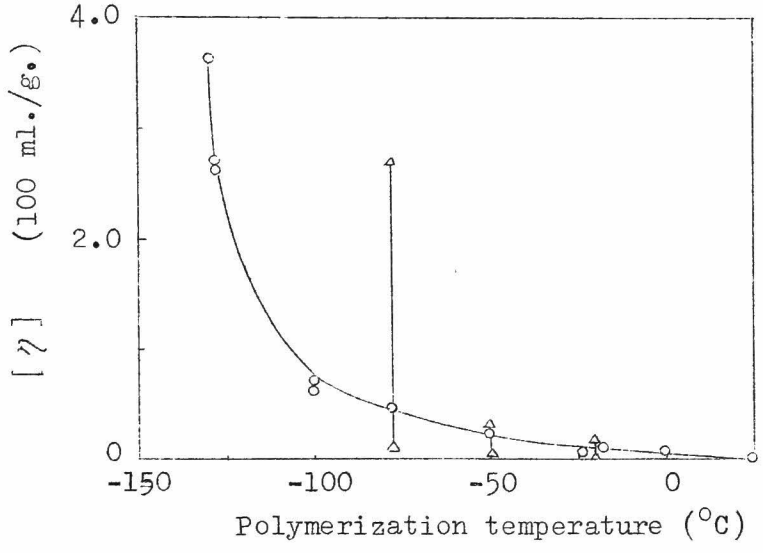

Fig.1-9 The relationship between $[\eta]$ of polymer and polymerization temperature (The comparison with the result obtained by Heiligmann et al.)
(○) : $[\eta]$ obtained by Heiligmann et al.
(△) : $[\eta]$ obtained in this work

From this Figure, it can be said that the polymer obtained in the present investigation has an extremely high intrinsic viscosity, and that the intrinsic viscosity of the polymers could be varied widely. The relatively high intrinsic viscosity here obtained corresponds to a molecular weight over a million, as calculated using equation (7-3).

Next, in an attempt to explain appearence of the

maximum value of the intrinsic viscosity in the low temperature polymerization, the polymerization system was divided into two parts, as follows:—

(1) Heterogeneous part—the part where the intrinsic viscosity and the polymerization rate increased with increasing amount of good solvent.

(2) Homogeneous part—the part where the intrinsic viscosity decreased, attained a maximum value, or remained contant with increasing amount of good solvent.

First of all in the heterogeneous part, when good solvent is utterly absent, the catalyst added precipitates and the polymer produced on the catalyst—solvent interface also precipitates and covers the catalyst surface. Polymerization rate and intrinsic viscosity of the polymer are therefore low. When an increasing amount of good solvent was added to this system, the polymer which covered the catalyst surface was swollen and diffusion of monomer to the active site thus facilitated. This effect gives rise to a fast, high-degree polymerization. When chloroform or methylene chloride is used as a good solvent, the increase in dielectric constant of the polymerization system also brings about fast polymerization. Furthermore, part of the added catalyst is dissolved

into the polymerization solvent when a good solvent is added. Then, both catalyst precipitated and catalyst dissolved can initiate the polymerization in the separate phase. In the solution, monomer diffusion takes place very readily and this brings about increase of the apparent propagation rate to give a high molecular weight polymer in fast polymerization. These ideas are supported by the fact, shown in Table 1-1, that the intrinsic viscosity of polymer precipitated is lower than that remaining in solution. The experimental findings regarding solvent effect in the present investigation appear to point essentially to what was found in polymerization of methyl vinyl ether, viz. activated polymerization, the important thing being whether a monomer can easily diffuse to an active site.

Next, with a view to securing explanations for the behaviors of the polymerization rate and intrinsic viscosity in a homogeneous system, the experimental results on them, as observed in mixed solvent containing over 40 vol.% of good solvent, are summarized in Table 1-3. Complete explanation of all the experimental results is hardly possible at the present stage. Chain breaking due to impurities in good solvent may explain

Table 1-3 Cationic polymerization of α-methylstyrene in a homogeneous system

(Solvent more than 40 vol.%)

		With increasing toluene, chloroform or methylene chloride		
Temp.(°C)↓ Solvent→		Toluene — n-hexane	Chloroform — n-hexane	Methylene chloride — n-hexane
-78	$[\eta]$	No appreciable change	Maximum	Decrease
	Rp	"	"	Increase
-50	$[\eta]$	"	Slight increase	Decrease
	Rp	"	Slight decrease	Increase
-20	$[\eta]$	"	Slight increase	Decrease
	Rp	"	"	Increase

what is found. However, even when highly purified solvent (water content about a mili mole/l.) was used, and two polymerizations were made, similar results were always obtained. Further the intrinsic viscosity maximum did not appear on polymerization at elevated temperatures. Here appearance of maximum values of the intrinsic viscosity and polymerization rate are characteristic of low temperature polymerization.

Since the characteristic behaviors of the intrinsic viscosity and the polymerization rate were observed in an apparently homogeneous system, solubility difference cannot explain the experimental results. Referring again to Table 1-3, changes in intrinsic viscosity and polymerization rate are small in toluene—n-hexane mixed solvent, where dielectric constant of the polymerization system does not vary with changing solvent composition, but change was clearly observed in methylene chloride—n-hexane mixed solvent in which variation of dielectric constant of the polymerization system is largest.

The change in chloroform—n-hexane mixed solvent was intermediate between the above two. In view of this, the effects of solvent on polymer intrinsic viscosity and polymerization rate may be explained in terms of the solvent dilectric constant.

It has been observed in the polymerization of styrene that the more polar the solvent, the higher the molecular weight of the resultant polymer. Comparing the solvent effect in the present investigation with that in styrene polymerization[1)], the solvent effect for the

intrinsic viscosity in the cationic polymerization of α-methylstyrene in methylene chloride—n-hexane mixed solvent was found to be just the reverse of that for styrene polymerization. This suggests that the mechanisms of the termination and transfer reactions in the cationic polymerization of α-methylstyrene are different from those in the styrene polymerization. However, occurrence of a maximum for the intrinsic viscosity when chloroform—n-hexane mixed solvent is used means that termination and transfer reactions with the same mechanisms as those in the styrene polymerization can also take place. This point can be clarified by determination of exact values of the termination and the transfer reaction constants, and explanations of the experimental results in the light of the rate constants will be given in the succeeding Section.

Finally, increase of intrinsic viscosity as polymerization proceeds, especially at the initial stage of the polymerization, will be discussed. Such behavior was observed in the polymerization of vinyl ether [3], where the long life of the propagating species is considered to be the cause. In the present investigation, a molecular weight distribution study showed that the polymer produced

at high conversion did not contain so much low molecular weight material, even with low intrinsic viscosity at the initial stage of the polymerization. This is explained by stepwise propagation of a long-lived propagating species, instead of production of the extremely high molecular weight polymer at the later stage of polymerization. However, loss of the low molecular weight part of the polymer during the fractionation may be also a reason for the molecular weight distribution here observed.

To summarize, the present investigation showed that in low temperature cationic polymerization of α-methylstyrene, the intrinsic viscosity of polymer can be varied widely and arbitrarily by changing the solvent composition, and that the modes of the variation of intrinsic viscosity and polymerization rate depend on solvent dielectric constant.

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Section 1.2 The Rate Constant Ratios of the Monomer Transfer Reaction and Unimolecular Termination Reaction

1. Introduction

When α-methylstyrene was polymerized by boron trifluoride etherate in various kinds of mixed solvents, the characteristic behavior of the intrinsic viscosity and the polymerization rate in relationship to solvent nature described in Section 1.1 was observed.

In cationic polymerization, the nature of the growing ion-pair, consisting of growing carbonium ion plus the anionic moiety of the catalyst, affects each of the elementary reactions. It has been qualitatively recognized from the measurement of polymerization rate and intrinsic viscosity of the polymer that the nature of the growing ion-pair is determined by the natures of the solvent, monomer, and catalyst. Previously a quantitative study has been made in our laboratory on the effects of catalyst and solvent on the termination and the transfer constant ratios in cationic polymerization of styrene at around room temperature[1] and it is the only quantitative investigation so far reported.

Clarifying the features characteristic of cationic polymerization generally involves knowing the behavior of the growing ion-pair. In the present investigations the termination and the transfer constant ratios were therefore determined for several polymerization conditions. Assuming that the change in rate constant ratio is due to variation in the nature of the growing ion-pair, the effect of polymerization conditions on the nature of the growing ion-pair was deduced from the experimental results on the rate constant ratios. Furthermore, in the following series of investigations the rate constant ratios were measured for several kinds of monomers, and the effects of the nature of the growing ion-pair were compared.

In this Section, cationic polymerization of α-methylstyrene was carried out by boron trifluoride etherate in a variety of solvents, and the rate constant ratios were calculated from the degree of polymerization of the resultant polymer, enabling the role of the solvent to be studied.

The monomer transfer reaction, solvent transfer reaction, and unimolecular termination reaction will now be defined. The monomer transfer reaction is the chain breaking reaction in the activated state in which one molecule of the growing chain and one molecule of monomer

participate. The solvent transfer reaction is similarly the chain breaking reaction where one molecule of growing chain and one molecule of solvent participate in the activated state. These two reactions are called the transfer reaction, without strict distinction between the transfer reaction and the termination one. On the other hand, the unimolecular termination reaction means the chain breaking reaction in which only one molecule of the growing chain participates in the activated state, and similarly there is no distinction between termination and transfer reaction. From a technical reason, in the kinetic treatment of the degree of polymerization, reaction between a growing cation and impurity (for example, water) is sometimes included in the term unimolecular termination reaction or solvent transfer reaction.

2. Experimental

2.1 Reagents

The methods of purifying the reagents were described in Section 1.1.

2.2 Procedure

2.2.1 Polymerization

Monomer and solvent were introduced into a 100 ml.

flask equipped with a long calcium chloride tube and a catalyst inlet, and cooled in a thermostatted low temperature bath. Polymerization was started by adding a given amount of catalyst through the inlet. Stopping polymerization and subsequent treatment of the polymer were described in Section 1.1.

2.2.2 The measurement of dielectric constant

The dielectric constant of α-methylstyrene was measured using high frequency Wheatstone bridge.[2] Dielectric constants of n-hexane, chloroform, and methylene chloride were taken from Morgan's data.[3] The dielectric constant of toluene was taken from Isnardi's data.[4]

To calculate the dielectric constant of mixed solvent from the dielectric constants of the pure solvents, Debye's equation was used for a mixture of two non-polar solvents, and Onsager's equation was used for a mixture containing a polar solvent.[5] Such physical constants as specific gravity and refractive index, which are necessary for the calculation, were obtained from the literature.[6] When the temperature range used in the present investigation was beyond that of the literature, extrapolation was resorted to.

2.3 Determination of molecular weight

In Chapter 7 the relationship between the intrinsic viscosity of the polymer in benzene at 30°C and its molecular weight as determined by osmotic pressure measurement was reported for a fractionated sample of poly-α-methylstyrene polymerized under the present conditions to be given by:—

$$[\eta] = 2.49 \times 10^{-4} \times \bar{M}_n^{0.65} \qquad (1\text{-}2)$$

This equation holds for molecular weights from 10^5 to 10^6, and therefore for polymers obtained at -50° and -70°C. On the other hand, for low molecular weight polymer obtained at -20°C, the intrinsic viscosity—molecular weight relationship reported by Bywater et al.[7] was used:—

$$[\eta] = 0.0105 + 1.787 \times 10^{-5} \times \bar{M}_n \qquad (1\text{-}3)$$

In the present investigation, the polymer molecular weight was calculated by substituting in equations (1-2) and (1-3) the intrinsic viscosity of unfractionated material. The molecular weight thus calculated is not the true number average molecular weight, consequently the rate constant ratio calculated using this molecular weight is not a true rate constant but a modified rate

constant ratio. According to the Flory's theory,[8] in the case of "most probable distribution" polymer, the ratio of the number average molecular weight ($\bar{M}_n$) to the viscosity average molecular weight ($\bar{M}_v$) is $1 : \left[(1+a)\Gamma(1+a)\right]^{1/a}$ where a is given by the equation $[\eta] = K\bar{M}_v^{a}$. Assuming "most probable distribution" for poly-α-methylstyrene obtained in the present investigation, the molecular weight calculated by equation (1-2) or (1-3) using the intrinsic viscosity of unfractionated sample is always $\left[(1+a)\Gamma(1+a)\right]^{-1/a}$ times $\bar{M}_n$. If a is assumed to be 0.65, then $\bar{M}_v$ is always 1.84 times $\bar{M}_n$. Therefore, provided that the condition that the molecular weight distribution of the polymer is always the same is satisfied, it does not matter if the rate constant ratios calculated from $\bar{M}_v$ are compared. However, a more detailed consideration seems to be important and it will be given in Chapter 9.

The variation of polymer intrinsic viscosity with conversion is also important. It is observed more clearly in low temperature polymerization which gives high molecular weight polymer. But when polymerizations were carried out at -78°C in toluene—n-hexane, chloroform—n-hexane or methylene chloride--n-hexane (all homogeneous systems), there was increase in intrinsic viscosity with increasing

conversion only in the initial stage of the polymerization and little change after conversion reached about 30%. This was described in Section 1.1. Since the same is also supposed hold for polymerizations at -50° and -20°C, the intrinsic viscosity of polymer obtained at over 30% conversion was measured.

3. Determination of the rate constant ratio.

3.1 Method of calculating the rate constant ratio

The elementary reactions in the present polymerization are given by equations (1-4)-(1-9), where * means the activated state, and C, M, S, S', S" and X represent catalyst, monomer, toluene, chloroform or methylene chloride, n-hexane and impurity, respectively. k_i, k_p, k_{tm}, k_t, k_{ts}, $k_{ts'}$, $k_{ts''}$, and k_{tx} denote the rate constants of initiation, propagation, monomer transfer, unimolecular termination, chain transfer to solvent S, solvent S', solvent S", and reaction with impurity, respectively.

$$C^* + M \xrightarrow{k_i} M^* \qquad (1\text{-}4)$$

$$\left.\begin{array}{lll} M^* + M & \xrightarrow{k_p} & M_2^* \\ \vdots & & \vdots \\ M_{n-1}^* + M & \xrightarrow{k_p} & M_n^* \end{array}\right\} \qquad (1\text{-}5)$$

$$M_n^* + M \xrightarrow{k_{tm}} Mn + M^* \qquad (1\text{-}6)$$

$$M_n^* + S(\text{or } S', S'') \xrightarrow{k_{ts}, k_{ts'}, k_{ts''}} Mn + S^*(\text{or } S'^*, S''^*) \qquad (1\text{-}7)$$

$$M_n^* \xrightarrow{k_t} M_n \qquad (1\text{-}8)$$

$$M_n^* + X \xrightarrow{k_{tx}} M_n \qquad (1\text{-}9)$$

As stated previously, for the convenience in calculation, reaction (1-9) is sometimes included in reaction (1-8). In this case, the unimolecular termination constant is represented by k_t', ($k_t' = k_t + k_{tx}[X]$).

From these equations, the reciprocal of the degree of polymerization is calculated thus:

$$1/\bar{p} = k_{tm}/k_p + k_{ts}[S]/k_p[M] + k_{ts}'[S']/k_p[M] + k_{ts}''[S'']/k_p[M] + k_t'/k_p[M] \qquad (1\text{-}10)$$

Plotting the reciprocal of the degree of polymerization against solvent or monomer concentration, the rate constant ratio can be calculated.

The volume of the polymerization solution was kept constant at 50 ml. and the monomer concentration was varied over a range 2 vol.% (0.154 mole/l.) to 20 vol.% (1.54 mole/l.); catalyst concentration was varied from 0.016 to 0.158 mole/l. The reason for using the above monomer concentration range was stated previously, too high a monomer concentration (more than 20 vol.%) entails various complexities. Polymerizations were carried out at -20°, -50° and -70°C. The following solvent systems

were used: n-hexane, toluene, chloroform, methylene chloride, toluene—n-hexane(euqal volumes), chloroform—n-hexane (equal volumes), and methylene chloride—n-hexane (equal volumes). Polymerizations were carried out for various monomer concentrations: to avoid change of dielectric constant and homogenity (or heterogenity) of the polymerization solution consequent upon change of monomer concentration, an appropriate amount of toluene was added to the solution as the monomer concentration was reduced.

Equation (1-10) has to be modified according to the kind of solvent. Below each case will be treated separately.

3.1.1 Toluene

Change of concentration of monomer in toluene does not cause the change in dielectric constant of the polymerization solution, because there is little difference between the dielectric constants of monomer and toluene. In equation (1-10), $[S'] = [S''] = 0$. Furthermore, accepting Plesch's view[9] that the unimolecular termination reaction can not occur energetically in a solvent of such low dielectric constant, k_t is zero, giving equation (1-11).

$$1/\bar{p} = k_{tm}/k_p + k_{ts}[S]/k_p[M] \qquad (1\text{-}11)$$

The reaction with any impurity present, (k_{tx} [X]), is included in the k_{ts} [S] term. Plotting $1/\bar{p}$ against [S] /[M] , the slope and the intercept of the straight line give respectively k_{ts}/k_p and k_{tm}/k_p.

3.1.2Equal volume mixed solventof toluene and n-hexane

As n-hexane is not a solvent for polymer and catalyst, 20 ml.of n-hexane were always used, and the monomer concentration was reduced by adding the right amount of toluene. Then, [S'] = 0 in equation (1-10), giving equation (1-12).

$$1/\bar{p} = k_{tm}/k_p + k_{ts}[S]/k_p[M] + k_{ts}''[S'']/k_p[M] + k_t'/k_p[M] \qquad (1\text{-}12)$$

Equation (1-12) was modified as in polymerization of styrene[10], to give equation (1-13).

$$1/\bar{p} = (k_{tm}/k_p - bk_{ts}/k_p) + (aVk_{ts}/k_p + k_t'/k_p)/[M] \qquad (1\text{-}13)$$

where:

$k_t' = k_t + k_{ts}''[S''] + k_{tx}[X]$

[S''] = constant (40 vol.% of n-hexane)

$a = 1000\ d_S/W_S$ $\qquad$ $b = d_S.W_m/d_m.W_S$

d_S and d_m are the specific gravity of toluene and monomer, respectively.

W_s and W_m are the molecular weights of toluene and monomer, respectively.

$V = V_s + V_m = 0.2$

V_s and V_m are the volume fraction of toluene and monomer, respectively.

In equation (1-13), k_{ts}/k_p is the rate constant ratio for chain transfer to toluene. If k_{ts}/k_p is always constant independent of solvent dielectric constant[11], k_{ts}/k_p obtained in equation (1-11) can be used in equation (1-13), too. Then by plotting $1/\bar{p}$ against $1/[M]$, k_{tm}/k_p and k_t'/k_p are determined.

3.1.3 Chloroform, methylene chloride, and n-hexane

40 ml. of each solvent were used with monomer and toluene. The monomer concentration was reduced by adding the right amount of toluene, when equation (1-13) holds. But when chloroform or methylene chloride is used,

$k_t' = k_t + k_{ts}'[S'] + k_{tx}[X.]$

3.1.4 Equal volume mixtures of chloroform and n-hexane and methylene chloride and n-hexane as the solvents.

20 ml. of chloroform or methylene chloride and 20 ml. of n-hexane were used with toluene and monomer. The monomer concentration was varied keeping the total volume of monomer plus toluene equal to 10 ml. Then too equation

(1-13) holds, but $k_t' = k_t + k_{ts}'[S'] + k_{ts}''[S''] + k_{tx}[X]$.

For all polymerization systems, the logarithm of the rate constant ratio was plotted against the reciprocal of the absolute temperature, and the activation energy and activation entropy differences were calculated. Extrapolating to -78°C the straight line plot of the logarithm of rate constant ratio against reciprocal of absolute temperature gave the rate constant ratio at that temperature.

3.2 Experimental results

Figs. 1-10 and 1-11 exemplify determination of the rate constant ratio according to equation (1-11) or (1-12).

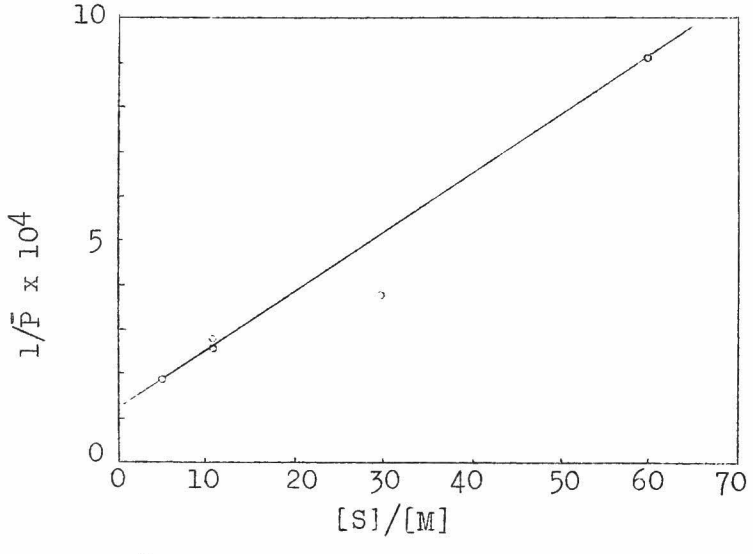

Fig. 1-10 The determination of the rate constant ratios by plotting $1/\bar{P}$ against [S]/[M]
Solvent: Toluene, -70°C, $k_{tm}/k_p = 1.22 \times 10^{-4}$, $k_{ts}/k_p = 0.13 \times 10^{-4}$

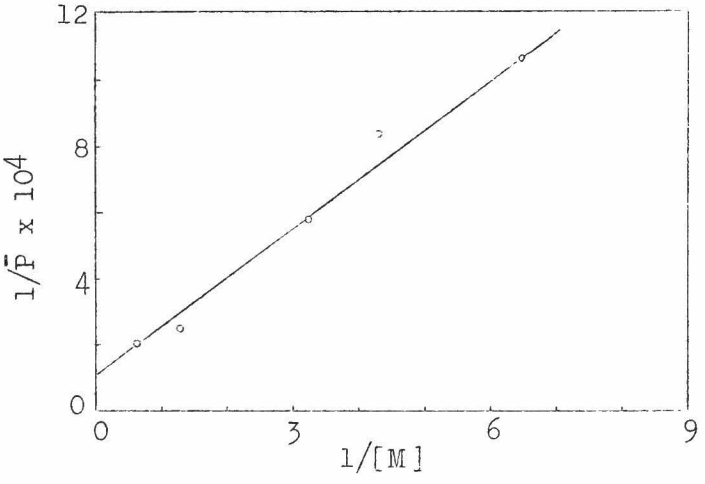

Fig.1-11 The determination of the rate constant ratios by plotting $1/\bar{P}$ against $1/[M]$
Solvent: Methylene chloride—n-hexane, -70°C,
$k_t'/k_p = 1.21 \times 10^{-4}$ $k_{tm}/k_p = 1.26 \times 10^{-4}$

Polymerizations were carried out in each solvent using four to six different monomer concentrations. The polymer degree of polymerization for each initial monomer concentration gave a linear plot which afforded rate constant ratios. Polymerizations in the same solvent were carried out at three different temperatures. Activation energy and activation entropy differences were found from Fig. 1-12.

Similar experiments were carried out in seven different kinds of solvent and the entire results are summarized in Table 1-4.

Table 1-4 The rate constant ratios

Solvent	Rate constant ratio	-20°C ($\times 10^{-2}$)	-50°C ($\times 10^{-3}$)	-70°C ($\times 10^{-4}$)	Activation energy difference (Kcal/mole)	Activation entropy difference (EU)	Rate constant ratio extrapolated to -78°C
n-Hexane	k_{tm}/k_p	4.75	9.10	35.2	5.2	14.7	1.9×10^{-3}
	k_t'/k_p	0.25	0.64	3.26	4.5	5.6	1.8×10^{-4}
Toluene	k_{tm}/k_p	1.12	1.00	1.22	9.1	26.9	4.8×10^{-5}
	k_{ts}/k_p	0.16	0.07	0.13	9.9	26.4	3.1×10^{-6}
Toluene—n-hexane (1 : 1 by volume)	k_{tm}/k_p	1.08	1.09	1.04	9.5	28.6	4.5×10^{-5}
	k_t'/k_p	0.50	0.73	1.99	6.4	14.3	9.6×10^{-5}
Chloroform	k_{tm}/k_p	0.76	1.09	0.56	10.3	28.4	2.7×10^{-5}
	k_t'/k_p	2.50	1.25	0.73	11.9	30.2	2.7×10^{-5}
Chloroform—n-hexane (1:1 by volume)	k_{tm}/k_p	1.94	2.01	1.48	9.9	32.4	7.1×10^{-5}
	k_t'/k_p	1.70	0.51	0.70	11.1	35.2	1.8×10^{-5}
Methylene Chloride	k_{tm}/k_p	2.60	2.59	2.41	9.5	30.6	1.1×10^{-4}
	k_t'/k_p	1.94	3.55	3.06	8.4	25.9	1.8×10^{-4}
Methylene Chloride—n-hexane (1:1 by volume)	k_{tm}/k_p	1.32	0.89	1.26	9.9	30.3	3.6×10^{-5}
	k_t'/k_p	1.78	0.76	1.21	10.2	31.8	3.6×10^{-5}

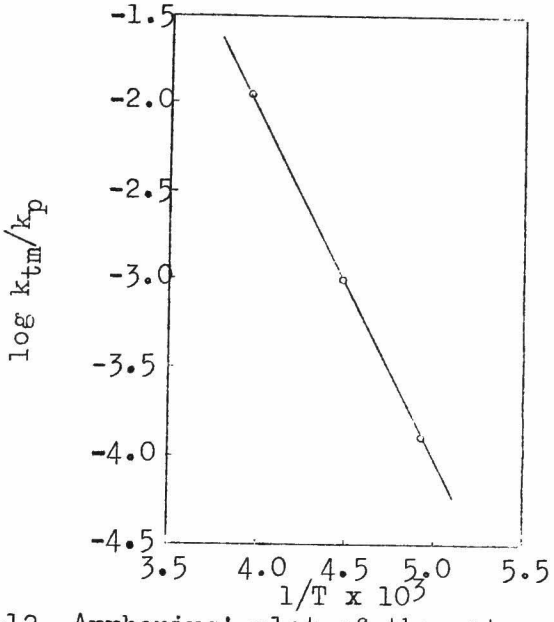

Fig. 1-12 Arrhenius' plot of the rate constant ratio k_{tm}/k_p in toluene,
$E_{tm}-E_p$ = 9.1 Kcal/mol, $S_{tm}-S_p$ = 26.9 EU

4. Discussion

4.1 Explanation in terms of rate constant ratio of the changes in polymerization rate and polymer intrinsic viscosity accompanying change of the solvent in cationic polymerization of α-methylstyrene

The experimental results in the cationic polymerization of α-methylstyrene carried out with a 20 vol.% initial monomer concentration, were described in Section 1.1., and these results have to be satisfactorily explained in accordance with the rate constant ratio here found when changing the monomer concentration.

4.1.1 n-Hexane

At all temperatures from -20° to -78°C, the rate constant ratios for this solvent were extremely large compared with those for other solvents. This falls into line with the very low molecular weight of the polymer produced in this solvent.

4.1.2 Toluene—n-hexane mixed solvent

At equal temperatures, k_{tm}/k_p in toluene was almost the same as that for equal volume of toluene—n-hexane. Furthermore, $k_{ts}[S]/k_p$ for toluene was almost the same as k_t'/k_p in the above mixed solvent at the same temperature. Since both reactions determining the molecular weight of polymer are insensitive to the change of solvent, the intrinsic viscosity of polymer obtained with a monomer concentration of 20 vol.% in toluene would be expected to be almost the same as that with the toluene—n-hexane mixture. and this was found to be the case (Fig. 1-2a, 1-8c, 1-8d).

Equation (1-14) for polymerization rate is deduced from equations (1-4)-(1-9), assuming a steady state:—

$$Rp = k_p \cdot k_i \cdot [C][M]^2/k_t \qquad (1\text{-}14)$$

If [M] (20 vol.%) and [C] are constant, Rp depends on $k_i.k_p/k_t$. In the present solvent system, the dielectric

constant of the system does not change with change in solvent composition (see Table 1-5). And the rate constant $k_i \cdot k_p/k_t$, too, is not affected by change in solvent composition. This leads to a polymerization rate insensitive to solvent composition, as shown in Section 1.1 (Figs. 1-3a, 1-8a, 1-8c).

4.1.3 Chloroform—n-hexane mixed solvent

With a solvent of higher dielectric constant (chloroform only), k_{tm}/k_p was smaller and k_t'/k_p larger over the temperature range -20° to -78°C. If k_t' is determined mainly by k_t (and this is probable), the dependency of k_t'/k_p on the solvent dielectric constant is in good agreement with the result in the styrene polymerization.[1] Calculating the molecular weight of polymer polymerized with an initial monomer concentration of 20 vol.% using the rate constant ratio in Table 1-4, the intrinsic viscosity of polymer produced in chloroform was found to be slightly larger than that in chloroform—n-hexane mixed solvent for all temperatures from -20° to -78°C. And this is in good agreement with the experimental results of Section 1.1 (Figs. 1-2b, 1-8a, 1-8b).

However, the appearance of a maximum intrinsic viscosity in chloroform—n-hexane mixed solvent cannot be

explained by the rate constant ratios of Table 1-4, as the rate constant ratio for chloroform 75%—n-hexane 25% is lacking. This will be discussed later in greater detail.

Regarding polymerization rate, among the rate constants determining it, k_i and k_t are supposed to be more sensitive to the variation of the solvent dielectric constant than is k_p. If it is assumed that k_i increases more rapidly than k_t with increase of solvent dielectric constant, the experimental result at -20°C (Fig. 1-8a) can be explained. If the reverse is assumed, the experimental result at -50°C (Fig. 1-8b) can be explained. However, neither explains the presence of a maximum polymerization rate at a certain solvent composition (chloroform 75 vol.%). This may be due to a different dielectric constant dependence of k_i and k_t.

4.1.4 Methylene chloride—n-hexane mixed solvent

Over the range -20°C to -78°C, both k_{tm}/k_p and k_t'/k_p were larger in a solvent of higher dielectric constant (methylene chloride). Therefore, when polymerization is carried out in the mixed solvent system, the intrinsic viscosity of polymer should decrease with increasing amount of methylene chloride independently of the monomer concentration at all temperatures, and this

was found to be the case (Fig. 1-2c).

Regarding polymerization rate, in a solvent as polar as methylene chloride, it is safe to assume that k_i increases much more than k_t, and this should lead to higher polymerization rate in methylene chloride than in the mixed solvent (Fig. 1-3c), which is what is found.

4.2 Relationship between solvent dielectric constant and rate constant ratio

It has been observed in the cationic polymerization of styrene[1] at room temperature that with increasing dielectric constant of solvent the monomer transfer reaction is suppressed and the unimolecular termination reaction is favored. In the present investigation the rate constant ratios listed in Table 1-4 were obtained, whence it was found that the relationship observed in the styrene polymerization did not hold in the α-methylstyrene polymerization, especially in respect of k_{tm}/k_p in solvents of higher dielectric constant. It is, therefore, necessary to discuss the rate constant ratio in relation to dielectric constant of solvent. Dielectric constants of solvent were determined as described in 2.2.1 and summarized in Table 1-5.

Table 1-5, Dielectric constant of the polymerization system

Solvent → Temp.(°C) ↓	α-Methylstyrene[a]	n-Hexane—monomer[b]	Toluene—monomer[b]	Chloroform—monomer[b]
-20	2.65	2.09	2.50	5.03
-50	2.72	2.13	2.58	5.68
-70	2.77	2.17	2.62	6.27
-78	2.78	2.18	2.64	6.58
Solvent → Temp.(°C) ↓	Methylene chloride—monomer[b]	Toluene—n-hexane—monomer[b],c)	Chloroform—n-hexane—monomer[b],c)	Methylene chloride—n-hexane—monomer[b],c)
-20	9.30	2.29	3.45	5.44
-50	10.68	2.35	3.79	6.16
-70	11.86	2.38	4.07	6.73
-78	12.31	2.40	4.21	6.97

a) Observed value b) Calculated value using the observed D.C. of monomer

c) n-Hexane 40 vol.%

4.2.1 Relationship between k_{tm}/k_p and the solvent composition

When k_{tm}/k_p was plotted against the solvent composition, Fig. 1-13 a, b, c were obtained.

There, the left half containing over 50% n-hexane is the heterogeneous part, where the precipitation of catalyst and polymer occurred.

The following points emerged from Fig. 1-12:

(1) With over 50% n-hexane content in the mixed solvent, the monomer transfer reaction occurs very easily. Since the dielectric constant of n-hexane is very low, as was deduced from the experimental results on the styrene polymerization, the lack of the solvation of the growing ion-pair gives a large k_{tm}/k_p.

(2) In spite of its relatively low dielectric constant, toluene gives a small k_{tm}/k_p. This is due to effective solvation of the growing ion-pair by the phenyl group rich in π-electron. It seems as effective as solvation by a solvent of high dielectric constant.

(3) The curves for methylene chloride—n-hexane have a minimum value at 50-50 vol.%. In other words, a wide variation in dielectric constant on changing

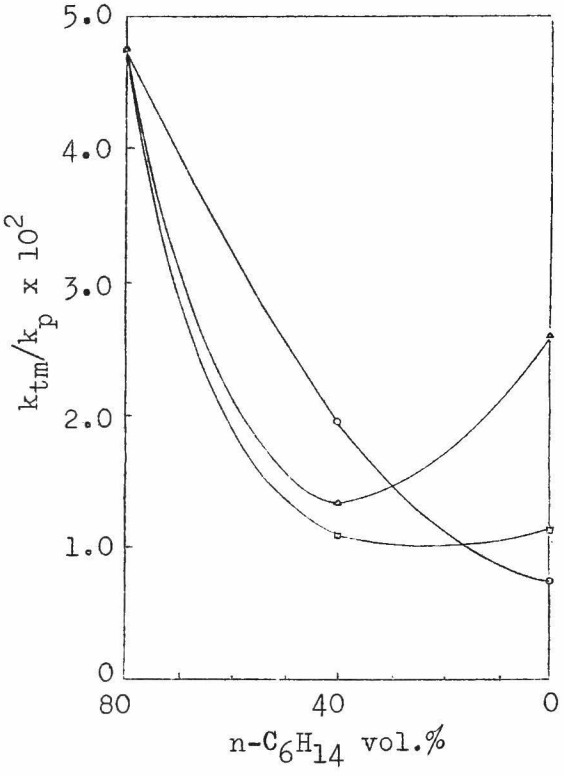

Fig.1-13a

Fig.1-13 The relationship between k_{tm}/k_p and the solvent composition
(□): Toluene—n-hexane mixture, [M] = 20 vol.%
(○): Chloroform—n-hexane mixture, [M] = 20 vol.%
(△): Methylene chloride—n-hexane mixture, [M] = 20 vol.%
a: -20°C, b: -50°C, c: -70°C

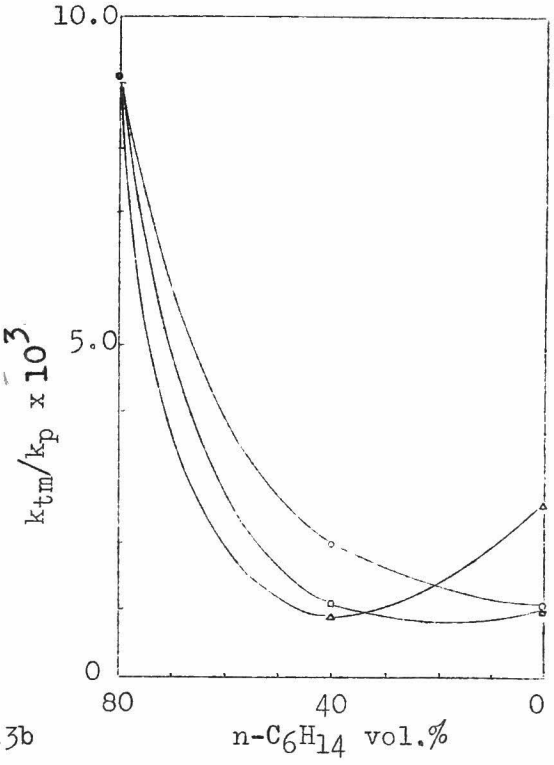

Fig.1-13b

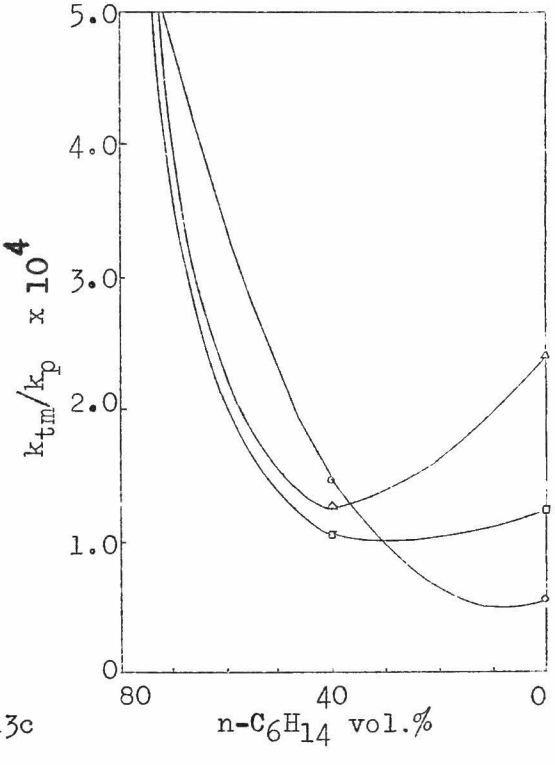

Fig.1-13c

solvent composition is possible with this combination, and subsequently the nature of the growing ion-pair can be varied widely, a certain degree of polarization being imparted to the ion-pair : where the monomer transfer reaction takes place with most difficulty. Applying this idea to the chloroform—n-hexane mixture, there may be a minimum in the curve of Fig. 1-13 c. If there is, the appearence of a maximum intrinsic viscosity with it can be explained by the operation of the two effects.

As implied above, discussion of the monomer transfer reaction in terms of degree of polarization of the growing ion-pair is very important. In an attempt at elucidation, k_{tm}/k_p was plotted against solvent dielectric constant (Fig. 1-14).

In view of the above-mentioned exceptional property of toluene, plotting was done only for aliphatic solvents. It is observed that the minimum value of k_{tm}/k_p is at dielectric constant ca. 6, independent of polymerization temperature. This corresponds to the intrinsic viscosity of polymer obtained at -78°C becoming a maximum with 50-50 vol.% of methylene chloride—n-hexane or in the chloroform-rich part of a chloroform—n-hexane mixture. The

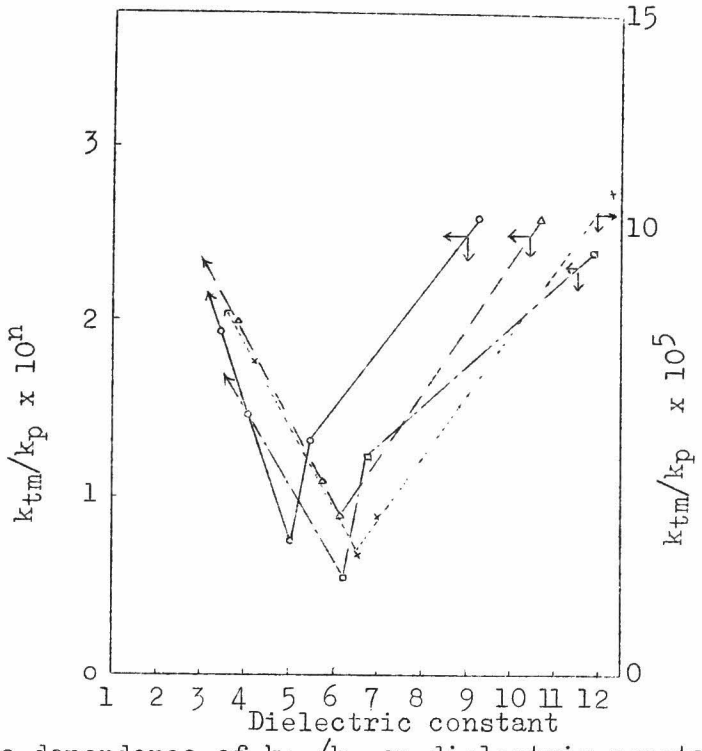

Fig.1-14 The dependence of k_{tm}/k_p on dielectric constant
(○): -20°C, n = 2 (△): -50°C, n = 3,
(□): -70°c, n = 4 (×): -78°C

reason for this experimental finding will be discussed later.

In Fig. 1-14, the behavior of k_{tm}/k_p in solvent of dielectric constant less than 6 is the same as was found for styrene polymerization.[1] This suggests occurrence of a monomer transfer reaction having the same mechanism that of styrene polymerization in α-methylstrene polymerization in solvent of dielectric constant less than 6. The nature of the monomer transfer reaction in solvent of dielectric constant above 6, will be discussed

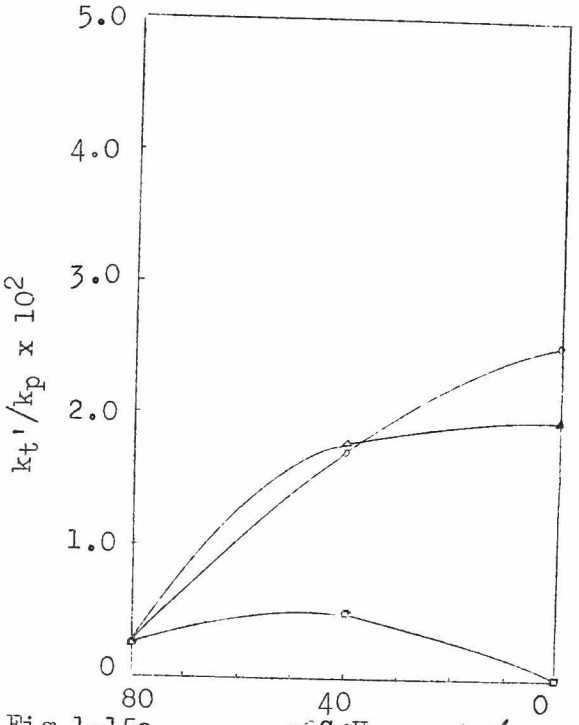

Fig.1-15a

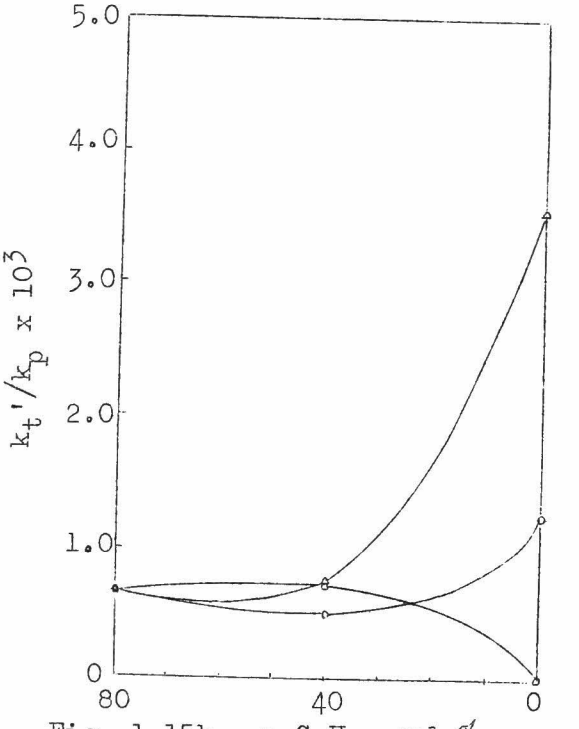

Fig. 1-15b

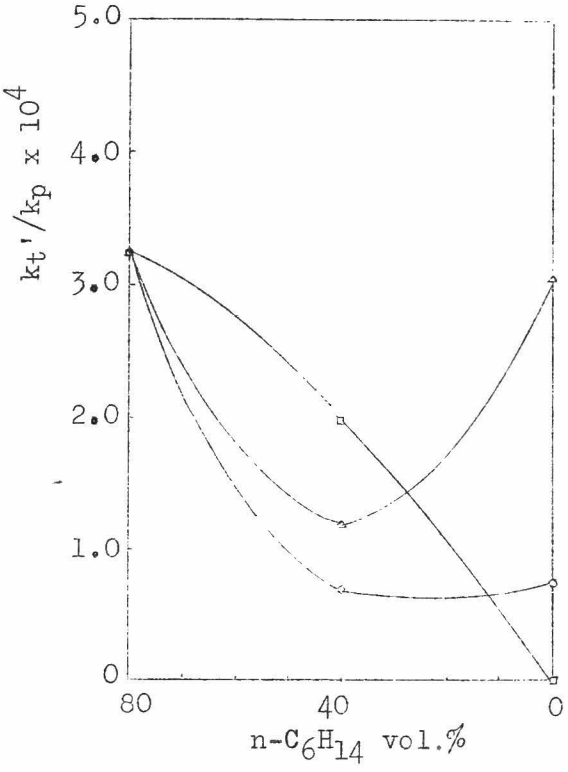

Fig. 1-15c

Fig. 1-15 The relationship between k_t'/k_p and the solvent composition

(□): Toluene—n-hexane mixture, [M] = 20 vol.%

(○): Chloroform—n-hexane mixture. [M] = 20 vol.%

(△): Methylene chloride—n-hexane mixture, [M] = 20 vol.%

a: -20°C, b: -50°C, c: -70°C

in detail later.

4.2.2 The relationship between k_t'/k_p and solvent composition

As in 4.2.1, k_t'/k_p was plotted against solvent composition and gave Fig. 1-15 a, b, c.

From Fig. 1-15 the following points emerged:—

(1) k_t'/k_p was large in the n-hexane-rich part. The styrene polymerization showed that a unimolecular termination reaction can scarcely occur in a solvent of low dielectric constant, such as n-hexane. In order to explain this contradiction, loss of activity of the growing ion by precipitation was assumed as the chain breaking reaction without participation of monomer. Consequently, the k_t' term in n-hexane includes the precipitation effect and is, therefore, large in spite of low dielectric constant. Table 1-4 shows that $(E_t' - E_p)$ and $(S_t' - S_p)$ in n-hexane are very small compared with those in other solvents, and that the nature of k_t' is also different. Furthermore, the expectation that the precipitation effect will be enhanced at lower temperature was fulfilled since the difference between k_t'/k_p in n-hexane and k_t'/k_p in other solvents increased with decreasing temperature.

These findings support the precipitation explanation.

(2) k_t'/k_p was large in methylene chloride-rich solvent: if one admits the assumption that k_t' consists mainly of k_t, this trend of k_t'/k_p accords well with the view that increase of dielectric constant facilitates unimolecular termination. In order to elucidate this point further, k_t'/k_p was plotted against dielectric constant of solvent (Fig. 1-16).

As stated above, n-hexane which shows an abnormal effect was omitted in this plot. In Fig. 1-16 k_t'/k_p increased remarkably when the solvent dielectric constant

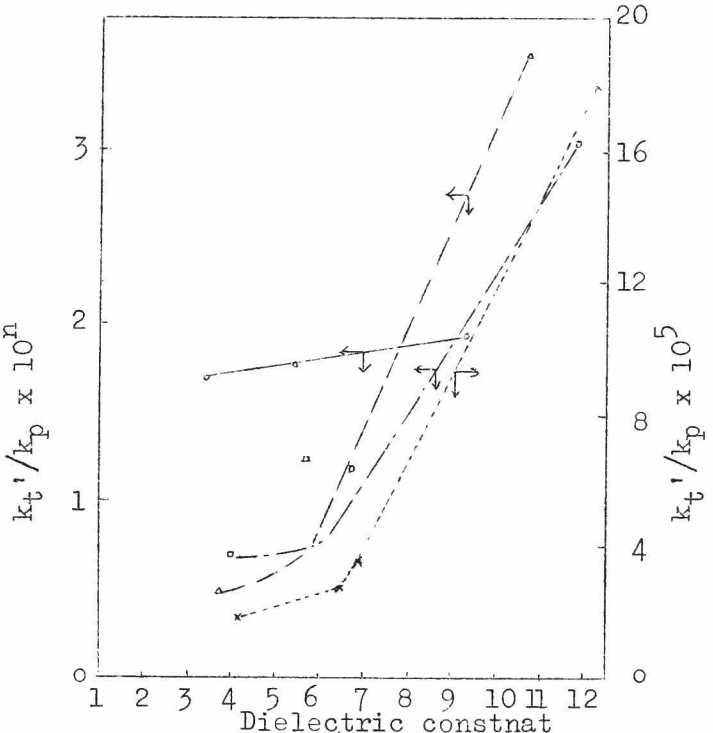

Fig.1-16 The dependence of k_t'/k_p on dielectric constant
(○): -20°C, n=2 (△): -50°C, n=3 (□): -70°C, n=4
(×): -78°C

rose above 6, and readiness with which the unimolecular termination in a polar solvent occurs was confirmed. On the other hand, k_t'/k_p tends to converge to a low value at low solvent dielectric constant. This supports the assumption made in calculating the rate constant, that k_t can be neglected in toluene having a low dielectric constant and not causing any special effect such as precipitation.

A discussion regarding activation energy and activation entropy in relation to solvent is essentially bound up with polymerization, but it would be premature to enter into a discussion here.

To sum up, the present investigation established that in cationic polymerization of α-methylstyrene the rate constant ratio could be calculated from the degree of polymerization of polymer on an assumption that k_t is zero in a solvent which giving a homogeneous polymerization and of low dielectric constant. The rate constant ratios obtained were plotted against solvent dielectric constant and it was found that k_{tm}/k_p was a minimum at dielectric constant about 6, and that k_t'/k_p became small in solvents of dielectric constant below 6 and became large at dielectric constant over 6. These tendencies were found

at all four temperatures used. These results suggest that the nature of the growing ion-pair is profoundly affected by the variation in solvent dielectric constant.

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Chapter 2 Isobutene

1. Introduction

There have been many studies of cationic polymerization of isobutene[1], and the polymerization kinetics and polymer structure have been elucidated. The author tried to obtain some information about the relationship between elementary reactions in cationic polymerization e.g., nature of the growing ion-pair, and the polymerization conditions, from the degree of polymerization, and the experimental results for α-methylstyrene was given in Chapter 1. Of the many investigations relating to isobutene, few have been carried out for the above purpose. Chapter 1 gave experimental results suggesting that the monomer transfer reaction in α-methylstyrene polymerization is partly the same as and partly different to that found in styrene polymerization. Since α-methylstyrene resembles in structure both styrene and isobutene, it is very interesting to study the effect of nature of the growing ion-pair on the polymerizations of isobutene, styrene and α-methylstyrene.

In this Chapter, the effect of the growing ion-pair of isobutene on the elementary reactions was investigated using the degree of polymerization of the resultant

polyisobutene, and the correspondence of the elementary reactions to the end group of the polymer was investigated. Furthermore, the results for isobutene polymerization were compared with those for other monomers, and the mechanisms of the monomer transfer and unimolecular termination reactions were discussed. In Chapter 1, the role of solvent in the cationic polymerization of α-methylstyrene was studied, while in this Chapter the role of the catalyst, in addition to the solvent effect, was studied and the role of the growing ion-pair in the cationic polymerization was clarified.

2. Experimental

2.1 Reagent

Isobutene (Phillips, purity 99.3 wt.%) was distilled from a cylinder at room temperature, dehydrated through a long potassium hydroxide tube, and condensed into a buret precooled to -78°C. A given amount of isobutene was taken from the buret.

Methylene chloride, chloroform, and n-hexane were used as polymerization solvents. The purification methods were described in Chapter 1.

Titanium tetrachloride (Extra pure) was distilled

into a small glass ampoule, which was broken in the polymerization solution to initiate the polymerization (b.p. 136°C/760mmHg).

Stannic chloride (Extra pure) was distilled from phosphorus pentoxide into a small glass ampoule, which was broken in the polymerization solution to initiate polymerization (b.p. 111.6-111.8°C).

Trichloroacetic acid (Guaranteed Reagent) was used as co-catalyst.

2.2 Procedure

2.2.1 Polymerization

40 ml.of solvent was introduced into a 100 ml.flask equipped with a long calcium chloride tube and a catalyst inlet. When co-catalyst was used, it was added to the solvent prior to addition of the catalyst. The flask was cooled to about -20°C, and isobutene cooled to -78°C was added from the buret. In order to compensate for the change in dielectric constant of the polymerization solution due to variation of monomer concentration, the concentration of monomer was reduced by adding the right amount of n-hexane. The polymerization solution thus prepared was cooled to the requisite temperature and the catalyst added to initiate the polymerization. In the

present polymerizations, the water content was found to be a few m mole/l. Polymerization was effected in a thermostatted low temperature bath. As in the α-methylstyrene polymerization, the polymerization was stopped when conversion exceeded 30%. The treatment of the polymer was described in Chapter 1.

2.2.2 Bromination

Unsaturation in the polymer was determined by bromination. A carbon tetrachloride solution of the polymer of known concentration was first prepared. To this a carbon tetrachloride solution of bromine of known concentration was added. After the mixture had stored four hours,[2),3)] potassium iodide was added to give iodine in place of the unreacted bromine. Aqueous sodium thiosulfate solution of known concentration was added in slight excess. The unreacted sodium thiosulfate was titrated with aqueous iodine-potassium iodide solution which was previously standardized against aqueous sodium thiosulfate solution. Calculation gave the numbers of double bonds in the polymer.

2.2.3 Infrared spectrum

A potassium bromide plate was made from exhaustively dehydrated potassium bromide, and a carbon disulfide

solution of the polyisobutene run on to it. The carbon disulfide was evaporated giving a thin polymer film-on-potassium bromide disk. After storing the film for a long time in a vacuum, it was subjected to infrared analysis using a Shimadzu IR-27 spectrometer.

2.3 Determination of the degree of polymerization and calculation of the rate constant ratio

Toluene was used as the solvent with most of polyisobutenes and the intrinsic viscosity of the resultant solution was measured at 30°C. The molecular weight of the polyisobutene was calculated using equation (2-1).[4]

$$[\eta] = 2.0 \times 10^{-4} \times \bar{M}_n^{0.67} \quad (\bar{M}_n = 7 - 1300 \times 10^3) \qquad (2\text{-}1)$$

Low molecular weight polyisobutene obtained at -20°C by using stannic chloride—trichloroacetic acid as the catalyst was dissolved in benzene and the intrinsic viscosity was determined at 30°C. The molecular weight of the polymer was calculated using equation (2-2).[4]

$$[\eta] = 6.1 \times 10^{-4} \times \bar{M}_n^{0.56} \quad (\bar{M}_n = 1 - 1300 \times 10^3) \qquad (2\text{-}2)$$

From the molecular weight of polymer calculated by equations (2-1) and (2-2), the rate constant ratios were

determined, as for α-methylstyrene polymerization. In the cationic polymerization using the solvent mentioned above, the chain transfer reaction to solvent may reasonably be neglected. Then equation (2-3) was derived for the relationship between the degree of polymerization and the initial monomer concentration, where $k_t' = k_t + k_{ts}[X] + k_{ts}[S]$, i.e.:—

$$1/\bar{p} = k_{tm}/k_p + k_t'/k_p \cdot 1/[M] \qquad (2\text{-}3)$$

k_t' containing the term for reactions with impurity and with solvent, if present, as well as for the unimolecular termination reaction. It was previously stated that in the polymerization of styrene k_t is considered to be very small for non-polar solvents.[5] If this also holds for polymerization of isobutene in n-hexane, equation (2-3) will become:—

$$1/\bar{p} = k_{tm}/k_p + k_{ts}/k_p \cdot [S]/[M] \qquad (2\text{-}3')$$

When polymerization is carried out in a polar solvent such as methylene chloride (methylene chloride 40 ml., monomer + n-hexane 10 ml.), k_t can no longer be neglected, and equation (1-12) should apply. The chain transfer constant ratio for n-hexane (k_{ts}/k_p) was determined using equation (2-3'), and introduced into equation (1-12).

This attempted evaluation failed because k_t'/k_p in methylene chloride was found to be negative, which was absurd. Hence instead of the chain transfer reaction to n-hexane, the unimolecular termination reaction term was assumed to predominate in k_t', i.e., equation (2-3) was used instead of equation (2-3').

Plotting the reciprocals of degree of polymerization against the reciprocals of initial monomer concentration, the rate constant ratios were calculated, by equation (3-3).

3. Results

3.1 The appearence of the polymerization system

The polymerization system had a pale yellow color when titanium tetrachloride was used as the catalyst, but was colorless when stannic chloride was used.

All of solvents used dissolved the catalyst to give homogeneous solutions. But sometimes in polymerization in methylene chloride, polymer formed around the catalyst immediately after the latter was added, covering it. Polyisobutene did not dissolve in methylene chloride. In polymerization at -20°C, low molecular weight polyisobutene precipitated as a jelly, but in polymerization

at $-78^{\circ}C$, the high molecular weight polyisobutene precipitated as a white mass.

Polymerization can usually attain 100% conversion.

3.2 Polymerization rate

In order to compare the dependency of the over-all polymerization rate on polymerization conditions, the conversion per unit m mole of catalyst per hour was calculated. The results are shown in Table 2-1 where the polymerization rate is an average one for 80-90% conversion. Conversion was but slightly affected by initial monomer concentration, and Table 2-1 gives results for polymerization with the initial monomer concentration of 0.23 mole/l. (2 vol.%).
Co-catalyst was added to keep the catalyst/co-catalyst ratio 3-4.

Table 2-1 shows that the polymerization rate was much higher when polymerization was initiated by titanium tetrachloride than when initiated by stannic chloride, and that trichloroacetic acid had an accelerating effect.

For discussion of the effect of solvent, dielectric constants of the solvents[6] at various temperatures are given in Table 2-2.

Table 2-1 The average reaction rate in the isobutene polymerization (%/m mole catalyst/hr.)
$[M]_0$ = 0.23 mole/l. [catalyst]/[TCA] = 3-4

Catalyst	$TiCl_4$			$TiCl_4$·TCA			$SnCl_4$·TCA		
Temp.(°C) Solvent	-20	-50	-78	-20	-50	-78	-20	-50	-78
$n\text{-}C_6H_{14}$	43	40	6	90	143	195	0	8.3	4.2
$CHCl_3$	45	44	226	268	289	848	10	23	47
CH_2Cl_2	73	171	191	82	662	301	41	144	77

Table 2-2 The dielectric constants of polymerization solvents

Solvent → / Temp.(°C) ↓	$n\text{-}C_6H_{14}$	$CHCl_3$	CH_2Cl_2
-20	1.965	5.65	11.00
-50	2.006	6.45	12.77
-78	2.046	7.58	14.89

Tables 2-1 and 2-2, show that the polymerization rate in non-polar n-hexane was smaller than in a polar solvent. Though the polymerization rate in methylene chloride was unexpectedly small because of polymer precipitation, the polymerization rate was in general larger in a more polar solvent.

Over the temperature range used in the present investigation, the general tendency for polymerization rate to increase at higher temperature was not observed. Plesch[7] observed an unusual effect of temperature on rate in cationic polymerization of isobutene: rate of polymerization of isobutene by titanium tetrachloride was a minimum at -50°C. He considered that lowering the temperature decreases the positive over-all activation energy and hence the total rate, while increasing the dielectric constant of the solvent with consequent increase in over-all polymerization rate. Below -50°C, the later effect predominates and the over-all polymerization rate has a negative activation energy. Table 2-1 shows the higher rate at lower temperatures in the present case. But the behavior of the polymerization rate, especially in polymerization at -78°C, is not quite identical with that reported by Plesch. However, allowing for a cut in polymerization rate at -78°C due to precipitation of polymer Plesch's mechanism satisfactorily explains the present results.

3.3 Degree of polymerization

Keeping the monomer concentration constant at 2.29 mole/l.(20 vol.%), the effects of catalyst and solvent on

polymer intrinsic viscosity were studied. As seen from Fig. 2-1 a, b, c, a solvent effect was scarecely observed when stannic chloride—trichloroacetic acid was used as the catalyst (the degree of polymerization of the polymer was low), but it was clearly marked when titanium tetrachloride was employed. It was also found that the more polar the solvent, the lower the intrinsic viscosity of the polymer. This is in accord with the experimental results obtained in α-methylstyrene polymerization with solvent of dielectric constant above 6, but the reverse of what obtained in styrene polymerization.[8)]

3.4 Relationship between polymerization conditions and the rate constant ratio

In order to ascertain the relationship between the nature of the growing ion-pair and the rate constant ratio, isobutene was polymerized at various monomer concentrations under twenty seven different conditions (three temperatures, three solvents, three catalysts). In each polymerization, the rate constant ratio was found using equation (2-3). Fig. 2-2 a, b, c. shows examples:—

The logarithms of the rate constant ratios were plotted against the reciprocals of the absolute temperatures to obtain the differences in activation energies:

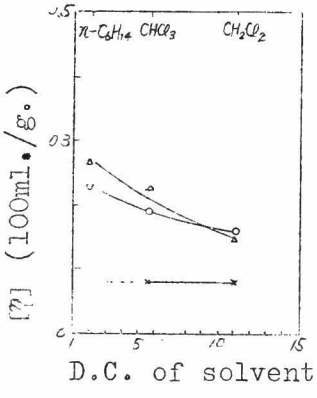


Fig. 2-1c

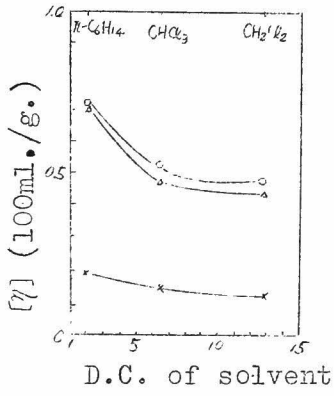


Fig. 2-1b

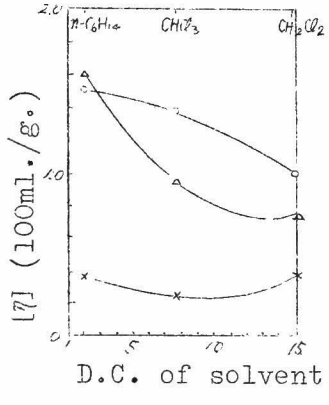


Fig. 2-1a

Fig. 2-1 The relationship between the intrinsic viscosities of polyisobutene and the dielectic constants of polymerization solvents

(○): $TiCl_4$ catalyst, $[TiCl_4]$ = 0.003-0.048 mole/l.

(△): $TiCl_4$·TCA catalyst, $[TiCl_4]$ = 0.005-0.008 mole/l. $[TiCl_4]/[TCA]$ = 3-4

(×): $SnCl_4$.TCA catalyst, $[SnCl_4]$ = 0.023-0.036 mole/l. $[SnCl_4]/[TCA]$ = 3-4

a: -78°C b: -50°C c: -20°C

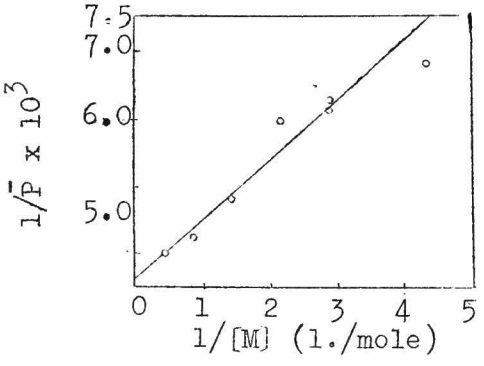


Fig. 2-2a

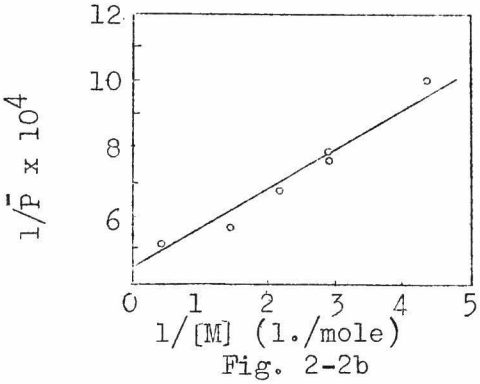


Fig. 2-2b

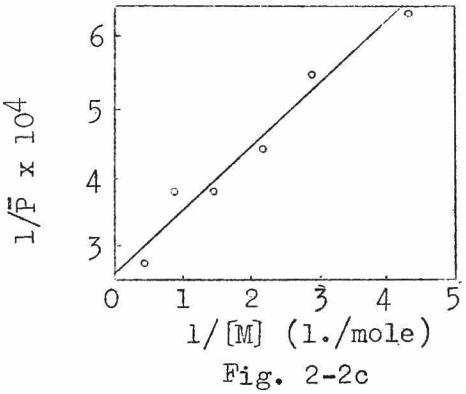


Fig. 2-2c

Fig. 2-2 The relationship between $1/\bar{P}$ and $1/[M]$
Polymerization temperature -50°C
a: $SnCl_4$·TCA—CH_2Cl_2 system
b: $TiCl_4$·TCA—$CHCl_3$ system
c: $TiCl_4$ —— $n\text{-}C_6H_{14}$ system

see Fig. 2-3.

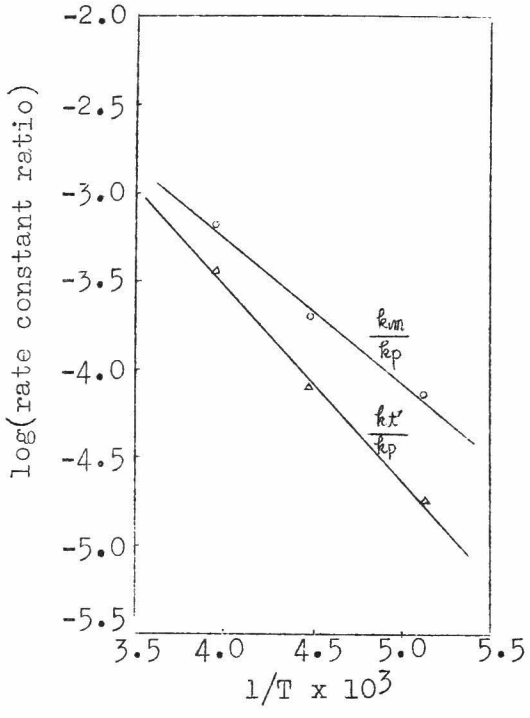


Fig. 2-3 The estimation of the activation energy differences using Arrhenius' plot $n\text{-}C_6H_{14}$—$TiCl_4$·TCA system

Complete results are summarized in Table 2-3.

3.5 Bromination of polymer

Determination of the number of double bonds by bromination was carried out on polymers obtained under different conditions. The results are given in Table 2-4.

Table 2-3 Summary of the reaction rate constant ratios($\times 10^{-4}$) and the activation energy differences

Catalyst→		$TiCl_4$			
Temp.(°C)→ Solvent ↓		-20	-50	-78	Activation energy differences (Kcal/mole)
$n\text{-}C_6H_{14}$	k_{tm}/k_p	10.3	2.60	0.80	4.2
	k_t'/k_p	5.2	0.90	0.48	4.0
$CHCl_3$	k_{tm}/k_p	12.0	3.00	1.00	4.6
	k_t'/k_p	7.6	1.48	0.70	4.0
CH_2Cl_2	k_{tm}/k_p	21.2	6.60	1.52	4.4
	k_t'/k_p	8.0	1.40	0.39	5.1

$TiCl_4$·TCA				$SnCl_4$·TCA			
-20	-50	-78	Activation energy differences (Kcal/mole)	-20	-50	-78	Activation energy differences (Kcal/mole)
6.6	2.00	0.72	3.7	—	17.0	6.7	2.7
3.6	0.80	0.18	5.0	—	10.5	2.5	4.3
25.2	4.48	1.56	4.6	60.0	22.8	8.1	3.4
2.0	1.04	0.56	2.1	77.0	11.2	9.0	3.4
26.9	5.68	2.44	4.2	60.0	36.0	5.7	3.9
1.3	0.56	0.38	2.2	54.0	9.0	3.3	4.8

Table 2-4 The relationship between the polymerization conditions and the numbers of double bond in a polymer molecule

Polymerization conditions			The numbers of double bond in a polymer molecule
Catalyst	Solvent	Temp.(°C)	
$SnCl_4$·TCA	$n\text{-}C_6H_{14}$	-78	0.61 0.99
	$CHCl_3$		1.71 2.12
	CH_2Cl_2		3.69 3.49
	CH_2Cl_2	-50	2.72
	$CHCl_3$	-20	0.89 1.35
	CH_2Cl_2		1.80 1.78
$TiCl_4$	CH_2Cl_2	-50	2.31
$TiCl_4$·TCA	CH_2Cl_2	-50	1.74
	$CHCl_3$	-20	3.06
	CH_2Cl_2		3.07

To calculate the number of double bonds, it is necessary to know the true molecular weight. As in the present investigation the intrinsic viscosity was determined on unfractionated samples, the viscosity average molecular weight was obtained instead of the number average molecular weight, leading to a larger number of double bonds. Furthermore, part of the bromine reacted may be consumed in side reactions e.g.,in substitution.[9] This again leads to a larger number of double bonds. Though these difficulties are inherent in the procedure, comparative values of the number

of double bonds may be valid. Table 2-4 shows that the polyisobutenes obtained here were mixtures of saturated and unsaturated polymers, and that the more polar the solvent, the higher the proportion of unsaturated polymers.

3.6 Infrared spectrum of polymer

The infrared spectrum of the polymers was studied by the method described in 2.2.3. A typical infrared spectrum is shown in Fig. 2-4.

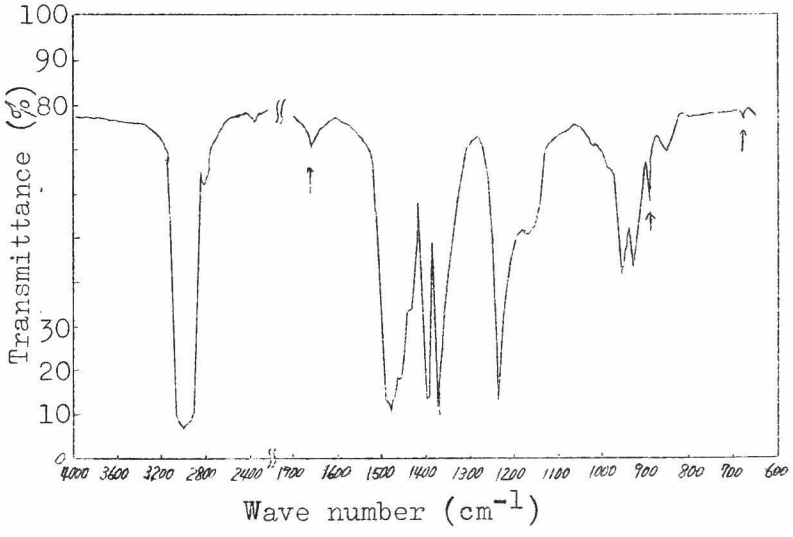


Fig. 2-4 Infrared spectrum of polyisobutene. Polymer was produced in CH_2Cl_2 at -20°C by $TiCl_4$·TCA, $[\eta]$ being 0.125.

Weak absorptions at wave numbers of 680, 895, 1660cm^{-1} are ascribed to an asymmetric disubstituted double bond. (as already reported by Dainton[10]). The presence of unsaturation in the polymer was confirmed by infrared spectroscopy as well as by bromination. Furthermore, since infrared analysis showed that the double bond is an asymmetric disubstituted one, it was thereby proved to exist at the polymer end. It is considered that the double bond is produced when the transfer or the termination reaction occurs by loss of a proton from the growing chain end.

For comparison, the infrared spectrum of poly-α-methylstyrene is shown in Fig. 2-5 a, b. From Fig. 2-5 a, very weak absorption was found at 895cm^{-1}. This can be ascribed to an asymmetric disubstituted double bond, as in polyisobutene. However, Sakurada[11] proposed to ascribe this absorption to crystallinity of polymer. In order to clarify this point, the poly-α-methylstyrene of Fig. 2-5 a was brominated. (It will be shown in Chapter 7 that the crystalline poly-α-methylstyrene cannot be produced under the polymerization condition to which Fig. 2-5 a relates). The infrared spectrum of the brominated polymer is shown in Fig. 2-5 b, where the absorption at 895cm^{-1} has disappeared. Hence, the absorption at 895cm^{-1} of poly-α-methylstyrene

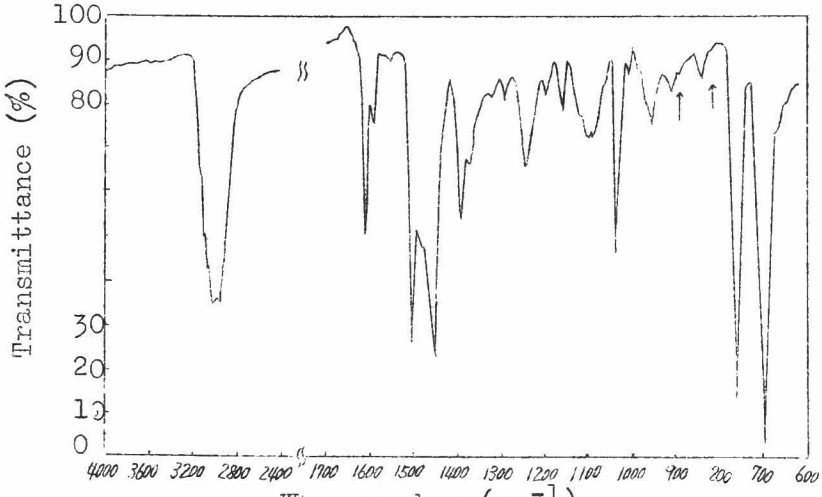


Fig. 2-5a

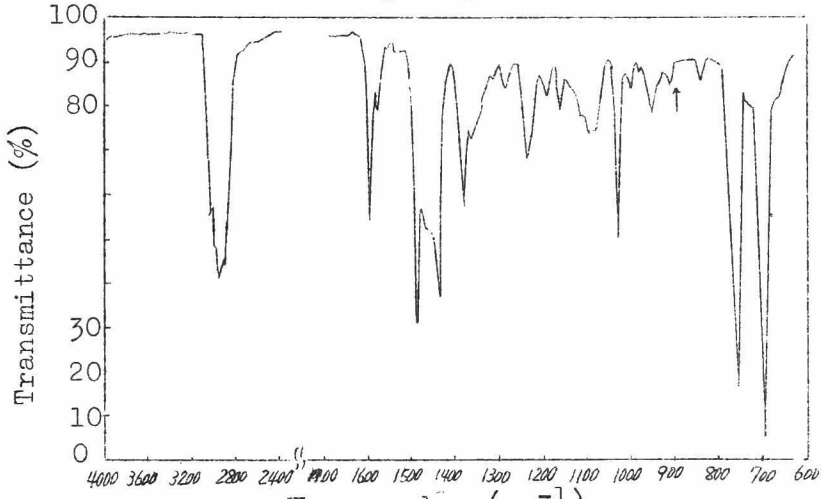


Fig. 2-5 b

Fig. 2-5 Infrared spectrum of poly-α-methylstyrene. Polymer was produced in CH_2Cl_2 at -20°C by $BF_3 \cdot O(C_2H_5)_2$, $[\eta]$ being 0.062.

a: Before bromination

b: After bromination

is ascribed to a double bond of the $R_1R_2C = CH_2$ type.

4. Discussion

The experimental results described above give some information about the polymerization mechanism for isobutene. However, the monomer transfer and the unimolecular termination reaction for which quantitative results were given will be discussed. The data summarized in Table 2-3 were plotted against solvent dielectric constant in Figs. 2-6 a, b, c and 2-7 a, b, c.

From these Figures, the effects of solvent and catalyst on the reactions can be inferred and are summarized as follows:—

(1) At -20°C to -78°C k_{tm}/k_p is larger the more polar the solvent, though when stannic chloride—trichloroacetic acid catalyst was used, the effect of dielectric constant was not clear.

(2) At -50°C and -78°C k_t'/k_p was affected little by solvent dielectric constant. But at -20°C, it was found to be dependent.

(3) Both k_{tm}/k_p and k_t'/k_p were much larger in polymerization by stannic chloride than when using titanium tetrachloride.

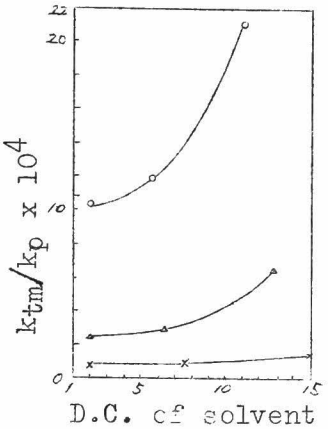


Fig. 2-6a

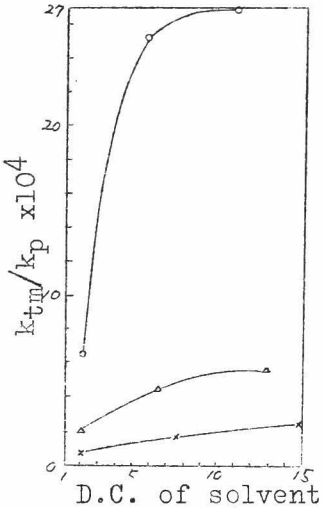


Fig. 2-6b

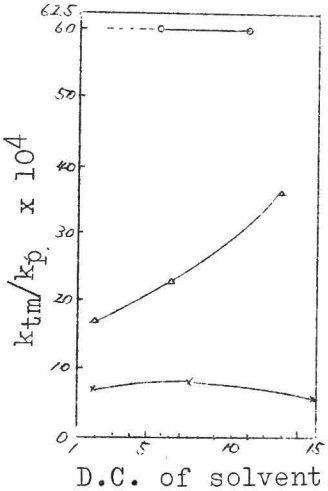


Fig. 2-6c

Fig. 2-6 The plot of k_{tm}/k_p versus the dielectric constants of polymerizing solvents in the isobutene polymerization
Polymerization temperature: (○): -20°C, (△): -50°C, (×): -78°C
a: $TiCl_4$ catalyst b: $TiCl_4$·TCA catalyst
c: $SnCl_4$.TCA catalyst

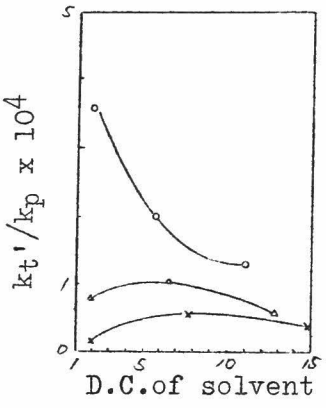


Fig. 2-7b

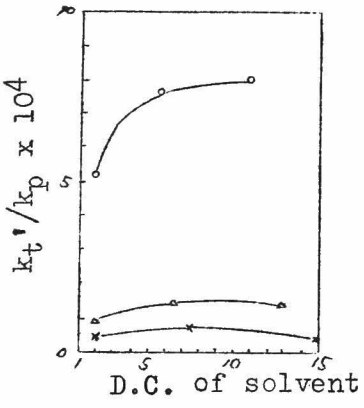


Fig. 2-7a

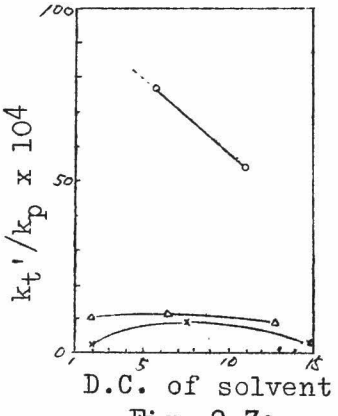


Fig. 2-7c

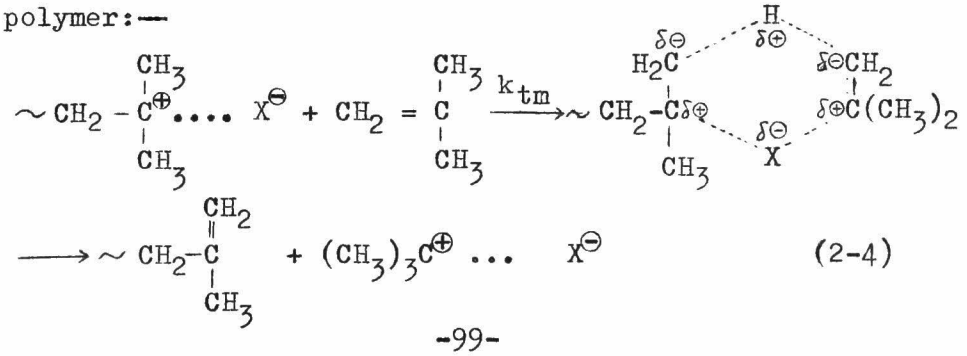
Fig. 2-7 The plot of k_t'/k_p versus the dielectric constants of polymerizing solvents in the isobutene polymerization
Polymerization temperature: (○): -20°C, (△): -50°C (×): -78°C
a: $TiCl_4$ catalyst, b: $TiCl_4$·TCA catalyst
c: $SnCl_4$·TCA catalyst

(4) Difference in catalyst (titanium tetrachloride or stannic chloride) was reflected in the rate constant ratio more than was difference in co-catalyst (water or trichloroacetic acid).

Hence it was concluded that the ion-pair consisting of carbonium ion plus counter anion produced from titanium tetrachloride or titanium tetrachloride—trichloroacetic acid is unreactive in the transfer and the termination reactions, and that the effect of solvent dielectric constant on rate constant ratio is regularly manifest for this growing ion-pair. On a basis of these conclusion, the following reaction mechanisms are proposed for the transfer and termination reactions:—

4.1 The monomer transfer reaction

The following mechanism can be offered for the monomer transfer reaction of isobutene since (1) k_{tm}/k_p increases in a more polar solvent (this suggests the ion-forming reaction) and (2) a terminal double bond is present in the polymer:—



(2-4)

Mechanism (2-4) can explain all of the experimental results obtained here and is essentially the same as that so far reported in the literature on cationic polymerization of isobutene.[12),13)] The presence of a double bond at the end of the polymer implies proton expulsion from the growing ion. There are two ways in which a proton can be expelled, that is, expulsion from a penultimate methyl group or from a penultimate methylene group. The double bond due to expulsion of a proton from a methylene group is a **trisub-**stituted double bond which is stabilized by hyperconjugation more than **disubstituted** double bond resulted from the methyl proton expulsion. If the reaction path were determined mainly by the stability of the product, proton expulsion would be expected to occur at the penultimate methylene group. However, infrared analysis shows the presence of an asymmetric di substituted double bond only. This suggests that in the monomer transfer reaction reaction path is determined by a steric factor rather than by the electrostatic one and this is why mechanism (2-4) is proposed.

A similar mechanism was proposed by Kennedy[13)] to explain his experimental results. He stated that in the activated state of reaction (2-4) dissociation of the

growing ion-pair is unnecessary. However, the present author suggested that the ion-pair necessarily dissociates in the activated state of the monomer transfer reaction, and based his view on the experimental results given above and on the ideas set out below. That the propagation reaction takes place when the growing carbonium ion attacks a β -carbon atom of a monomer and that the monomer transfer reaction takes place when the counter anion attacks an α -carbon atom of a monomer molecule may possibly explain the experimental results, but these possibilities remain to be investigated.

Mechanism (2-4) includes the process of extraction of a proton from a methyl group and that of ion-pair dissociation. These process should be accelerated by increase in dielectric constant of the medium, and this is in good agreement with what is found experimentally. Next, the experimental result that k_{tm}/k_p with stannic chloride is larger than k_{tm}/k_p with titanium tetrachloride will be discussed. The natures of the monomer transfer reaction and propagation reaction were considered vis a vis the nature of the growing ion-pair. The propagation reaction is facilitated by dissociation of the ion-pair into free ions, because in the propagation step a monomer is inserted between

a growing cation and its counter anion.[14),15)] Taking into account k_{tm}/k_p being larger in a more polar solvent, the dissociation of the ion-pair into free ions is more important in the monomer transfer reaction than in the propagation reaction. Then the effect of catalyst (counter anion) on k_{tm}/k_p is reduced to the effect of the counter anion on ion-pair dissociation. The difference between $SnCl_4 \cdot CCl_3COO^{\ominus}$ and $TiCl_4 \cdot CCl_3COO^{\ominus}$ lies in the nature of metal atom. Due to the lesser electropositivity of Sn and its larger ionic radius as compared with Ti, $SnCl_4 \cdot CCl_3COO^{\ominus}$ is more stable and more easily dissociated from the carbonium ion than is $TiCl_4 \cdot CCl_3COO^{\ominus}$. Hence, the monomer transfer reaction is more important in polymerization by stannic chloride than by titanium tetrachloride. The effects of catalyst and solvent are thus explained in relation to the nature of the growing ion-pair, and it can be concluded that in isobutene polymerization, the free ion form is more important in the monomer transfer reaction than in the propagation reaction.

In cationic polymerization of styrene, it was found that the less polar the solvent and the stronger the catalyst, the larger k_{tm}/k_p.[11)] When this experimental fact is considered in relation to the nature of the ion-pair, it can

be concluded that in styrene polymerization the ion-pair form is more important in the monomer transfer reaction than in the propagation reaction. This fact suggests that a different mechanism operates in the styrene monomer transfer reaction. The mechanism of the reaction and the role of the growing ion-pair in the latter will be discussed in Chapters 3 and 4.

For convenience it is proposed to name the monomer transfer reactions of isobutene and styrene the isobutene-type and the styrene-type respectively. The mechanism of the monomer transfer reaction in α-methylstyrene polymerization (Chapter 1) can tentatively be explained as follows, focussing on that reaction. In the polymerization of α-methylstyrene, k_{tm}/k_p increases with increasing solvent dielectric constant for dielectric constant above 6, but decreases with increasing dielectric constant of solvent at dielectric constant below 6. α-Methylstyrene has a methyl group which is connected with the isobutene-type monomer transfer reaction and a phenyl group which is connected with the styrene-type monomer transfer reaction. Therefore, in a polar solvent the isobutene-type monomer transfer reaction (free ion form important) and in a non-polar solvent the styrene-type monomer transfer reaction

(ion-pair form important) are considered to occur. The weak absorption at 895cm^{-1} in the infrared spectrum of poly-α-methylstyrene in Fig. 2-5a is taken as the evidence of occurrence of the isobutene-type monomer transfer reaction.

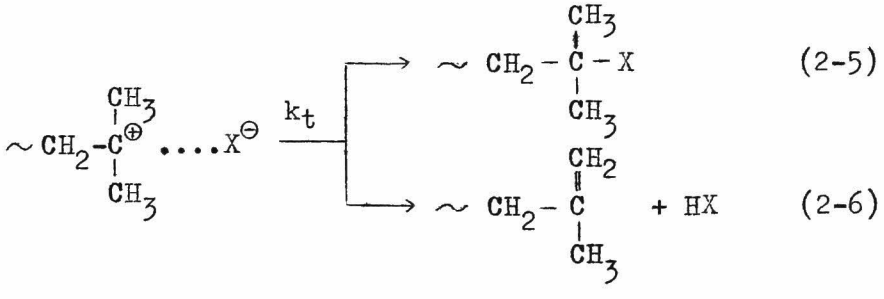
However, another explanation, propagation reaction explanation, could be given for the solvent effect on the k_{tm}/k_p value of α-methylstyrene. As will be seen in Chapter 11, the composition of the n-hexane—methylene chloride mixed solvent profoundly affects the propagation constant of isobutene in copolymerization of isobutene with styrene. There the reactivity (that is, k_p) of isobutene was found to increase with increasing solvent dielectric constant. Similar experimental results were also found by Overberger[16] in the cationic copolymerization of isobutene and p-chlorostyrene. Both isobutene and α-methylstyrene are α, α'-disubstituted ethylene. A solvent effect for the monomer reactivity ratio in the copolymerization of α,α'-disubstituted ethylene has also been observed by Smets et al.[17] in the field of anionic copolymerization. A tentative explanation of such a solvent effect was given by Mizote,[18] who considered the relationship between the solvent as it affects the nature of the growing ion-pair and the effect of the latter on the steric requirements at the propagating step. So in the case of the experimental results with α-methylstyrene, this explanation

of Mizote's, regarding effect of solvent on k_p, may hold instead of the above explanation relating to k_{tm}.

4.2 The unimolecular termination reaction

As described earlier, k_t'/k_p includes the unimolecular termination (k_t), the solvent transfer ($k_{ts}[S]$) and the reaction with impurity ($k_{tx}[X]$) terms. For the reason stated previously $k_{ts}[S]$ can be neglected, and $k_{tx}[X]$ can also be neglected because [X] is extremely small (less than a few m mole/l). k_t was considered to be a predominant term in k_t'.

Two different mechanisms can be put forward for the unimolecular reaction, as was done by Plesch:—[12),19)]



(2-5)

(2-6)

Reaction (2-5), which is an ion neutralization process, is facilitated by a non-polar solvent. On the other hand, reaction (2-6), which is an ion-forming reaction, occurs readily in a polar solvent. The following experimental results for k_t'/k_p can be explained in terms of

the above considerations:

(1) k_t'/k_p depends but little on solvent dielectric constant of solvent.

(2) Polyisobutene is a mixture of unsaturated polymers and saturated polymers.

The double bond shown in Table 2-4 is produced partly by the reaction (2-4) and partly by the reaction (2-6). Since such a polymerization condition as the initial monomer concentration was not accurately known in the present investigation, the unsaturation could not be correlated with α-value as in Chapter 5. Distinction between a double bond between from reaction (2-4) and one from reaction (2-6) was not made.

To summarize: it was established that, contrary to the case of styrene, the degree of polymerization of polyisobutene was higher when polymerization was carried out in a less polar solvent by a stronger catalyst. This difference was ascribed to difference between monomer transfer reaction mechanisms. Occurrence of an isobutene-type and of a styrene-type monomer transfer reaction was recognized. The effect of the nature of the growing ion-pair on the transfer and the termination reactions was discussed.

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Chapter 3 Ortho- and Para-methoxystyrene

1. Introduction

The effect of the nature of the growing ion-pair on the monomer transfer and unimolecular termination reactions under various conditions of cationic polymerization have been investigated in Chapters 1 and 2: tentative mechanisms were proposed for both reactions in the polymerization of isobutene. Styrene, the cationic polymerization of which has long been an object of study, has also been studied in our laboratory and a monomer transfer reaction differing in mechanism from that for isobutene has been deduced. Hence it is very interesting to investigate the mechanism of the monomer transfer reaction for styrene and its derivatives.

Aromatic nuclei with a considerable nucleophilic activity interact with a growing carbonium ion, since it is found experimentally that aromatic hydrocarbons can act as a chain transfer agent or as a molecular termination agent for cationic polymerization[1], and that para-substituted toluene is detected in the cationic polymerization of styrene in toluene.[2] Since styrene is an aromatic monomer, it is possible that the phenyl group of styrene

reacts with a growing carbonium ion. These considerations showed that in the polymerization of styrene and its derivatives, the growing ion-pair undergoes a transfer reaction involving the phenyl group of the monomer.

In the present chapter the effects of ortho- and para-substituents on the monomer transfer and termination reactions in the polymerization of styrenes are studied. (i) The monomer transfer and unimolecular termination constant ratios were estimated under the various conditions; (ii) The reaction site of the monomer transfer reaction was investigated by comparing the results of calculation by molecular orbital theory with the experimental results; (iii) The end groups of the polymer were identified by infrared analysis and were interpreted in term of the mechanism of the monomer transfer and the unimolecular termination reaction.

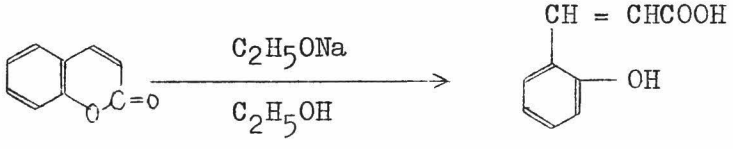
Using these approaches, the effects of the substituents on the monomer transfer and unimolecular termination reactions in the cationic polymerization of styrene and its derivatives were elucidated. The role of the reactivity of the growing ion-pair in the monomer transfer reaction is discussed.

2. Experimental

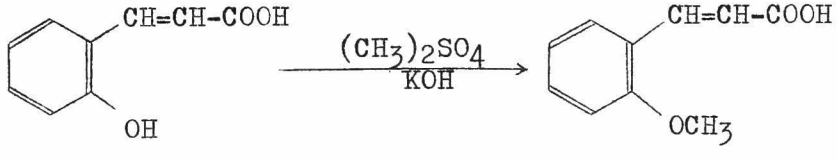
2.1 Synthesis of monomers

p-Methoxystyrene was synthesized from anisole and paraldehyde by a procedure reported elsewhere.[3] Monomer was purified and distilled just before use. (b.p. 82°-84°C/6mmHg, lit. 92°-93°C/13mmHg).

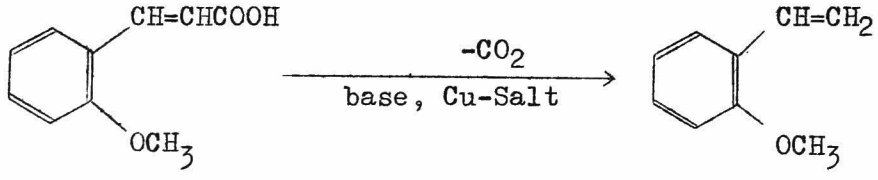
o-Methoxystyrene was synthesized from coumarin. Commercial coumarin was dissolved in ethyl alcohol and hydrolyzed by sodium ethoxide to give o-hydroxycinnamic acid. The procedure including the purification of the product were reported by Corsons.[4]



o-Hydroxycinnamic acid was dissolved in aqueous potassium hydroxide solution and methylated by dimethylsulfate to give o-methoxycinnamic acid. This procedure and the purification of the product were reported by Rengaswami et al.[5]



o-Methoxystyrene was obtained by the decarboxylation of o-methoxycinnamic acid. The procedure and purification of the product were reported by Marvel et al.[6)]



The monomer was washed repeatedly with alkali and water, then dried over anhydrous potassium carbonate, and distilled twice just before use.

Physical properties of o-methoxystyrene and the intermediates are summarized in Table 3-1. Use of the above synthetic route avoided isomeric by-products. The yield of o-methoxystyrene was 25-40% theoretical.

2.2 Reagents

Carbon tetrachloride, chloroform, methylene chloride and sometimes 1,2-dichloroethane were used as polymerization solvents. Boron trifluoride etherate was used as the polymerization catalyst. The purifications of chloroform, methylene chloride and boron trifluoride etherate have previously been described.

1,2-Dichloroethane (Guaranteed reagent) was washed

Table 3-1 Physical Properties of o-Methoxystyrene and Intermediates of Preparation

Materials	Observed value	Literature or theoretical value
o-Hydroxy-cinnamic acid	m.p.: 205°C (d.) C% : 66.50 H% : 5.18	m.p.: 207-8°C (d.) C% : 65.85 H% : 4.91
o-Methoxy-cinnamic acid	m.p.: 186°C C% : 67.50 H% : 5.68 b.p.: 92°C/9.5mmHg 78°C/7.5mmHg 72°C/4.8mmHg	m.p.: 185-6°C C% : 67.40 H% : 5.60 b.p.: 60.8°-62°C/3mmHg
o-Methoxy-styrene	n_D: 1.5619 (16.2°C) 1.5580 (26.5°C) 1.5530 (36.0°C) $d^{30°}$: 0.9987 C% : 80.49 H% : 7.59	n_D : 1.5566 (20°C) C% : 80.56 H% : 7.51

repeatedly with aqueous sodium hydroxide solution and water, dried over calcium chloride, and distilled from phosphorus pentoxide twice just before use (b.p. 83.0°C).

Carbon tetrachloride (Guaranteed reagent) was washed repeatedly with concentrated sulfuric acid, water, 10% aqueous sodium hydroxide solution and water, dried over

phosphorus pentoxide, and distilled twice from the latter just before use (b.p. 76.3 - 76.5°C).

2.3 Polymerization procedure

Known quantities of solvent and monomer, total volume 50 ml., were measured into a 100 ml. falsk with a catalyst inlet (syringe). The flask opened to the air via a calcium chloride tube, and was immersed in a thermostatted bath. By adding catalyst polymerizations were carried out at 30°, 0°, -20° and -50°C, and appeared to proceed homogeneously.

Polymerization was stopped by pouring the polymerizing solution into ammoniacal methyl alcohol. The polymer was precipitated by adding large quantities of methyl alcohol, and it was then washed repeatedly with methyl alcohol, and dried at 40°C in a vacuum.

2.4 Molecular weight determination

Polymer intrinsic viscosity was determined in toluene at 30°C. The following equations were used to calculate the molecular weight:—

poly- o-methoxystyrene :
$$[\eta] = 6.40 \times 10^{-5} \times \bar{M}_w^{0.71} \qquad (3\text{-}1)$$

poly- p-methoxystyrene :
$$[\eta] = 1.66 \times 10^{-4} \times \bar{M}_w^{0.65} \qquad (3\text{-}2)$$

where $\bar{M}_w$ is the weight average molecular weight. These equations were obtained from light-scattering measurements on fractionated samples in methyl ethyl ketone solution.

3. Results

3.1 Estimation of the ratio of the rate constants for the monomer transfer and spontaneous termination reactions.

The method of determining the rate constant ratios was described in detail in Chapter 1. Taking into account occurrence of monomer transfer reaction (3-3), unimolecular termination reaction (3-4) and reaction with adventitious impurities (3-5) in the cationic polymerization of methoxystyrenes, the reciprocal of the number-average degree of polymerization ($1/\bar{p}$) of the polymer obtained in the present system is given by equation (3-6). Solvent transfer reactions, which could also affect $\bar{p}$, could be neglected for the solvent used here.

Monomer transfer: $$P_n^+ + M \xrightarrow{k_{tm}} P_n + M^+ \quad (3\text{-}3)$$

Unimolecular termination: $$P_n^+ \xrightarrow{k_t} P_n \quad (3\text{-}4)$$

Reaction with impurity: $$P_n^+ + X \xrightarrow{k_{tx}} P_n(+X^+) \quad (3\text{-}5)$$

$$1/\bar{p} = k_{tm}/k_p + k_t'/k_p \cdot 1/[M] \quad (3\text{-}6)$$

$$(k_t' = k_t + k_{tx}[X])$$

In the above equations, M and [M] represent monomer and its concentration (mole/l.), X and [X] represent impurity and its concentration (mole/l.), and Pn denotes polymer having a $\bar{p}$ value of n. k_p, k_{tm}, k_t, and k_{tx} are the rate constants for propagation, monomer transfer, spontaneous termination and reaction with impurity, respectively. Thus, by measuring $\bar{p}$ for various [M] values and plotting $1/\bar{p}$ against $1/[M]$, k_t'/k_p and k_{tm}/k_p can be found from the slope and intercept of the straight line of equation (3-6). To this end, cationic polymerizations of methoxystyrenes were carried out varying the concentration of p-methoxystyrene over the range 1ml/50ml. to 7ml/50ml. ([M] = 0.149 - 1.04 mole/l.), and the o-methoxystyrene concentration over the range 1ml/50ml. to 5ml/50ml. ([M] = 0.149 - 0.746 mole/l.). Dielectric constants of o-methoxystyrene was measured by high frequency bridge method[7] and found to be 4.26 at 30°C, 4.58 at 0°C and 4.78 at -20°C, which are almost the same as those of chloroform.[8] The dielectric constant of p-methoxystyrene is also assumed to be almost the same as that of chloroform. Hence the dielectric constant of the chloroform solution is independent of [M]. In carbon tetrachloride, methylene chloride or 1,2-dichloro-

ethane solutions, the dielectric constant may be kept the same by adding the right amount of chloroform as [M] is reduced.

Examples of the determination of rate constant ratios by using equation (3-6) are shown in Figs. 3-1 and 3-2. The rate constant ratios determined under the various polymerization conditions are listed in Table 3-2.

Table 3-2 The rate constant ratios. ($\times 10^{-3}$)($BF_3 \cdot O(C_2H_5)_2$)

Solvent	Rate const. ratio	30°C	0°C	-20°C	-50°C
		o-Methoxystyrene			
CCl_4	k_{tm}/k_p	2.80	3.33	3.21	
	k_t'/k_p**)	~0	~0	0.087	
CH_2Cl_2	k_{tm}/k_p	2.92	3.80	3.24	3.10
	k_t'/k_p**)	2.38	1.08	0.60	0.35
		p-Methoxystyrene			
CCl_4	k_{tm}/k_p	5.60	4.40	3.10	
	k_t'/k_p**)	1.45	0.98	0.38	
$CHCl_3$	k_{tm}/k_p	4.40	3.68	3.10	
	k_t'/k_p**)	1.70	0.66	0.59	
CH_2Cl_2	k_{tm}/k_p	1.86*)	1.60	1.20	
	k_t'/k_p**)	0.77*)	0.43	0.27	

*) Values estimated in $(CH_2Cl)_2$

**) Dimension mole/l.

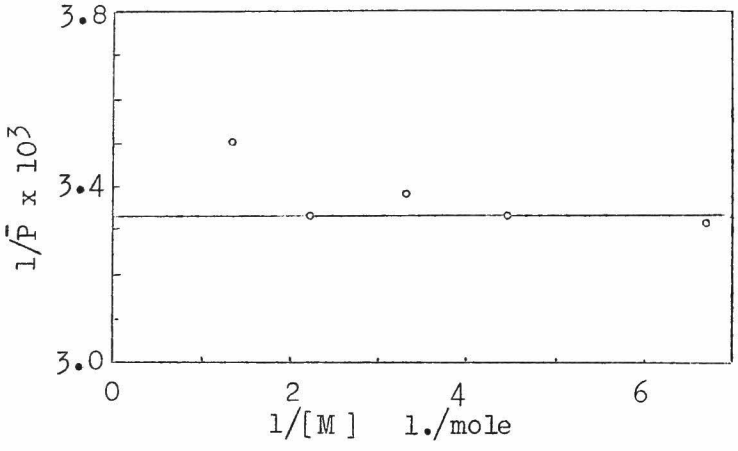


Fig. 3-1 The plot of $1/\bar{p}$ versus $1/[M]$
Polymerization of p-methoxystyrene in carbon tetrachloride at 0°C
$k_{tm}/k_p = 3.33 \times 10^{-3}$ $k_t'/k_p \simeq 0$

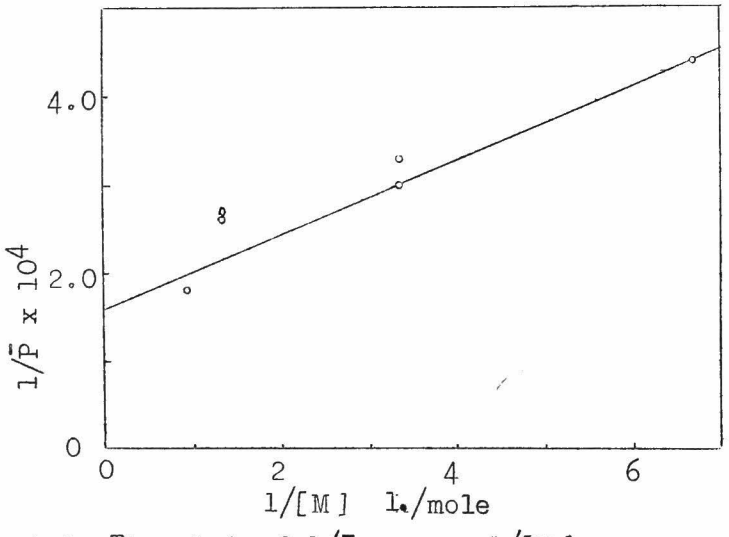


Fig. 3-2 The plot of $1/\bar{p}$ versus $1/[M]$
Polymerization of p-methoxystyrene in methylene chloride at 0°C, $k_{tm}/k_p = 1.60 \times 10^{-4}$
$k_t'/k_p = 0.43 \times 10^{-4}$

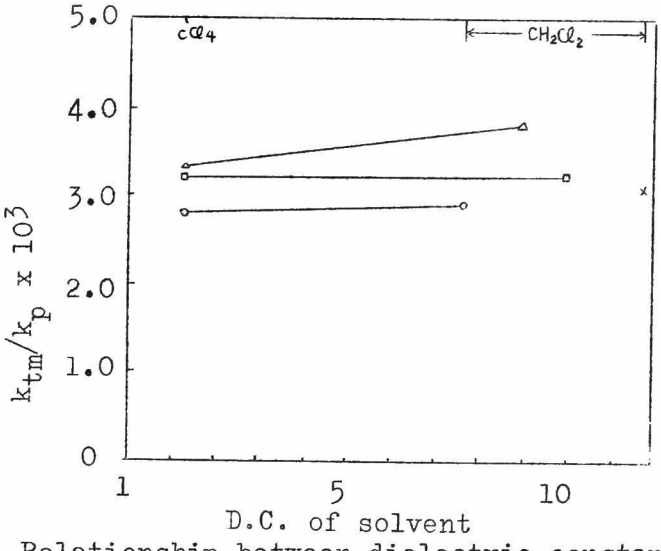


Fig. 3-3 Relationship between dielectric constant of the solvent and k_{tm}/k_p of o-methoxystyrene, (○): 30°C, (△): 0°C, (□): -20°C, (×): -50°C

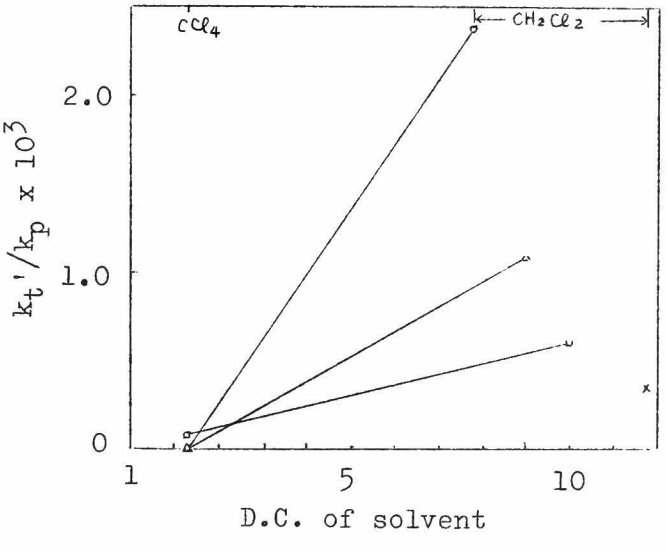


Fig. 3-4 Relationship between dielectric constant of the solvent and k_t'/k_p of o-methoxystyrene (○): 30°C, (△): 0°C, (□): -20°C, (×): -50°C

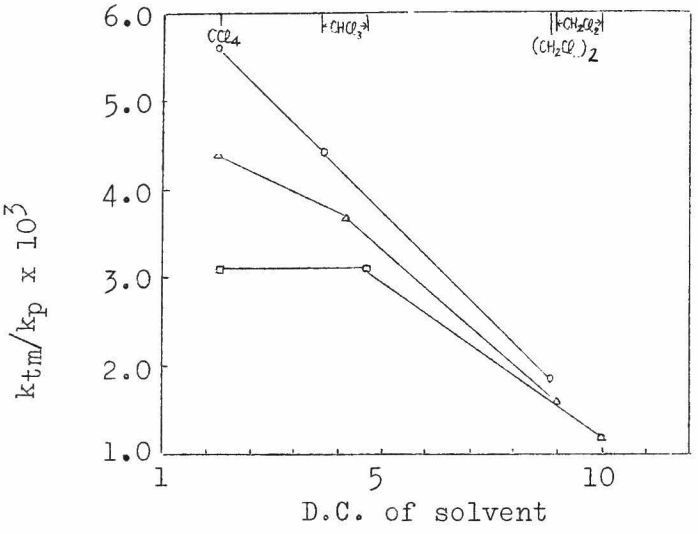


Fig. 3-5 Relationship between dielectric constant of the solvent and k_{tm}/k_p of p-methoxystyrene
(○): 30°C, (△): 0°C, (□): -20°C

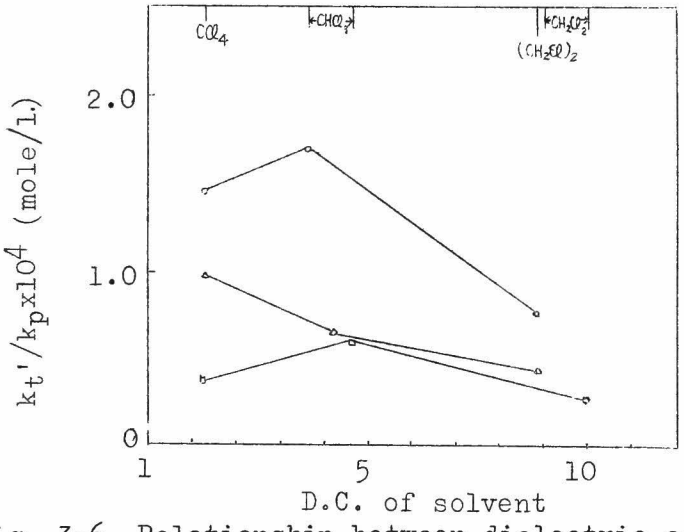


Fig. 3-6 Relationship between dielectric constant of the solvent and k_t'/k_p of p-methoxystyrene
(○): 30°C, (△): 0°C, (□): -20°C

[In Figs.3-3, 4, 5, and 6, rate constant ratios at various temperatures are plotted against D.C. of the solvent at each temperature. The change of D. C. of the solvent with temperature is shown in the figures.]

The rate constant ratios are plotted against dielectric constant of the solvent in Figs 3-3, 3-4, 3-5, and 3-6.

In the polymerization of o-methoxystyrene, k_{tm}/k_p was independent of both polymerization temperature and solvent dielectric constant, while k_t'/k_p decreased with decreasing polymerization temperature and decreasing solvent dielectric constant. k_t'/k_p was almost zero in carbon tetrachloride.

In the polymerization of p-methoxystyrene, k_{tm}/k_p decreased with decreasing polymerization temperature and with increasing solvent dielectric constant which is the same tendency as is observed in the cationic polymerizations of styrene.[9] k_t'/k_p decreased with decreasing polymerization temperature, but did not correlate well with the solvent dielectric constant.

From the rate constant ratios estimated at varying monomer concentration, it may be expected that in the cationic polymerization of p-methoxystyrene by boron trifluolide etherate $\bar{p}$ will increase with increasing solvent dielectric constant, and similarly for polymerization of o-methoxystyrene at higher monomer concentration; this was what was found experimentally.

3.2 Comparison between k_{tm}/k_p of styrene, o-methoxystyrene and p-methoxystyrene

A main object of this study was to investigate the electronic and steric effects of the methoxy group on the monomer transfer reaction. The values of $(k_{tm})_o$ $(k_{tm})_s$, $(k_{tm})_p/(k_{tm})_s$, and $(k_{tm})_o/(k_{tm})_p$, where the suffixes s, o, and p denote styrene, o- and p-methoxystyrene respectively, were calculated to investigate the effects of the substituents. The calculation was carried out according by the method used in Chapter 10 for the determining of the ratio of chain transfer constant with toluene.

Referring to monomers A and B,

$$(k_{tm})_A/(k_{tm})_B = (k_{tm}/k_p)_A/(k_{tm}/k_p)_B \times (k_p)_A/(k_p)_B \qquad (3\text{-}7)$$

$$(k_p)_A/(k_p)_B \approx (r_A/r_B)^{\frac{1}{2}} \qquad (3\text{-}8)$$

where r_A and r_B are the monomer reactivity ratios in the copolymerization of A and B. Equation (3-8) will be discussed again in more detail in Chapter 10. So:—

$$(k_{tm})_A/(k_{tm})_B = (k_{tm}/k_p)_A/(k_{tm}/k_p)_B \times (r_A/r_B)^{\frac{1}{2}} \qquad (3\text{-}9)$$

In order to estimate the ratios (k_{tm}/k_p) for A and B, monomers A and B must be homopolymerized under the

same conditions, and A and B must be copolymerized under the same conditions as those in the homopolymerization to obtain the values of r_A and r_B.

The values of $(k_{tm}/k_p)_o$ and $(k_{tm}/k_p)_p$ are given in Table 3-2, and values of $(k_{tm}/k_p)_s$ which previously reported from our laboratory[9] are listed in Table 3-3.

Table 3-3 k_{tm}/k_p in the polymerization of styrene $BF_3 \cdot O(C_2H_5)_2$, 30°C

Solvents used in Ref. 9	$10^2 k_{tm}/k_p$	Corresponding solvents used in the present investigation
Benzene	0.82	CCl_4
Dichloroethane 30 vol.% + benzene	0.80	$CHCl_3$
Dichloroethane 60 vol.% + benzene	0.60	CH_2Cl_2

In all strictness it must be mentioned that the solvents used in the polymerization of styrene (left-hand column of Table 3-3) was not the same as those used in the polymerizations of methoxystyrenes (right-hand column of Table 3). However, the correspondence is probably fairly close in view of the similar solvent dielectric constants.

Monomer reactivity ratios are listed in Table 3-4; the data for o-methoxystyrene—p-methoxystyrene and styrene—o-methoxystyrene copolymerizations were determined by the present author as described in Chapter 10. Copolymerization of p-methoxystyrene with styrene was effected by boron trifluoride etherate in chloroform at 30°C. The compositions of the copolymers were determined by infrared analysis, using the ratio of optical densities $D_{825}cm^{-1}/(D_{825}cm^{-1} + D_{700}cm^{-1})$. The values of r_1 and r_2 were found by the cross-section method. The corresponding copolymer composition curve is shown in Fig. 3-7. The k_p ratios could be calculated from the values of r_1 and r_2 thus obtained, and are listed in Table 3-4. Despite the difference between polymerization conditions used in homopolymerization and copolymerization, the numerical values in Tables 3-2, 3-3, and 3-4 were assumed to be applicable to equation (3-10).

The k_{tm} ratios, which are listed in Table 3-5, were calculated by inserting the data shown in Tables 3-2, 3-3, and 3-4 in equation (3-10).

It will be seen from Table 3-5 that the value of $(k_{tm})_p/(k_{tm})_s$ lies between 0.2 and 0.6 and that the value of $(k_{tm})_o/(k_{tm})_s$ lies between 1.5 and 2.2.

Table 3-4 Monomer reactivity ratios and ratios of k_p (Solvent: $CHCl_3$)

M_1	M_2	Polymerization condition	r_1	r_2	$k_{p_1}/k_{p_2} \simeq (r_1/r_2)^2$
p-Methoxystyrene	o-Methoxystyrene	30°C, $BF_3 \cdot O(C_2H_5)_2$	2.9±0.7	0.35±0.03	2.88
p-Methoxystyrene	o-Methoxystyrene	-20°C, $BF_3 \cdot O(C_2H_5)_2$	3.9±1	0.35±0.09	3.35
p-Methoxystyrene	o-Methoxystyrene	-78°C, $BF_3 \cdot O(C_2H_5)_2$	6.4±0.4	0.45±0.05	3.78
p-Methoxystyrene	Styrene	30°C, $BF_3 \cdot O(C_2H_5)_2$	38	0.5	8.72*)
o-Methoxystyrene	Styrene	30°C, $SnCl_4 \cdot CCl_3CO_2H$	3.9±0.7	0.20±0.02	4.39
o-Methoxystyrene	Styrene	-20°C, $BF_3 \cdot O(C_2H_5)_2$	3.6±0.8	0.11±0.04	5.70

*) The reliability of the data is low because of the great difference between the reactivity of M_1 and that of M_2.

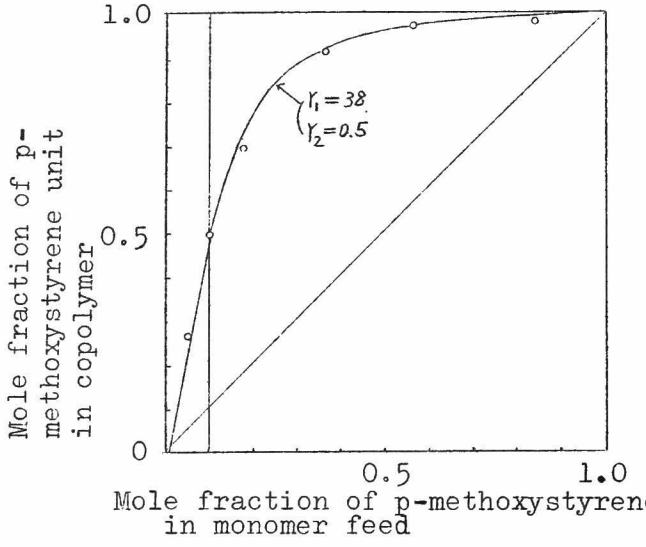


Fig. 3-7 Copolymer composition curve for copolymerization of p-methoxystyrene (M_1) and styrene (M_2) in chloroform by $BF_3 \cdot O(C_2H_5)_2$ at 30°C

Table 3-5 Ratios of k_{tm} and of R_M' ($BF_3 \cdot O(C_2H_5)_2$)

M_1	M_2	Polym. cond. Solvent/°C	$\frac{k_{tm} \text{ of } M_1}{k_{tm} \text{ of } M_2}$	$\frac{R_M' \text{ of } M_1}{R_M' \text{ of } M_2}$
p-Methoxystyrene	Styrene	CCl_4/30	0.58	5.0
		$CHCl_3$/30	0.47	4.1
		CH_2Cl_2/30	0.26	2.2
o-Methoxystyrene	Styrene	CCl_4/30	1.50	8.3
		CH_2Cl_2/30	2.14	11.9
p-Methoxystyrene	o-Methoxystyrene	CCl_4/30	0.58	0.90
		CH_2Cl_2/30	0.18	0.28
		CCl_4/-20	0.32	0.50
		CH_2Cl_2/-20	0.14	0.22

However, these values cannot be directly discussed because both R_M' (the reactivity of a monomer in the monomer transfer reaction) and R_I' (the reactivity of a growing ion in the monomer transfer reaction) must be taken into account. To ascertain $(R_M')_A/(R_M')_B$, the relationship "$k_{tm} = R_I' \cdot R_M'$" was assumed, which will be discussed in Chapter 10 in more detail.

Therefore, the following relationships obtain:—

$$(k_{tm})_A/k_{tm})_B = (R_M')_A(R_I')_A/(R_M')_B(R_I')_B \qquad (3\text{-}11)$$

$$(R_M')_A/(R_M')_B = (k_{tm})_A/(k_{tm})_B \cdot (R_I')_B/(R_I')_A$$

To determine $(R_I')_B/(R_I')_A$, the ratio of the reactivities of the growing ions in the transfer reaction to toluene was used, the data for which will be reported in Chapter 10; see Table 3-6.

Table 3-6 The comparison of R_I', the reactivity of growing ion

Cation 1	Cation 2	$\frac{R_I' \text{ of cation 1}}{R_I' \text{ of cation 2}}$
p-Methoxystyrene	Styrene	0.082 - 0.15
o-Methoxystyrene	Styrene	0.15 - 0.20
p-Methoxystyrene	o-Methoxystyrene	0.64

Thus, the values of $(R_M')_A/(R_M')_B$ could be calculated and are shown in Table 3-5. It was found that the presence of a methoxy group increased the value of R_M' the effect being greater for ortho- than for para-substitution.

Logarithms of r_1 values (Table 3-4) obtained in the boron trifluoride etherate copolymerization of p-methoxystyrene (M_1) and o-methoxystyrene (M_2) in chloroform are plotted in Fig. 3-8 against 1/T. A linear relationship was obtained from which $(\Delta H_{12} - \Delta H_{11})$ was found to be 0.86 Kcal/mole and $(\Delta S_{11} - \Delta S_{12})$ was found to be 0.69 cal/deg./mole. The latter is nearly zero, the value usually found in other copolymerizations.[10] The similar plot for r_2 was not made because the values were scattered.

3.3 Molecular orbital calculations

To investigate theoretically the propagation and monomer transfer reactions of o- and p-methoxystyrene, the stabilization energy, $(\Delta E)r,s$, based on π conjugation between the position r in the monomer and the position s in the ion, was calculated from second order perturbation theory to be:[11]

$$(\Delta E)_{r,s} = \left(\sum_{m}^{occ} \sum_{n}^{unocc} - \sum_{m}^{unocc} \sum_{n}^{occ} \right) \frac{(a_r^m)^2 (b_s^n)^2 (\Delta\beta)^2}{Fn - Fm} \qquad (3\text{-}12)$$

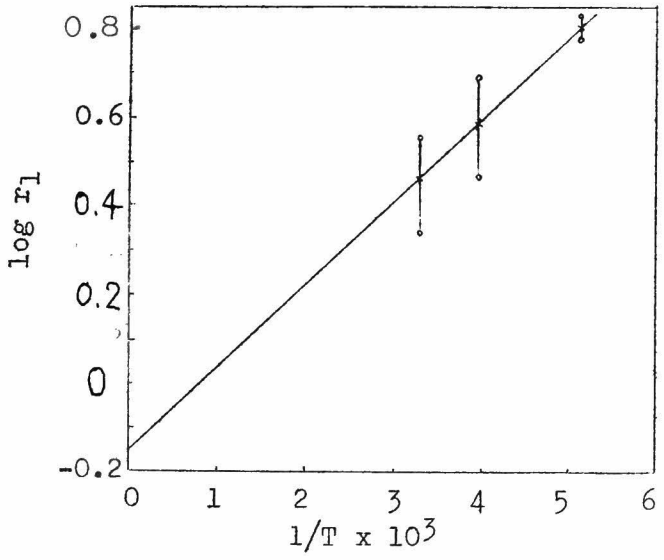


Fig. 3-8 The plot of log r_1 versus 1/T

r_1 is for the copolymerization of p-methoxystyrene(M_1) and o-methoxystyrene(M_2) in chloroform by $BF_3 \cdot O(C_2H_5)_2$.

x means the averaged value of r_1

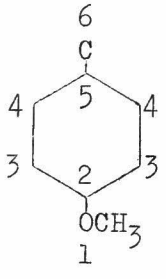
$r_1 = 6.4$ (-78°C) $r_1 = 3.9$(-20°C) $r_1 = 2.9$(30°C)

⌇ means the range of the error in r_1.

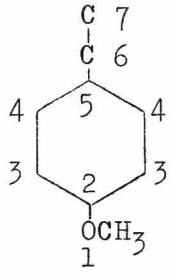
Here, a_r^m and b_s^n are the coefficients of the r-th and the s-th atomic π-orbitals in the m-th and n-th molecular orbitals of a monomer and an ion, respectively; Fm and Fn are the eigenvalues of the m-th and n-th molecular orbitals, respectively; $\Delta\beta$ is the resonance integral of an incipient bond between a monomer and an ion; and $\sum^{occ}$ and $\sum^{unocc}$ denote the summation over all the occupied and the unoccupied orbitals, respectively. It has been assumed

that the larger the absolute value of $(\Delta E)_{r,s}$ the more easily the reaction occurs.

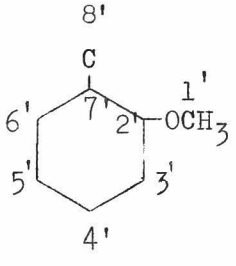
To deduce the position of carbonium ion attack in the propagation and monomer transfer reactions, the frontier electron density was calculated, regarding the methoxy group as equivalent to an atom. The values of the Columb and resonance integrals used in the present molecular orbital calculation were taken as[12]:—



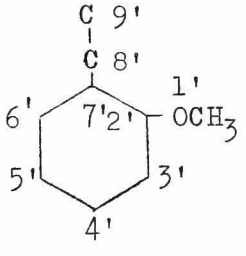
p-Methoxystyrene cation



p-Methoxystyrene monomer



o-Methoxystyrene cation



o-Methoxystyrene monomer

Fig. 3-9 Molecular orbital calculations

$$\alpha_1 = \alpha + 0.6\beta$$
$$\alpha_2 = \alpha + 0.05\beta$$
$$\beta_{12} = \beta_{21} = 0.55\beta$$

The calculated electron densities are given in Fig. 3-10.

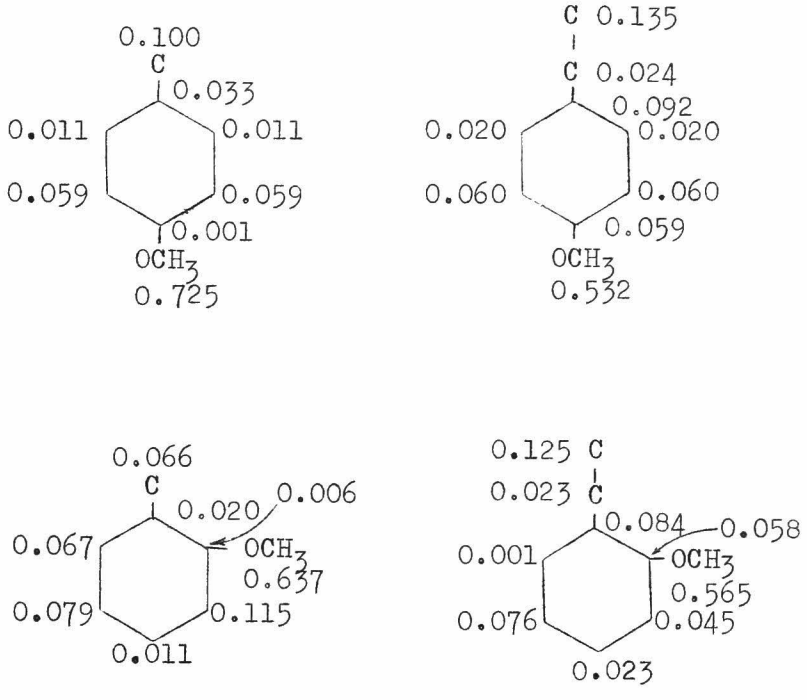


Fig. 3-10 The frontier electron densities

Carbonium ion attack was considered to take place at the position of maximum electron density in the monomer(otherwise at the methoxy group) to bring about the propagation

reaction, and at that in the phenyl group to give rise to the monomer transfer reaction. The following values were therefore calculated:

for copolymerization $(\Delta E)_{7,6}$, $(\Delta E)_{9',8'}$, $(\Delta E)_{9',6}$, $(\Delta E)_{7,8'}$

for monomer transfer reaction $(\Delta E)_{3,6}$ $(\Delta E)_{5',8'}$

Results are shown in Table 3-7. From the calculation it was found that $(\Delta E)_{7,6}$ was smaller than $(\Delta E)_{9',6}$ (absolute value) and $(\Delta E)_{9',8'}$ was larger than $(\Delta E)_{7,8'}$ (absolute value). The rate constants k_{11}, k_{12}, k_{22}, and k_{21} are determined by $(\Delta E)_{7,6}$, $(\Delta E)_{9',6}$, $(\Delta E)_{9',8'}$, and $(\Delta E)_{7,8'}$ respectively. Therefore, value r_2 may be expected to be larger than unity and r_1 smaller than unity. On the other hand, $(\Delta E)_{3,6}$ was found to be larger than $(\Delta E)_{5',8'}$ (absolute value). The rate constants $(k_{tm})_o$ and $(k_{tm})_p$ are determined respectively by $(\Delta E)_{5',8'}$ and $(\Delta E)3,6$, so it may be expected that $(k_{tm})_p/(k_{tm})_o$ will be larger than unity. The experimental results were, however, completely contrary to these predictions.

3.4 Infrared spectroscopy of the polymers

To investigate the end groups of poly-o- and p-methoxystyrenes, the infrared spectra of the polymers

Table 3-7 Relationship between $(\Delta E)_{r,s}$, (r_1, r_2)*) and k_{tm}-ratio

Cation	Monomer	$(\Delta E)_{r,s}$	r_1 and r_2 in chloroform at 30°C	k_{tm} of o-MS/k_{tm} of p-MS** in CH_2Cl_2 at 30°C
p-Methoxystyrene (M_1)	p-Methoxystyrene (M_1)	$(\Delta E)_{7,6} = -0.9078_2$	$r_1 = 2.9 \pm 0.7$	
	o-Methoxystyrene (M_2)	$(\Delta E)_{9',6} = -0.9112_0$		
o-Methoxystyrene (M_2)	o-Methoxystyrene (M_1)	$(\Delta E)_{9',8'} = -0.9060_2$	$r_2 = 0.35 \pm 0.03$	
	p-Methoxystyrene (M_1)	$(\Delta E)_{7,8'} = -0.9033_6$		
P-Methoxystyrene	p-Methoxystyrene	$(\Delta E)_{3,6} = -0.6854_6$		0.18
O-Methoxystyrene	o-Methoxystyrene	$(\Delta E)_{5',8'} = -0.6733_4$		

*) Values obtained by using $BF_3 \cdot O(C_2H_5)_2$

**) MS = Methoxystyrene

were examined.

As was seen in Table 3-2, k_{tm}/k_p and $k_{t'}/k_p$ values for o-methoxystyrene are sufficiently large to give low molecular weight polymer even under less severe polymerization conditions. This is convenient for end group analysis.

Poly-o-methoxystyrene obtained under the present polymerization conditions gave weak infrared absorptions at 900 cm^{-1} and 970 cm^{-1}, as shown in Fig. 3-11a. The absorption at 900 cm^{-1} also appears strongly with the monomer too, but is absent with the polymer obtained by thermal polymerization, while the absorption at 970 cm^{-1} is not found in the monomer but is present in thermally polymerized polymer, as shown in Fig. 3-11c. Both absorptions are very weak in the polymer of higher molecular weight as shown in Fig. 3-11b, and disappeared on bromination of the polymer as shown in Fig. 3-11d. Though the changes in the infrared absorption spectrum of polymer accompanying bromination were slight, the facts led the author to conclude that these absorptions are due to a terminal double bond. The absorption at 900 cm^{-1} may be ascribed to a terminal vinyl group and the absorption at 970 cm^{-1} to terminal trans double bond.[13)]

p-Methoxystyrene gave polymers of higher molecular weight under the present conditions, making end group analysis difficult. So poly-p-methoxystyrene was fractionated and the lower molecular weight fractions were analyzed by infrared spectroscopy. The polymer had a weak absorption at 900 cm^{-1}, as shown in Fig. 3-12a, and this disappeared on bromination. The same absorption was strong in the monomer. It may possibly be due to the terminal vinyl group. A weak absorption at 960 cm^{-1}, absent in the monomer, could be detected in the polymer. This suggests the presence of a trans double bond, as in poly-o-methoxystyrene. However, this absorption appeared also in the polymer of higher molecular weight as shown in Fig. 3-12b, so, a definite conclusion could not be reached.

In addition to these absorptions, poly-o- and p-methoxystyrene of lower molecular weight gave a weak absorption at 680-690 cm^{-1}, absent both from polymers of higher molecular weight and from monomer. Bromination of the polymer caused it to disappear, and it is considered to be due to a terminal cis double bond.[13)]

The presence of the very weak absorptions at 870 cm^{-1} in poly-o-methoxystyrene may be attributed to a 1,2,4-trisubstituted phenyl group.[13)]

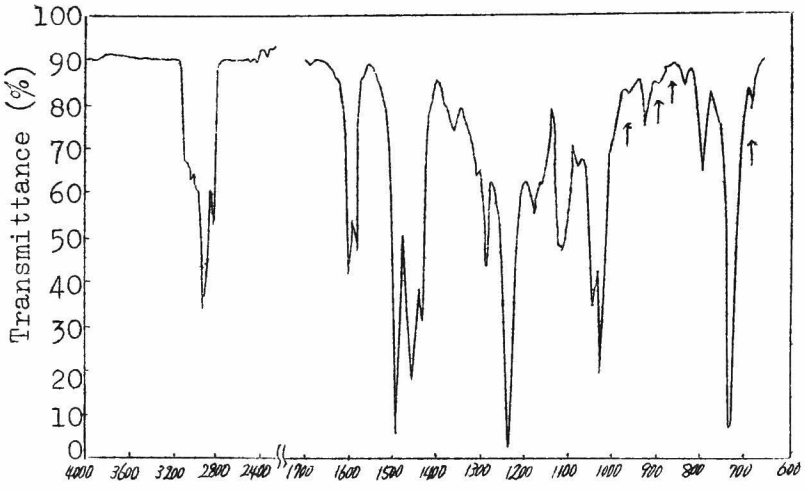


Fig. 3-11a

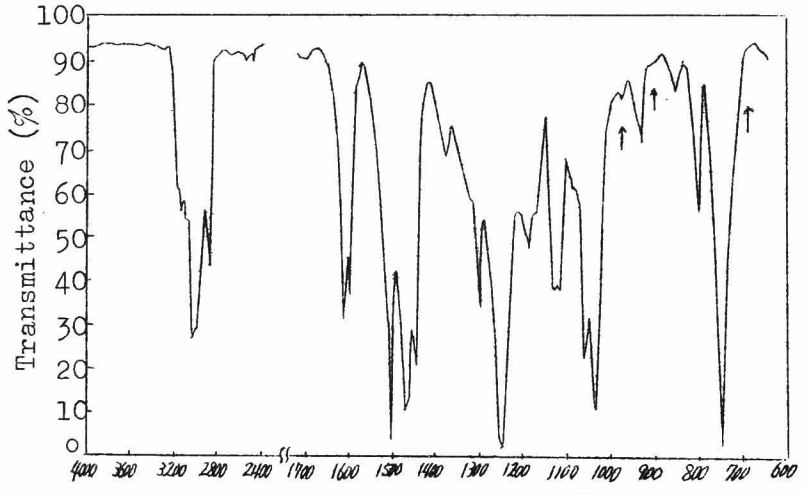


Fig. 3-11b

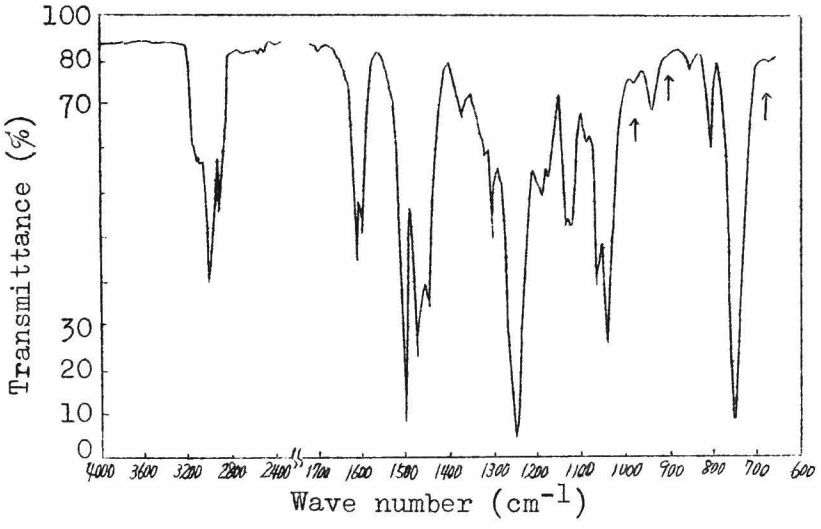


Fig. 3-11c

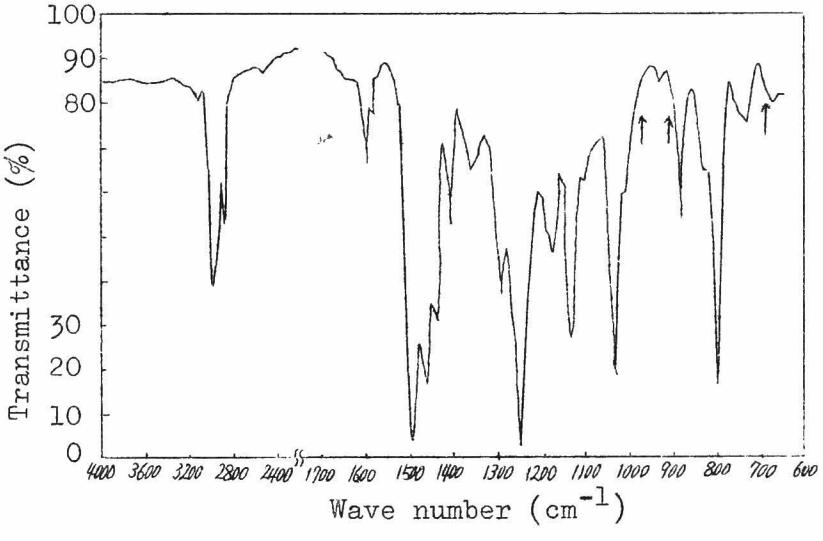


Fig. 3-11d

Fig. 3-11 Infrared spectra of poly-o-methoxystyrene
a: Low molecular weight polymer, $[\eta]$= 0.028, Polymerization condition: 30°C, CCl_4, $BF_3 \cdot O(C_2H_5)_2$
b: High molecular weight polymer, $[\eta]$ = 0.142
Polymerization condition: 30°C, CH_2Cl_2, $BF_3 \cdot O(C_2H_5)_2$
c: Polymer obtained by thermal polymerization, $[\eta]$ = 0.140
d: Brominated polymer of sample a.

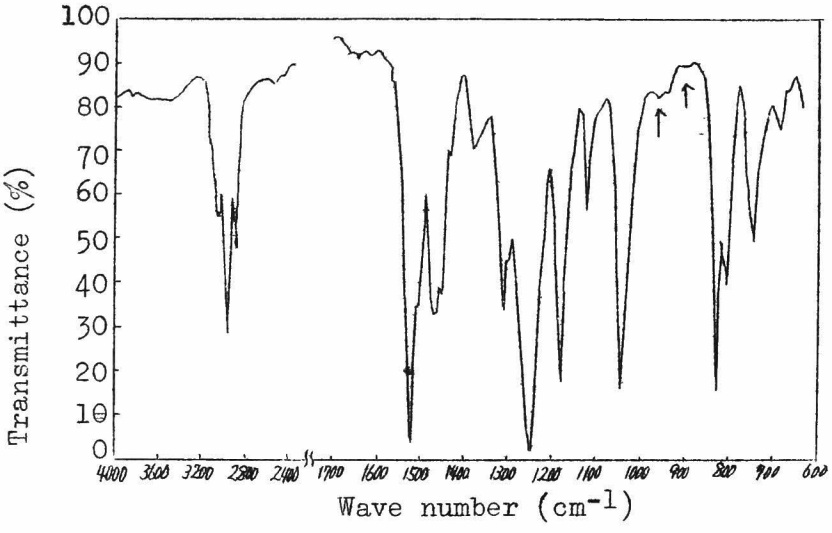


Fig. 3-12a

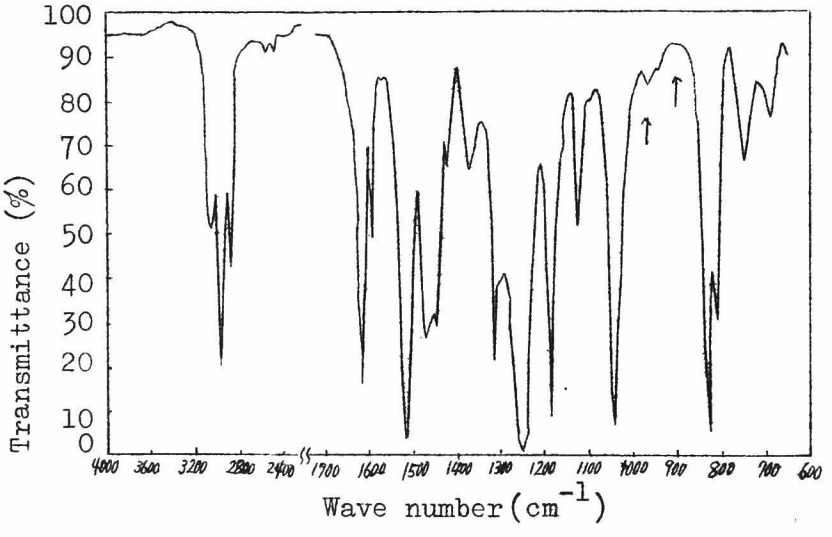


Fig. 3-12b

Fig. 3-12 Infrared spectra of poly-p-methoxystyrene
a: Low molecular weight polymer, $[\eta] = 0.152$
Polymerization condition: $30^{\circ}C$, $(CH_2Cl)_2$, $BF_3 \cdot O(C_2H_5)_2$
b: High molecular weight polymer, $[\eta] = 2.13$
Polymerization condition: $-20^{\circ}C$, CCl_4, $BF_3 \cdot O(C_2H_5)_2$

4. Discussion

4.1 Monomer transfer reaction in cationic polymerizations of methoxystyrenes

The following conclusions were drawn concerning the change in reactivity of styrene derivatives in the monomer transfer reaction (R_M') due to the methoxy group:

(i) The reactivity of p-methoxystyrene in the propagation reaction is more than ten times greater than that of styrene (Table 3-4). On the other hand, the reactivity of p-methoxystyrene in the monomer transfer reaction is only two to five times greater than that of styrene (Table 3-5).

(ii) The reactivity of o-methoxystyrene in the propagation reaction is only five times greater than that of styrene (Table 3-4). On the other hand, the reactivity of o-methoxystyrene in the monomer transfer reaction is ten times greater than that of styrene (Table 3-5).

(iii) It is easier to study the monomer transfer reaction using o-methoxystyrene since the reactivity of o-methoxystyrene for this reaction is usually larger than that of the p-isomer.

(iv) The β-carbon of the vinyl group and the carbon atom of highest electron density in the phenyl group are

considered to constitute the reaction site between a carbonium ion and a monomer. The reaction might also be expected to occur on the oxygen of the methoxy group. However, this possibility was neglected for three reasons; (1) although the electron density is apparently relatively larger at this position, the electron releasing effect of oxygen gives this atom a slight positive charge, which hinders the access of the carbonium ion, (2) the reaction between the carbonium ion and oxygen is highly sterically hindered, (3) the hypothesis that the reaction site is the oxygen atom cannot explain the difference between o- and p-isomers in the effect of the substituents on R_M'.

In the light of these facts, the following propositions can be discussed.

(A) "Monomer transfer reaction takes place at the phenyl group of a monomer"

If the monomer transfer reaction occurs at the vinyl group of a monomer, the effects of the methoxy group on the propagation and the monomer transfer reaction should be the same. However, the effect of the methoxy group is dependent on its position of

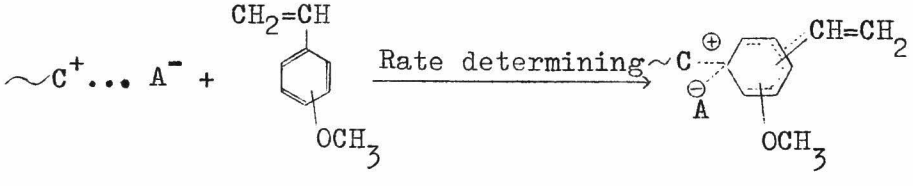
substitution (see (i) and (ii)). This indicates that the reaction occurs at the phenyl group (see (iv)). Let us now consider this possiblity in detail. From the molecular orbital calculation, the monomer transfer reaction is expected to occur at the carbon atom 3 (Fig. 3-9) in the polymerization of p-methoxystyrene. In view of the steric effect, the introduction of the p-methoxy group will promote the reaction at the vinyl group (propagation reaction) more than the sterically hindered reaction at the carbon atom 3 (monomer transfer reaction). On the other hand, in the polymerization of o-methoxystyrene, the monomer transfer reaction is expected to occur at the carbon atom 5' (Fig. 3-9). In this case, the introduction of the o-methoxy group will accelerate the reaction at the carbon atom 5' more than the reaction at the vinyl group. These expectations were confirmed by the present investigation (see (i), (ii), and (iii)). Overberger et al.[14] reported that the ratio of the reactivities of chain transfer reagents was about 1.2 for p-xylene/toluene and about 9.4 for o-xylene/toluene in the cationic polymerization of styrene by stannic chloride. The experimental results obtained in the

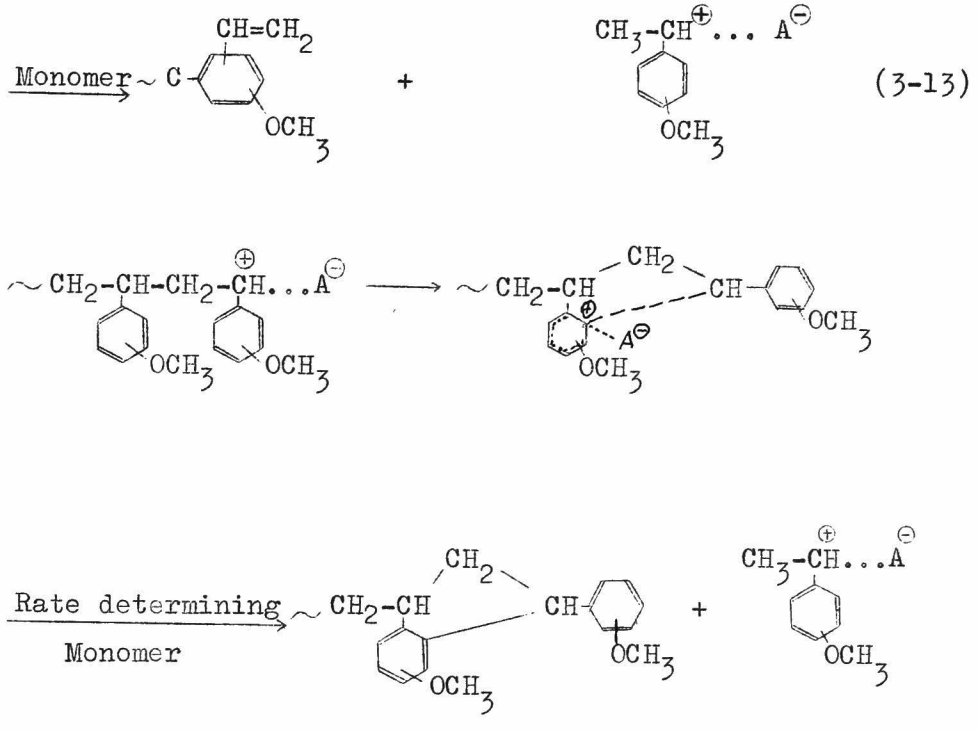
present investigation thus agree well with those obtained by Overberger et al., and also with those previously obtained in our laboratory.[15)]

Molecular orbital calculation gave a large value for $-(\Delta E)_{3,6}$ than for $-(\Delta E)_{5',8'}$ (Table 3-6). In practice, however, the value of $(k_{tm})_o/(k_{tm})_p$ was found to be larger than unity (Table 3-5). This discrepancy is due to the steric effect. The same phenomenon in chain transfer reaction towards an aromatic compound was observed in our laboratory[16)] in the molecular orbital approach to the transfer reaction.

(B) "Monomer transfer reaction consists mainly in reaction between a carbonium ion and a free monomer"

In the above investigations, it was tacitly assumed that the monomer transfer reaction takes place at the phenyl group of a free monomer (mechanism (3-13)). However, there is an alternative mechanism for the reaction (mechanism (3-14)):





(3-13)

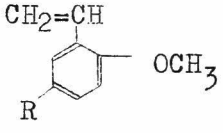
(3-14)

Reaction (3-14) gives a substituted indane structure at the polymer end. In the cationic polymerization of styrene and its derivatives, this reaction was proposed as a possible $\bar{p}$-determining reaction by some workers,[17),18),19),20)] and was rejected by others.[21),22)] In the polymerization of methoxystyrenes, it is clear that for both electronic and steric reasons the o-methoxy group should enhance reaction (3-14) less than the p-methoxy group. However, this does not agree with the experimental results (see (iii)). Moreover, the terminal vinyl groups

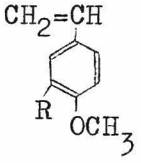
which were detected in the polymer can be formed only by reaction (3-13). These two facts imply that the monomer transfer reaction proceeds at least in part by mechanism (3-13).

Reaction (3-13) could also introduce following 1,2, 4-trisubstituted benzene at the end of the polymer:—

poly-o-methoxystyrene

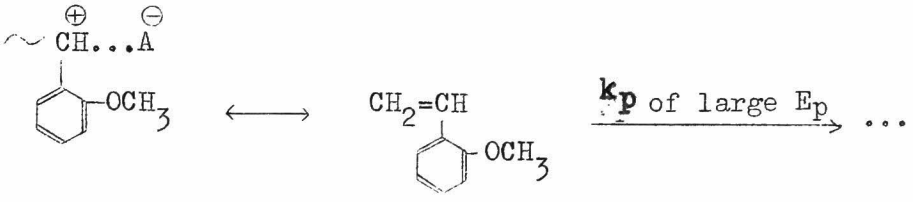


poly-p-methoxystyrene

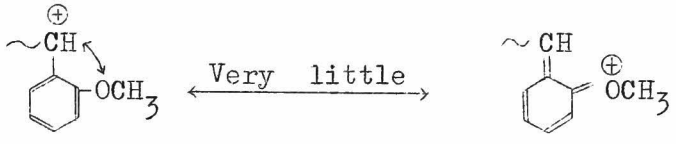


Therefore, infrared absorptions for these structures are to be expected at 805-825 cm^{-1} and 870-885 cm^{-1} 13). Only a very weak absorption could be observed in the spectrum of the fractionated poly-o-methoxystyrene.

The value of k_{tm}/k_p for the polymerization of o-methoxystyrene was independent of the polymerization temperature (Table 3-2). This unusual result is due to the relatively low value of E_{tm} and relatively high value of E_p. The latter may be ascribed to two effects; (A) the repulsion between the o-methoxy group near the growing ion and the vinyl group of an attacking monomer.



(B) The deviation from a planar form of the growing end caused by interaction of the carbonium ion with the o-methoxy group, and the consequently low contribution of resonance stabilization.



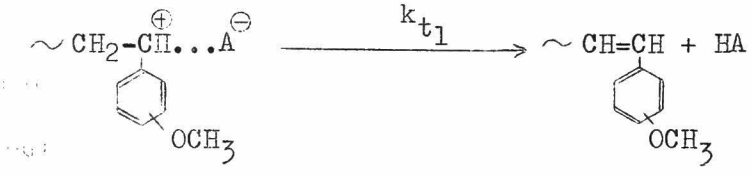
These effects were reflected in the following observations:

(A') Although a value of r_2 larger than unity and a value of r_1 smaller than unity in the cationic copolymerization of p-methoxystyrene (M_1) with o-methoxystyrene (M_2) are to be expected from the molecular orbital approach (Table 3-7), the reverse relationship was found experimentally.

(B') It may be seen from Fig. 3-8 that the entropy and potential energy of the transition state are higher in the addition of M_2 to $M_1^{\oplus}$ than in that of M_1 to $M_1^{\oplus}$.

4.2 Unimolecular termination reaction in cationic polymerizations of the two methoxystyrenes

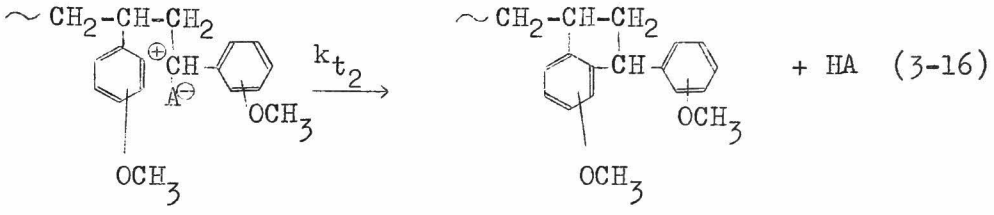
There is some ambiguity about the nature of the unimolecular termination reaction because k_t' is made up of k_t and $k_{tx}[X]$(see 3.1). But in polymerization of o-methoxystyrene, k_t'/k_p was nearly equal to zero in a solvent of low dielectric constant such as carbon tetrachloride (Table 3-2), suggesting that mechanism (3-15) here predominates. The proton expulsion reaction would be expected to be depressed by a decrease in solvent dielectric constant.



(3-15)

In polymerization of p-methoxystyrene, k_t'/k_p was not greatly affected by change in solvent dielectric constant, suggesting that, in addition to reaction (3-15), there occurs another reaction of different mechanism for which a low solvent dielectric constant is permissible. Thus, reaction (3-16) may be used to explain the unimolecular termination reaction of p-methoxystyrene: it is essentially the same as the monomer transfer reaction in that it is an alkylation by the growing ion.

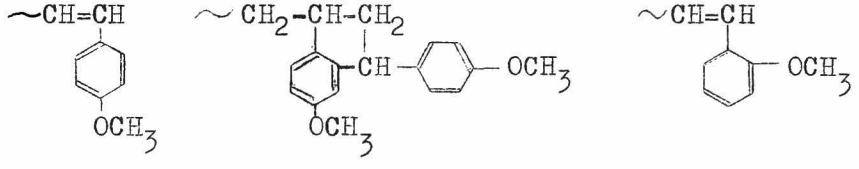
Therefore reaction (3-16) will be accelerated by a decrease



(3-16)

in solvent dielectric constant. The o-methoxy group would sterically inhibits reaction (3-16), but no experimental evidence was found to this. The unimolecular termination reaction will thus produce the following end groups:

Poly-p-methoxystyrene poly-o-methoxystyrene



(I) (II) (III)

The infrared absorptions at 680 cm^{-1} (cis double bond) and at 960-970 cm^{-1} (trans double bond) in poly-o- and p-methoxystyrene are due to end groups (I) and (III), confirming mechanism (3-15) above. However, absorptions attributable to the end group (II) were not found for poly-p-methoxystyrene.

4.3 The monomer transfer reaction of styrene and its derivatives

It was found that in cationic polymerizations of styrene and methoxystyrenes the monomer transfer constant ratio (k_{tm}/k_p) increases with increasing solvent dielectric constant, and that in the polymerization of styrene k_{tm}/k_p increases, the stronger the Lewis acid as catalyst. For the reason stated in Chapter 2, these facts suggest that k_{tm}/k_p increases with change of the growing end into ion-pair form, contrary to what obtains with isobutene. From the reaction kinetics and infrared analysis, the mechanism of the styrene-type monomer transfer reaction is considered to be (3-13).

Kanoh et al.[23] consider that in the propagation reaction of styrene and its derivatives, it is necessary for the growing end to dissociate into free ions.

However, the monomer transfer reaction (3-13) is essentially an alkylation, and proceeds via the displacement mechanism proposed by Brown.[24] In the monomer transfer reaction, therefore, dissociation into free ions is not always important, but bond formation between the growing ion and the phenyl group of a monomer is important. Thus, the change of the growing ion into the ion-pair form

greatly depresses the propagation reaction, but does not affect the monomer transfer reaction. These mechanisms imply that k_{tm}/k_p is higher, the lower the solvent dielectric constant and the stronger the Lewis acid catalyst.

The effects of the electron withdrawing substitution on the styrene-type monomer transfer reaction will be described in the next chapter.

To sum up, investigation of the effects of the methoxy substitution of styrene on k_{tm}/k_p established that in the monomer transfer reaction of styrene and its derivatives the growing ion reacts with the phenyl groups of a monomer, and that the change of the growing end into ion-pair form facilitates the monomer transfer reaction.

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Chapter 4 Ortho- and Para-chlorostyrene

1. Introduction

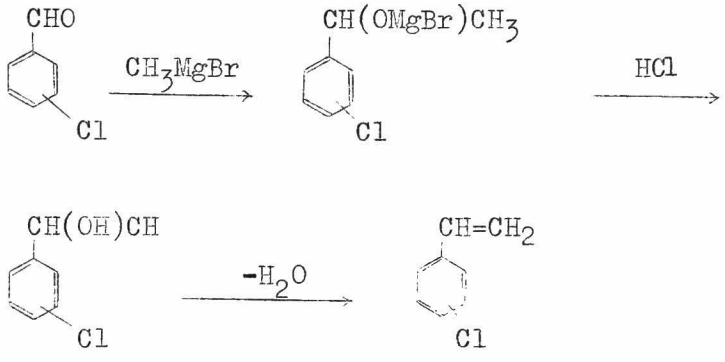
In order to investigate the mechanism of the monomer transfer reaction in the cationic polymerizations of styrene and its derivatives, the electronic steric effect of the substituent on the transfer and termination reactions were investigated. In the preceding Chapter, the effect of electron donating substituent (methoxy group) was investigated. As a consequence, a tentative mechanism was proposed to the styrene-type monomer transfer reaction, in which the reaction of the growing cation with the phenyl group of the monomer is important. In this Chapter, the electronic and steric effects of an electron withdrawing substituent such as a chlorine atom were investigated and the validity of the mechanism of the styrene-type monomer transfer reaction previsouly proposed was discussed.

2. Experimental

2.1 Reagent

o- and p-Chlorostyrene were synthesized by the method of Brooks[1] from o- and p-chlorobenzaldehyde (Heydon

Newport) respectively, these being distilled just before use. The synthetic route was as following:



The above synthetic route avoided isomers as by-products. Physical properties of the monomers, the starting materials and the intermediates are summarized in Table 4-1

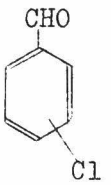
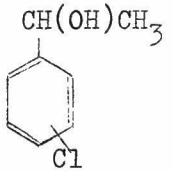
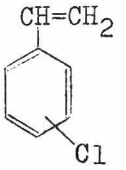
o- and p-Chlorostyrene were washed repeatedly with alkali and water, then dried over anhydrous potassium carbonate, and distilled twice just before use.

Styrene was washed repeatedly with alkali and water, then dried over sodium sulfate, distilled in a vacuum, dried over metallic sodium, and again distilled (b.p. 55°C/32mm).

The toluene, chloroform and dichloroethane used as solvent were purified as stated previously, special care being taken to remove water.

Benzene was purified in the same way as toluene

Table 4-1 The physical properties of monomers, intermediates and starting materials

Materials	Physical properties	Ortho-isomer	Para-isomer	
	m.p. (°C)	11 —	46-47 —	lit.
	b.p. (°C)	208 112-113 (18mm)	213 108-111(25mm)	lit. obs.
	n_D	— 1.5652 (21°C)	— —	lit. obs.
	b.p. (°C)	108-109 (7mm) 113 (12mm)	87-89 (2mm) 115-116 (10mm)	lit. obs.
	n_D	1.5457 (20°C) 1.5440 (21°C)	1.5633 (20°C) 1.5357 (25°C)	lit. obs.
	b.p. (°C)	60-61 (4mm) 75 (13mm)	53-54 (3mm) 71-72 (11mm)	lit. obs.
	n_D	1.5648 (20°C) 1.5645 (20°C) 1.5602 (30°C)	1.5658 (20°C) 1.5643 (25°C) 1.5604 (30°C)	lit. obs. obs.
	$d^{30°C}$	1.100 1.105	1.090 1.084	lit. obs.
Yield from aldehyde		~ 70%	~ 70%	obs.

(b.p. 79.8°C).

Stannic chloride as catalyst and trichloroacetic acid as co-catalyst were purified as described in Chapter 2.

2.2 Procedure

2.2.1 Polymerization

Polymerizations were carried out in a 100 ml. flask immersed in a thermostatted bath at 30°C, using stannic chloride—trichloroacetic acid as catalyst, and stopped by the addition of a large amount of methanol. The precipitated polymer was washed repeatedly with methanol and dried in a vacuum at 40°C.

The polymerization rate was measured using a dilatometer at 30°C. The volume decrease of monomer was found to be 14.2% for o-chlorostyrene and 15.4% for p-chlorostyrene.

2.2.2 The determination of the molecular weight

The molecular weight ($\bar{M}$) or the degree of polymerization ($\bar{P}$) of polymer was calculated from the intrinsic viscosity using equations (4-1), (4-2), and (4-3).

poly-p-chlorostyrene

$$\bar{P}_n = 16.98 \times 10^2 \times [\eta] - 45.1 \qquad (4\text{-}1)$$

The molecular weight range : 800 - 4400

poly-o-chlorostyrene

$$\bar{P}_n = 5.72 \times 10^2 \times [\eta] - 8.2 \qquad (4\text{-}2)$$

The molecular weight range : 1100-2200

polystyrene[2)]

$$[\eta] = 2.27 \times 10^{-4} \times \bar{M}_n^{0.72} \qquad (4\text{-}3)$$

The molecular weight range : 1000-10000

Equations (4-1) and (4-2) were found by measuring the freezing point depression of a benzene solution of unfractionated sample and the intrinsic viscosity in toluene at 30°C. Equation (4-3) was reported by Pepper on the relationship between the intrinsic viscosity of benzene solution at 25°C and the molecular weight determined by the freezing point depression measurement.

A lot of intrinsic viscosity—molecular weight equations have been reported for low molecular weight polystyrene and low molecular weight polystyrene derivatives. Plotting logarithms for the equations for polystyrene[2),3)] and for poly-α-methylstyrene,[4),5)] practically parallel straight lines were obtained. They greatly resemble the straight line obtained for the logarithmic plot of equation (4-2) (poly-o-chlorostyrene). They are all shown in Fig. 4-1.

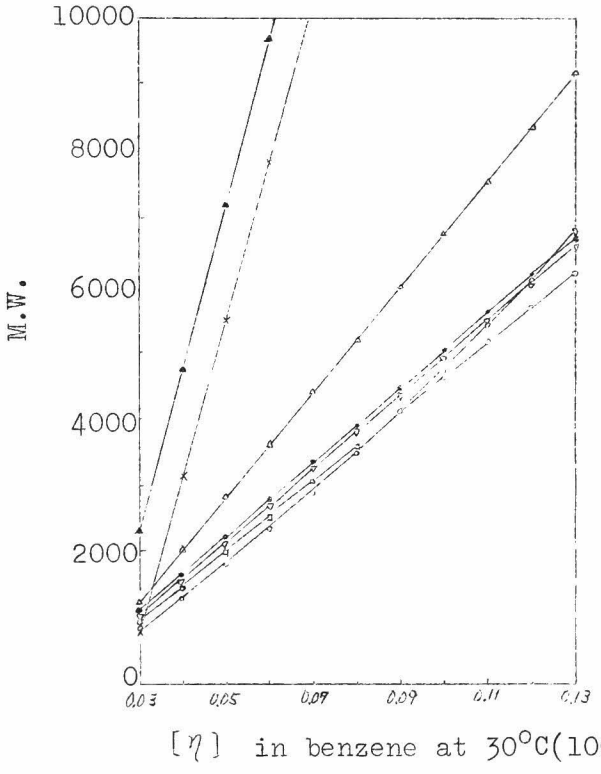


Fig. 4-1 The comparison between various intrinsic viscosity-molecular weight equations for polystyrene derivatives
(○): Polystyrene (Pepper)[2]
(▽): Polystyrene (Mathieson)[3]
(□): Poly-α-methylstyrene (Mathieson)[4]
(●): Poly-α-methylstyrene (Bywater)[5]
(×): Poly-p-chlorostyrene
(▲): Poly-o-methoxystyrene[6]
(△): Poly-o-chlorostyrene

However, the equation (4-1) for poly-p-chlorostyrene had a very steep slope when plotted logarithmically, and behaved differently from others. Furthermore, it has

been reported that the very similar graphs are obtainable for high-molecular poly-p-methoxystyrene, poly-p-chlorostyrene and polystyrene[7]. These experimental results suggest that the abnormal behavior of equation (4-1) when plotted logarithmically may be due to its incorporating considerable experimental error. Now assuming that an intrinsic viscosity—molecular weight relationship similar to that for other polystyrene derivatives holds for poly-p-chlorostyrene, the rate constant ratios in the polymerization of poly-p-chlorostyrene were calculated tentatively using equation (4-2) instead of equation (4-1). It was indeed found that the absolute value of the rate constant ratio was different, but the discussions on the basis of the rate constant ratio were not seriously affected even if equation (4-2) was used instead of equation (4-1). The calculation of the rate constant ratio by equation (4-1) did not therefore greatly affect the relevant discussion, even if some experimental error entered into equation (4-1). The intrinsic viscosity ($30^{\circ}C$, toluene)—number averaged molecular weight (determined by vapor pressure depression) relationship for low molecular weight poly-o-methoxystyrene behaved, very similarly to equation (4-1) when plotted logarithmically.

3. Results

3.1 The measurement of the polymerization rate

The polymerization rates (R_p) of o- and p-chlorostyrene have hitheto rarely been measured. In this investigation, the cationic polymerizations of o- and p-chlorostyrene were carried out at 30°C in benzene or dichloroethane with various monomer concentration [M], catalyst concentrations [C], co-catalyst concentrations [Co] and co-catalyst/catalyst ratios. The effects of changes in these variables on the polymerization rate and length of the induction period (t_i) being studied.

3.1.1 The rate of polymerization of p-chlorostyrene

The polymerization was carried out in benzene with variation of the monomer concentration, the concentrations of catalyst and co-catalyst being kept constant. The time—conversion curves are shown in Fig. 4-2.

The maximum polymerization rate was calculated from a tangent to the curve, and was plotted against the square of the monomer concentration, when it gave a straight line. This is shown in Fig. 4-3. For polymerization in benzene, the polymerization rate was thus shown to be proportional to the square of the initial monomer concentration.

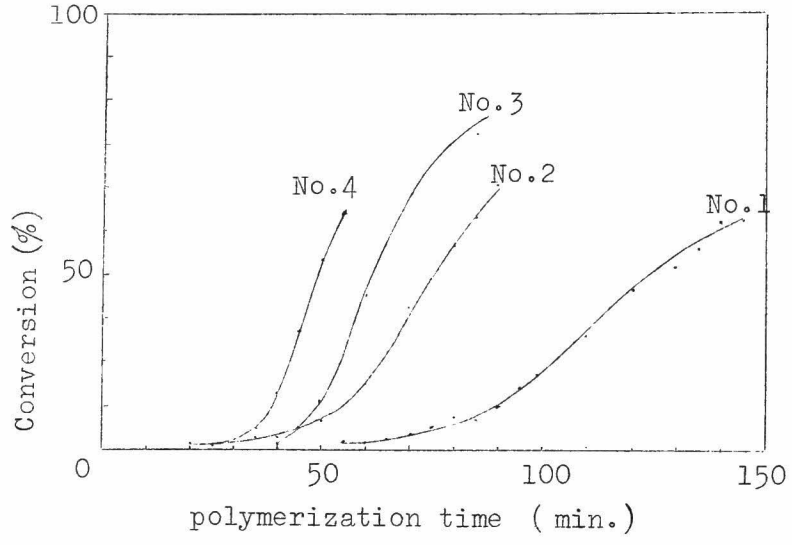


Fig. 4-2 Time—conversion curves for the polymerization of p-chlorostyrene at 30°C in benzene

[M] mole/l.

No. 1 0.550 No. 2 0.826 No.3 1.10 No.4 1.38

[c] = 15 m mole/l. $[C_0]$ = 10 m mole/l.

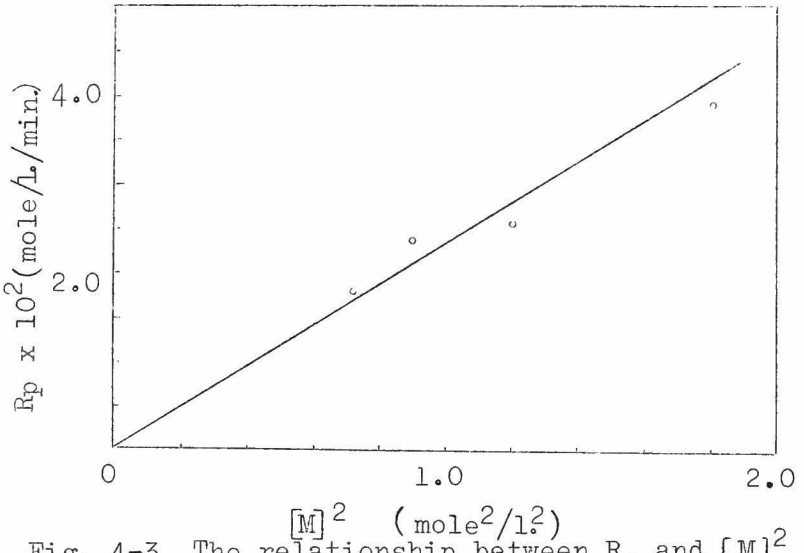


Fig. 4-3 The relationship between R_p and $[M]^2$ in the polymerization of p-chlorostyrene at 30°C in benzene

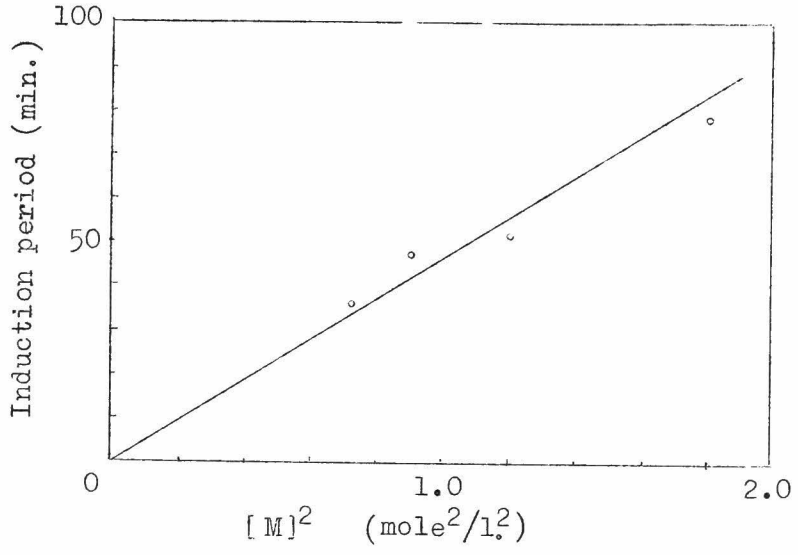


Fig. 4-4 The relationship between t_i and $1/[M]$ in the polymerization of p-chlorostyrene at 30°C in benzene

In Fig. 4-4 the length of the induction period was plotted against the reciprocal of the monomer concentration and the proportionality between them was evident.

Next, polymerizations were carried out at various catalyst concentrations, while the monomer concentration and the catalyst/co-catalyst ratio were kept constant. The time—conversion curves are shown in Fig.4-5.

The maximum polymerization rate was calculated from a tangent to the curve and plotted against the catalyst concentration to give a straight line. The linear relationship between the polymerization rate and the catalyst

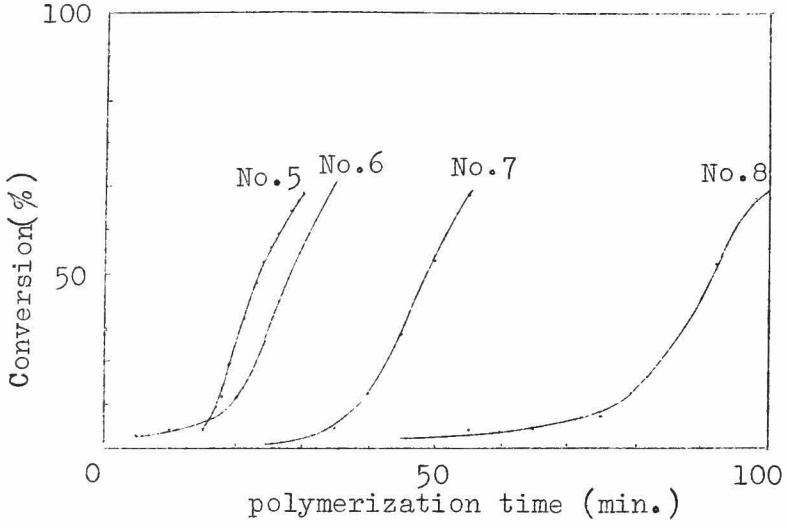


Fig. 4-5 Time—conversion curves for the polymerization of p-chlorostyrene at 30°C in benzene

	[C] m mole/l.	[Co] m mole/l.
No.5	30	20
No.6	22.5	15
No.7	15	10
No.8	8	5

[M] = 1.38 mole/l.

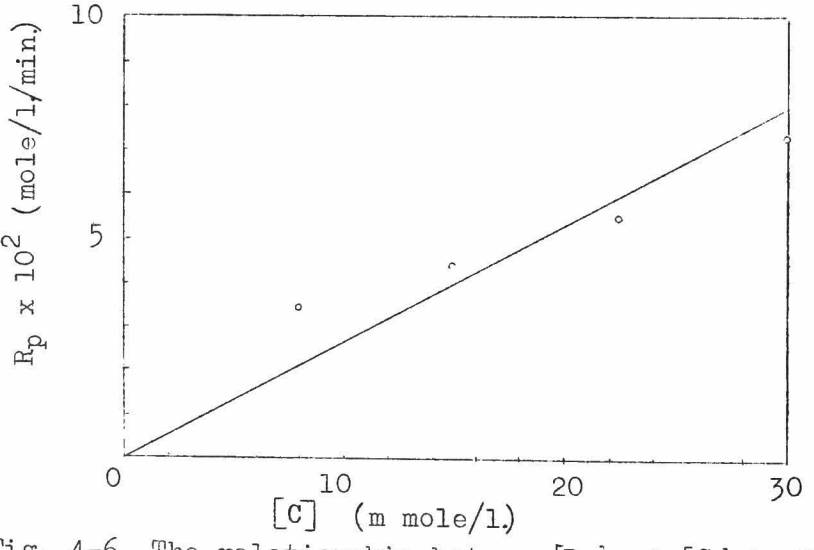


Fig. 4-6 The relationship between $[R_p]$ and [C] in the polymerization of p-chlorostyrene at 30°C in benzene with constant [Co]/[C]

concentration is shown in Fig. 4-6.

The length of the induction period was plotted against the reciprocal of the catalyst concentration. The relationship between them is shown in Fig. 4-7.

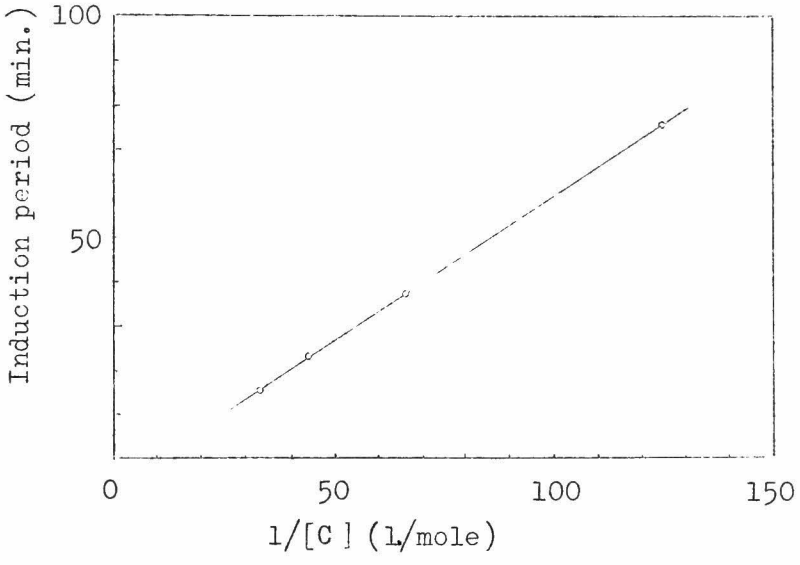


Fig. 4-7 The relationship between t_i and 1/[C] in the polymerization of p-chlorostyrene at 30°C in benzene with constant [Co]/[C]

From these experimental results it was established that in the cationic polymerization of p-chlorostyrene in benzene at 30°C using stannic chloride —trichloroacetic acid as catalyst the following equations hold,

$$R_p = K[M]^2[C]$$

$$T_i = K'/[M][C]$$

These relationships were likewise observed in the cationic polymerization of styrene in benzene using stannic chloride as catalyst.[8)]

Next, polymerizations of p-chlorostyrene were carried out in dichloroethane at various monomer concentrations, while the concentrations of catalyst and co-catalyst were kept constant. The time—conversion curves are shown in Fig. 4-8.

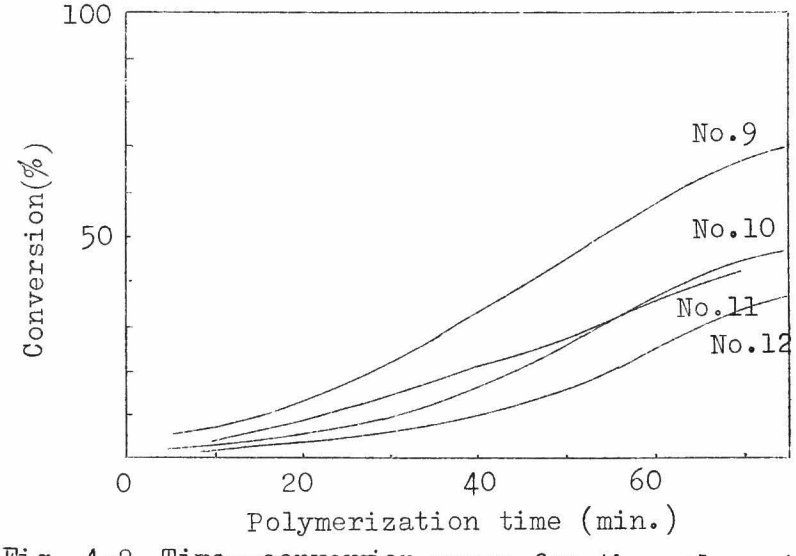


Fig. 4-8 Time—conversion curve for the polymerization of p-chlorostyrene at 30°C in dichloroethane

[M] mole/l.

No. 9	0.550	No. 10	0.826
No.11	1.10	No. 12	1.38

[C] = 1 m mole/l.
[Co] = 0.5 m mole/l.

The maximum polymerization rate was calculated from a tangent to the curve and plotted against the monomer concentration, when a straight line was obtained as shown in Fig. 4-9

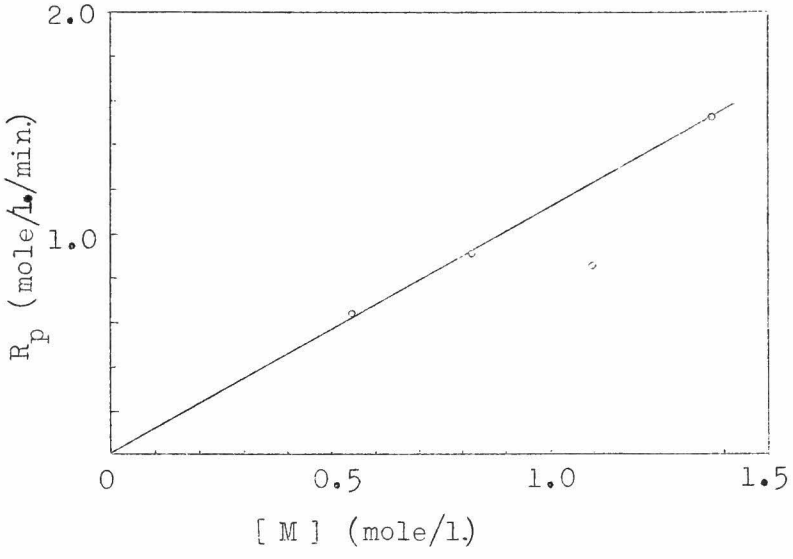


Fig. 4-9 The relationship between R_p and [M] in the polymerization of p-chlorostyrene at 30°C in dichloroethane

Then, the proportionality of polymerization rate to the monomer concentration was proved for dichloroethane, this differing from the proportionality to the square of monomer concentration observed in the styrene polymerization.[8)]

3.1.2 The polymerization rate of o-chlorostyrene

o-Chlorostyrene was polymerized in benzene at 30°C using stannic chloride—trichloroacetic acid as catalyst. The time—conversion curves are shown in Fig. 4-10. For the comparison, the time—conversion curve of p-chlorostyrene is shown in Fig. 4-10.

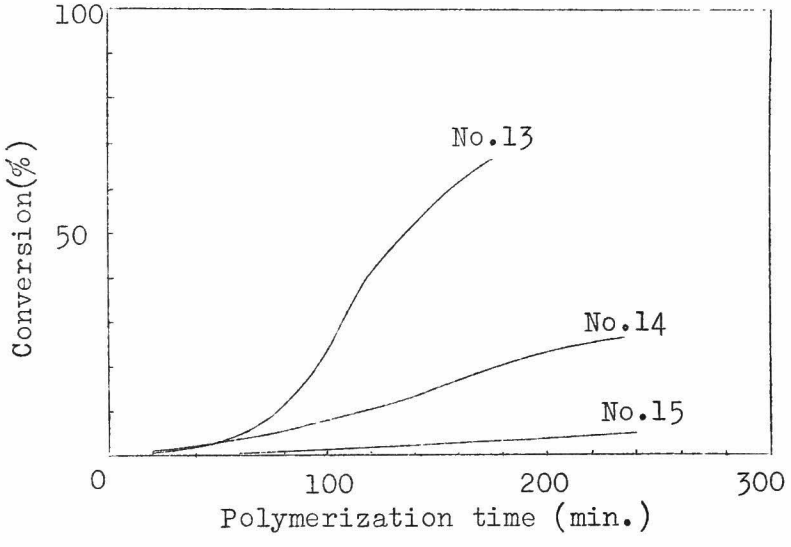


Fig. 4-10 Time—conversion curves for the polymerization of p-chlorostyrene (No.13) and o-chlorostyrene (No.14 and 15) at 30°C in benzene

	[M] mole/l.	[C] m mole/l.	[Co] m mole/l.
No.13	1.38	11.6	5.1
No.14	3.17	53	18.5
No.15	3.17	26.5	9.3

As is clearly shown in the Figure, the polymerization rate of o-chlorostyrene is much less than that of p-chlorostyrene. How the rate of polymerization of o-

chlorostyrene depended on the monomer concentration and catalyst concentration were not studied.

3.1.3 The rate of polymerization of styrene

Fig. 4-11 shows the time — conversion curves for the polymerization of styrene in dichloroethane at 30°C using stannic chloride—trichloroacetic acid as catalyst.

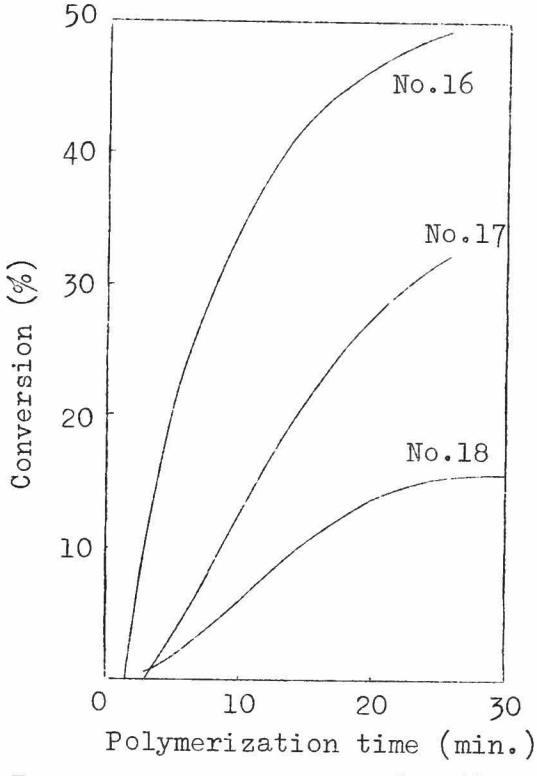


Fig. 4-11 Time—conversion curves for the polymerization of styrene at 30°C in dichloroethane

[M] = 1.45 mole/l.

	[C] m mole/l.	[Co] m mole/l.
No.16	0.5	0.25
No.17	0.25	0.25
No.18	0.25	0.125

3.1.4 The effect of co-catalyst/catalyst ratio on the polymerizations of o- and p-chlorostyrene.

o-Chlorostyrene was polymerized in dichloroethane at 30°C with changing co-catalyst/catalyst ratio, while the monomer concentration was kept constant. The time—conversion curves are shown in Fig. 4-12.

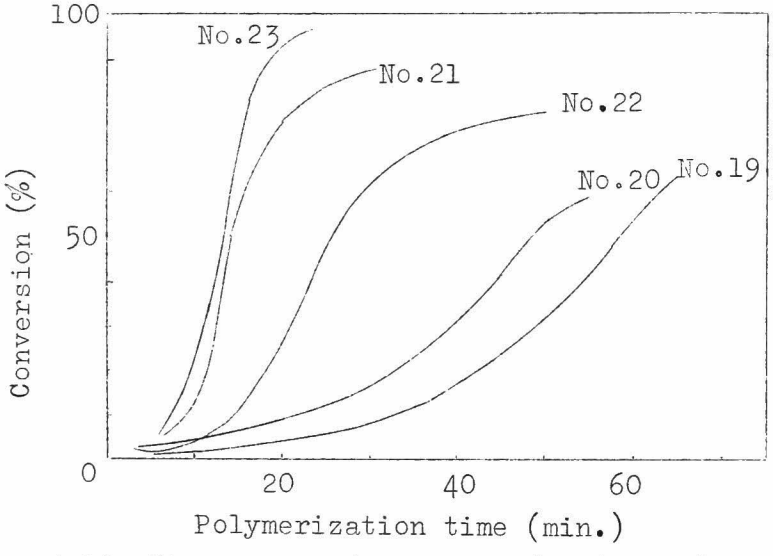


Fig. 4-12 Time—conversion curves for the polymerization of o-chlorostyrene at 30°C in dichloroethane

[M] = 1.31 mole/l.

	[C] m mole/l.	[Co] m mole/l.	[Co]/[C]
No.19	2	0.5	0.25
No.20	2	1	0.5
No.21	2	2	1
No.22	2	4	2
No.23	4	2	0.5

Similarly p-chlorostyrene was polymerized in dichloroethane at 30°C, and the effect of co-catalyst/catalyst ratio was studied. The time—conversion curves

are shown in Fig. 4-13.

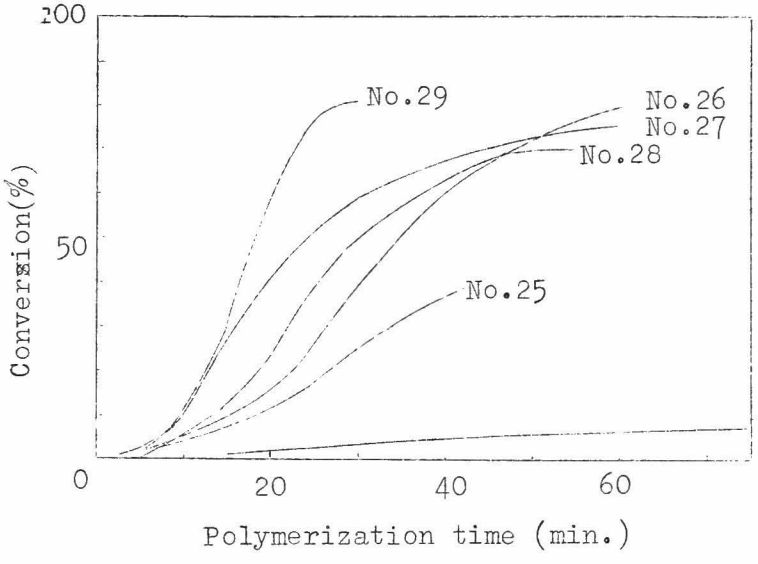


Fig. 4-13 Time—conversion curves for the polymerization of p-chlorostyrene at 30°C in dichloroethane
[M] = 1.38 mole/l.

	[C] m mole/l.	[Co] m mole/l.	[Co]/[C]
No.24	1	0	0
No.25	1	0.25	0.25
No.26	1	0.5	0.5
No.27	1	1.0	1
No.28	1	2.0	2
No.29	2	1.0	0.5

The effect of the co-catalyst/catalyst ratio on the cationic polymerizations of styrene, o- and p-chlorostyrene by stannic chloride— trichloroacetic acid as catalyst was discussed in terms of the polymerization rate calculated from a tangent to the time—conversion

curve shown in Figs. 4-11, 4-12 and 4-13. These polymerization rates are shown in Fig. 4-14, which also gives the degree of polymerization of the polymer. From that Figure it was ascertained that the polymerization rate reached a maximum at a co-catalyst/catalyst ratio of about unity, and that the degree of polymerization of resultant polymer was not essentially affected by the co-catalyst/catalyst ratio over the range employed in the present investigation.

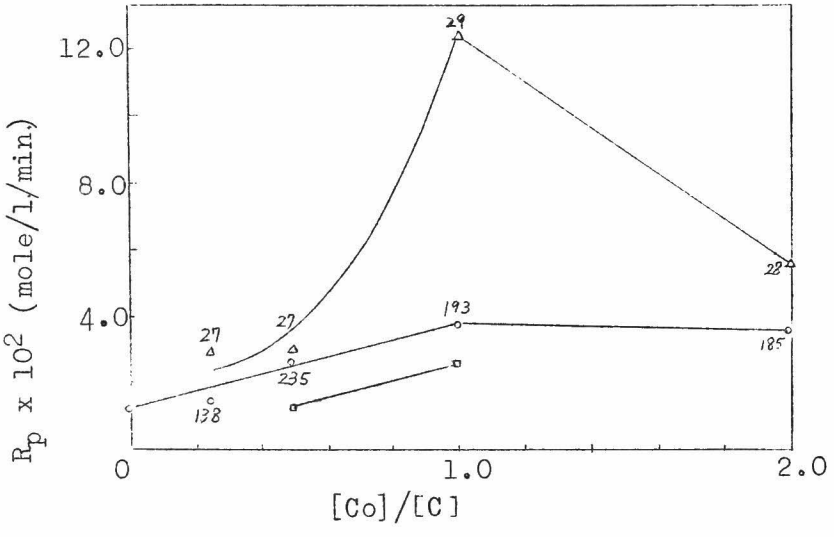


Fig. 4-14 The dependence of R_p and $\bar{P}$ on [Co]/[C]in the polymerization at 30°C in dichloroethane. The figures are the average degree of polymerization of polymers.

	[M] mole/l.	[C] m mole/l.
(○): p-chlorostyrene	1.38	1
(△): o-chlorostyrene	1.31	2
(□): styrene	1.45	0.5

3.1.5 The comparison of the polymerization rates of styrene, o-chlorostyrene and p-chlorostyrene

The polymerization rates of three monomers were compared. As is seen from Table 4-2, the polymerization rates fall in the order styrene > p-chlorostyrene > o-chlorostyrene. Later, in Chapter 10, the monomer reactivity of these three monomers in the cationic copolymerization will be shown to be in the order of styrene > o-chlorostyrene > p-chlorostyrene, which does not coincide with the order of the polymerization rate. The reason of the discrepancy is not clear at present.

3.2 The determination of the rate constant ratio

3.2.1 The transfer and termination constant ratio in the polymerization of p-chlorostyrene

In order to obtain rate constant ratios, polymerizations of p-chlorostyrene were carried out in 25 ml. of benzene or dichloroethane using various concentrations of monomer. The right amount of chloroform was added to avoid change in dielectric constant when monomer concentration was reduced. Here determination of the rate constant ratio in benzene will be shown by way of example.

The dielectric constant of the system is probably low (ca. 2.5), when the unimolecular termination reaction

Table 4-2 The comparison of maximum rate of the polymerization of styrene, o-chlorostyrene and p-chlorostyrene

Monomer	Solvent	[M] mole/l.	[C] m mole/l.	[Co] m mole/l.	$R_p \times 10^2$ mole/l./min.	Time—conv. curve
o-Chlorostyrene	C_6H_6	3.17	53	18.5	0.46	No.14
	"	3.17	26.5	9.3	0.08	No.15
p-Chlorostyrene	"	1.38	11.6	5.1	1	No.13
"	"	1.38	22.5	15	5.50	No. 6
Styrene	$(CH_2Cl)_2$	1.45	0.5	0.25	10	No.16
o-Chlorostyrene	"	1.31	2	1	3	No.20
o-Chlorostyrene	"	1.38	2	1	5	No.29

may reasonably be neglected[9], leading to eq. (4-4), where [S

$$\frac{1}{\bar{P}} = \frac{k_{tm}}{k_p} + \frac{k_{ts}}{k_p} \cdot \frac{[S]}{[M]} \qquad (4\text{-}4)$$

is the concentration of benzene (here constant). When the reciprocal of the degree of polymerization of polymer ($\bar{P}$) was plotted against [S]/[M]or 1/[M], a straight line was obtained, the intercept of which gave the monomer transfer constant ratio k_{tm}/k_p and the slope the chain transfer constant ratio for benzene k_{ts}/k_p. These relationships are evident in Fig. 4-15.

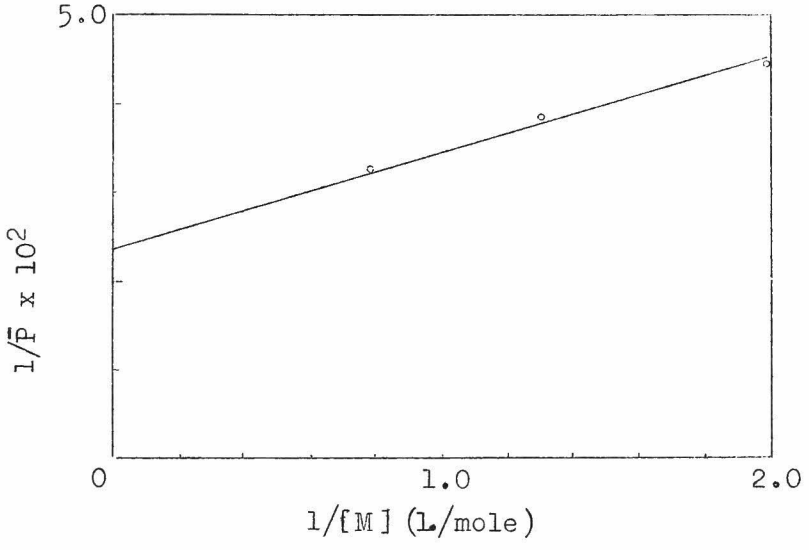


Fig. 4-15 The plot of $1/\bar{p}$ versus 1/[M]
p-Chlorostyrene—benzene—30°C—$SnCl_4 \cdot CCl_3COOH$
[C] = 11.3 m mole/l. [Co] = 5 m mole/l.
$k_{tm}/k_p = 2.36 \times 10^{-2}$ $k_{ts}/k_p = 1.22 \times 10^{-3}$

3.2.2 The transfer and the termination constant ratio of o-chlorostyrene

Since it can be assumed that dielectric constant of o-chlorostyrene is almostly the same as that of chloroform, polymerization of 12 ml.of o-chlorostyrene in 18 ml.of benzene or dichloroethane was carried out, and the right amount of chloroform was added when the monomer concentration decreased. A high monomer concentration was required to obtain a measurable polymerization rate (cf. 3.1). In consequence, the approximate value of dielectric constant of the system was ca. 3.5, when the unimolecular termination reaction is no longer negligible.[9] Then, eq. (4-5) holds. Plotting the reciprocal of the degree of polymerization versus [S]/[M], a straight line was obtained from which k_{tm}/k_p could be determined.

$$1/\bar{P} = k_{tm}/k_p + (k_{ts}/k_p + k_t'/k_p \cdot 1/[S])\,[S]/[M] \quad (4\text{-}5)$$

In eq. (4-5), $k_{t'} = k_t + k_{tx}[X]$ where k_t and k_{tx} are the rate constants for the unimolecular termination and the reaction with impurity, respectively. These relationships are clear in Fig. 4-16.

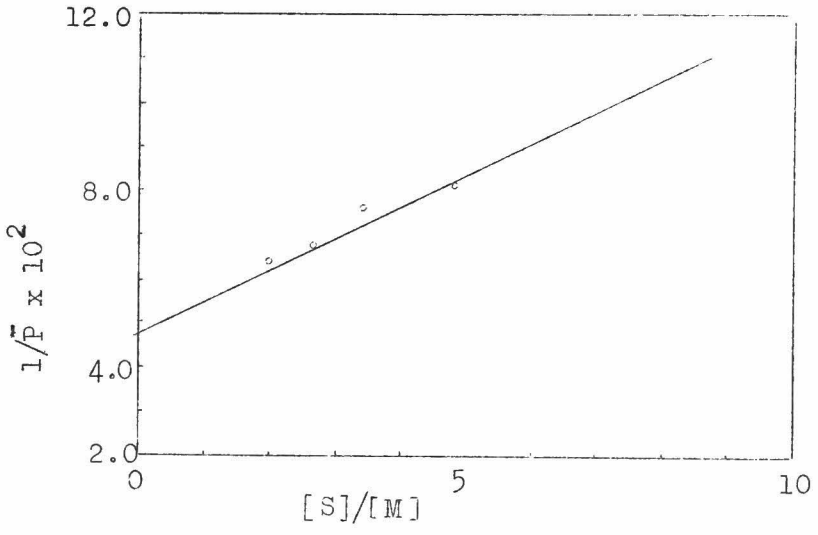


Fig. 4-16 The plot of $1/\bar{P}$ versus [S]/[M]
o-Chlorostyrene—benzene—30°C—$SnCl_4 \cdot CCl_3COOH$
[C] = 35 m mole/l. [Co] = 14 m mole/l.
$k_{tm}/k_p = 4.80 \times 10^{-2}$ $k_{ts}/k_p + k_t/k_p[S]$
$= 0.72 \times 10^{-2}$

k_{tm}/k_p was obtained similarly in dichloroethane.

3.2.3 The transfer and the termination reaction in the polymerization of styrene

The cationic polymerization of styrene by stannic chloride as catalyst has been widely investigated and the rate constant ratios have been determined in various solvents.[10] However, the rate constant ratio in polymerization by stannic chloride — trichloroacetic acid has seldom been reported. Hence the present work on the polymerization of styrene using stannic chloride —

trichloroacetic acid.

Styrene was polymerized at 30°C using stannic chloride — trichloroacetic acid as catalyst in toluene, toluene — chloroform mixed solvent and dichloroethane, and the rate constant ratios were determined. The results of polymerization in toluene will be given by way of example.

Since toluene has almostly the same dielectric constant as styrene, the polymerization was carried out keeping the total volume of styrene and toluene 30 ml. and changing the monomer concentration. The reciprocal of the degree of polymerization of polymer is given by eq. (4-6),

$$1/\bar{P} = k_{tm}/k_p + k_r k_p \cdot [r]/[M] \qquad (4\text{-}6)$$

where [r] represents the concentration of toluene and k_r stands for the chain transfer constant to toluene. Fig. 4-17 shows the plot of $1/\bar{P}$ against [r] / [M]. The rate constant ratio was determined similarly in dichloroethane.

The rate constant ratios for three kinds of monomers, thus determined, are shown in Table 4-3.

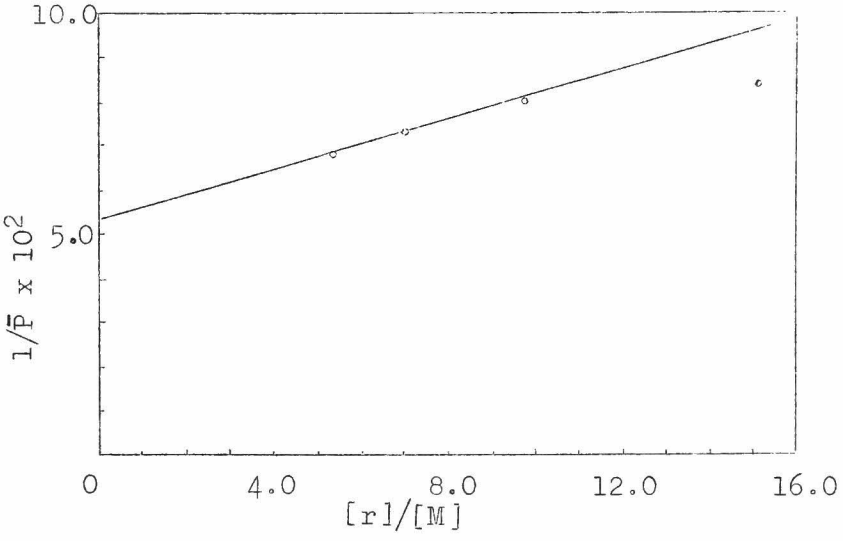


Fig. 4-17 The plot of $1/\bar{P}$ versus $[r]/[M]$
styrene—toluene—30°C—$SnCl_4 \cdot CCl_3COOH$
$k_{tm}/k_p = 5.35 \times 10^{-2}$, $k_r/k_p = 2.80 \times 10^{-3}$
[C] = 20 m mole/l. [Co] = 8 m mole/l.

Table 4-3 The monomer transfer constant ratios ($k_{tm}/k_p \times 10^2$)

D.C.* of the system	o-Chlorostyrene	p-Chlorostyrene	Styrene
2.5	—	2.36	5.35
3.5	4.80	—	1.45
9.8	3.12	3.60	5.82

* Approximate values of dielectric constants of the polymerization systems, assuming that $\bar{\varepsilon} = \sum_i v_i \varepsilon_i$, where $\bar{\varepsilon}$ is the approximate value, ε_i is dielectric constant of i th component and v_i is volume fraction of i th component.

3.3 The infrared spectrum of polymer

In order to ascertain the polymer end group the infrared spectrum of polymer was investigated. The infrared spectrum of poly-o-chlorostyrene obtained in the present investigation is shown in Fig. 4-18. The number average molecular weight of this polymer was ca. 10. Weak absorptions at 910, 990 and 1640 cm^{-1} may be ascribed to a vinyl double bond.[11] This view is supported by the fact that these absorptions appear strongly with monomer and disappear when the polymer has been brominated. The infrared spectrum of poly-o-chlorostyrene after bromination is shown in Fig. 4-19.

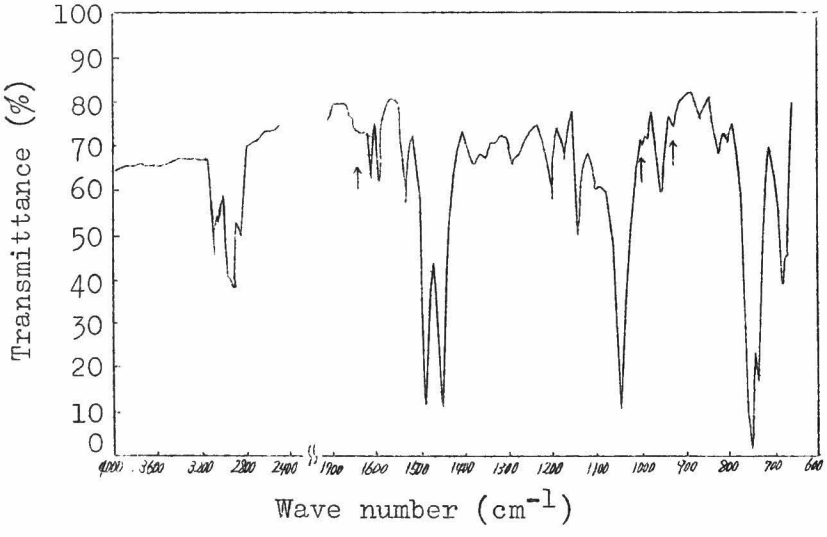


Fig. 4-18 The infrared absorption spectra of poly-o-chlorostyrene. $\overline{P}_n \simeq 10$

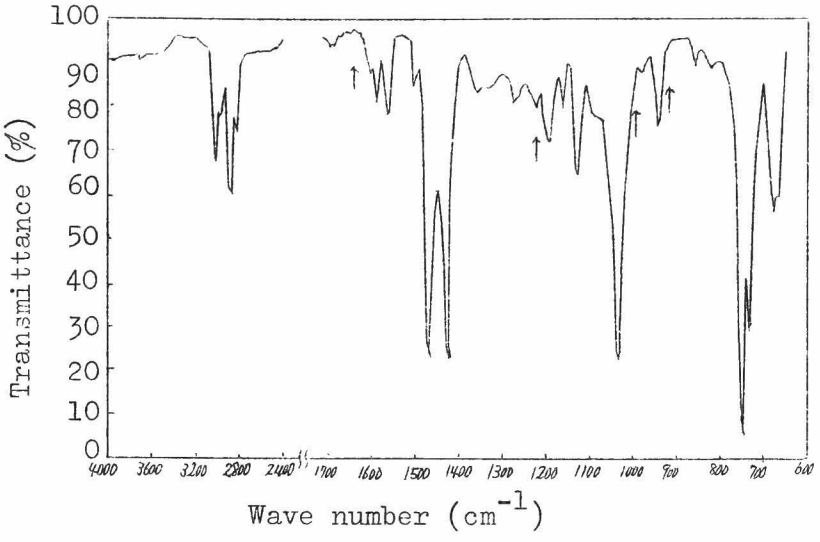


Fig. 4-19 The infrared absorption spectra of brominated poly-o-chlorostyrene

After bromination the absorptions described above disappeared and instead a new absorption appeared at 1220 cm^{-1}, which has not been assigned with certainty. It may be due to a harmonic absorption by an aliphatic carbon–bromine bond which shows an absorption at about 600 cm^{-1}.[11]

The infrared spectrum of poly-p-chlorostyrene is shown in Fig. 4-20. This polymer was produced in benzene and had a degree of polymerization of about 30. It also shows absorptions at 910 and 990 cm^{-1}, which are ascribed to a vinyl double bond[11] because they appears strongly in monomer and disappear after bromination of the polymer.

The infrared spectrum of brominated poly-p-chlorostyrene is shown in Fig. 4-21. A new weak absorption at 1220 dm^{-1} appeared in the infrared spectrum of brominated poly-p-chlorostyrene, analogous to the case of poly-o-chlorostyrene.

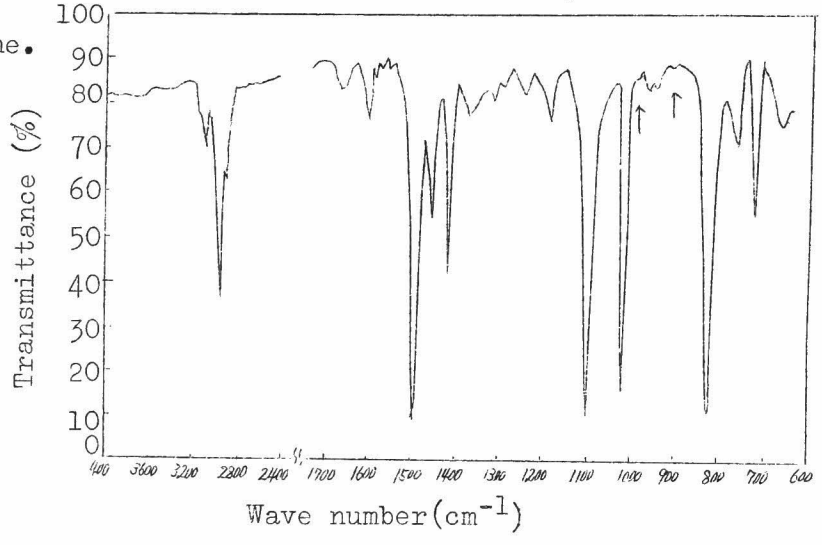


Fig. 4-20 The infrared absorption spectra of poly-p-chlorostyrene $\overline{P}_n \simeq 30$

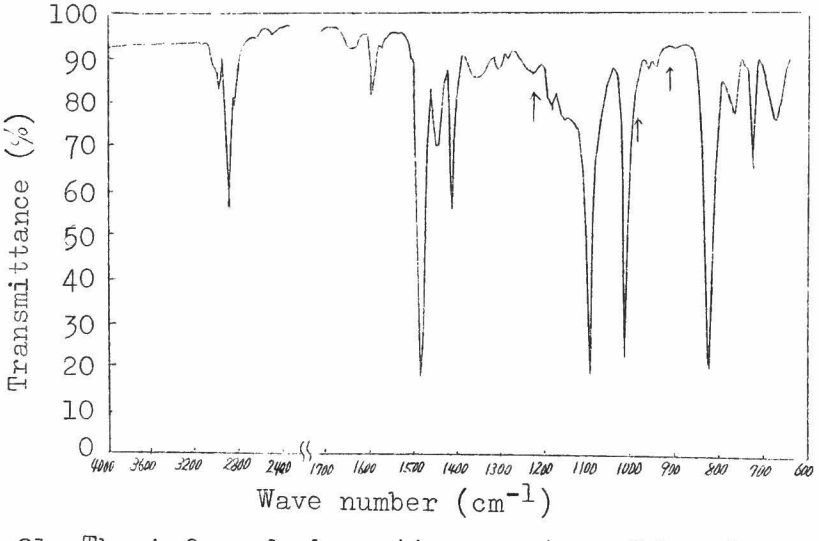


Fig. 4-21 The infrared absorption spectra of brominated poly-p-chlorostyrene

4. Discussion

Discussions will be given regarding the mechanism of the monomer transfer reaction of chlorostyrenes. In the cationic polymerizations of o- and p-chlorostyrene under the various conditions, k_{tm}/k_p decreased with increasing dielectric constant of solvent as shown in Fig. 4-3, which is a characteristic feature for the styrene-type monomer transfer reaction. As a result of the investigation on the monomer transfer reaction for methoxystyrenes in the previous Chapter, it was suggested that the reaction of the growing ion-pair with the phenyl group of monomer is important in the styrene-type monomer transfer reaction. In order to investigate the validity of this mechanism for the polymerization of chlorostyrenes, the electronic and steric effect of chlororine atom were considered by comparing k_{tm}/k_p of chlorostyrenes with that of styrene.

The approximate value of the ratio of the monomer transfer constants (k_{tm}) for chlorostyrene and styrene under the same condition was calculated by eq. (4-7) which was put forward in the previous Chapter,

$$\frac{(k_{tm})_{ClSt}}{(k_{tm})_{St}} = (k_{tm}/k_p)_{ClSt}/(k_{tm}/k_p)_{St} \times \left(r_{ClSt}/r_{St}\right)^{\frac{1}{2}} \quad (4\text{-}7)$$

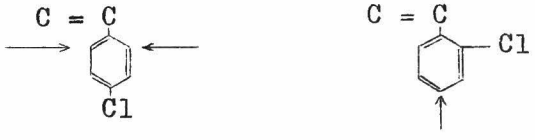
where r_{ClSt} and r_{St} are the monomer reactivity ratios in the cationic copolymerization of chlorostyrene and styrene carried out under the same condition as when k_{tm}/k_p was determined. The experimental results of the copolymerization will be described in Chapter 10. The ratio of k_{tm} is shown in Table 4-4. But as noted in Chapter 3, no conclusion is drawn from k_{tm} because the magnitude of k_{tm} is determined by the reactivities of an attacking ion and a monomer. Then, R_M' of chlorostyrene was calculated according to eq. (3-13) by inserting R_I' determined in Chapter 10, R_M' of styrene being taken as unity. The results are shown in Table 4-4.

Table 4-4 The comparison of monomer transfer constant

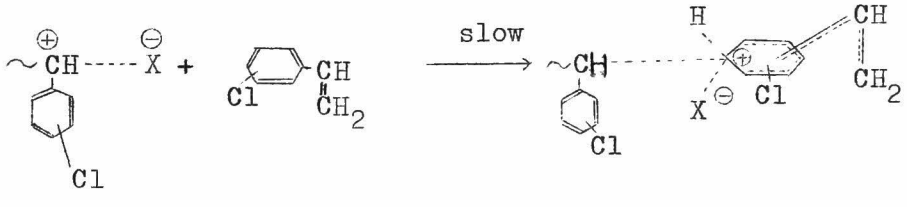
Monomer		Comparison of k_{tm}*	Comparison of R_M'
M_1	M_2	k_{tm} of M_2/k_{tm} of M_1	R_M' ofM_2/R_M' of M_1
Styrene	p-Chlorostyrene	0.14-0.18	0.03
Styrene	o-Chlorostyrene	1.56-2.15	0.10
o-Chlorostyrene	p-Chlorostyrene	0.07-0.12	0.33
Styrene	p-Chlorostyrene	0.20-0.25	—
Styrene	o-Chlorostyrene	2.52-3.48	—
o-Chlorostyrene	p-Chlorostyrene	0.06-0.10	—

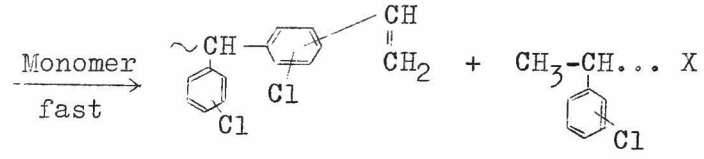
* The data in upper column were obtained in solvent of low D. C. (Ca.3), and other data were obtained in solvents of high D.C. (Ca. 9).

Judging from R_M' ratio, chlorostyrenes have much smaller reactivity as a chain transfer reagent than styrene. This is due to the decrease of electronegativity of the phenyl group induced by the inductive effect of chlorine atom. On the other hand, the comparison between o- and p-chlorostyrene showed that o-chlorostyrene is superior to p-isomer as chain transfer reagent. This is due partly to the larger electron density[12] and partly to the smaller steric hindrance at the reaction site (indicated by arrow) in the case of o-chlorostyrene as compared with that of p-chlorostyrene.

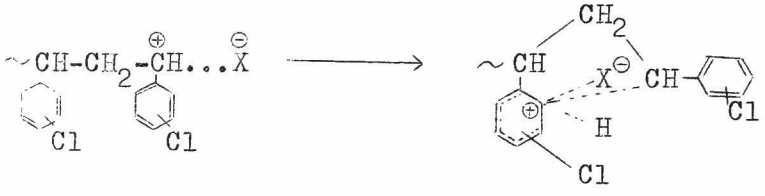


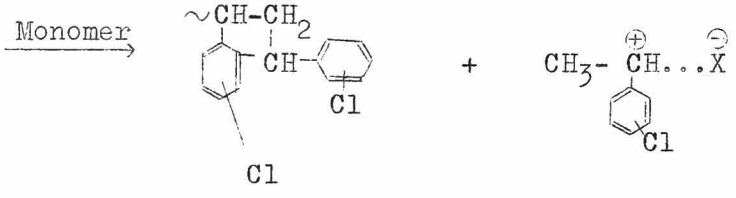
As described in the previous Chapter, there are the following two possibilities (eq. (4-8) and (4-9)) in the styrene-type monomer transfer reaction, in which a growing cation attacks the phenyl group:—





(4-8)





(4-9)

Pepper[13] was inclined to consider that eq. (4-9) represents the mechanism. Both reactions are essentially the same and are not easily distinguished by the present kinetic investigation. However, the larger reactivity of o-chlorostyrene as a chiin transfer agent in the monomer transfer reaction compared with p-chlorostyrene, as shown in Table 4-4, is satisfactorily explained on a basis that the reaction (4-8) takes place at least in part. Thus the kinetic investigation supports the mechanism of the styrene-type monomer transfer reaction proposed in Chapter 3.

Spectroscopic analysis of the polymer structure also supports the above conclusion, that is,that a vinyl double bond can be incorporated only by reaction (4-8). As the result of the reaction (4-8), a 1,2,4-trisubstituted benzene has to be formed both in poly-p-chlorostyrene and in poly-o-chlorostyrene. The absorption due to the trisubstituted benzene should appear in the wave number range between 800 and 900 cm^{-1}. With poly-p-chlorostyrene a strong absorption at 820 cm^{-1} interfered with the analysis. In poly-o-chlorostyrene three weak absorptions were detected in that region. There is some support for the view that some of those absorptions may be assigned to trisubstituted benzene[11], but no definite conclusion can be drawn because there is no simple method of identification such as brominating the double bond.

Now the facility of the monomer transfer reaction will be discussed in relationship to the ion-pair—free ions equilibrium of the growing end. As has already been made clear, k_{tm}/k_p in the cationic polymerization of styrene and its derivatives is smaller for polymerization in a more polar solvent by a milder catalyst to give a high molecular weight polymer. This will

be discussed in relation to reaction (4-8).

Let us consider the solvent effect with reaction (4-8). It has been recognized in cationic polymerization of styrene the propagation reaction is facilitated by the dissociation of the ion-pair into free ions induced by the increase of dielectric constant of solvent.[14] The decrease of k_{tm}/k_p in the more polar solvent is therefore ascribed to either the decrease of k_{tm} or the increase of k_{tm} to less extent than k_p. Reaction (4-8) is a kind of Friedel-Crafts reaction. Brown et al.[15] from their kinetic investigation proposed that the Friedel-Crafts reaction is not accelerated in the above way by the increase of dielectric constant of solvent. Brown stated in this connection that the Friedel-Crafts reaction does not proceed through substitution mechanism but proceeds through a displacement mechanism, and that the attacking species need not be free ion. Since the free ion form is more important in the propagation reaction than in the reaction (4-8), k_{tm}/k_p became smaller in more polar solvent. This view is supported by an experiment[16] in which, by changing the solvent from carbon tetrachloride to dichloroethane, k_p was increased more than k_{tm} to bring about decrease in k_{tm}/k_p.

Table 4-5 The polymerization of p-methoxystyrene by iodine at 30°C[16]

Polymerization in CCl_4		
k_{tm}/k_p	k_p l/mole/min.	k_{tm} l/mole/min.
2.6×10^{-2}	7.4	1.9×10^{-1}

Polymerization in $(CH_2Cl)_2$		
k_{tm}/k_p	k_p l/mole/min.	k_{tm} l/mole/min.
0.25×10^{-2}	3.5×10^{2}	8.8×10^{-1}

Next, the effect of the counter ion on reaction (4-8) will be discussed. It was established that the free ion form is important in the propagation reaction, while the styrene-type monomer transfer reaction can take place without dissociating the ion-pair. The reactivity of the growing ion is required to be large in the monomer transfer reaction, where a new bond is formed between a cation and a phenyl group. The growing end, consisting of a reactive carbonium ion or a reactive counter anion, tends to form an ion-pair. Thus it can be said that the monomer transfer reaction occurs more easily on the growing end of ion-pair form . The effect of catalyst on the reactivity of an ion-pair was considered in

relationship to stannic chloride and titanium tetrachloride as examples. The stability of $SnCl_4 \cdot X^{\ominus}$ is possibly larger than that of $TiCl_4X^{\ominus}$ for the reason given in Chapter 2. Consequently, the ion-pair $C^{\oplus}\ldots TiCl_4X^{\ominus}$ is considered to be more reactive in the monomer transfer reaction. The more acidic catalyst, titanium tetrachloride, therefore gives larger k_{tm}/k_p.

There should be a lot to be explained about the effect of catalyst on the reactivity of the growing end. But it is obvious that the nature of counter anion is not directly connected with the reactivity of catalyst in the initiation reaction, but must be discussed from the stand point of the stability of anion (as above). For example, in the cationic polymerization of isobutene by titanium tetrachloride, which gives a large polymerization rate, k_{tm}/k_p was smaller than with stannic chloride which gives a small polymerization rate (in both cases, the co-catalyst was trichloroacetic acid.). If this experimental result is ascribed to difference of the catalystic activity in the initiation reaction, k_{tm}/k_p should become larger when titanium tetrachloride—water is used in place of titanium tetrachloride—trichloroacetic acid, but the reverse was obtained. This is

satisfactorily explained by assuming a difference in counter anion stability, viz. allowing for the change distribution, $TiCl_4 \cdot CCl_3COO^{\ominus}$ is to be regarded as more stable and dissociating into free ions more readily than $TiCl_4 \cdot OH^{\ominus}$.

The monomer transfer reaction in which the free ion form is important is thus accelerated when trichloroacetic acid is used as the co-catalyst.

It was established in the present investigation as a result of investigation of the electronic and the steric effect of the chlorine atom on the monomer transfer reaction that the monomer transfer reaction takes place by the interaction of the growing cation with the phenyl group of monomer. The mechanism of the styrene-type monomer transfer reaction was thus supported. Furthermore, from the effect of the polymerization condition on k_{tm}/k_p for styrene and its derivatives, it was deduced that the ion-pair form is more important in the monomer transfer reaction than in the propagation reaction.

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Chapter 5 Methyl Vinyl Ether

1. Introduction

From foregoing experimental facts it was recognized that the nature of the growing ion-pair affects the transfer and termination reaction in the cationic polymerization, and mechanisms for the transfer and the termination reactions were proposed for isobutene and styrene derivatives. In the polymerization of styrene derivatives, the monomer transfer reaction takes place by attack of a growing ion-pair on an electronegative phenyl group of monomer. Alkyl vinyl ethers have ethereal oxygen in themselves which is nucleophilic enough to act as the transfer and termination agent[1] in the cationic polymerization. It has been reported by Eley[2] and Schidknecht[3] that ethereal oxygen forms a complex with cationic catalysts. The equilibrium constant between iodine and alkyl vinyl ethers is very large compared with that between iodine and styrene derivatives.[4] It is therefore very interesting to investigate the effects of catalyst and solvent on the degree of polymerization of polymer in the cationic polymerization of such monomers. In order to investigate the transfer and termination

reactions in polymerization of monomers with an electron donating substituent, the polymerizations were carried out with alkyl vinyl ether. In this Chapter, the experimental results for methyl vinyl ether will be described.

2. Experimental

2.1 Reagent

Methyl vinyl ether (Mitsubishi Chemical Co.) was bubbled repeatedly through aqueous potassium hydroxide solution and water, dried through a long calcium chloride tube, and condensed in a buret cooled with dry ice—methanol. Monomer was added to a precooled flask containing a given amount of solvent.

Boron trifluoride etherate and stannic chloride-trichloroacetic acid were used as catalysts, and were purified in the way previously described.

Carbon tetrachloride, chloroform and methylene chloride were used as solvents. They were purified in the way previously described, special case being taken to remove water.

2.2 Procedure

40 ml. of solvent were put in a 100 ml. flask and monomer was added. When the monomer concentration is

changed, the dielectric constant of the polymerization solution is changed, and in order to avoid this, the right amount of chloroform, which is considered to have about the same dielectric constant as monomer, was added with decreasing the monomer concentration. The total volume of polymerization solution was 50 ml.

Polymerization solution was prepared in a 100 ml. flask fitted with a long calcium chloride tube and the catalyst inlet, and cooled to a given temperature. The polymerization was started by adding the catalyst through the inlet, and stopped by adding ammoniacal petroleum ether. The polymer was separated as a liquid phase, which was washed repeatedly with hot water, and dried in a vacuum at 40°C.

The bromination of polymer was carried out just as described in Chapter 2.

The hydrolysis of the end group of the polymer and the subsequent determination of the amount of aldehyde eliminated were carried out as follows.[5] To 50 ml. of aqueous polymer solution with a concentration of 0.002-0.005 mole/l., 50 ml. of N/100 aqueous hydroxylamine hydrochloride solution were added, and the mixture allowed to react for two days. Any acetal group present,

was hydrolyzed by the hydrogen chloride, and the resultant aldehyde was trapped by the hydroxylamine hydrochloride simultaneously, hydrogen chloride in amount corresponding to aldehyde was eliminated, and this hydrogen chloride was titrated by N/100 aqueous sodium hydroxide solution. The titration was carried out using pH meter containing a glass electrode. The neutralization point for sodium hydroxide and hydrogen chloride eliminated after hydrolysis was found from the titration curve. Moles of aldehyde were calculated from the amount of alkaline solution needed for the neutralization.

2.3 The calculation of the rate constant ratio

In order to calculate the rate constant ratio, polymerizations were carried out changing the monomer concentration over the range 1 ml./90 ml. (0.28 mole/l.) to 10 ml./50 ml. (2.76 mole/l.). From the relationship between the initial monomer concentration ([M]) and the degree of polymerization of polymer ($\bar{P}$), the monomer transfer constant ratio k_{tm}/k_p and the unimolecular termination constant ratio k_t'/k_p were calculated using equation (5-1).

$$1/\bar{P} = k_{tm}/k_p + k_t'/k_p \cdot 1/[M] \qquad (5\text{-}1)$$

where $k_t' = k_t + k_{tx}[X]$ and [X] represents the impurity.

The molecular weight of polymer was calculated from the intrinsic viscosity of the polymer in benzene at 30°C, using equation (5-2).

$$[\eta] = 1.84 \times 10^{-4} \times \bar{M}_w^{0.72} \qquad (5\text{-}2)$$

Equation (5-2) gives a molecular weight somewhat higher than does the equation reported by Manson et al.[6] However, in this investigation equation (5-2) was used. In the present polymerization, the degree of polymerization of polymer is determined by the monomer transfer reaction and the unimolecular termination reaction, the ratio of $\bar{M}_w/\bar{M}_n$ is considered to be about 2. Discussions given below assume $\bar{M}_w/\bar{M}_n = 2$.

3. Results

3.1 General features

The polymerization system was yellow or dark brown. The color of the system was darker, the higher the catalyst/monomer ratio, the more polar the solvent and the higher the temperature. The color almost vanished when the terminating agent was added to the system. However, when the polymerization system was colored strongly, the resulting polymer was colored pale yellow.

The reason for the coloration is not known. But even when the polymerization system and the resulting polymer were colored, the polymer dissolved readily in benzene and there was no difference between the Huggins' k' primes for colored polymer and colorless polymer. So it is safe to assume that there is no serious difference between the structures of the two types of polymer. Polymerizations could reach 100% conversion.

The effects of solvent dielectric constant and of catalyst on the intrinsic viscosity of the polymer in the cationic polymerization of methyl vinyl ether are shown in Fig. 5-1.

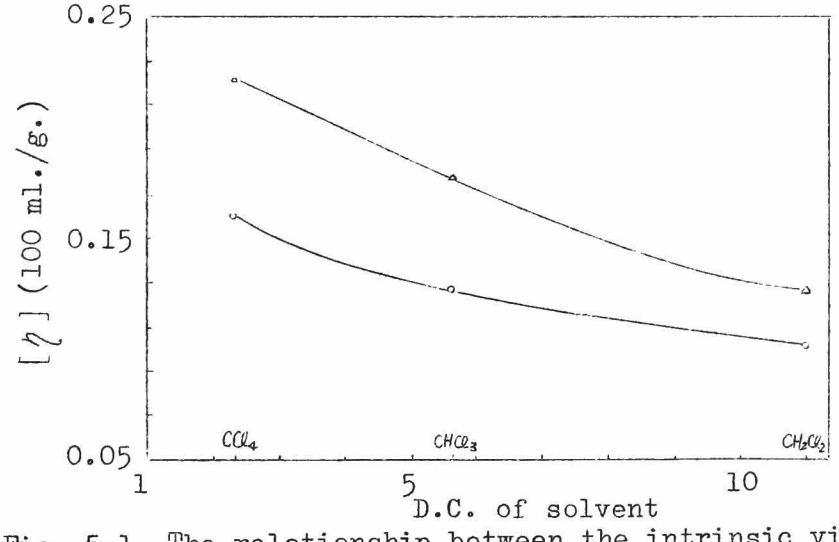


Fig. 5-1 The relationship between the intrinsic viscosity of polymethyl vinyl ether and the dielectric constant (D.C.) of solvent at -20°C
[M] = 0.83 mole/l. (3 ml/50 ml.)
Catalyst (△): $BF_3 \cdot O(C_2H_5)_2$ 60-90 m mole/l.
(○): $SnCl_4 \cdot CCl_3COOH$ 2 - 3 m mole/l.

The intrinsic viscosity of polymer decreased with increasing dielectric constant of solvent and increasing catalyst acidity. The effect of solvent was the same as in the isobutene polymerization, and the effect of catalyst was the same as in the styrene polymerization.

3.2 The calculation of the rate constant ratio

In order to explain the behavior of the degree of polymerization of polymer shown in Fig. 5-1, the effect of polymerization conditions on the transfer and the termination reaction must be known. So a number of rate constant ratios were calculated from the degree of polymerization of polymer using equation (5-1). Cases of determination of the rate constant ratio are shown in Fig. 5-2 a and b.

Rate constant ratios were determined for 10 kinds of polymerization conditions and these are listed in Table 5-1. Since carbon tetrachloride freezes at -50°C, polymerization in that solvent was not carried out at that temperature.

Plotting the data of Table 5-1 against dielectric constant of solvent, Fig. 5-3 a and b were obtained. From those Figures it was established that either the

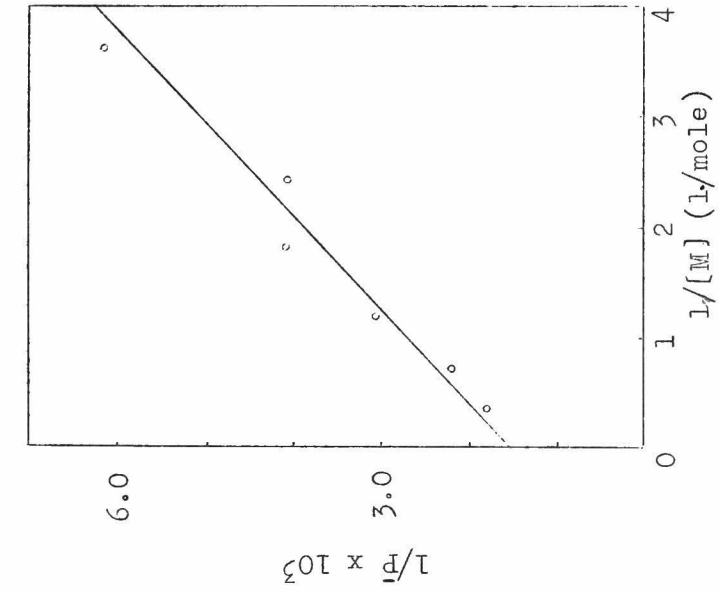


Fig.5-2a

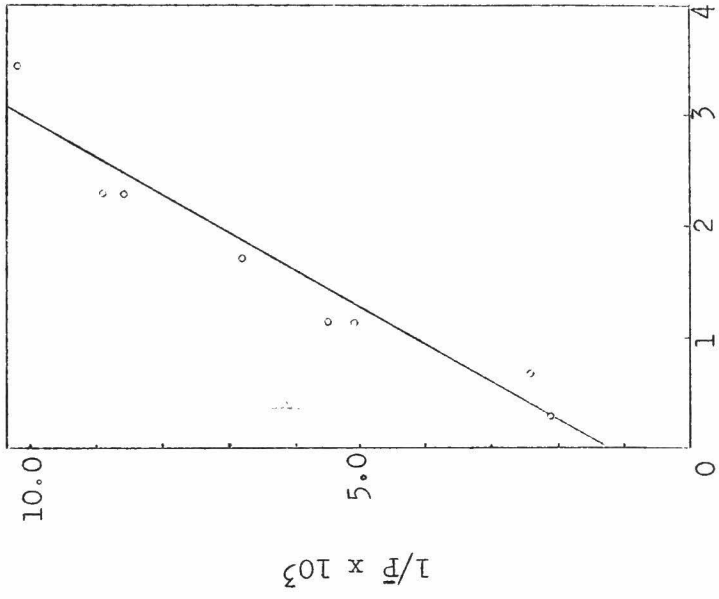


Fig. 5-2b

Fig.5-2 The estimation of the rate constant ratio by equation (5-1)

a: $CCl—BF_3 \cdot O(C_2H_5)_2$, -20°C

$k_{tm}/k_p = 1.54 \times 10^{-3}$ $k_t'/k_p = 1.17 \times 10^{-3}$

b: $CH_2Cl_2—SnCl_4 \cdot CCl_3COOH$, -50°C

$k_{tm}/k_p = 1.28 \times 10^{-3}$ $k_t'/k_p = 2.92 \times 10^{-3}$

Table 5-1 The summary of the rate constant ratios

Catalyst	$SnCl_4 \cdot CCl_3COOH$				$BF_3 \cdot O(C_2H_5)_2$			
Rate Const. Ratio	$k_{tm}/k_p \times 10^3$		$k_t'/k_p \times 10^3$		$k_{tm}/k_p \times 10^3$		$k_t'/k_p \times 10^3$	
Temp.(°C)	-20	-50	-20	-50	-20	-50	-20	-50
CCl_4	2.14	—	2.42	—	1.54	—	1.17	—
$CHCl_3$	2.40	1.20	3.02	2.63	2.29	0.60	1.44	1.24
CH_2Cl_2	3.20	1.28	4.40	2.92	3.12	0.64	3.20	1.52

monomer transfer reaction or the unimolecular termination reaction is promoted when polymerization is carried out with a more polar solvent, at higher temperature or using a more acidic catalyst (stannic chloride—trichloroacetic acid).

The ratio α of the two kinds of molecular weight-determining reactions can be calculated from the rate constant ratios of Table 5-1 using equation (5-3). α is the approximate ratio (differential form) of the number

$$\alpha = k_{tm}[M]/(k_{tm}[M] + k_t') \qquad (5\text{-}3)$$

of the polymer end groups produced by the monomer transfer reaction against the total number of the polymer end groups. $(1 - \alpha)$ is, therefore, the corresponding ratio

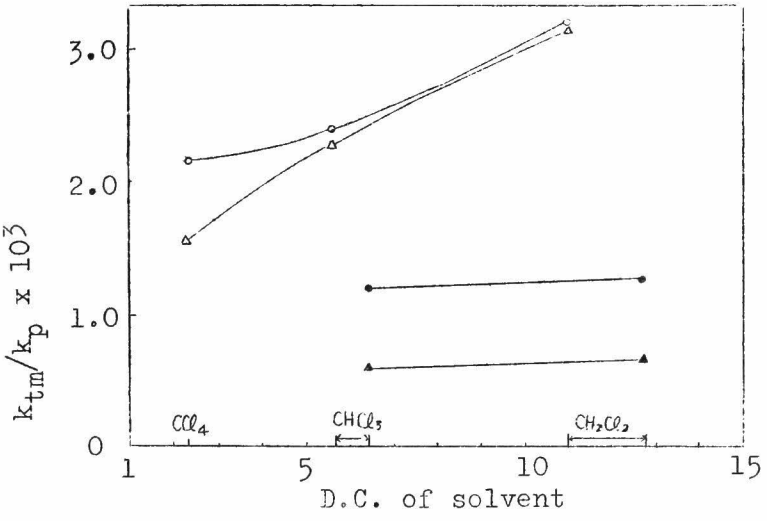


Fig. 5-3a

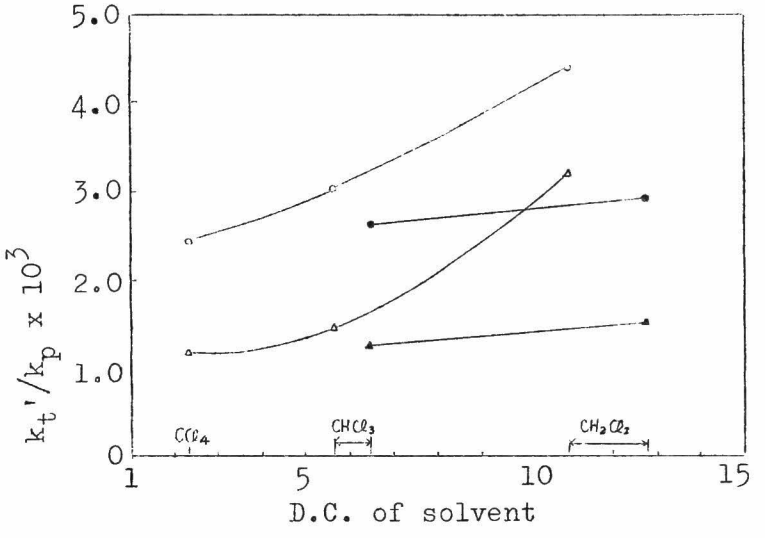


Fig. 5-3b

Fig. 5-3 The relationship between the rate constant ratio and the dielectric constant of solvent

(○): $SnCl_4 \cdot CCl_3COOH$, -20°C
(●): $SnCl_4 \cdot CCl_3COOH$, -50°C
(△): $BF_3 \cdot O(C_2H_5)_2$, -20°C
(▲): $BF_3 \cdot O(C_2H_5)_2$, -50°C

a: k_{tm}/k_p
b: $k_{t'}/k_p$

for the number of the polymer end groups produced by the unimolecular termination reaction.

In order to correlate α with end group structure, bromination of polymer was carried out and the results were compared with α in Table 5-2. It is clear that the number of double bond in polymer correlates with the monomer transfer reaction.

In order to obtain further information about the end group structure produced by the transfer and the termination reactions, hydrolysis of the polymer end group was carried out and the production of acetaldehyde was investigated. If acetal, ketal and vinyl ether type bond are present in the polymer, they are hydrolyzed by acid to give aldehyde (or ketone) and alcohol. By titrating the aldehyde produced information is afforded regarding the end group structure of the polymer. Bisulfite method and hydroxylamine methods are used for the determination of carbonyl group. In this investigation the latter method was used because it is more exact. The experimental procedure was described in 2.2. Fig. 5-4 a and b, exemplified the results. Fig. 5-4 a shows the pH-curve of the titration by N/100 aqueous sodium hydroxide solution of the mixture of N/100 aqueous

Table 5-2 The estimation of numbers of double bonds in polymethyl vinyl ether by the bromination method

Polymerization condition				Molecular weight of polymer*	Molecular weight of polymer**	Number of c=c/one polymer molecule***	α
Solvent	Catalyst	Temp.(°C)	[M](mole/l.)				
$CHCl_3$	$SnCl_4$·TCA****	-20	0.83	8710	4360	0.29	0.40
CH_2Cl_2	"	"	1.38	12080	6040	0.38	0.50
CCl_4	$BF_3 \cdot O(C_2H_5)_2$	"	0.83	20620	10310	0.35	0.52
$CHCl_3$	$SnCl_4$·TCA	-50	2.90	28920	14460	0.38	0.57
CH_2Cl_2	"	-20	2.76	11730	5870	0.47	0.66
CCl_4	"	"	2.76	32410	16200	1.30	0.71
CH_2Cl_2	$BF_3 \cdot O(C_2H_5)_2$	"	2.76	6330	3170	0.80	0.73

* Viscosity average molecular weight ($\bar{M}_v$) calculated from eq. (5-2).

** Calculated number average molecular weight ($\bar{M}_n$), assuming $\bar{M}_v=\bar{M}_w=2\ \bar{M}_n$.

*** Values based on corrected molecular weight (column 6).

**** TCA = trichloroacetic acid.

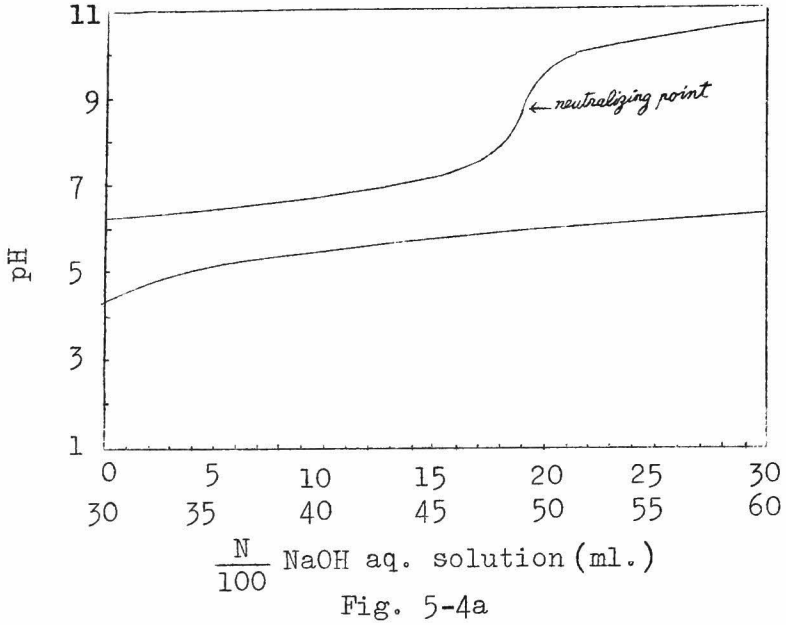


Fig. 5-4a

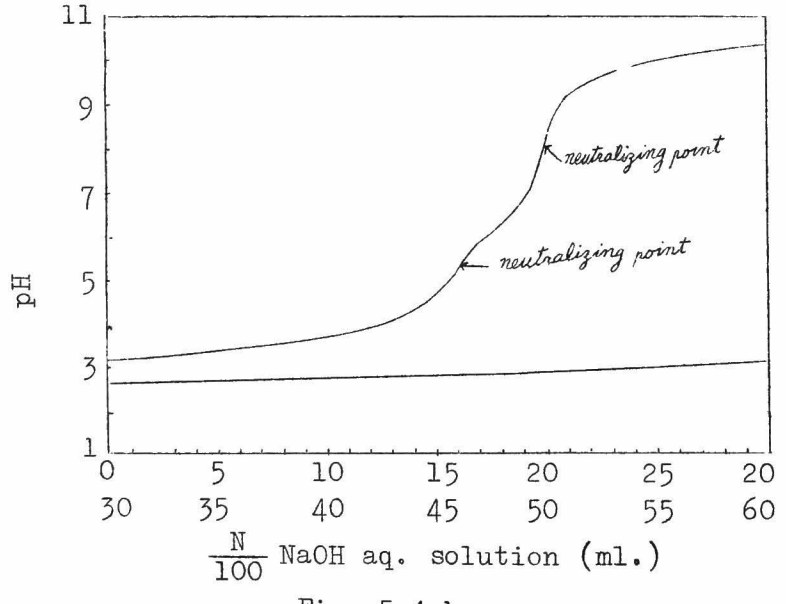


Fig. 5-4 b

Fig. 5-4 The determination of carbonyl group in polymer. the titration of $NH_2OH \cdot HCl$ by NaOH
a: H_2O 50 ml., $\frac{1}{100}$N $NH_2OH \cdot HCl$ aq. solution 50 ml.
b: aqueous solution of polymer 50ml.(conc. 1.3225g/50ml.), $\frac{1}{100}$N $NH_2OH \cdot HCl$ aq. solution 50 ml.

hydroxylamine hydrochloride solution (50 ml.) and distillated water (50 ml.). Neutralization occurred at pH 8.65, and 49.0 ml. of aqueous sodium hydroxide solution were used. Fig. 5-4 b shows the pH-curve in titration by N/100 aqueous sodium hydroxide solution of the mixture of N/100 aqueous hydroxylamine hydrochloride solution (50 ml.) with aqueous polymer solution (50 ml.). 50 ml. of aqueous sodium hydroxide solution were necessary to neutralize the hydrogen chloride in the system (neutralizing point was pH 8.08). Hydrogen chloride corresponding to 1 ml. of N/100 aqueous sodium hydroxide solution (50-49 = 1) is considered to be included in polymer. The neutralization at pH of 5.25 is correlated with free hydrogen chloride. 46.0 ml. of N/100 aqueous sodium hydroxide solution were consumed to neutralize free hydrogen chloride. Then 45.0 ml. of N/100 aqueous sodium hydroxide solution (46.0-1.0 = 45.0) corresponds to the aldehyde produced by hydrolysis. The calculation showed that 4.59×10^{-4} moles of aldehyde were produced by hydrosis of the polymer. A duplicate experiment gave 4.64×10^{-4} moles aldehyde, and 4.61×10^{-4} moles was taken as the mean. The experimental results are given in Table 5-3. This Table also gives values of α.

Table 5-3 The hydrolysis of polymethyl vinyl ether and the determination of aldehyde group

Polymerization condition				Molecular weight of polymer*	Molecular weight of polymer**	Number of aldehyde/ molecule***	α
Solvent	Catalyst	Temp.($^{\circ}$C)	[M]mole/l.				
$CHCl_3$	$BF_3 \cdot O(C_2H_5)_2$	0	1.38	9470	4730	1.65	0.85
$CHCl_3$	$SnCl_4$.TCA	0	0.69	5980	2990	0.97	0.42

* $\bar{M}_v$ in Table 5-2 column 5.

** $\bar{M}_n$ in Table 5-2 column 6.

*** Values based on $\bar{M}_n$.

Polymers for hydrolysis were made at $0^{\circ}C$ in order to secure a low molecular weight polymer. The α value was calculated from the rate constant ratios at $0^{\circ}C$, which were found by extrapolation of the rate constant ratios at -20° and $-50^{\circ}C$ to $0^{\circ}C$, using an Arrhenius' plot. Linear relationships between log (rate constant ratio) and the reciprocal of T are obtained in polymerizations of α-methylstyrene and isobutene. This relationship is expected to hold for methyl vinyl ether.

It is seen from Table 5-3 that the polymer produced in a system where the monomer transfer reaction predominates gives more aldehyde by hydrolysis than is obtained in other cases.

4. Discussion

4.1 Relationship between degree of polymerization and polymerization conditions.

From Table 5-1 and Fig. 5-3 it is seen that k_{tm}/k_p and k_t'/k_p behave similarly on changing the polymerization condition, that is, both increase with polymerization in more polar solvent and when using a more acidic catalyst. This corresponds to an experimental fact shown in Table 5-1, viz. that the intrinsic viscosity

of polymethyl vinyl ether was lower when the polymerization was carried out in more polar solvent or by a more acidic catalyst. So in order to get polymethyl vinyl ether of high molecular weight, polymerization should be carried out in less polar solvent, or using a less acidic catalyst.

4.2 The monomer transfer reaction

(1) Monomer extraction of a proton from the penultimate carbon is one of the possible mechanisms for the monomer transfer reaction. But it was rejected because in the bimolecular elimination reaction of branched alkyl halides to give an olefin, 1-olefin is the major product, due to the steric effect, and because with the cationic polymerizations of isobutene[7] and α-methylstyrene[8], the asymmetric disubstituted double bond predominates over the trisubstituted double bond. In the present polymerization, (2) the cleavage of the ether-bond of monomer by a growing ion-pair is proposed as an alternative mechanism for the monomer transfer reaction.

The cleavage of the ether bond of monomer by a growing ion-pair is essentially the same as Friedel-Crafts reaction in that a highly reactive ionic species is necessary. Since the use of stannic chloride—trichloro-

acetic acid as catalyst, which forms a more reactive ion-pair, resulted in larger k_{tm}/k_p value than boron trifluoride etherate, which forms a less reactive ion-pair, the experimental result is in good agreement with the above view.

The proposed mechanism[9] of the ether cleavage by acid catalyst is:—

$$R_1\text{-}O\text{-}R_2 + H^{\oplus} \underset{}{\overset{\text{fast}}{\rightleftharpoons}} R_1\text{-}\overset{\oplus}{O}(H)\text{-}R_2$$

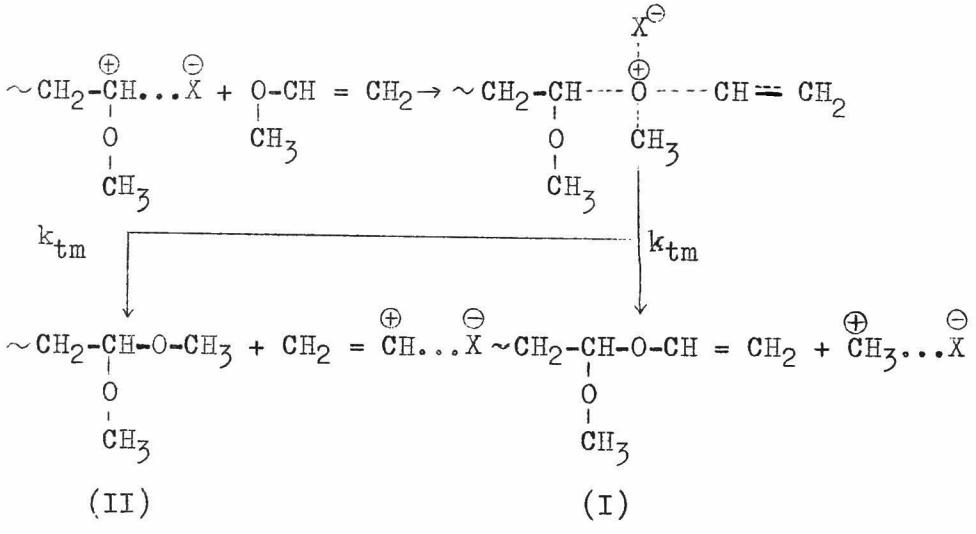
$$R_1\text{-}\overset{\oplus}{O}(H)\text{-}R_2 \overset{\text{slow}}{\rightleftharpoons} R_1^{\oplus} + R_2OH$$

$$R_1^{\oplus} + H_2O \overset{\text{fast}}{\rightleftharpoons} ROH + H^{\oplus}$$

As an evidence for this mechanism, there is cited experimental fact[10] that the relative rate constants for hydrolysis of acetal prepared from formaldehyde and an alcohol lie in increasing order methyl 1 < ethyl 8.5 < n-propyl 9.4 < isopropyl 47.2, methyl being taken as 1. The less reactive the alkyl cation, the larger the rate constant. This result shows that the carbon—oxygen bond breaking step is the rate determining one. Bearing this in mind, the increase of dielectric constant of solvent is considered to facilitate the ether cleavage

reaction more than the propagation reaction. Then, the observed solvent effect for k_{tm}/k_p was also explained by the above mechanism.

If a view is taken that the monomer transfer reaction is brought about by reaction of a growing cation with a nucleophilic ethereal oxygen of the monomer, end group (I) or (II) will be introduced in the polymer.



The end group (I) has a double bond, but the end group (II) does not. Since the number of double bond in polymer was proportional to the α value, i.e., the monomer transfer reaction (vide Table 5-2), the end group structure should be of type (I).

In the acid catalyzed ether cleavage reaction, the group broken off is generally the lower molecular weight

one of the two carbon-oxygen bonds.[11] The question arises what is broken here is whether the $CH_2 = CH\text{-}O$ bond or the $CH_3\text{-}O$ bond, and in this connection, both unsaturation factor and molecular weight factor have to be taken into account. If the molecular weight rule held here, the $CH_3\text{-}O$ bond would be broken to give an end group of type (I), and this obtained.

When end group (I) is hydrolyzed, two moles of aldehyde will be produced:—

$$\sim CH_2\text{-}\underset{\underset{\underset{CH_3}{|}}{O}}{\overset{|}{CH}}\text{-}O\text{-}CH = CH_2 \xrightarrow[H_2O]{\overset{\oplus}{H}} \sim CH_2\text{-}\underset{O}{\overset{\|}{C}}H + CH_3CHO + CH_3OH$$

As shown in Table 3, the polymer obtained under conditions corresponding to $\alpha = 0.85$ produced 1.65 moles of aldehyde when hydrolyzed. It is safe to conclude that if polymer is produced under conditions such that $\alpha = 1$ (monomer transfer reaction only) two moles of aldehyde will be produced, corresponding exactly to what would be expected theoretically. Further, in Table 5-3, the polymer obtained under conditions corresponding to $\alpha = 0.42$ produced 0.97 moles of aldehyde when hydrolyzed. It is further assumed that if the polymer is produced under

the conditions of $\alpha = 0.5$ one mole of aldehyde will be produced. $\alpha = 0.5$ means that the end group of half the polymer was produced by the monomer transfer reaction. Assuming that the polymer end group produced by the unimolecular termination reaction does not give rise to aldehyde when hydrolyzed (and as this was established later), the above result means that the polymer end group produced by the monomer transfer reaction gives two moles of aldehyde when hydrolyzed. This is again in good agreement with what would be expected theroetically. The end group (I) is the only one that has a double bond and produces two moles of aldehyde when hydrolyzed.

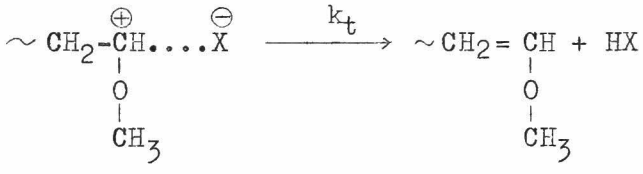
It has never been reported that a carbonium ion having an ether group attacks another ether to give an acetal. However, the experimental observations that ether acts as an inhibitor in the cationic polymerization of styrene[1] and that a strong complex is formed between oxygen of vinyl ether and cationic catalysts,[2] suggest strong carbonium ion affinity of ethereal oxygen of the monomer and affords some support for the above mechanism for the monomer transfer reaction.

4.3 The unimolecular termination reaction

The following three reactions are proposed for the

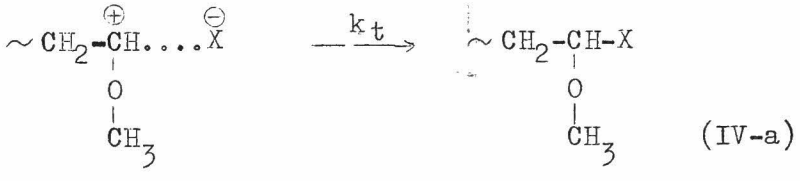
unimolecular termination reaction:—

(1) Unimolecular catalyst regeneration by a loss of proton from the penultimate carbon to the counter anion.

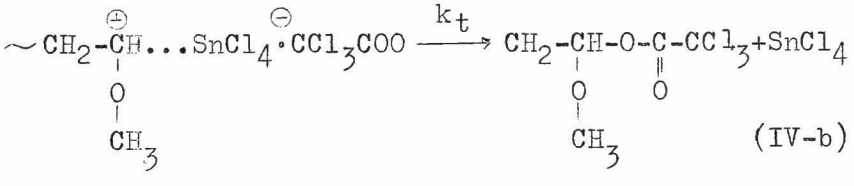


(III)

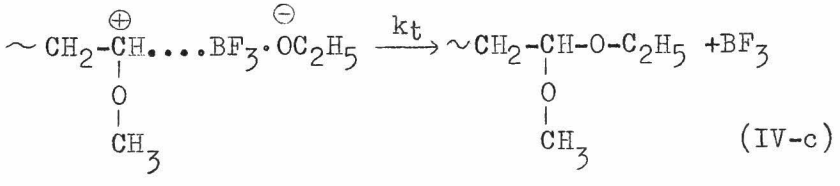
(2) Recombination of the growing cation with the counter anion or with part of the counter anion.



(IV-a)

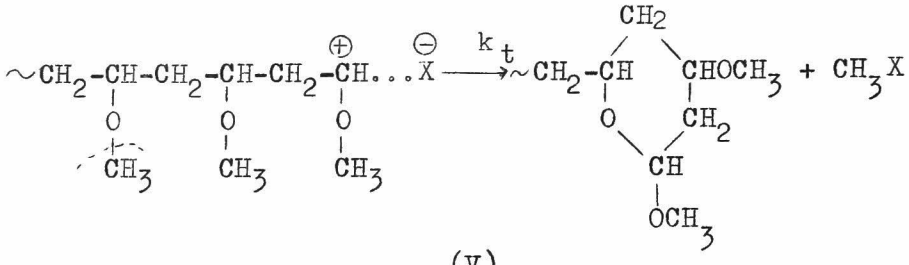


(IV-b)



(IV-c)

(3) Unimolecular cleavage of an ether bond in the growing chain by a rear reaction of the growing cation.



(V)

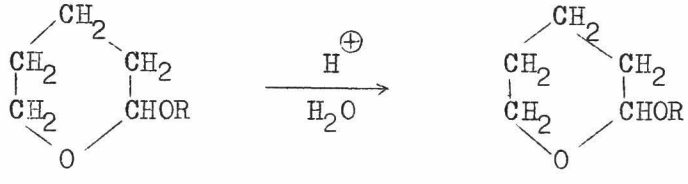
The mechanism (1) is discarded because the mechanism (1) gives a double bond in the polymer, while Table 5-2 suggests that the polymer end produced by the unimolecular termination reaction does not have the double bond.

The mechanism (2) is also discarded because it gives a polymer end which gives aldehyde when hydrolyzed, while Table 5-3 suggests that the polymer end produced by the unimolecular termination reaction does not produce aldehyde when hydrolyzed.

The mechanism (3) fulfills the requirements about the double bond (Table 5-2) and the aldehyde (Table 5-3). The end group (V) does not have a double bond and does not produce aldehyde when hydrolyzed. Mechanism (3) is essentially the same as the mechanism of the monomer transfer reaction. As shown in Table 5-1 and Fig. 5-2,

$k_{t'}/k_p$ was found to behave just like k_{tm}/k_p with the change of polymerization conditions, and this further supports mechanism (3). So, the mechanism of the unimolecular termination reaction was concluded to be mechanism (3) giving end group (V).

Lots of tetrahydropyran derivatives of type (VI) are known. (VI) is hydrolyzed by acid catalyst to give (VII). This does not contradict with the mechanism (3).



(VI) (VII)

Reaction of the growing cation with polymer comes to be considered in connection with the mechanism of the monomer transfer and the unimolecular termination reaction. Reaction between two macromolecules such as these is expected to occur to a considerable extent in polymerizations at high monomer concentration and high conversion. But with the present polymerization conditions it can be neglected kinetically, as was confirmed by the straight line shown in Fig. 5-2 a and b. The absence of the analogous

reaction in styrene polymerization, that is, of chain branching caused by reaction of a growing ion with the phenyl group or with tertiary hydrogen of a dead polymer was shown by Plesch[12] and Overberger.[13] Hence reaction between two macromolecules can be kinetically neglected in the polymerization under the less severe conditions.

To conclude, it was established in the present investigation that in the cationic polymerization of methyl vinyl ether, the degree of polymerization of the polymer decreases the higher the temperature, the stronger the catalyst and the more polar the solvent, and that this is due to marked occurrence of either the monomer transfer reaction or the unimolecular termination reaction under the given conditions. Taking together into account the analysis of the polymer end group, it was concluded that the monomer transfer reaction is ether cleavage of monomer by a growing ion-pair, and that the unimolecular termination reaction is ether cleavage of a growing ion by a rear reaction to give acetal in the polymer.

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Chapter 6 Isobutyl and Tertiarybutyl Vinyl Ether

1. Introduction

Lower alkyl vinyl ethers are the reactive monomer group in cationic polymerization and have long been the subject of investigation.[1] It was found in Chapter 5 that particularly in the cationic polymerization of methyl vinyl ether, the degree of polymerization is smaller, the more polar the solvent used, which is the reverse of what obtains in the styrene polymerization.[2] Transfer and termination reactions were found to be enhanced in the more polar solvent, and reaction mechanisms for both reactions were proposed where interaction of a growing ion with ethereal oxygen of monomer is important. Hence, it is to be expected that the nature of the alkyl group of the monomer will have inductive, mesomeric and steric effects on the reactions. So when attempting to clarify the reaction mechanism, it is very important to investigate the effects of alkyl groups on the transfer and the termination reactions. In the present Chapter, the polymerizations of isobutyl and t-butyl vinyl ether were investigated on the same basis as the methyl vinyl ether polymerization, and the results were compared.

2. Experimental

2.1 Reagent

Isobutyl and t-butyl vinyl ether (Mitsubishi Chemical Co.) were washed repeatedly with 5 % aqueous sodium hydroxide solution and water until they gave no color with ammonium molybdate, then dried over potassium hydroxide, and distilled twice from sodium metal just before use (b.p.: iosbutyl vinyl ether 81.8-82°C, lit. 83.2°C, t-butyl vinyl ether 77-78°C, lit. 75°C).

Purification of solvent and catalyst was effected as described previsouly.

2.2 Polymerization

The polymerization technic was almostly the same as that employed in Chapter 5. Polymerizations were carried out using boron trifluoride etherate as catalyst in n-hexane, chloroform and methylene chloride. Precooled monomer solution was added to precooled catalyst solution to initiate the polymerization, because using the ordinary method, i.e. the addition of catalyst to precooled monomer solution, polymer precipitates to make the system heterogeneous. Catalyst concentration ranged from 2.0 to 6.0 m mole/l.and monomer concentration 2 to 20 vol.%. The monomer concentration was reduced by adding right amount

of chloroform in order to avoid variation of dielectric constant of the polymerization solution. Chloroform was considered to have about the same dielectric constant as the vinyl ethers. Isobutyl vinyl ether was polymerized at -20° and -50°C, and t-butyl vinyl ether at -50° and and -78°C. Polymerizations were stopped by the addition of ammonia in methanol.

2.3 Calculation of the rate constant ratio

Polymerizations were carried out varying the initial monomer concentration [M], and the reciprocal of the degree of polymerization of the resultant polymer was plotted against the reciprocal of the monomer concentration. Using equation (6-1) the rate constant ratios were calculated;—

$$1/\bar{P} = k_{tm}/k_p + k_t'/k_p \cdot 1/[M] \qquad (6\text{-}1)$$

where $k_t' = k_t + k_{tx}[X]$, and the solvent transfer reaction was neglected.

The molecular weight of the polymer was calculated from the intrinsic viscosity of a benzene solution at 30°C, using equation (6-2) and equation (6-3).

Polyisobutyl vinyl ether

$$[\eta] = 7.55 \times 10^{-5} \times \bar{M}_w^{0.75} \qquad (6\text{-}2)$$

Poly-t-butyl vinyl ether

$$[\eta] = 2.04 \times 10^{-4} \times \bar{M}_w^{0.64} \qquad (6\text{-}3)$$

3. Results

3.1 Relationship between polymerization conditions and the intrinsic viscosity of polymer

The dependency of the intrinsic viscosity of the polymer on the polymerization conditions, especially on the dielectric constant of solvent, was investigated, and the experimental results are shown in Fig. 6-1 a and b. Either isobutyl or t-butyl vinyl ether gives polymer of lower molecular weight in a solvent of higher dielectric constant, and the same tendency was found in isobutene polymerization, but the reverse obtained with styrene[2].

3.2 Relationship between polymerization conditions and the rate constant ratio

Examples relating to determination of the rate constant ratios using equation (6-1) are given in Fig. 6-2 a and b.

The rate constant ratios were determined in three kinds of the solvents of different polarities, viz., n-hexane, chloroform and methylene chloride, and the results

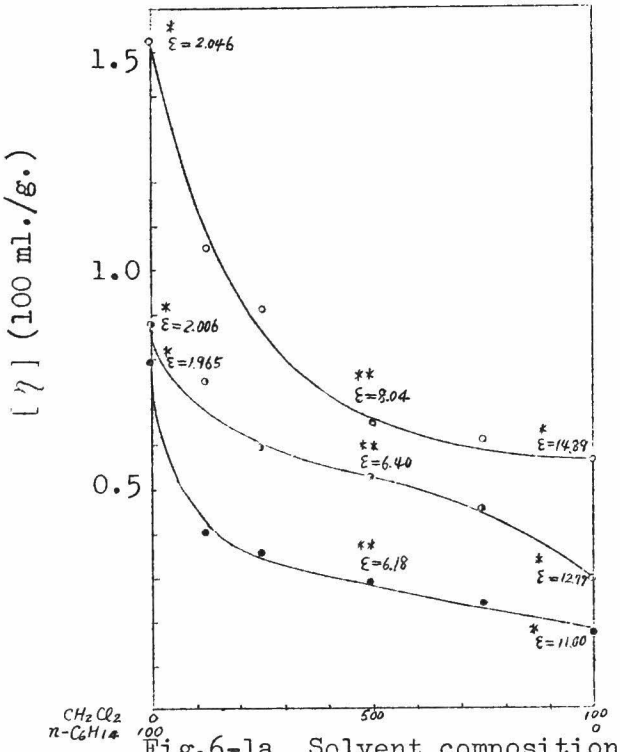


Fig.6-1a Solvent composition (vol.%)

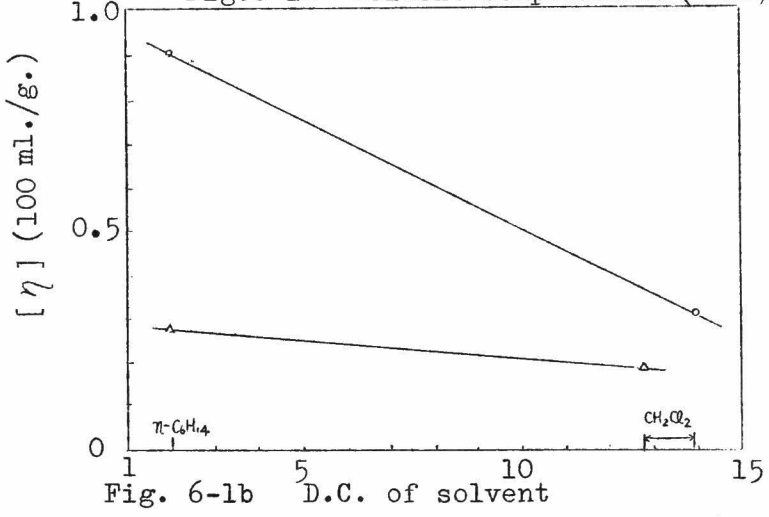


Fig. 6-1b D.C. of solvent

Fig. 6-1 The relationship between the polarity of solvent and the intrinsic viscosity of the polymer

a: Isobutyl vinyl ether, (○):-78°C, (◑):-50°C, (●):-20°C
[M] = 20 vol.%, $BF_3 \cdot O(C_2H_5)_2$ catalyst

* Dielectric constant of $n\text{-}C_6H_{14}$ and CH_2Cl_2 reported by S. O. Morgan and H. H. Lowry.

** Dielectric constant of mixed solvent calculated from Onsagar's theory

b: t-Butyl vinyl ether, (○):-78°C, (△):-50°C
[M] = 20 vol%, $BF_3O(C_2H_5)_2$ catalyst

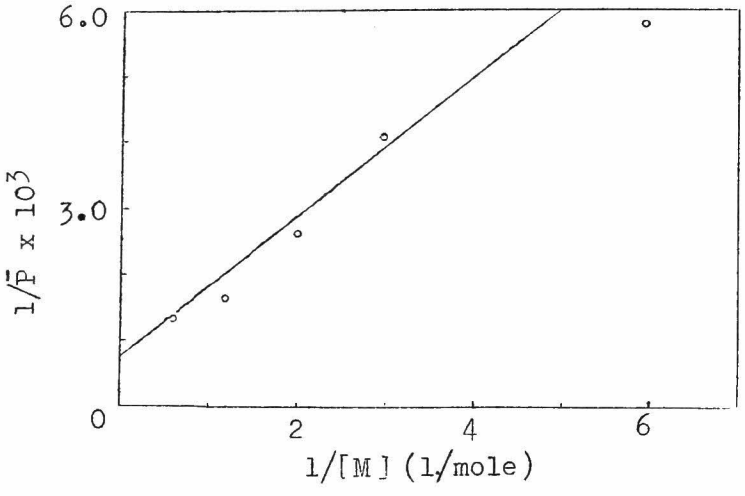


Fig. 6-2a

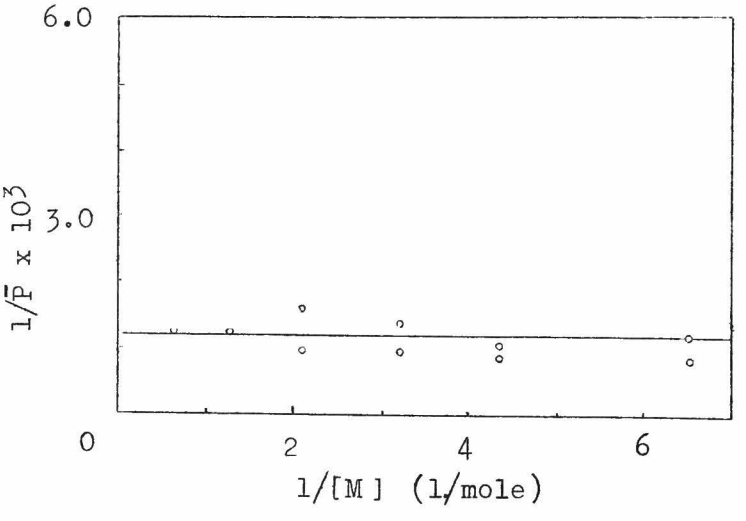


Fig. 6-2b

Fig. 6-2 The relationship between $1/\bar{P}$ and $1/[M]$
a: Isobutyl vinyl ether, -50°C, CH_2Cl_2
b: t-Butyl vinyl ether, -50°C, n-C_6H_{14}

are summarized in Table 6-1.

Table 6-1 The rate constant ratios under the various polymerization conditions

Rate constant ratio	$k_{tm}/k_p \times 10^4$		$k_t'/k_p \times 10^4$	
Monomer	Isobutyl vinyl ether			
Temp.(°C)→ / Solvent↓	-20	-50	-20	-50
$n\text{-}C_6H_{14}$	2.0	2.0	5.3	1.2
$CHCl_3$	4.7	5.8	9.6	4.7
CH_2Cl_2	7.4	7.5	12.1	10.6
Monomer	t-Butyl vinyl ether			
Temp.(°C)→ / Solvent↓	-50	-78	-50	-78
$n\text{-}C_6H_{14}$	12.0	2.0	0	0
CH_2Cl_2	7.6	7.6	4.8	7.0

Since boron trifluoride etherate did not dissolve completely into n-hexane over the temperature range -20° to -78°C, it was necessary to shake the polymerization solution continuously.

Plotting the rate constant ratios against the dielectric constant of solvent gave Fig. 6-3 a and b and Fig. 6-4 a and b.

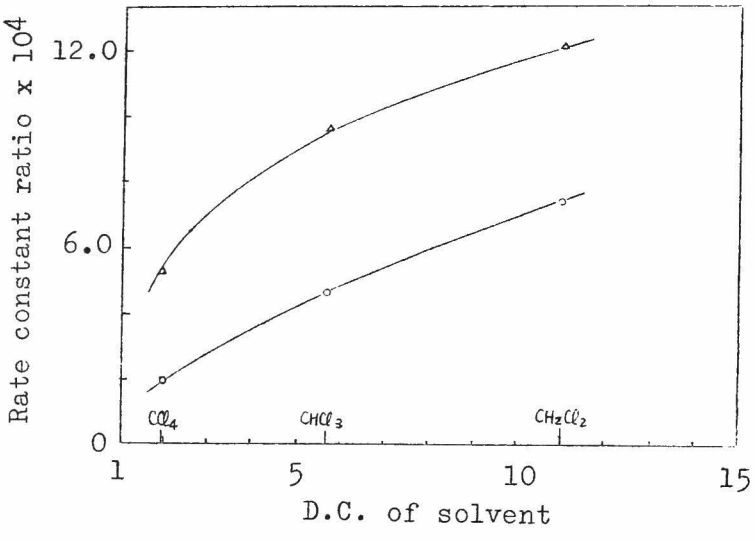


Fig. 6-3a

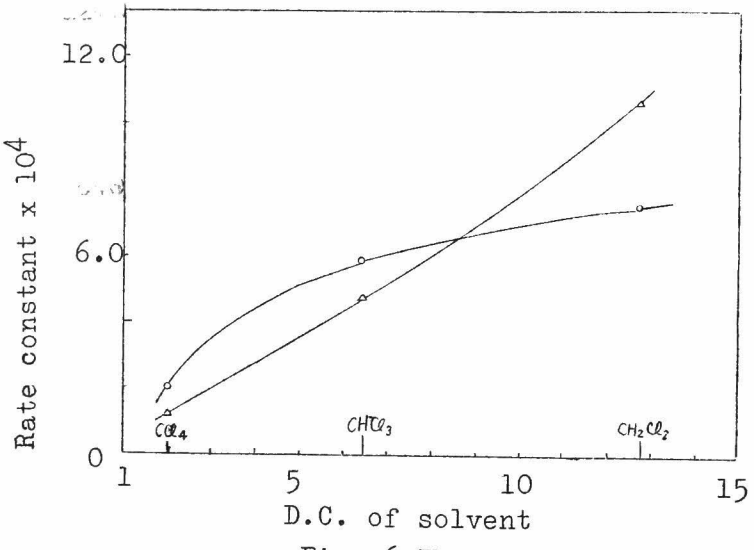


Fig. 6-3b

Fig. 6-3 The plot of k_{tm}/k_p and k_t'/k_p versus the dielectric constant of solvent in the polymerization of isobutyl vinyl ether

(○): k_{tm}/k_p (△): k_t'/k_p

a: -20°C, b: -50°C

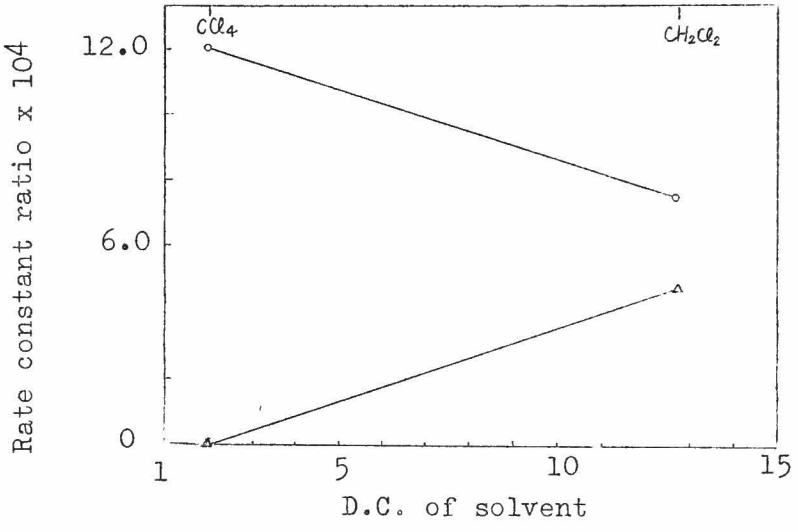


Fig. 6-4a

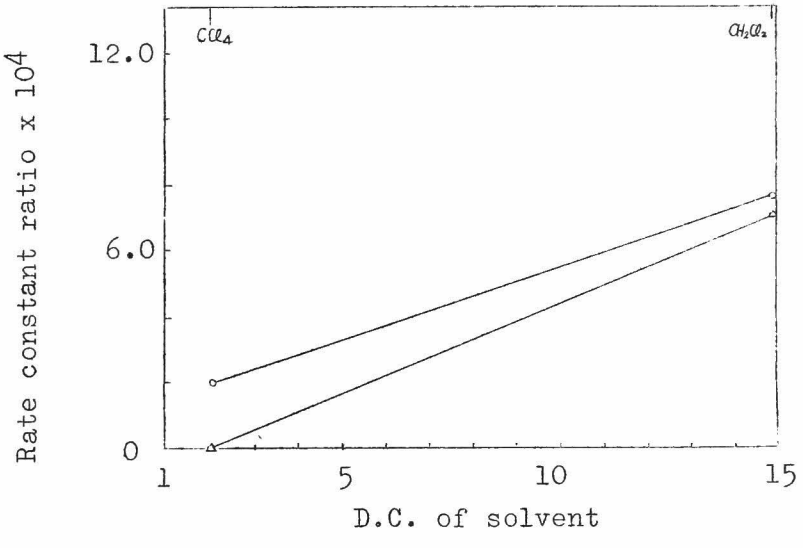


Fig. 6-4b

Fig. 6-4 The plot of k_{tm}/k_p and k_t'/k_p versus the dielectric constant of solvent in the polymerization of t-butyl vinyl ether

(○): k_{tm}/k_p , (△): k_t'/k_p

a: -50°C b: -78°C

Generally, it was observed, with a single exception that either the monomer transfer reaction or the unimolecular termination reaction is favoured in a polar solvent. The same was observed in the methyl vinyl ether polymerization, and afforded a kinetic explanation of why polymerization in polar solvent gave a polymer of low molecular weight.

Polymerizations were also carried out using stannic chloride— trichloroacetic acid as the catalyst, But reactions other than polymerization predominated: particularly in the polymerization of t-butyl vinyl ether a methanol insoluble polymer was not obtained under the present conditions. Similar results was observed in other experiments with t-butyl vinyl ether. The effect of catalyst on polymerization was not therefore investigated.

3.3 The structure of the end group of polymer

In order to investigate the end group structure, polyisobutyl vinyl ether was brominated and hydrolyzed. The experimental results are shown in Table 6-2. As seen in Table 6-1, isobutyl vinyl ether gives a polymer of considerably high molecular weight in polymerization at temperatures as high as -20°C. As polymers of high

Table 6-2 The analysis of the terminal structure of polyisobutyl vinyl ether

Polymerization condition				Molecular weight of polymer*	Number of c=c/one polymer molecule**	Number of aldehyde/ one polymer molecule**	α***(-20°C)
Solvent	Catalyst	Temp.(°C)	[M]mole/l.				
$CHCl_3$	$BF_3 \cdot O(C_2H_5)_2$	40	0.808	12800	0.78	—	0.28
$CHCl_3$	$SnCl_4$	40	0.808	11900	0.60	—	—
$CHCl_3$	$BF_3 \cdot O(C_2H_5)_2$	30	0.404	17600	—	0.53	0.17
$CHCl_3$	$SnCl_4$	30	0.808	22500	—	0.65	—

* Calculated number average molecular weight ($\bar{M}_n$), assuming $\bar{M}_v=\bar{M}_w=2\bar{M}_n$.

** Values based on the calculated number average molecular weight.

*** $\alpha = k_{tm}[M]/(k_{tm}[M] + k_t')$

molecular weight are not convenient for end group analysis, the samples for end group analysis were prepared by polymerization at 30° or 40°C. The bromination was carried out as in the case of polymethyl vinyl ether. The hydrolysis of polyisobutyl vinyl ether, and determination of the resultant aldehyde were carried out almostly exactly as with polymethyl vinyl ether. However, since polyisobutyl vinyl ether is not as soluble in water as polymethyl vinyl ether, the hydrolysis was carried out in carbon tetrachloride with mixing with aqueous hydroxylamine—hydrochloride by continuous agitation. Distillated water was added to the mixture on titration to make titration more precise.[3)]

Table 6-2 showed that some of the polyisobutyl vinyl ether contains double bond and some does not, and that some of the polyisobutyl vinyl ether does not produce aldehyde when hydrolyzed. Since the rate constant ratios were not determined at 30° or 40°C, true value of α could not be calculated. In Table 6-2, α at -20°C is listed, assuming that α does not so greatly change with changing the temperature from -20°C to 30°C or 40°C (judging by the rate constant ratios tabulated in Fig. 6-1). Allowing for the way in which the number of double bonds and aldehyde groups depend on α, the conclusion reached in

Chapter 5, that the end group produced by the monomer transfer reaction ($\alpha = 1$) has a double bond and produces two moles of aldehyde, holds good here too.

The end group of the polymer was also studied by infrared spectroscopy. Infrared spectra of poly-t-butyl vinyl ether are shown in Fig. 6-5 a, b and c. From case of the end group of polymethyl vinyl ether, vinyl type double bonds and the acetal bonds are to be expected to be present at the ends of poly-t-butyl vinyl ether.

It has been reported that the vinyl group of alkyl vinyl ethers has two absorptions at 960 and 810 cm^{-1}.[4] The poly-t-butyl vinyl ether obtained here has a weak absorption at 950 cm^{-1}, which was not detectable in a high molecular weight polymer and disappeared on bromination. These experimental facts suggest that this absorption is due to a terminal vinyl group. However, some absorptions due to the crystallinity have been found for this polymer, and the absorption band at 950 cm^{-1} was ascribed to a syndiotactic structure.[5] But the assignment of that absorption is not at present unequivocal.

Furthermore, absorption due to acetal bonding would be expected to appear at about 1100 cm^{-1}.[6] But this is not distinct from the strong absorption due to aliphatic

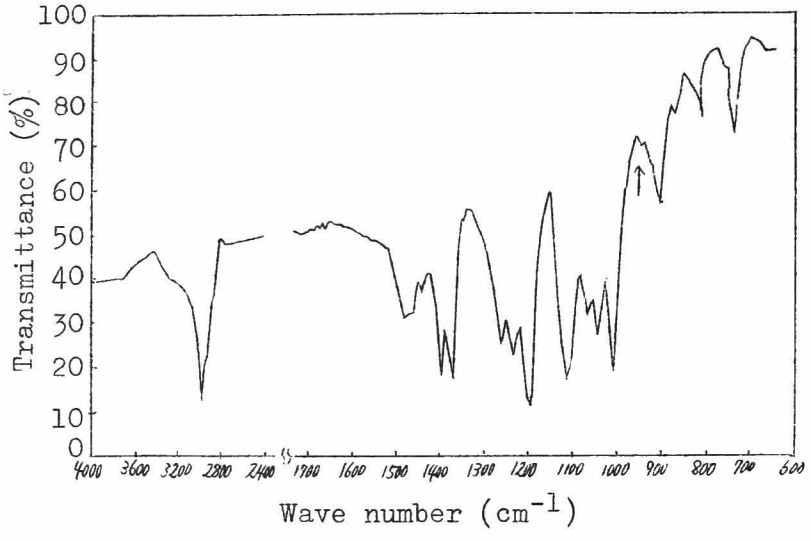


Fig. 6-5a

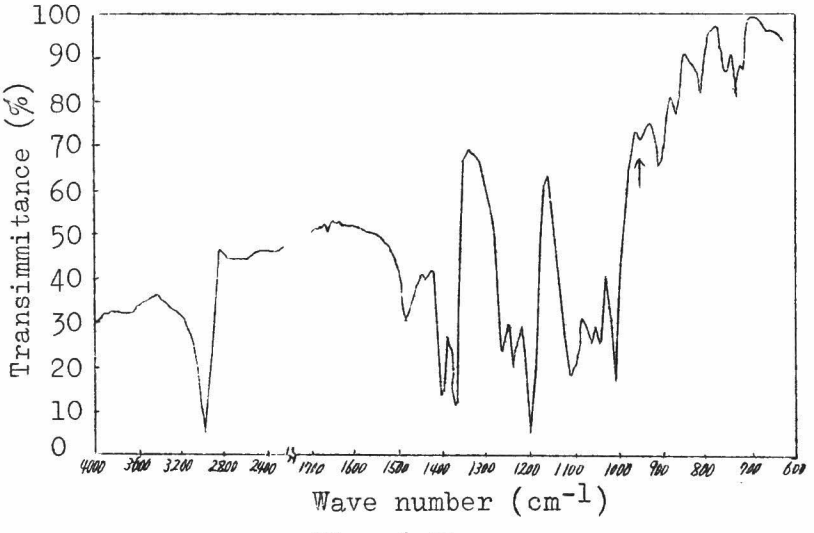


Fig. 6-5b

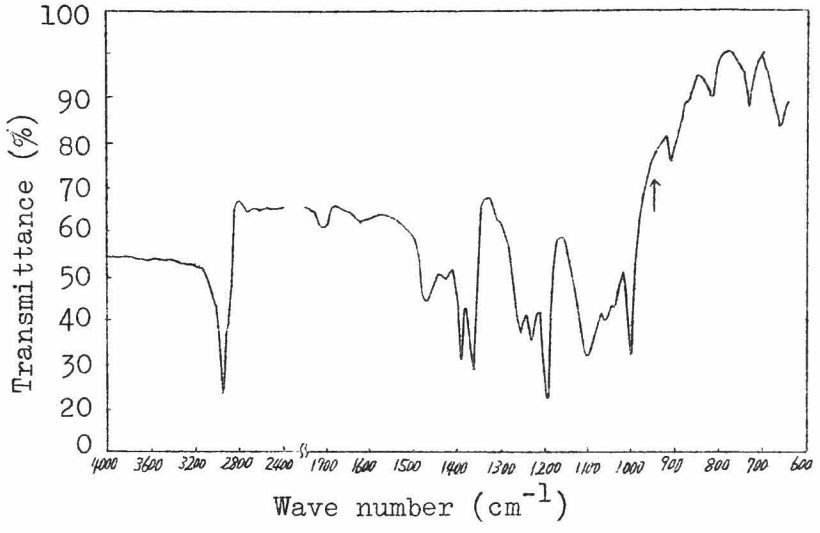


Fig. 6-5c

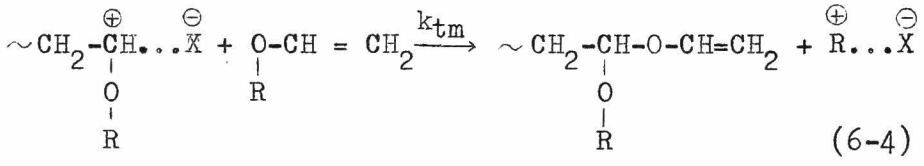
Fig. 6-5 The infrared spectra of poly-t-butyl vinyl ether

a: High molecular weight polymer, $[\eta]$ = 1.140, produced by $BF_3 \cdot O(C_2H_5)_2$ in n-C_6H_{14} at -78°C
b: Low molecular weight polymer, $[\eta]$ = 0.154, produced by $BF_3 \cdot O(C_2H_5)_2$ in CH_2Cl_2 at -78°C
c: Brominated polymer of sample b.

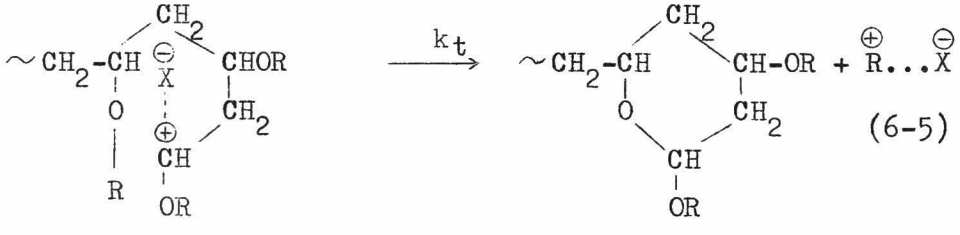
ether which appears at about 1100 cm^{-1}. For the above reasons the end group could not be satisfactorily studied by the infrared spectroscopy.

4. Discussion

From the experimental results on methyl vinyl ether polymerization, reaction (6-4), in which a growing ion-pair reacts with ethereal oxygen of a monomer, was proposed for the monomer transfer reaction, and reaction (6-5), in which a growing ion-pair reacts with ethereal oxygen of the same growing ion-pair, by the rear reaction, was proposed for the unimolecular termination reaction (R=CH_3).



(6-4)



(6-5)

On the other hand, in cationic polymerization of isobutyl and t-butyl vinyl ether the effect of dielectric constant of solvent on the transfer and the termination

reaction was found to be the same as was observed in methyl vinyl ether polymerization, as is seen from Fig. 6-4 and Fig. 6-5. Furthermore, in the polymerizations of butyl vinyl ethers using stannic chloride—trichloroacetic acid as the catalyst, polymers of high molecular weight were not obtained, and it was found from the elementary analysis of the reaction product that reaction between the catalyst and ethereal oxygen was promoted more than when boron trifluoride etherate was used as the catalyst. On the basis of this experimental fact it is conceivable that in the polymerization of butyl vinyl ethers too, the transfer and the termination constant ratios will increase when a stronger Lewis acid is used as the catalyst, analogous to what was found for the polymerization of methyl vinyl ether. The resultant polyisobutyl vinyl ether was proved to have an end group which contains a double bond and produces aldehyde when hydrolyzed. This end group was found experimentally to be given by the monomer transfer reaction. From these experimental findings it was established that the monomer transfer reaction and the unimolecular termination reaction in the cationic polymerization of butyl vinyl ethers (R = i-C_4H_9 or t-C_4H_9) are reactions (6-4) and (6-5) respectively, just as in

methyl vinyl ether polymerization.

The largest difference in the experimental results between methyl vinyl ether and butyl vinyl ethers exists in respect of the following, viz., that with the former k_{tm}/k_p and k_t'/k_p were affected by the polymerization temperature rather than by the polymerization solvent and that both reactions need considerable amounts of activation energy even in a solvent as polar as methylene chloride. However, in the polymerization of butyl vinyl ethers, the rate constant ratios were affected by solvent rather than by polymerization temperature, and both reactions needed considerable amounts of activation energy in a non polar solvent such as n-hexane, but did not need so much activation energy in such a polar solvent as methylene chloride. Since just the same mechanisms (6-4) and (6-5) are operative for the monomer transfer and unimolecular termination reactions in the polymerizations of methyl vinyl ether and butyl vinyl ethers, the above difference must be due to the difference in the nature of the alkyl group.

Comparing the methyl group with isobutyl and t-butyl group, the inductive effect of butyl groups is larger than methyl group. As consequence, the ethereal oxygen

of butyl vinyl ether is more electronegative than that in methyl vinyl ether, so in the former case the carbonium ion attack is facililated, particularly. During the breaking process of carbon—oxygen bonding, alkyl cation or alkyl cation-like state will appear in the activated state. In that case isobutyl and t-butyl cations are less reactive than the methyl cation, which makes the energy level of the activation state in the ether cleavage reaction of butyl vinyl ethers lower than with methyl vinyl ether. If the polarity of the solvent is high enough to stabilize the cation by the solvation, the energy level will be lowered yet further. This is a possible explanation of the effects of solvent and temperature on the transfer and termination reaction in the polymerization of butyl vinyl ethers.

In copolymerization of isobutyl vinyl ether(M_1) with methyl vinyl ether (M_2) with boron trifluoride etherate as the catalyst at -78°C, the monomer reactivity ratio r_1 was 1.6, and r_2 was 0.4. If the equation (10-10) holds, the ratio of the propagation constant is ca. 2. This leads to the conclusion that the absolute values of the rate constant, k_{tm} and k_t' for isobutyl vinyl ether, are smaller than those for methyl vinyl ether, though the

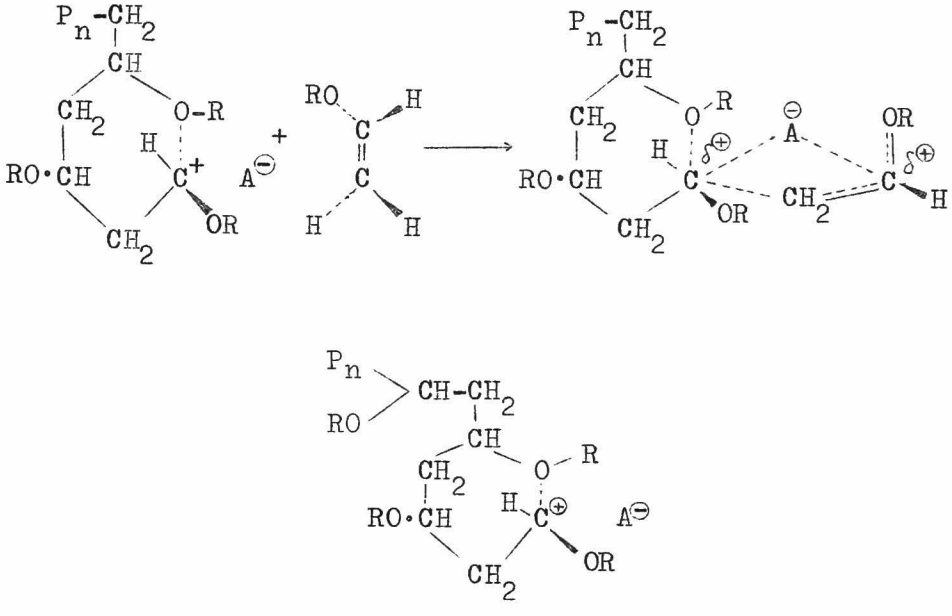
activation energies of those reactions in the case of isobutyl vinyl ether are considered to be smaller than with methyl vinyl ether. This should be explicable in terms of the frequency factor.

As is seen from Table 6-1 and Table 5-1, k_{tm}/k_p in the polymerization of alkyl vinyl ether is larger the more polar the solvent. Since k_p is considered to increase with increasing solvent dielectric constant[7], the increase of k_{tm}/k_p should be due to the larger increase of k_{tm} as compared with k_p with the increase in polarity of the solvent. This suggests a need for high polarity in solvating alkyl cation produced during the course of the monomer transfer reaction, a view which was confirmed by experimental results obtained by Kanoh et al.[8] It follows from Table 6-3, that k_{tm} increases more than k_p with increasing solvent polarity.

Table 6-3 Polymerization of isobutyl vinyl ether by iodine at 30°C[8]

Solvent	k_{tm}/k_p	k_p l/mole/min.	k_{tm} l/mole/min.
CCl_4	0.25×10^{-2}	7.4	1.7×10^{-2}
$(CH_2Cl)_2$	0.36×10^{-2}	3.9×10^{2}	1.4

To conclude the discussion the problem of the stereospecific polymerization of an alkyl vinyl ether will be considered. In low temperature homogeneous cationic polymerizations, an alkyl vinyl ether successfully produces a stereospecific polymer.[9] Regarding this, Bawn and Ledwith[10] proposed the following mechanism for stereospecific propagation with an alkyl vinyl ether,



The growing carbonium ion makes six-membered ring and is stabilized by rear reaction. The entering monomer attacks the carbonium ion always from the counter ion side. Then the counter ion $A^{\ominus}$ interacts with either newly-formed carbonium ion or the previously-existed carbonium ion,

and stabilizes by rear reaction on the same side as the latter. By this mechanism, a monomer can be incorporated into a growing chain without changing the steric configuration of the carbonium ion.

If both of the mechanisms for stereospecific polymerization proposed by Bawn et al. and for the unimolecular termination reaction proposed by the present author are correct, there should be some correlation between stereospecificity and the degree of polymerization of polymer. Glusker et al.[11] reported on the contribution of the rear reaction, by a six-membered ring formation, to anionic stereospecific polymerization of methyl methacrylate, and found a correlation between stereospecificity of poly methyl methacrylate and molecular weight of polymer. So, the relationship between stereospecificity and the molecular weight of the present polymer would be interesting to investigate.

To conclude, it was explained how, in view of the present investigation and the experimental results of Chapter 5, the alkyl vinyl ether gives a low molecular weight polymer in the polymerization in a polar solvent. The effect of solvent dielectric constant on the transfer and termination reactions was found to be manifest markedly

in the order of methyl < isobutyl < t-butyl vinyl ether. This phenomenon was explained in term of the inductive effect of alkyl groups.

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Part 3 The Properties of Polymer

The investigations described in Part 2 are in principle based on the molecular weight of polymer. To complete the investigation, the fundamental problems regarding the molecular weight of polymer must be solved. In connection with this, the molecular weight—intrinsic visocisty relationship and the molecular weight distribution during the course of polymerization were here studied. Furthermore, polymer stereospecificity and the abnormal behavior of the molecular weight—intrinsic viscosity relationship because of chain branching were investigaged.

Chapter 7 Poly-α-methylstyrene

Section 7.1 Stereospecific Polymer

1. Introduction

Schildknecht[1] reported that high molecular weight crystalline polyalkyl vinyl ether could be produced by the low temperature polyphase polymerization. It has been reported from our laboratory[2] that a stereospecific polymer of alkyl vinyl ether is produced by low temperature homogeneous cationic polymerization, and the mechanism of the stereospecific polymerization was interpreted in

relationship to the nature of the growing ion-pair. At that time, α-methyl-p-methylstyrene[3] was the only monomer that gave a crystalline polymer on low temperature cationic polymerization.

α-Methylstyrene is a rather reactive monomer for cationic polymerization and would be expected to have about the same reactivity as methyl vinyl ether which has relatively low reactivity among alkyl vinyl ethers. Though the extensive investigations had been carried out on polyalkyl vinyl ether little was known about the structure of poly-α-methylstyrene polymerized by homogeneous cationic polymerization. Schildknecht[1] also reported that methyl vinyl ether gave a crystalline polymer when using n-hexane mixed with a little amount of chloroform or toluene, that is, by activated polymerization. But the basis of the solvent effect is not clear.

In this investigation the low temperature cationic polymerization was carried out in a variety of mixed solvents and the properties of the resultant polymer were studied. As consequence, various interesting properties were observed for polymer produced by low temperature polymerization. This Chapter describes

experimental results.

2. Experimental

The purification of the reagents and the polymerization procedures are described in Section 1.1.

Polymerizations were carried out in the mixed solvent of n-hexane (non-solvent for the polymer) with toluene, chloroform and methylene chloride (solvent for the polymer). Boron trifluoride etherate was used as the catalyst. For comparison, stannic chloride and aluminum chloride were also used.

Experimental technics for the measurement of the properties of polymer will be described later.

3. Results

3.1 The experimental condition giving benzene-insoluble polymer

When the effect of the solvent composition on the degree of polymerization of poly-α-methylstyrene was being investigated by polymerizing at -78°C by boron trifluoride etherate in n-hexane—chloroform mixed solvent, it was found that poly-α-methylstyrene produced in mixed solvent rich in chloroform was partially insoluble in benzene at room temperature. Though the polymer was

insoluble in benzene which has been hitherto considered to be a good solvent of poly-α-methylstyrene, the polymer dissolved in hot benzene (above 40°C), toluene, xylene, chloroform and methylene chloride. The conditions for the production of cold benzene-insoluble polymer are given below.

The effect of the monomer concentration on the production of cold benzene-insoluble polymer was investigated. When 10, 20, and 30 ml. of α-methylstyrene were polymerized in chloroform 60 ml.—n-hexane 20 ml. mixed solvent at -78°C by boron trifluoride etherate, there was little difference between the solubilities of the polymer and a quantitative relationship between monomer concentration and the amount of cold benzene-insoluble fraction of the polymer was not obtained.

Next, the effect of extent of conversion on solubility was investigated. 20 ml. of monomer were polymerized in the above condition. Cold benzene-insoluble material was present when the polymerization was stopped at the conversion of 70.9% and 76.4%, but absent when the conversion was 46.6% and 58.7%. There was no great difference in the intrinsic viscosities of these polymers. Therefore, when conversion was increased, polymer solubility was

Table 7-1 The condition for the formation of the polymer insoluble in benzene

Temp.	-20°C impossible	-50°C very low possibility	-78°C possible
Solvent (mixture with n-hexane)	Toluene	n-Hexane 100% — impossible — 0% Toluene 0% — 100%	
	Chloroform	n-Hexane 100% — possible — 0% Chloroform 0% — 100%	
	Methylene chloride	n-Hexane 100% — possible — 0% Methylene chloride 0% — 100%	
Catalyst	$AlCl_3$ impossible	$SnCl_4$ impossible	$BF_3 \cdot O(C_2H_5)_2$ possible

The concentration of monomer was 20%.

The benzene-soluble polymer was formed only when three conditions for temperature, solvent composition, and catalyst were fulfilled.

lowered.

The solubility of polymer in cold benzene depended on the polymerization temperature, the kind of catalyst, the solvent composition and the conversion, but was independent of the catalyst concentration and the intrinsic viscosity of polymer. The ratio of the cold benzene insoluble part to the soluble part of the poly-α-methylstyrene depended slightly on the condition of polymer precipitation and was not strictly constant.

3.2 The solubility of polymer

The solubility of polymer produced using chloroform 80 ml.—monomer 20 ml. and boron trifluoride etherate at -78°C ($[\eta]$ = 1.69) was measured. Table 7-2 gives qualitative results.

Besides the experiments shown in Table 7-2, the solubility of polymer obtained using the mixed solvent n-hexane 20 ml.—chloroform 60 ml. other conditions being the same ($[\eta]$ = 1.78) was measured, and results resembling those of Table 7-2 were obtained. The special features brought out by Table 7-2 is that the initially cold benzene-insoluble polymer did not precipitate out when left standing after dissolving once in hot benzene, and that the film formed from the hot benzene solution

Table 7-2 The solubility of poly-α-methylstyrene

Weight of polymer(mg.)	Solvent*	Method for dissolving the polymer	Result
200	Benzene	Standing at room temp.	Most part of polymer did not dissolve.
100	"	"	"
800	Toluene	"	A transparent solution was given in a few hours.
200	Benzene	Polymer was dissolved by heating and the solution was left standing at room temperature.	"
800	"	"	A solution like diluted milk was given, which did not show any change for standing.
200	"	Polymer was dissolved by heating, and solvent was vaporized to make a film, which was immersed in the solvent at room temperature	Polymer was dissolved in two days.
800	"	"	A little part of polymer did not dissolve.

* Solvent 20 ml.

of the initially cold benzene-insoluble polymer dissolved up in cold benzene.

The rate of solution of the polymer insoluble in cold benzene was measured at room temperature, and the results are shown in Table 7-3.

Table 7-3 The rate of solution of poly-α-methylstyrene in benzene at room temperature

Time for standing (hr.)	Solubility (wt.%)	
	A*	B**
24	89.3	61.2
48	91.5	71.3
72	—	73.1
120	92.7	75.0
163	—	76.0

* Sample A ($[\eta]$ = 1.69) was produced under the condition as:—
chloroform 80 ml., monomer 20 ml., -20°C, $BF_3 \cdot O(C_2H_5)_2$

** Sample B was produced under the same condition as for sample A, $[\eta]$ = 1.02

Depending on the polymerization condition, the part insoluble in cold benzene could exceed 30%. In cold benzene it was like a gel, and its shape did not change even after the standing for more than seven years with

occasional shaking.

The fraction of the sample B insoluble in cold benzene mentioned in Table 7-3 was separated and dried in a vacuum at room temperature. It was again immersed in cold benzene. Then only 17.1 % of polymer was extracted by cold benzene, and the rest, 82.9%, was present as a gel.

As will be shown in the next Section, the cold benzene-insoluble polymer behaved the same as the cold benzene-soluble polymer in solution after solution by heating.

3.3 The chemical structure of polymer

Since the cold benzene-insoluble polymer dissolves easily into hot benzene, toluene and other organic solvents, the insolubility of polymer is not due to crosslinking. The difference of the end group caused by the chain transfer reaction in the different solvent may give rise to the difference of the solubility. Polymer produced at -78°C was extracted with benzene, and the elementary analysis and infrared spectrum of the cold benzene-soluble part and the insoluble part were investigated. No difference was found between them. As these

polymers had high molecular weights they could not conveniently be analysed for end groups. Then the polymerization was effected at -20°C in toluene and chloroform. Low molecular weight polymer can be obtained and the solvent transfer reaction, if it obtains, occur frequently. The infrared spectra of these polymers were studied, but no difference was found. So it was concluded that the difference in solubilities is not due to a difference in polymer end group.

The stereospecificity of polymer is considered to be the cause of the abnormal solubility. It was reported[4] that a stereospecific poly-α-methylstyrene obtained with a Ziegler type catalyst showed an absorption at 885 cm^{-1} due to the crystallinity. The cold benzene-insoluble poly-α-methylstyrene obtained at -78°C with boron trifluoride etherate in chloroform 50%—n-hexane 50% ($[\eta] = 1.45$) showed a weak absorption at 895 cm^{-1}. This absorption was weaker for polymer obtained at -50°C in n-hexane 50%—methylene chloride 50% (D.P.= 591) Fig. 2-5a shows how this absorption was much weaker with the polymer obtained at -20°C. The relationship between degree of light absorption and polymerization temperature falls into line with what has been reported

by Sakurada[4], and the absorption may be due to the crystallinity. In Chapter 2, however, this absorption was found to disappear after the bromination, and it was ascribed to terminal vinylidene type double bond. Bywater et al.[5] also came to the same conclusion about it. But allowing for the high molecular weight of polymer obtained at -78°C, the absorption at 895 cm^{-1} in cold benzene-insoluble polymer is ascribable to crystallinity, as Sakurada[4] suggested. So a more plausible conclusion is that the absorption at 895 cm^{-1} sometimes corresponds to crystallinity and sometimes to a vinylidene type of double bond. In the case of the high molecular weight polymer obtained at low temperature, the absorption should be ascribed to crystallinity, and infrared spectroscopy showed the polymer insoluble in cold benzene to be crystalline.

3.4 The X-ray diagrams of the polymer

Above the relationship of the unusual solubility of the polymer in benzene to crystallinity was considered. Since the same solubility phenomenon was also observed with polystyrene, the idea of a connection became more plausible. The polymer film was produced

from hot benzene solution of the cold benzene-insoluble polymer produced at -78°C by boron trifluoride etherate in the mixed solvent of chloroform 75%—n-hexane 25%. The film was submitted to X-ray analysis. Likewise X-ray analysis was carried out on film from the cold benzene-insoluble part and from the cold benzene-soluble part. As shown in Table 7-4, the cold benzene-insoluble part gave a clearer diagram than the cold benzene-soluble part. The results for poly-α-methyl-p-methylstyrene[3], which was the only polymer that was reported to be crystalline, are also shown in Table 7-4. A close resemblance was observed between the two polymers.

In order to obtain a fiber diagram for this polymer, it was stretched and submitted to X-ray analysis. The polymer was oriented a little by the stretching to about two or six times the original length. But on stretching to over ten times the original length, the X-ray pattern became diffuse, and using the same procedure, poly-α-methylstyrene did not yield a fiber diagram.

It was found that when this polymer was heated in air above 130°C the intrinsic viscosity fell and the X-ray diagram of the polymer showed a halo. After heating at 200°C for 30 hours, polymer which was originally

Table 7-4 The comparison of the X-ray diagram between the benzene-insoluble polymer and soluble polymer

Original sample		Residue after extraction		Extracted polymer		Poly-isopropenyl toluene[3]
Intensity	Spacing A	Intensity	Spacing A	Intensity	Spacing A	Spacing A
Very strong	8.74	Very strong	8.74	Very strong	8.74	10.1
"	5.02	"	5.02	Relatively strong	5.22	6.6
Very weak	3.70	Weak	3.75	—	—	5.3
Weak	3.08	Middle	3.08	—	—	3.4

Table 7-5 The X-ray diagram of a stretched film of benzene-insoluble fraction

Stretched 1.5-2.2 times as long as original			Stretched 7-9 times as long as original		
Intensity	Spacing A	Note	Intensity	Spacing A	Note
Very strong	9.27	Arc formation	Very strong	9.07	Diffuse
Very strong	5.12		Strong	5.12	
Very very weak	—		—	—	
Very weak	3.1	Orientation to meridian	Weak	3.1	

insoluble dissolved easily in cold benzene.

The commonly employed crystallization technics such as the boiling in non-solvent with subsequent stretching, or thermal treatment with subsequent stretching, were applied to the polymer in order to obtain a fiber diagram, but all of these methods failed to secure the fiber diagram; see Table 7-7.

Failure to secure a fiber diagram by stretching, thermal treatment, swelling in non-solvent and combinations of these may be due to lack of complete separation of the crystalline part.

For the comparison, the X-ray diagrams of powder of low molecular weight polymer obtained at -20°C in chloroform, and of sodium initiated polymer, were studied, but a diagram as clear as the polymer of low temperature polymerization was not obtained. The polymer produced at -78°C by boron trifluoride etherate in toluene—n-hexane mixed solvent did not show as sharp a diagram as the polymer insoluble in cold benzene. These facts are shown in Table 7-8.

The specific gravities of a film of the poly-α-methylstyrene produced in chloroform and in toluene were measured and are shown in Table 7-9. The specific gravity

Table 7-6 The X-ray diagram of the benzene-insoluble fraction after thermal treatment

Thermally treated at 100°C for 30 min.				Thermally treated at 130°C for 30 min.			
Intensity	Spacing A	Note	Change at thermal treatment	Intensity	Spacing A	Note	Change at thermal treatment
Very strong	8.95	No change	No change	Very strong	9.01	Slightly diffuse	Slight expansion
Very strong	5.12			Relatively strong	5.16		
Very weak	3.71		Solid mass	—	—		Soft mass
Weak	3.11			Very weak	3.1		
Thermally treated at 150°C for 30 min.				Thermally treated at 200°C for 30 min.			
Intensity	Spacing A	Note	Change at thermal treatment	Intensity	Spacing A	Note	Change at thermal treatment
Very strong	9.01	Diffuse	Large expansion	Very strong	9.07	diffuse	Large expansion
Strong	5.22			Strong	5.22		
—	—		Very soft	—	—		Very soft
—	—			—	—		

Table 7-7 The X-ray diagram of the benzene-insoluble part after various ways of treatment

Stretching after swelling in MEK			Stretching after heating		
Intensity	Spacing A	Note	Intensity	Spacing A	Note
Very strong	9.07	No fibre diagram	Very strong	9.07	No fibre diagram
Relatively strong	5.12		Relatively strong	5.12	
Very very weak	—		Very very weak	—	
Very weak	3.1		Very weak	3.1	

Table 7-8 The X-ray diagram of poly-α-methylstyrene obtained under a variety of conditions

Polymer obtained by Na			Polymer obtained in $CHCl_3$ at $-20^{\circ}C$		
Intensity	Spacing A	Note	Intensity	Spacing A	Note
Very strong	9.07		Very strong	9.01	
Very strong	5.12		Relatively strong	5.18	slightly
—	—		—	—	diffuse
Very weak	3.1		Very very weak	—	

Polymer obtained in $C_6H_5CH_3$—n-C_6H_{14} at $-78^{\circ}C$		
Intensity	Spacing A	Note
Very strong	9.42	
Strong	5.02	Slightly
—	—	diffuse
—	—	

was determined by the float method in aqueous sugar solution. There was no difference of the specific gravity, though there was some difference of the solubility.

Table 7-9 Specific gravity of poly-α-methylstyrene

Sample	Specific gravity		
	Before stretching	After stretching	Stretching ratio
A-1	1.06_0	1.07_3	2.1
A-2	1.05_8	1.06_9	2.0
B	1.06_3	1.06_5	2.2
C	1.06_2	—	—

A: Film of benzene-insoluble part of a polymer produced in $CHCl_3$ by $BF_3 \cdot O(C_2H_5)_2$.
B: Film of benzene-soluble polymer produced in toluene by $BF_3 \cdot O(C_2H_5)_2$.
C: Film of benzene-soluble polymer produced in toluene by $AlCl_3$

For the specific gravity of poly-α-methylstyrene Sakurada[4] reported a value of 1.0609-1.0634. He did not find that it varied with polymerization catalyst. He also reported that thermal treatment increased the specific gravity a little, and ascribed this to a shift of the polymer molecules to a more closely-packed state. This is closely correlated with the slight increase of the specific gravity by the stretching evidenced in Table 7-9, and the above explanation may possibly hold

here too. There is also correlation with the orientation as shown by the X-ray diagram, on stretching several-fold.

3.5 Viscosities of solutions in toluene and chloroform.

The unusual solubility of the polymer cannot be completely ascribed to crystallinity, because the results of X-ray analysis were not perfectly unambiguous and there was no difference in behavior between solutions of the polymer soluble in cold benzene and that insoluble in cold benzene. The conformation of the polymer during the polymerization process is important. In other words, the experimental results are explained by entanglement of polymer occurring during the propagation step, it not being disentangled by contacting with benzene, though entanglement was non-existent after it had dissolved in benzene by heating. Next, information about expansion of polymer molecules during the polymerization is important in connection with investigating the possibility of entanglement. Since it is difficult to measure viscosity at $-78^{\circ}C$ (polymerization temperature), the solvent dependency of the intrinsic viscosity of a fractionated sample was measured at $30^{\circ}C$. The experimental results are shown in Table 7-10. The intrinsic visocisty of polymer

Table 7-10 The relationship between $[\eta]$ of polymer and the solvent used in the measurement of $[\eta]$

Solvent	$[\eta]$ at 30°C	
Toluene	1.41	0.49
Chloroform	1.54	0.53
Benzene	1.53	0.53

in chloroform is 1.1 times as great as that in toluene. One would expect the polymer to be more expanded in chloroform than in toluene.

4. Discussion

It was found in the present investigation that the polymer produced at high conversion in the low temperature polymerization contains the part insoluble in cold benzene. The unusual solubility is not due to cross-linking or difference in end group structure: it was considered to be due to crystallinity and polymer entanglement. These two possibilities will be discussed here in more detail.

The experimental facts that the benzene-insoluble polymer was obtained in the polymerization at high

conversion and that after dissolving by heating it behaved in solution like the benzene-soluble polymer support the entanglement hypothesis. This means that entaglement of polymer chain took place only during the propagation step. This view is also supported by the fact that more polymer insoluble in cold benzene was formed in chloroform than in toluene, and by the fact that poly-α-methylstyrene expands more in chloroform than in toluene. A similar effect of solvent on the entanglement of polymer has been reported in the radical polymerization of acrylamide.[6] As seen in Section 7.2, poly-α-methylstyrene is expanded in the solution due to the presence of α-methyl group, which is appropriate for occurrence of entanglement. The failure of the X-ray diagram to show orientation on stretching may be explained by entanglement of the polymer chains.

However, there are some experimental facts which cannot be explained by entanglement but can only be explained by stereoregularity of polymer.

Stereoregularity in the polymer was indicated by certain experimental facts. Firstly, the benzene-insoluble fraction of polymer gave a sharp X-ray diagram, while the benzene-soluble fraction gave a diffuse one.

Next, a certain polymerization solvent and only boron trifluoride etherate gave the benzene-insoluble polymer. This suggests that the nature of the growing ion-pair was affected by the polymerization conditions, and determined the propagation step and the stereospecificity of polymer. It does not appear plausible that the polymer entanglement would be affected by the nature of the growing ion-pair. If it is considered that the polymer insoluble in cold benzene obtained here is a stereospecific poly-α-methylstyrene, the present polymerization would be explained by the mechanism proposed for the stereospecific polymerization of alkyl vinyl ether by low temperature homogeneous cationic polymerization.[2] The behavior of the stereospecific poly-α-methylstyrene obtained here closely resembles that of the isotactic one obtained using a Ziegler-type catalyst.[4] To secure an isotactic polymer in homogeneous cationic polymerization, moderate ionic character of the growing ion-pair, low temperature and repulsion between substituents are necessary.[2] The experimental conditions giving the benzene-insoluble polymer, i.e., polymerization by boron trifluoride etherate in mixed solvent comprising chloroform—n-hexane rich in chloroform or of

methylene chloride—n-hexane rich in n-hexane, are conditions imparting a moderately ionic character to the ion-pair. Poly-α-methylstyrene insoluble in cold benzene was produced only at low temperature. Furthermore, as expected from the low ceiling temperature for α-methylstyrene,[7] considerable repulsion between substituents may exist in the propagation step. Hence, conditions for the production of isotactic polymer are fulfilled.

Sakurada investigated the properties of poly-α-methylstyrene produced under the various conditions. Glass transition temperature,[4] infrared spectroscopy,[4] X-ray[8] and nuclear magnetic resonance studies[9] of the polymer showed that stereoregularity of polymer is affected by the polymerization catalyst in a decreasing order $Al(C_2H_5)_3 \cdot TiCl_4 \geq BF_3 \cdot O(C_2H_5)_2 \geq TiCl_4 > K \approx Na$. He reported[8] that the powder X-ray diagram of poly-α-methylstyrene obtained by $Al(C_2H_5)_2 \cdot TiCl_4$ and $BF_3 \cdot O(C_2H_5)_2$ was amorphous though both polymers showed stereoregularity on measurement of physical properties. However, the intensity ratio of the inner ging (9.1 A) and the outer ring (5.4 Å) of the powder X-ray diagram changed with tacticity of polymer, though it remained amorphous. Furthermore, he observed that the intensity

ratio changed according to crystallization treatment. Summarizing, he concluded that since poly-α-methylstyrene is harder than polystyrene because of the presence of an α-methyl group, crystallization of poly-α-methylstyrene is highly hindered despite its stereoregularity, and that as stated above the tacticity of the polymer affected the amorphous X-ray diagram.

The effect of the polymerization catalyst on the solubility in benzene of poly-α-methylstyrene obtained in the present investigation was found to be in the decreasing order: boron trifluoride etherate > stannic chloride, aluminum chloride > sodium, which is the same order as that observed by Sakurada.[8] The experimental facts that though the X-ray diagram of the benzene-insoluble part showed a slight orientation, it did not give a fiber diagram on stretching and that the crystalline part seemed to be destroyed by extremely large stretching will be explained on the basis suggested by Sakurada.[8] Poly-p-chlorostyrene,[10] poly-p-iodostyrene,[11] poly-p-methylstyrene[10),12] and poly-o-methoxystyrene[13] were reported to be less crystallizable polymer in spite of their stereoregularity. And poly-α-methylstyrene may be added to this group.

As stated above, entanglement and stereoregularity were suggested as the reason for the polymer's being insoluble in cold benzene. Since neither factor working separately can explain all of the experimental results, it is reasonable to consider that they operate simultaneously. It is not impossible to assume that chain entanglement at the propagation step takes place more easily when stereospecific propagation occurs. But there is no independent evidence to support this view.

To conclude, it was established in the present investigation that a polymer insoluble in cold benzene was produced under polymerization conditions at -78°C using boron trifluoride etherate in chloroform — n-hexane (chloroform-rich) or in methylene chloride — n-hexane (n-hexane-rich). The fraction insoluble in cold benzene gave a sharper X-ray diagram than the soluble fraction, which suggests the fraction insoluble in cold benzene is stereospecific. But a fiber diagram was not obtained even after various crystallization treatments, suggesting that the cold benzene-insoluble fraction is less crystallizable in spite of its stereospecificity. On the other hand, the entanglement of the polymer chain was suggested as another cause of the insolubility in cold benzene.

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Section 7.2 The Molecular Weight

1. Introduction

It was found in Section 1.1 that poly-α-methylstyrenes having a wide range of molecular weights were obtained by cationic polymerization in mixed solvents. However, the intrinsic viscosity—molecular weight relationship of high molecular weight poly-α-methylstyrene was not then reported. Heiligmann[1] calculated the molecular weight of poly-α-methylstyrene of large intrinsic viscosity using the equation[3] reported for low molecular weight polystyrene, and the true molecular weight could not be calculated. Hence in this investigation, the molecular weight of fractionated poly-α-methylstyrene was determined by the osmotic pressure measurement.

It was observed in Section 7.1 that the proportion of polymer insoluble in cold benzene depended on the polymerization conditions. It was investigated whether there is some difference between the solution properties of polymer soluble in cold benzene and insoluble polymer, and it was found that there is no difference between the solution properties, so use of the same intrinsic viscosity—molecular weight equation for both types of

polymer was confirmed to be satisfactory.

It is interesting to compare poly-α-methylstyrene with polystyrene in connection with the effect of α-methyl group. The effect of α-methyl group on the expansion of polymer in solution was investigated vis-a-vis the polymer entanglement proposed in Section 7.1.

2. Experimental and Results

2.1 Preparation and fractionation of sample

The poly-α-methylstyrene soluble in cold benzene was prepared under the following conditions.

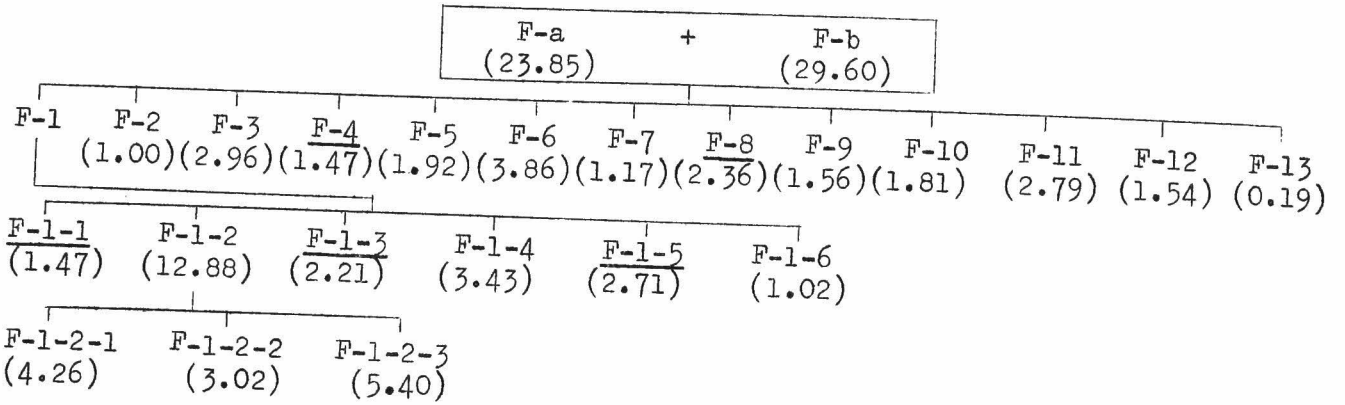
Table 7-11 The preparation of benzene-soluble poly-α-methylstyrene

Sample	Monomer ml.	Toluene ml.	n-Hexane ml.	Temperature °C	Conversion %	$[\eta]$
F-a	40	120	40	-78	64.7	1.20
F-b	40	120	40	-50 - -60	82.7	0.78

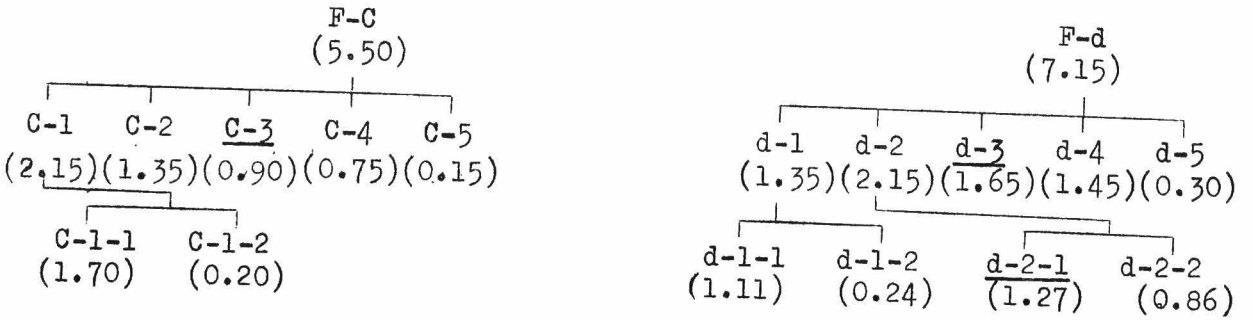
23.85 g. of sample F-a and 29.60 g. of sample F-b were dissolved into mixed solvent comprising benzene (2 l.) and toluene (1.7 l.), and fractionated by precipitating with methanol. Poly-α-methylstyrene was fractionated into twenty fractions as shown in Table 7-12.

Table 7-12 The fractionation of poly-α-methylstyrene
(weight : g.)

(a) Benzene-soluble polymer



(b) Benzene-insoluble polymer



The molecular weights of the fractions underlined were measured. In the present fractionation experiment the molecular weight distribution curve calculated using the intrinsic viscosity—molecular weight equation given below clearly exhibited two peaks.

In order to obtain poly-α-methylstyrene containing the benzene-insoluble part, the polymerization was carried out under the following donditions:—

Monomer	20 ml.	Chloroform	60 ml.
n-Hexane	20 ml.		
Boron trifluoride etherate			0.3 ml.
Polymerization temperature			$-78^{\circ}C$

Run No.	Conversion	$[\eta]$
F-C	90.7%	1.64
F-D	76.4%	1.03

Using the method described in the previous Section, poly-α-methylstyrene thus obtained was divided into parts soluble and insoluble in cold benzene, the insoluble material amounting to about fifty percent of the original by weight. The polymer insoluble in cold benzene was fractionated into several fractions employing the same procedure as was used with samples F-a and

F-b. The course of the fractionation is shown in Table 7-12. Almost all of these fractions were readily soluble in benzene at room temperature.

2.2 Measurement of osmotic pressure

The osmotic pressure of the benzene solution of poly-α-methylstyrene was carried out by using Gee-type osmometer at 30 $\pm$ 0.01°C. Denitrated collodion film made from collodion with which ethylcellosolve was mixed in amount depending on the drying temperature was used as semipermeable film. The measurements were carried out on five fractions of the polymer soluble in cold benzene and three fractions of insoluble material. With the polymer insoluble in cold benzene measurements were carried out with a few samples because fractionation of this polymer was considered to be incomplete. A linear relationship was not observed between the concentration of polymer, C, and π/C, which suggests a need to take into account the third term of equation (7-1).

$$\pi/C = (\pi/C)_0 \ (1 + \Gamma_2 C + \Gamma_3 C^2 + \ldots.) \qquad (7\text{-}1)$$

Assuming that Γ_3 equals $g\Gamma_2^2$ and g equals 0.25 as general case[3], equations (7-2) and (7-2') were derived.

$$(\pi/C)^{\frac{1}{2}} = (\pi/C)_o^{\frac{1}{2}} [\, 1 + (\Gamma_2/2)C \,] \qquad (7\text{-}2)$$

$$= (\pi/C)_o^{\frac{1}{2}} [\, 1 + (A_2M/2)C \,] \qquad (7\text{-}2')$$

Then, $(\pi/C)^{\frac{1}{2}}$ was plotted against C as is shown in Fig. 7-1.

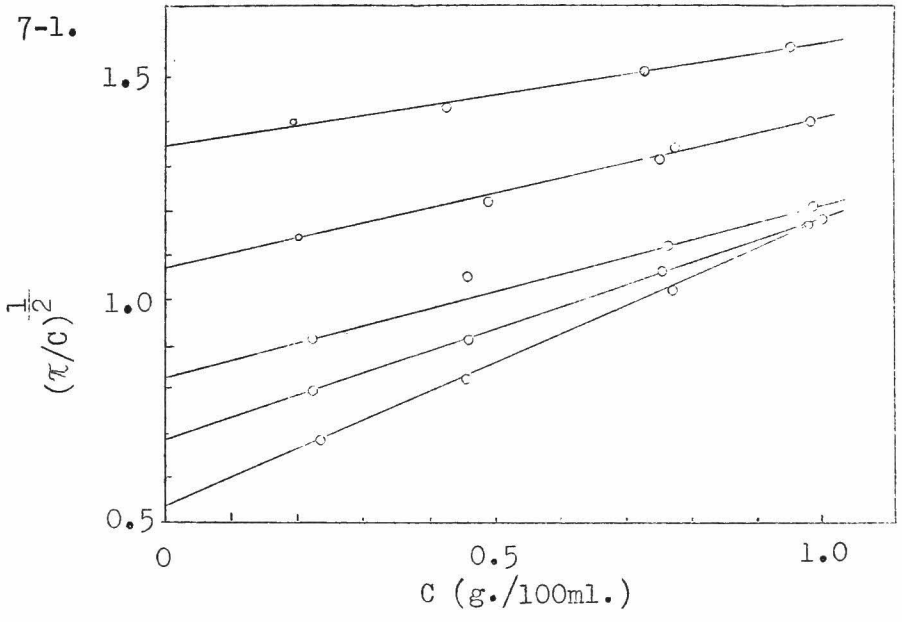


Fig. 7-1 Osmotic pressure measurement of benzene-soluble poly-α-methylstyrene

The experimental results from Fig. 7-1 are summarized in Table 7-13.

Though it is to be expected[4] that the second virial coefficient A_2 will decrease with increase in molecular weight of polymer, a clear relationship between A_2-value and the molecular weight was not observed in this experiment, as is seen from Table 7-13.

Table 7-13 The results of osmotic pressure measurement

Sample No.	$[\eta]$	$(\pi/c)_o$ *	$\bar{M}_n$	$\bar{M}_n$ calculated by eq.(7-3) from $[\eta]$	A x 10^4
Benzene-soluble polymer					
F-1-1	1.80	28.3	910000	920000	2.56
F-1-3	1.29	48.2	534000	550000	2.64
F-1-5	0.99	65.3	394000	366000	2.54
F-4	0.75	116.6	220000	239000	2.67
F-8	0.53	179.6	143000	139000	2.77
Benzene-insoluble polymer					
d-2-1	1.32	56.5	455000	567000	2.67
c-3	1.18	54.1	475000	477000	2.23
d-3	0.99	88.0	292000	366000	2.34

* $(\pi/c)_o$ is expressed as $(g/cm^2)/(g/cm^3)$

The relationship between intrinsic viscosity and molecular weight of polymer is shown in Fig. 7-2. This relationship is essentially the same for polymer soluble or insoluble in the cold benzene. To obtain the intrinsic viscosity—molecular weight equation, logarithmic

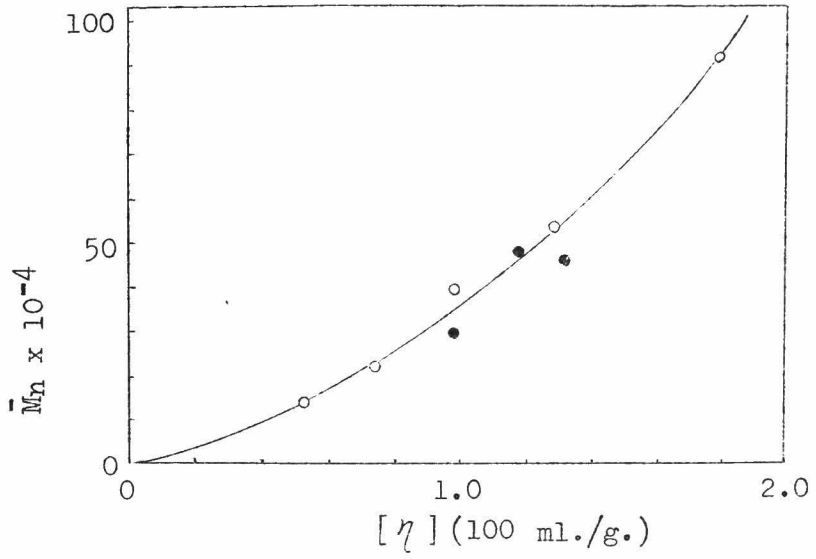


Fig. 7-2 The relationship between the intrinsic viscosity of benzene solution at 30°C and the molecular weight of poly-α-methylstyrene

(○) : Benzene-soluble polymer,
(●) : Benzene-insoluble polymer

plots of the intrinsic viscosity and the molecular weight was made using polymer insoluble in cold benzene, vide Fig. 7-3.

A straight line was obtained, from which the intrinsic viscosity—molecular weight equation, as determined by the least square method was found to be:—

$$[\eta] = 2.49 \times 10^{-4} \times \bar{M}_n^{0.647} \qquad (7\text{-}3)$$

The intrinsic viscosity value of the polymer on which the osmotic pressure measurement was made, was inserted

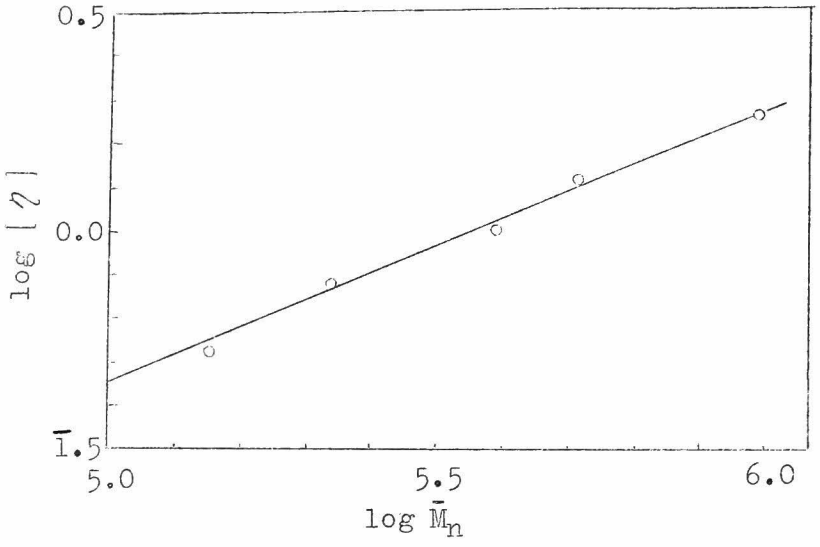


Fig. 7-3 The logalithmic plot of the intrinsic viscosity against the molecular weight of benzene-soluble poly-α-methylstyrene

in equation (7-3) and the corresponding molecular weight calculated, and this was compared with the practical molecular weight. The two were in good agreement.

2.3 The behavior of stereospecific polymer and the expanded chain of poly-α-methylstyrene

The composition of the critical consolute mixture comprizing benzene and methanol was determined at 30°C according to Shultz's method.[5] The polymer precipitation temperatures were determined on four kinds of poly-α-methylstyrene with different molecular weight (755000, 532600, 209600, and 74950), using benzene—methanol mixture

of three different compositions, and for four kinds of polymer concentration (0.4, 0.3, 0.2 and 0.1 g./100ml.) From these experiments Fig. 7-4 was obtained, which gives the content of methanol in the critical consolute mixture which precipitates polymer of infinite molecular weight at infinite dilution and 30°C. The composition of θ-solvent at 30°C was found to be methanol 20.64 vol. % and benzene 79.36 vol.%.

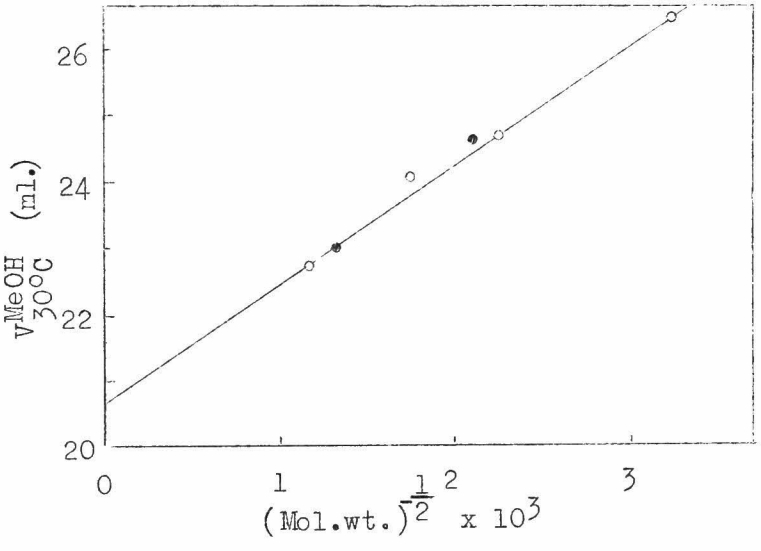


Fig. 7-4 The relationship between the molecular weight and the composition of mixed solvent on the precipitation point at 30°C
(○): Benzene-soluble polymer
(●): Benzene-insoluble polymer

For comparison, the measurements were carried out with polymer insoluble in cold benzene too. The experimental results are plotted in Fig. 7-4.

Next, the intrinsic viscosities of four fractionated poly-α-methylstyrenes were measured in θ-solvent, and are represented as $[\eta]_\theta$ in Table 7-14.

Table 7-14 The viscosity measurement in θ solvent

Sample No.	$\bar{M}_n$ from eq.(7-3)	$[\eta]^{30^\circ C}_{\text{benzene}}$	$[\eta]_\theta$	$\alpha^3=[\eta]/[\eta]_\theta$
1-2	755000	1.58	0.798	1.98
1-4	389400	0.97	0.578	1.67
5	209600	0.67	0.428	1.57
8	74950	0.355	0.260	1.37

The number average molecular weight of these polymers calculated by equation (7-3) was plotted against in Fig. 7-5. The straight line in Fig. 7-5 corresponds to the relationship " $[\eta]_\theta \propto \bar{M}^{0.50}$ ". So the following relationship was confirmed for θ-solvent.

$$[\eta]_\theta = 7.68 \times 10^{-4} \times \bar{M}^{0.50} \qquad (7\text{-}4)$$

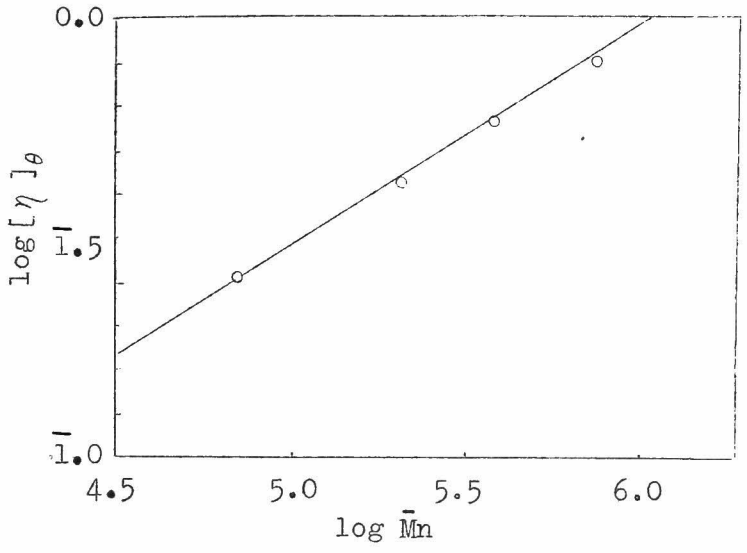


Fig. 7-5 The logalithmic plot of the molecular weight against $[\eta]_\Theta$ (30°C)
The straight line is drawn theoretically, the slope being 1/2.

3. Discussion

The intrinsic viscosity—molecular weight equation was determined for benzene solutions of the fractionated poly-α-methylstyrene obtained in this investigation. This equation showed clearly that the molecular weights of poly-α-methylstyrenes obtained in Section 1.1 were from about fifty thousand to about two million. The molecular weight of poly-α-methylstyrene found by Heiligmann et al.[1] is as high as several million as deduced from its intrinsic viscosity. Though they cal-

culated the molecular weight distribution by using the relationship "$[\eta] \propto \bar{M}$", their results should be greatly modified.

For poly-α-methylstyrene other intrinsic viscosity—molecular weight equations have been reported since equation (7-3) was given. The followings are representative:—

$$[\eta] = 7.81 \times 10^{-5} \times \bar{M}_w^{0.73} \qquad (7\text{-}5)^{6)}$$

$25^{\circ}C$, Toluene solution

Molecular weight: $(3\text{-}60) \times 10^4$

Polymer obtained by sodium naphthyl

at $-78^{\circ}C$ in tetrahydrofuran.

Molecular weight determined by

Archibald method

$$[\eta] = 1.08 \times 10^{-4} \times \bar{M}^{0.71} \qquad (7\text{-}6)^{7)}$$

$30^{\circ}C$, Toluene solution

Molecular weight: $(3\text{-}66) \times 10^4$

Polymer was obtained by sodium naphthyl

at $-78^{\circ}C$ in tetrahydrofuran.

Molecular weight determined by

osmotic pressure and light scattering.

$$[\eta] = 1.1 \times 10^{-3} \times \bar{P}_w^{0.87} \qquad (7\text{-}7)^{8)}$$

30°C, Toluene solution

Degree of polymerization : 860-4100

Polymer obtained using sodium metal

and fractionated in benzene-isopropanol system.

Molecular weight determined by

light scattering.

In Fig. 7-6 equations (7-3), (7-5), (7-6) and (7-7) are shown together for the comparison. Taking into account

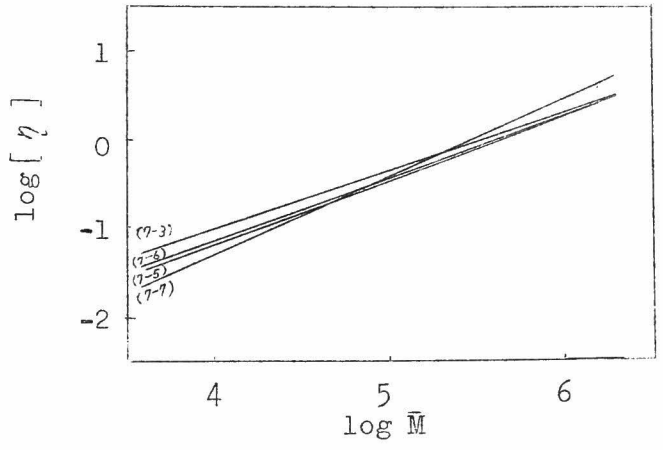


Fig. 7-6 Comparison between the intrinsic viscosity—molecular weight equations for poly-α-methylstyrene

that equation (7-5) and equation (7-6) relate to the intrinsic viscosity at 25°C and 30°C respectively, both straight lines are in very close agreement. Furthermore,

taking into account that equation (7-3) concerns the intrinsic viscosity in benzene and that the intrinsic viscosity of poly-α-methylstyrene is larger in benzene than in toluene (cf. Table 7-10), the agreement among equations (7-3), (7-5) and (7-6) is fairly good, especially in the high molecular weight range. Equation (7-7) shows a slightly different behavior to the others.

The properties of the polymer insoluble in cold benzene seem to be essentially the same as those of the polymer soluble in cold benzene when it has once been dissolved. The results shown in Table 7-13 would suggest that the A_2-values for the polymer soluble in cold benzene are slightly larger than those for the insoluble polymer. But because, as was mentioned above, fractionation of the insoluble polymer was not complete, the matter has been left for further study.

Danusso[9] measured the osmotic pressure of toluene solutions of isotactic polystyrene and atactic polystyrene at 30°C, and calculated the A_2-values. He found that the A_2-value for isotactic polystyrene was smaller than that for atactic polystyrene if the two molecular weights were the same. If the relationship between A_2-value and steric configuration found by Danusso holds for other

polymers, and if the poly-α-methylstyrene insoluble in cold benzene obtained here is isotactic, the small difference between the A_2-values in Table 7-13 might have some significance.

Next, poly-α-methylstyrene will be compared with polystyrene. Little has been reported on measurement of osmotic pressure of benzene solutions of polystyrene at 30°C, which are very relevant to the present work. Flory[10] measured the osmotic pressure of toluene solutions of polystyrene and found an A_2-value of 2.19×10^{-4} for polystyrene of molecular weight 158×10^4, and 5.13×10^{-4} for polystyrene of molecular weight 7.20×10^4. Danusso[9] measured the osmotic pressure of toluene solutions of polystyrene at 30°C, and found that A_2-values for atactic polystyrene of 2.95×10^{-4} for a molecular weight 85×10^4, and 5.00×10^{-4} for a molecular weight 7.6×10^4. Assuming that the A_2-value of polystyrene does not change on the changing the solvent from toluene to benzene, it follows that the A_2-value of poly-α-methylstyrene is smaller than that of polystyrene.

Comparing the volume expansion factor $\alpha^3 \equiv [\eta]/[\eta]_\theta$ for poly-α-methylstyrene with that for polystyrene in benzene solution, it was found that α^3 for polystyrene

was clearly larger than α^3 for poly-α-methylstyrene. Flory[11] reported on polystyrene that $\alpha^3 = 1.70$ (molecular weight : 63100) and $\alpha^3 = 3.16$ (molecular weight: 838000) from measurement of $[\eta]_\theta$ in cyclohexane at 34°C and intrinsic viscosity in benzene at 25°C. These values were compared with those of poly-α-methylstyrene listed in Table 7-14, though the intrinsic viscosity of poly-α-methylstyrene was measured at 30°C. Then it was found that α^3 for polystyrene was larger than for poly-α-methylstyrene, and that benzene is a better solvent for polystyrene than for poly-α-methylstyrene.

In order to ascertain the effect of the α-methyl group on the chain expansion of poly-α-methylstyrene, the end-to-end distance of the polymer in the θ-solvent should be discussed. From equation (7-4), K equals 9.68×10^{-4}, which is related to the mean square of the end-to-end distance of polymer, $\langle \bar{r}_o^2 \rangle$, and the universal parameter Φ by equation (7-8).

$$K = \Phi \left(\langle \bar{r}_o^2 \rangle / M \right)^{3/2} \qquad (7\text{-}8)^{12)}$$

Putting $\Phi = 2.1 \times 10^{21}$ [13]

$$\left(\langle \bar{r}_o^2 \rangle / M \right)^{1/2} = 772.5 \times 10^{-11} \quad A \qquad (7\text{-}9)$$

Taking the carbon-carbon distance of the main chain as 1.54 A and the bond angle 109.5°, and assuming free rotation of the main chain around a carbon-carbon bond, the mean square of the end-to-end distance of polymer $\langle \bar{r}^2_{of} \rangle$ would be

$$(\langle \bar{r}^2_{of} \rangle / M)^{1/2} = 283 \times 10^{-11} \text{ A} \qquad (7\text{-}10)$$

For poly-α-methylstyrene at 30°C, equation (7-11) is derived from equations (7-9) and (7-10),

$$(\langle \bar{r}^2_{o} \rangle / \langle \bar{r}^2_{of} \rangle)^{1/2} = 2.73 \qquad (7\text{-}11)$$

This value is larger than 2.44 (25°C) or 2.33 (70°C) for polystyrene[14], which clearly means that in poly-α-methylstyrene there is some steric hindrance of free rotation of main chain due to the methyl group.

Sirianni[7] studied the intrinsic viscosity in θ-solvent—the molecular weight equation for poly-α-methylstyrene obtained by sodium naphtyl in tetrahydrofuran at -78°C with a sharply-defined molecular weight and for polystyrene sharply fractionated, and found that the two equations were the same. So for poly-α-methylstyrene and polystyrene which have the same chain length, the former exhibits an intrinsic viscosity which is higher

by about 10% than that exhibited by the latter. Therefore, it was concluded that the α-methyl group in poly-α-methylstyrene hinders the free rotation of the polymer chain and makes the chain more expanded.

Kurata et al.[10] calculated the chain expansion of poly-α-methylstyrene in θ-solvent on the basis of Sirianni's data, $(\langle \bar{r}_o^2 \rangle / \langle \bar{r}_{of}^2 \rangle)^{1/2}$ being found to be 2.30 ± 0.10 if the universal parameter Φ was taken as 2.87×10^{21}. The same authors[10] calculated $(\langle \bar{r}_o^2 \rangle / \langle \bar{r}_{of}^2 \rangle)$ for atactic polystyrene as 2.22 ± 0.05 ($\sim 30^{\circ}C$) and 2.15 ($70^{\circ}C$), using a Φ-value of 2.87×10^{21}. These calculated results again show that in θ-solvent the poly-α-methylstyrene chain is more expanded than that of polystyrene.

In conclusion, the following points were demonstrated by the present investigation. With a benzene solution of the fractionated sample from high molecular weight poly-α-methylstyrene produced by low temperature cationic polymerization, measurement of intrinsic viscosity and the osmotic pressure gave the following equation,

$$[\eta] = 2.49 \times 10^{-4} \times \bar{M}_n^{0.647}$$

This equation enables the molecular weight of poly-α-

methylstyrene to be calculated.

For a critical consolute solution consisting methanol 20.6 vol.% and benzene 79.4 vol.% at 30°C, the following relationship was obtained:—

$$[\eta]_\theta = 7.68 \times 10^{-4} \times \bar{M}^{0.50}$$

Using this equation and equation (7-8) $(\langle \bar{r}_o^2 \rangle / \langle \bar{r}_{of}^2 \rangle)^{1/2}$ was calculated as 2.73, which suggests that in θ-solvent, poly-α-methylstyrene is more expanded, due to α-methyl group, than is polystyrene. The behavior of the polymer insoluble in cold benzene in solution was almostly the same as that of the polymer soluble in cold benzene, after it was once dissolved.

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Chapter 8 The Molecular Weight and Molecular Weight Distribution of Polystyrene Obtained by Cationic Polymerization

1. Introduction

It is generally difficult to produce polystyrene of high molecular weight by cationic polymerization at room temperature. This is mainly due to a marked occurrence of the transfer reactions at high temperatures. It was reported from our laboratory[1] that the monomer transfer reaction is important in determining the molecular weight of polystyrene in cationic polymerization by stannic chloride in a non-polar solvent. Litt,[2] however, re-calculated those experimental results and showed that the monomer transfer reaction is of minor importance in polymerization of styrene in dichloroethane.

These arguments are based on the average molecular weight of polystyrene calculated from the intrinsic viscosity. To discuss the above in more detail, information on the molecular weight distribution of polystyrene is therefore needed. Atkins et al.[3] found that polystyrene obtained by stannic chloride-catalyzed polymerization has long branched chains, due to a chain transfer reaction to polymer, and pointed the inapplicability of

the normal intrinsic viscosity — molecular weight equations to that kind of polystyrene. Furthermore, Overberger et al.[4] have found an increase of weight average molecular weight of polystyrene with the increase of polymerization conversion, and have ascribed it to appearance of chain branching caused by a polymer transfer reaction. All of those polymerization were carried out in nitrobenzene or in nitrobenzene—carbontetrachloride. On the other hand, it was reported from our laboratory that the intrinsic viscosity of polystyrene decreased with increasing conversion when styrene was polymerized in dichloroethane with stannic chloride or boron trifluoride complex as the catalyst, and that there was no evidence for chain branching.[1),5)]

The present investigation was carried out in order to obtain information about the polymer and monomer transfer reactions in cationic polymerization of styrene, for which purpose the intrinsic viscosity —molecular weight relationship for polystyrene and the variation of polymer molecular weight during polymerization were studied.

As consequence, evidence for chain branching due to the polymer transfer reaction was not found in polymerization of styrene in dichloroethane, but was found with a

solvent mixture containing nitrobenzene. Furthermore, it was confirmed that there is a monomer transfer reaction under the polymerization conditions.

2. Experimental and Results

2.1 Relationship between intrinsic viscosity and molecular weight for polystyrene obtained by cationic polymerization

All of the polymerizations of styrene in which Atkins et al.[3] and Overberger et al.[4] found the chain branching were carried out using stannic chloride as the catalyst in carbon tetrachloride—nitrobenzene mixed solvent. In the present investigation, therefore, the intrinsic viscosity—molecular weight relationship was studied for polystyrene produced in dichloroethane. As will be seen later, polystyrene obtained in dichloroethane does not have branched chains.

Polystyrene was produced under the conditions shown in Table 8-1. A 2 % solution of polystyrene in benzene was fractionated at 30°C by adding methanol. The first addition of methanol to the polymer solution caused some polystyrene (P-1) to separate, leaving a solution (S-1). The solid fraction (P-1) was again dissolved in benzene and fractionated, by addition of methanol, into polystyrene

Table 8-1 Conditions synthesizing polystyrene for the determination of molecular weight

(Initial monomer concentration: 30 vol.%,
Solvent : dichloroethane 70 vol.%,
Polymerization temperature : -20°C)

Sample No.	Conversion	Catalyst concentration	Fractionated into
L-A	42%	4.4 m mole/l.	12 fractions
L-B	95%	5.6 m mole/l.	16 fractions

(P-2) and solution (S-2). The solution (S-2) was mixed with solution (S-1) and subjected to further fractionation.[6] The results of fractionation are summarized in Table 8-2. The intrinsic viscosity of each fraction in benzene or methyl ethyl ketone at 30°C is also shown in Table 8-2.

The molecular weight of some of the polystyrene fractions were found by a light scattering method, a Shimadzu light scattering photometer of the Brice type being used. Measurements were made for wave length of 436 m μ in methyl ethyl ketone at room temperature, using a semi-octagonal cell and the triangle method. The apparatus was calibrated on standard polystyrene[7] obtained from the Committee for Molecular Weight Deter-

mination of the High Polymer Society of Japan or by using a Shimadzu standard diffuser. The refractive index concentration gradient for the polymer ($\partial n/\partial C$) obtained from literature was taken as 0.231 (C: g./ml.).[8)]

Table 8-3 summarizes the weight average molecular weight and the second virial coefficient thus obtained. In Table 8-3, molecular weights of polystyrenes free from chain branching and calculated using the intrinsic viscosity—molecular weight equation reported by Atkins et al.[3)] are also shown, the two sets of values of molecular weight being in good agreement.

Using the results shown in Table 8-3, the relationships between the intrinsic viscosity and weight average molecular weight, and between the second virial coefficient and weight average molecular weight, for the present polystyrene are graphed in Figs. 8-1 and 8-2, respectively.

It is seen from Fig. 8-1, that whenever the polymerization is carried out in dichloroethane, no abnormality is noticed in intrinsic viscosity—molecular weight relationship even with polystyrene produced at high conversion. The conversion does not seem to affect the second virial coefficient, though the experimental error

Table 8-2 The fractionation of polystyrene obtained by low temperature polymerization (Polymerization condition is described in Table 8-1)

(a) Fractionation of polystyrene obtained in low conversion.

Sample No.	Weight fraction	$[\eta]^{30^\circ C}_{MEK}$	$[\eta]^{30^\circ C}_{Benzene}$
LA-2-1	8.34%	0.437	0.777
LA-1	8.12	0.365	0.604
LA-3	1.19	0.356	0.590
LA-4	7.86	0.351	0.580
LA-5	10.24	0.345	0.567
LA-2-2	9.44	0.334	0.540
LA-6	14.61	0.334	0.540
LA-7	12.30	0.304	0.475
LA-8	11.92	0.254	0.395
LA-9	10.66	0.201	0.300
LA-10	4.75	0.122	0.180
LA-11	0.56	0.050	0.076

(b) Fractionation of polystyrene obtained in high conversion

Sample No.	Weight fraction	$[\eta]^{30^\circ C}_{MEK}$	$[\eta]^{30^\circ C}_{Benzene}$
LB-1	2.78%	0.392	0.707
LB-2	9.44	0.352	0.620
LB-3	7.05	0.336	0.569
LB-4	1.19	0.323	0.553
LB-5	9.50	0.294	0.526
LB-6	7.74	0.270	0.466
LB-7	8.83	0.265	0.416
LB-8	8.21	0.238	0.380
LB-9	8.32	0.220	0.335
LB-10	8.60	0.195	0.294
LB-11	6.61	0.170	0.251
LB-12	6.93	0.141	0.204
LB-13	5.19	0.118	0.168
LB-14	5.83	0.102	0.125
LB-15	3.15	—	0.086
LB-16	0.65	—	0.055

Table 8-3 Weight average molecular weight of fractionated polystyrene
Measurement by light scattering of MEK solution at room temperature

Sample No.	$\bar{M}_w \times 10^{-4}$	A_2 Room temp. MEK $\times 10^4$	$[\eta]^{30°C}_{MEK}$	$[\eta]^{30°C}_{Benzene}$	$\bar{M}_w \times 10^{-4}$ from Atkins' eq.[3]
LA-2-1	28.9	1.33	0.437	0.777	27.6
LA-1	20.1	1.27	0.365	0.604	20.0
LA-6	16.5	1.37	0.334	0.540	17.4
LA-7	12.7	1.87	0.304	0.475	14.7
LA-8	11.4	1.73	0.254	0.395	10.6
LB-1	24.0	1.31	0.392	0.707	22.9
LB-2	20.0	1.42	0.352	0.620	19.1
LB-5	14.7	1.92	0.294	0.526	13.7
LB-6	12.2	1.62	0.270	0.466	11.8
LB-8	9.2	1.69	0.238	0.380	9.38

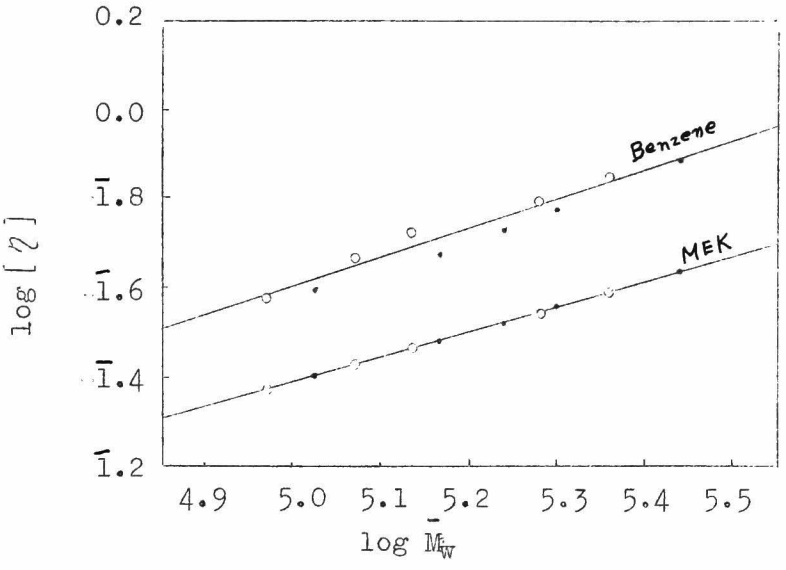

Fig. 8-1 Relationship between $[\eta]$ and $\bar{M}_w$ on the fractionated polystyrene obtained in cationic polymerization
(●): LA-polymer (low conversion)
(○): LB-polymer (high conversion)

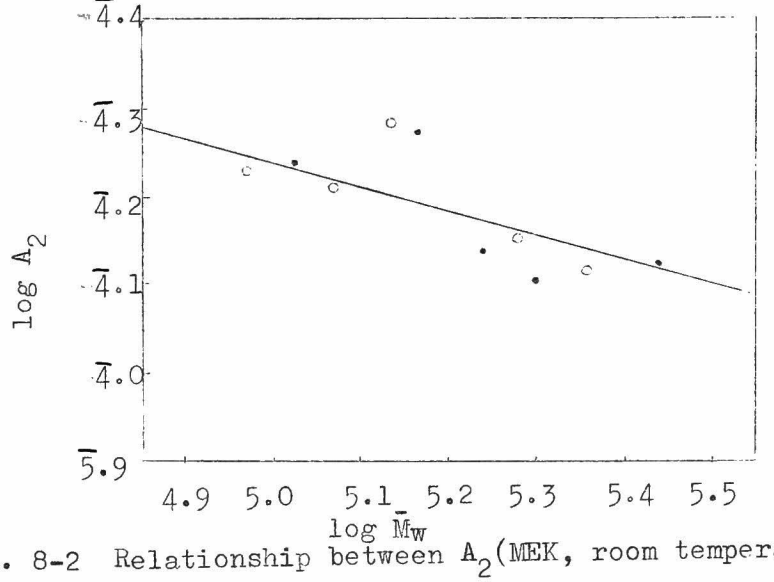

Fig. 8-2 Relationship between A_2(MEK, room temperature) and $\bar{M}_w$ on the fractionated polystyrene obtained in cationic polymerization
(●): LA-polymer (low conversion)
(○): LB-polymer (high conversion)

in the latter makes precise discussion difficult.

For the fractionated polystyrene produced in dichloroethane using stannic chloride as the catalyst the equations below hold between the weight average molecular weight and the intrinsic viscosity in benzene or methyl ethyl ketone, independent of the polymerization conversion. Of these that for methyl ethyl ketone solution agrees fairly well with Atkin's equation[3] found at 25°C,

$$[\eta]^{30^\circ C}_{MEK} = 3.9 \times 10^{-4} \times \bar{M}_w^{0.56} \qquad (8\text{-}1)$$

$$[\eta]^{30^\circ C}_{Benzene} = 2.27 \times 10^{-4} \times \bar{M}_w^{0.65} \qquad (8\text{-}2)$$

Fig. 8-1 shows that in the molecular weight range, there is no abnormality due to chain branching. Hence it can safely be concluded that polystyrene produced in dichloroethane does not have branched chains.

2.2 Variation in molecular weight of polystyrene as polymerization progresses

If chain branching appears during polymerization, as Overberger et al.[4] proposed, it might be expected that the weight average molecular weight of polymer would increase with increasing polymerization conversion.

Unless the polymer transfer reaction occurred decrease of molecular weight of polymer produced at high conversion due to decrease of monomer concentration might be expected (if polymer molecular weight is controlled by the monomer transfer reaction only, it will not change with conversion.).

In the present investigation, styrene was polymerized using boron trifluoride etherate or stannic chloride as the catalyst, in dichloroethane, nitrobenzene or nitrobenzene—carbon tetrachloride, and the molecular weight of the polystyrene was studied in relation to conversion.

Polymerizations were carried out under dry nitrogen in a flask equipped with rubber cap. A known amount of the polymerizing solution was taken from the falsk by a syringe through the rubber film at suitable intervals. Polymer was precipitated in a large amount of methanol. Conversion and the intrinsic viscosity in benzene at 30°C were determined. Reagents were purified as described previously. The water content in the polymerization system was as low as 0.8-4 m mole/l.

The experimental results are shown in Figs. 8-3, 8-4, 8-5, 8-6 and 8-7. As is clear from Fig. 8-3, the intrinsic viscosity of polystyrene decreases with increasing

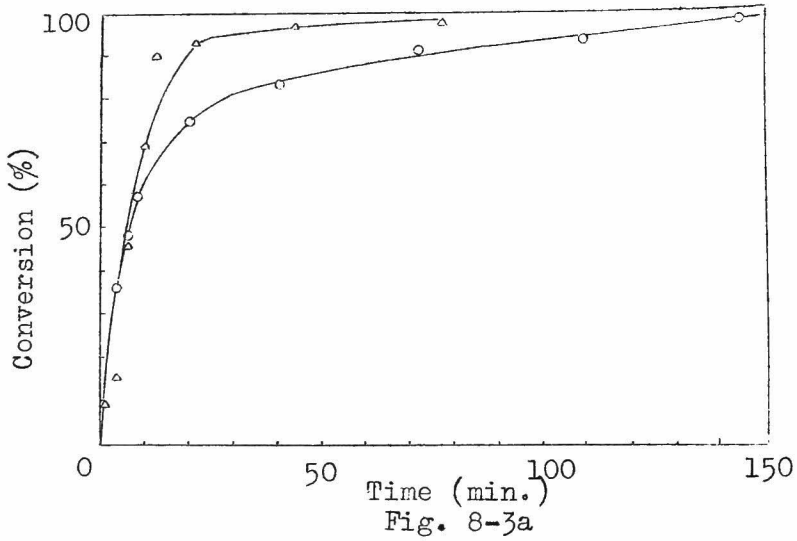

Fig. 8-3a

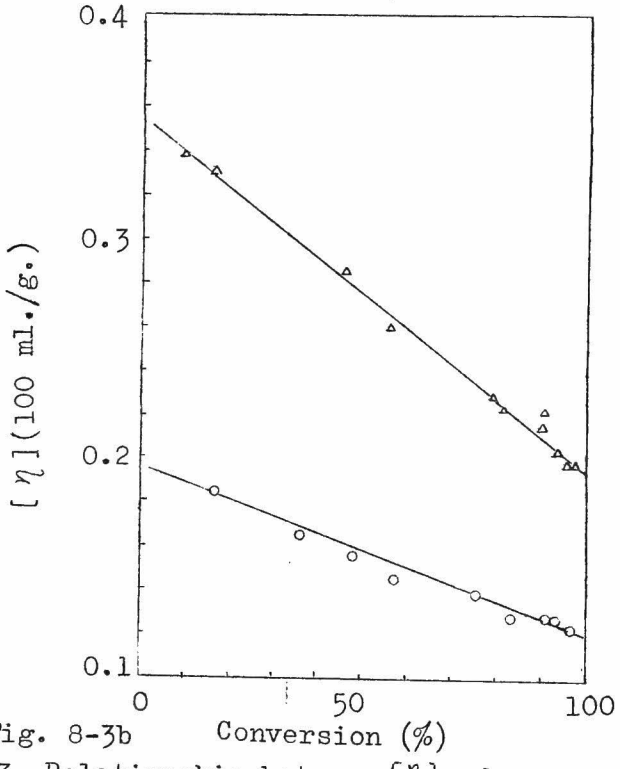

Fig. 8-3b

Fig. 8-3 Relationship between $[\eta]$ and conversion in dichloroethane, $BF_3 \cdot O(C_2H_5)_2$, $[M]_0$= 20 vol.%

a: Time—conversion curve

b: Relationship between $[\eta]$ and conversion

(○: $[BF_3 O(C_2H_5)_2]_0$= 6.5 m mole/l., $[H_2O]_0$= 9.7 m mole/l. Temp.=30°C

(△: $[BF_3 \cdot O(C_2H_5)_2]_0$= 5.9 m mole/l., $[H_2O]_0$= 1.61 m mole/l. Temp. =0°C

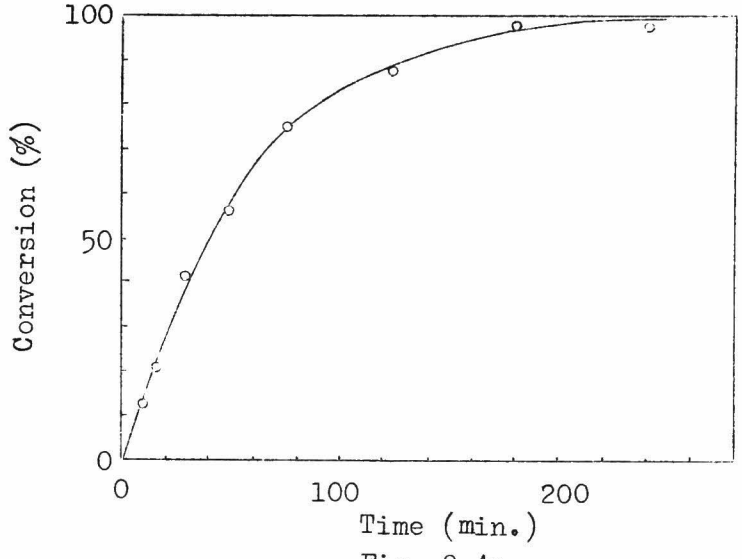

Fig. 8-4a

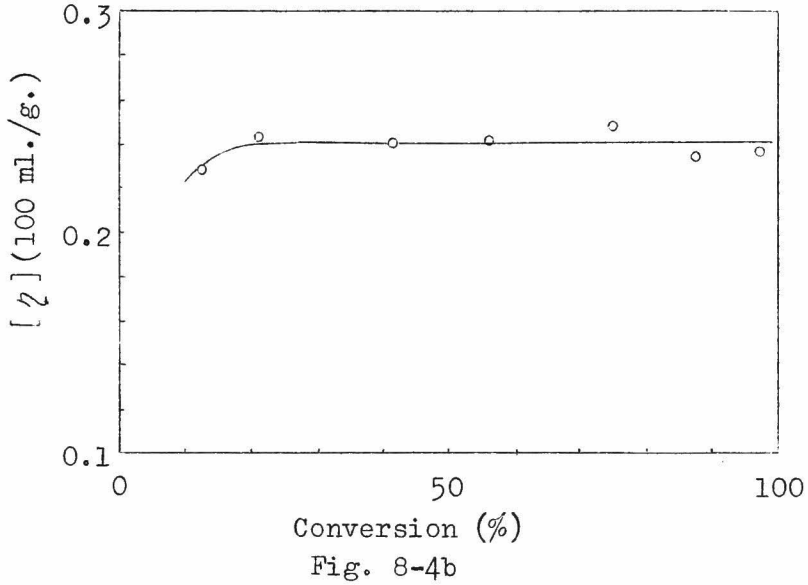

Fig. 8-4b

Fig. 8-4 Relationship between $[\eta]$ and conversion in nitrobenzene—carbon tetrachloride mixed solvent (1:1)
$[SnCl_4]_o$ = 24 m mole/l., $[M]_o$ = 20 vol.%, Temp.=0°C
a: Time — conversion curve
b: Relationship between $[\eta]$ and conversion

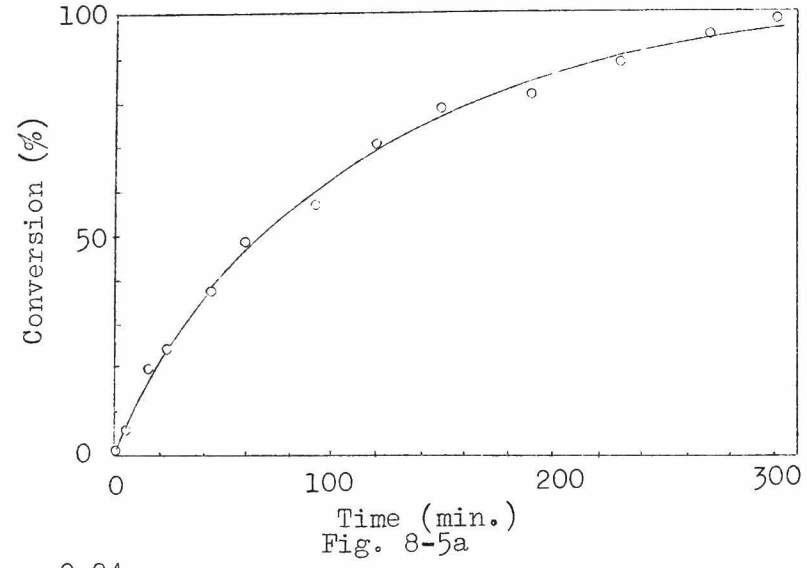

Fig. 8-5a

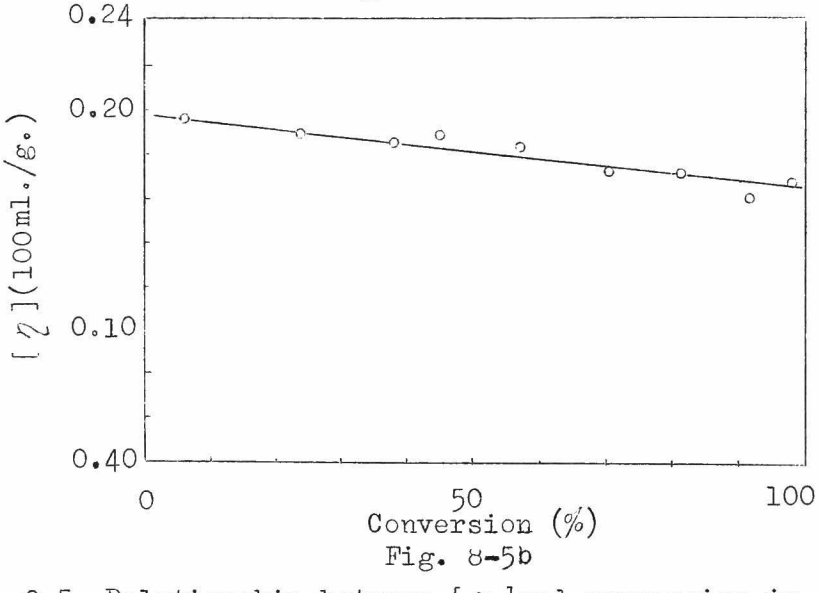

Fig. 8-5b

Fig. 8-5 Relationship between [η] and conversion in nitrobenzene—carbon tetrachloride mixed solvent (1:1)
$[BF_3 \cdot O(C_2H_5)_2]_0$ = 11.9 m mole/l.,
$[M]_0$ = 20 vol.%, Temp. = 30°C
a: Time—conversion curve
b: Relationship between [η] and conversion

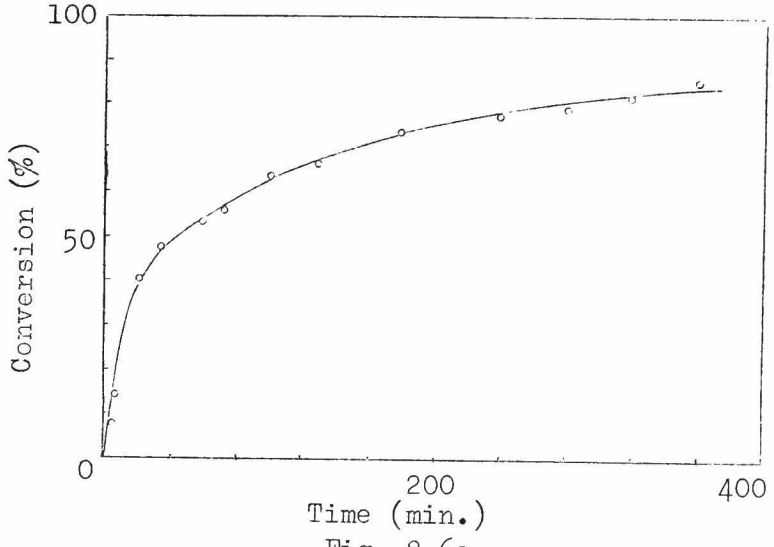

Fig. 8-6a

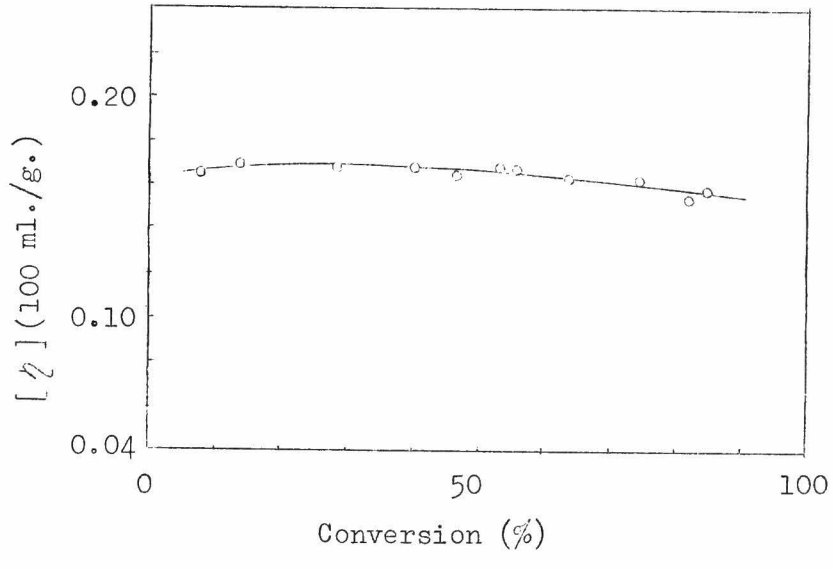

Fig. 8-6b

Fig. 8-6 Relationship between $[\eta]$ and conversion in nitrobenzene
$[SnCl_4]_o$ = 1.0 m mole/l., $[M]_o$ = 20 vol.%,
$[H_2O]_o$ = 3.7 m mole/l., Temp.^{o} = 30°C
a: Time—conversion curve
b: Relationship between $[\eta]$ and conversion

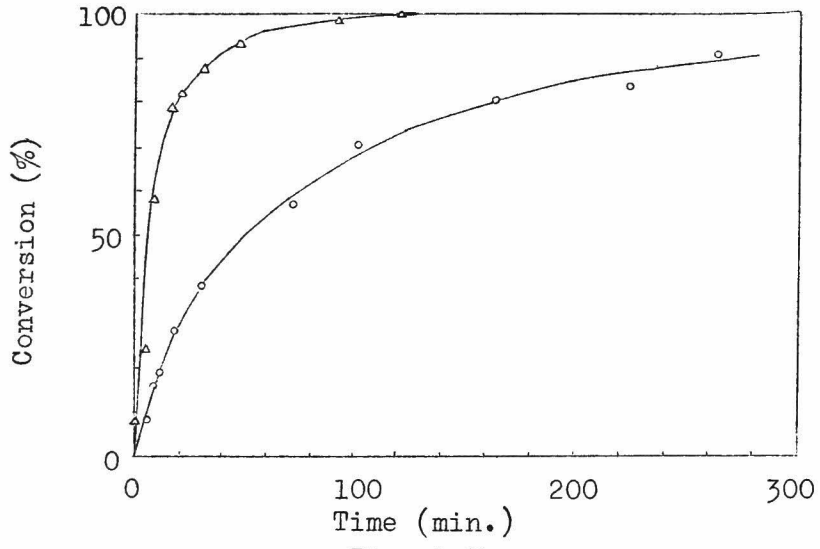

Fig. 8-7a

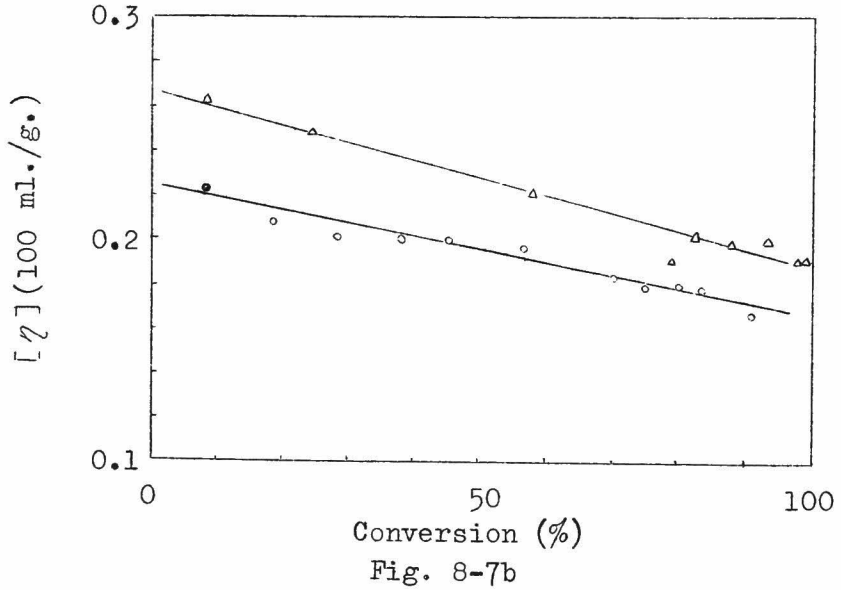

Fig. 8-7b

Fig. 8-7 Relationship between $[\eta]$ and conversion in nitrobenzene, $BF_3 \cdot O(C_2H_5)_2$, $[M]_o$ = 20 vol.%, $[H_2O]_o$ = 0.8 m mole/l.

a: Time—conversion curve

b: Relationship between $[\eta]$ and conversion

(○): $[BF_3 \cdot O(C_2H_5)_2]_o$ = 1.0 m mole/l., Temp. = 30°C

(△): $[BF_3 \cdot O(C_2H_5)_2]_o$ = 4.0 m mole/l., Temp. = 10°C

conversion in dichloroethane. The results shown here are for boron trifluoride etherate-catalyzed polymerization. The same results were obtained with stannic chloride-catalyzed polymerization, as previously reported from this laboratory[1]. On the other hand, with polymerization in nitrobenzene or in nitrobenzene—carbon tetrachloride, the polymer intrinsic viscosity did not decrease with increasing conversion in the polymerization caused by stannic chloride as is seen in Figs. 8-4 and 8-6. In polymerization in nitrobenzene or in nitrobenzene—carbon tetrachloride and catalyzed by boron trifluoride etherate, the polymer intrinsic viscosity decreases to a minor extent compared with polymerization in dichloroethane, as is seen from Figs. 8-5 and 8-7.

Now the question whether the intrinsic viscosity measured gives the molecular weight is an important one. So polystyrene was prepared in systems where the polymer intrinsic viscosity decreased with conversion (boron trifluoride etherate—dichloroethane) and where it did not (stannic chloride—nitrobenzene—carbon tetrachloride). The weight average molecular weights of the polystyrenes thus obtained were measured by an ultracentrifuge. Here the weight average molecular weight was measured instead

of the number average molecular weight, as the latter includes more experimental error than does the former, owing to the possibility of losing low molecular weight polystyrene when polymer obtained at high conversion is recovered from the polymerization solution by adding methanol. The extent of polymer recovery in the precipitation method was investigated by weighing the polymer recovered by evoporating the methanol of the filtrate and it was found that about 1% of the total polymer would be lost in it. The ultracentrifuge was used instead of light scattering for the molecular weight measurement, as with the latter method the effect of impurity (dust etc.) is large particularly with low molecular weight polystyrenes. The light scattering method was used in addition for high molecular weight polystyrene. Measurement of molecular weight by the ultracentrifuge was carried out in methyl ethyl ketone solution using Archibald method[9] with a Spinco ultracentrifuge. Molecular weights of the present polystyrenes were found using 15,000 to 20,000 r.p.m. Fig. 8-8 shows that the apparent molecular weights were determined at different polymer concentrations; the true molecular weight was estimated by extrapolating the polymer concentration to zero.

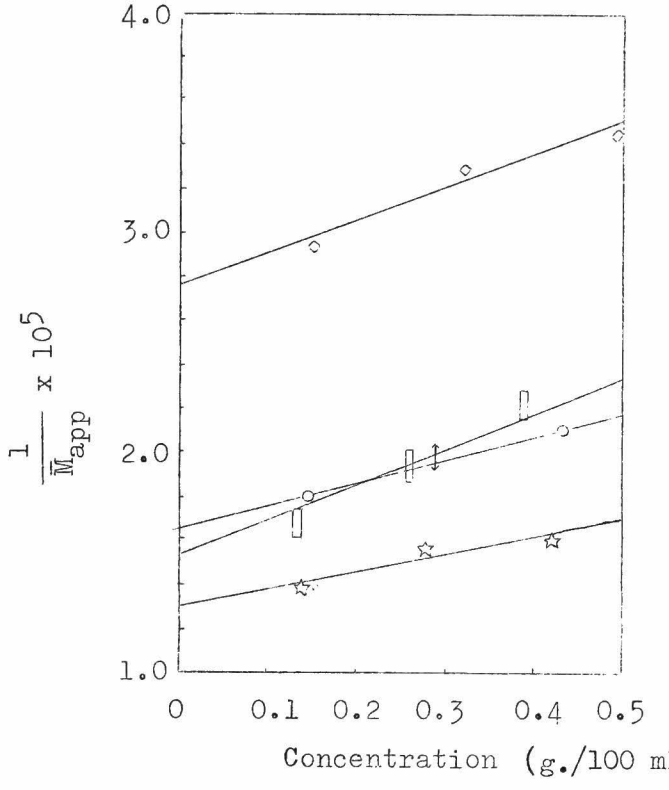

Fig. 8-8 Molecular weight measurement by Archibald method, styrene (20%)—$(CH_2Cl)_2$ (80%)—$BF_3 \cdot O(C_2H_5)_2$ —0°C

(☆): Conversion 9.0%, $[\eta] = 0.338$, $\bar{M}_w = 7.6 \times 10^4$

(◇): Conversion 97.5%, $[\eta] = 0.197$, $\bar{M}_w = 3.6 \times 10^4$

Styrene(20%)—CCl_4(40%)—$C_6H_5NO_2$(40%)—$SnCl_4$—0°C

(○): Conversion 41.8%, $[\eta] = 0.240$, $\bar{M}_w = 6.1 \times 10^4$

(□): Conversion 97.8%, $[\eta] = 0.237$, $\bar{M}_w = 6.5 \times 10^4$

Molecular weights of unfractionated polystyrene as determined by the ultracentrifuge and light scattering methods are listed in Table 8-4.

Experimental results shown in Table 8-4 are plotted in Fig. 8-9. Polystyrenes obtained in dichloroethane fit well on a straight line, whereas those obtained in nitrobenzene—carbon tetrachloride deviate from a straight line at the higher molecular weight. This would suggest that with the latter there is chain branching. Fig. 8-9 gave equation (8-2') relating weight average molecular weight and intrinsic viscosity of unfractionated polystyrene, equation (8-9) differs from equation (8-2) only in respect of experimental error,

$$[\eta]^{30^{\circ}C}_{\text{Benzene}} = 1.0 \times 10^{-4} \times \bar{M}_w^{0.72} \qquad (8\text{-}2')$$

2.3 Variation of the molecular weight of polystyrene during polymerization and estimation of the monomer transfer constant ratio

As stated previously, polymer molecular weight should be constant during polymerization if the monomer transfer reaction controls molecular weight, as shown in Figs. 8-4 and 8-6. Putting $\bar{P}$ for the average degree of

Table 8-4 Relationship between $[\eta]$ and $\bar{\bar{M}}_w$ of unfractionated polystyrenes prepared under various conditions

Sample No.	Solvent	Catalyst	$[M]_o$ (vol.%)	Polymn. temp.(°C)	Conversion (%)	$[\eta]^{30°C}_{Benzene}$	$\bar{\bar{M}}_w \times 10^{-4}$	Method of determining $\bar{\bar{M}}_w$
	$(CH_2Cl)_2$	$BF_3 \cdot O(C_2H_5)_2$ 5.9 m mole	20	0	9.0	0.338	7.6±0.9	A
					97.5	0.197	3.6±0.3	
	CCl_4—$C_6H_5NO_2$ 1:1	$SnCl_4$ 24 m mole	20	0	41.8	0.240	6.1±0.7	A
					97.8	0.237	6.5±0.9	
HB	$(CH_2Cl)_2$	$SnCl_4$	20	30	89.5	0.183	3.4	A
LA'	$(CH_2Cl)_2$	$SnCl_4$	20	-20	32.6	0.502	14.7	LS
LB'	$(CH_2Cl)_2$	$SnCl_4$	20	-20	96.7	0.380	10.3	LS

A: Archibald method, LS: Light scattering method

polymerization of polymer produced instantaneously and $\bar{\bar{P}}_n$ for the number average degree of polymerization of total polymer, $\bar{\bar{P}}_n$ is given by:[1),10)]

$$\bar{\bar{P}}_n = \int_{[M]_o}^{[M]_f} dM \Big/ \int_{[M]_o}^{[M]_f} 1/\bar{P}\, dM \qquad (8\text{-}3)$$

$$1/\bar{\bar{P}}_n = k_{tm}/k_p + k_t'(\ln[M]_o - \ln[M]_f)/k_p([M]_o - [M]_f) \qquad (8\text{-}4)$$

where k_p and k_{tm} are the rate constants for the propagation and the monomer transfer reactions respectively, k_t' is the sum of the rate constants for all of transfer and termination reactions not involving monomer, $[M]_o$ and $[M]_f$ are the initial and residual (at the time of measurement) monomer concentrations respectively.

Plotting conversions and molecular weights found from Figs. 8-3, 8-4, 8-5, 8-6 and 8-7 gave k_{tm}/k_p and k_t'/k_p of equation (8-4). The calculation results are plotted in Fig. 8-10 and the resultant rate constant ratios are summarized in Table 8-5.

At the inttial stage of polymerization, degree of polymerization of polymer will be given by equation (8-5).

$$1/\bar{P}_n = k_{tm}/k_p + k_t'/k_p \cdot 1/[M]_o \qquad (8\text{-}5)$$

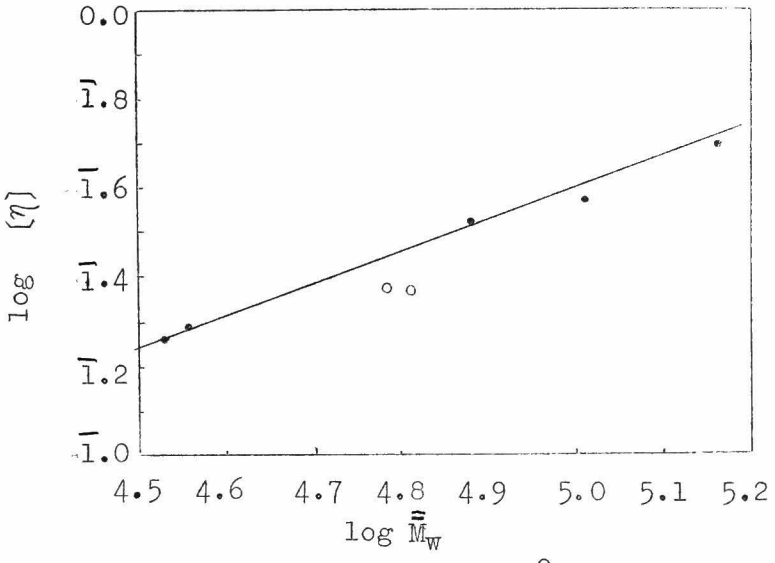

Fig. 8-9 Relationship between [η] (30°C, benzene) and $\bar{M}_w$ of unfractionated polystyrene prepared under various conditions

(●): polymer obtained in dichloroethane
(○): polymer obtained in nitrobenzene—carbon tetrachloride (1:1) mixed solvent

By determining the degree of polymerization of polymer obtained for various initial monomer concentrations, k_{tm}/k_p and k_t'/k_p could be calculated using equation (8-5). Since many investigations employing the above method have been reported from our laboratory,[11] details of the estimation of rate constant ratios are not given here, and only the results of calculation are shown in Fig. 8-11 and Table 8-5.

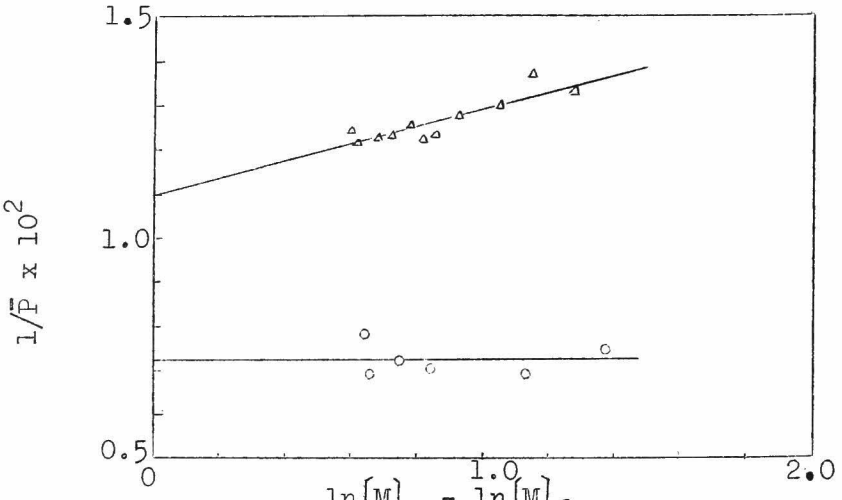

Fig. 8-10a

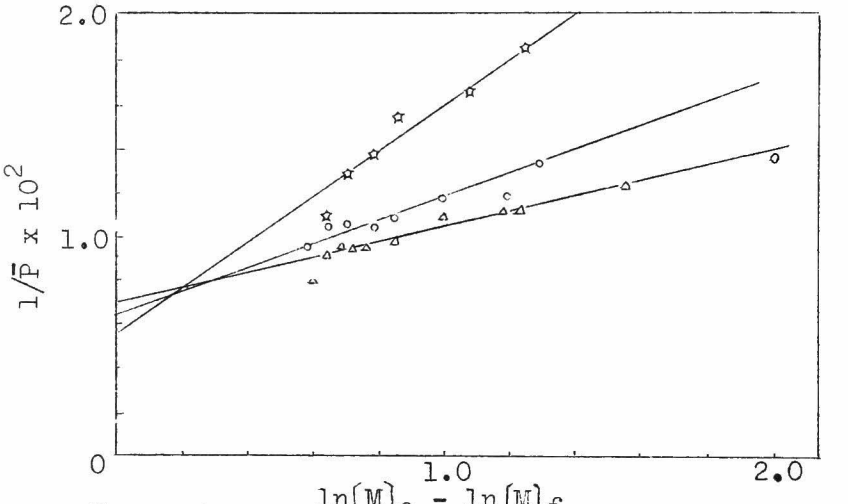

Fig. 8-10b

Fig. 8-10 The plot of $1/\bar{P}$ against $(\ln[M]_o - \ln[M]_f)/([M]_o - [M]_f)$ according to equation (8-4)

a : Polymerization by $SnCl_4$

(○): $C_6H_5NO_2$ —CCl_4, 0°C, $k_{tm}/k_p = 0.74 \times 10^{-2}$, $k_t'/k_p \simeq 0$

(△): $C_6H_5NO_2$, 30°C, $k_{tm}/k_p = 1.16 \times 10^{-2}$ $k_t'/k_p = 0.13 \times 10^{-2}$

b : Polymerization by $BF_3 \cdot O(C_2H_5)_2$ at 30°C

(○): $C_6H_5NO_2$—CCl_4, $k_{tm}/k_p = 0.66 \times 10^{-2}$ $k_t'/k_p = 0.50 \times 10^{-2}$

(△): $C_6H_5NO_2$, $k_{tm}/k_p = 0.73 \times 10^{-2}$, $k_t'/k_p = 0.30 \times 10^{-2}$

(☆): $(CH_2Cl)_2$, $k_{tm}/k_p = 0.53 \times 10^{-2}$, $k_t'/k_p = 1.04 \times 10^{-2}$

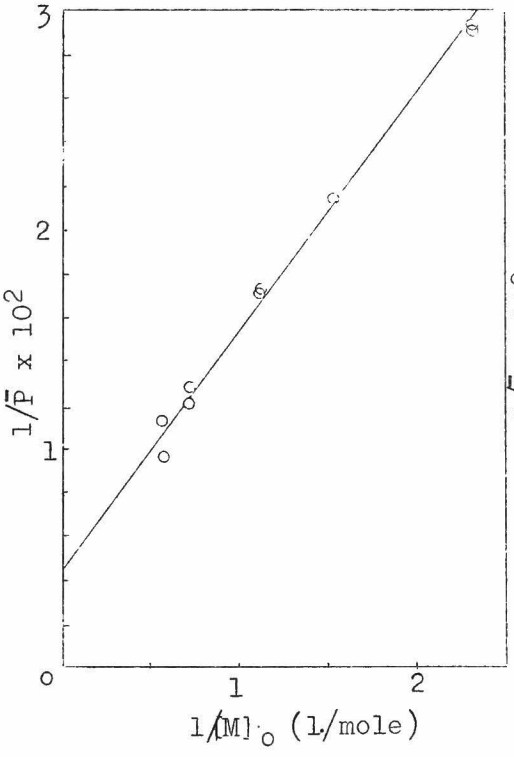

Fig. 8-11b

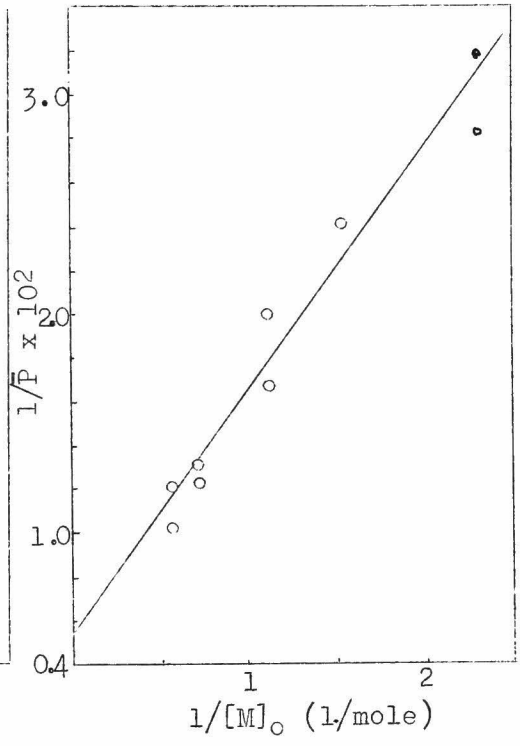

Fig. 8-11a

Fig. 8-11 Relationship between $1/\bar{P}$ and $1/[M]_0$
a: $[SnCl_4]$ = 1 m mole, 30°C, Styrene —CCl_4 20%, $C_6H_5NO_2$ 80%, k_{tm}/k_p = 0.52 x 10^{-2}
k_t'/k_p = 1.08 x 10^{-2}
b: $[BF_3.O(C_2H_5)_2]$ = 1 m mole, 30°C, Styrene —CCl_4 20%, $C_6H_5NO_2$ 80%, k_{tm}/k_p = 0.40 x 10^{-2},
k_t'/k_p = 1.13 x 10^{-2}

Table 8-5 Comparison of the transfer constant ratio calculated from the variation of degree of polymerization during the course of polymerization with that calculated from the relationship between the initial monomer concentration and the degree of polymerization[a].

Solvent	Catalyst	k_t'/k_p (mole/l.)$\times 10^2$		$k_{tm}/k_p \times 10^2$		k_t'/k_{tm} (mole/l.)	
		From the course of polymn.	From $[M]_o$	From the course of polymn.	From $[M]_o$	From the course of polymn.	From $[M]_o$
$(CH_2Cl)_2$	$BF_3 \cdot O(C_2H_5)_2$	1.04	0.86[c]	0.53	0.51[c]	2.0	1.7
$(CH_2Cl)_2$	$SnCl_4$	0.48	0.41[d]	0.43	0.51[d]	1.1	0.80
$C_6H_5NO_2$—CCl_4	$BF_3 \cdot O(C_2H_5)_2$	0.50	— [e]	0.66	—	0.76	—
1:1	$SnCl_4$[b]	~0	—	0.74	—	~0	—
$C_6H_5NO_2$	$BF_3 \cdot O(C_2H_5)_2$	0.30	1.13	0.73	0.40	0.41	2.8
$C_6H_5NO_2$	$SnCl_4$	0.13	1.08	1.16	0.52	0.11	2.1

a) Comparison was carried out on the molecular weights calculated using Pepper's equation (8-20).
b) Only in this system polymerization temperature was 0°C, in other systems 30°C.
c) $k_{tm}/k_p = 0.009 \times 10^{-2}$ was used.
d) $k_{ts}/k_p = 0.28 \times 10^{-2}$ was used.
e) — means that no polymerization was carried out.

Table 8-5, also gives data for the stannic chloride—dichloroethane system previously reported from our laboratory[1]. The transfer constant ratios calculated from the variation of molecular weight during polymerization and those derived when varying the initial monomer concentration agree well when dichloroethane is the solvent (see Table 8-5), but do not when nitrobenzene or nitrobenzene—carbon tetrachloride is. In these latter, polystyrene of unexpectedly higher molecular weight is produced at higher conversions, implying occurrence of chain transfer to polymer when nitrobenene is present.

This finding is in accord with the finding that polystyrene of molecular weight unexpectedly higher than its intrinsic viscosity would lead one to expect is produced in nitrobenzene (see Fig. 8-9).

2.4 Molecular weight distribution of polystyrene produced by cationic polymerization

The experimental results of the foregoing sections showed that there is no polymer transfer reaction in dichloroethane. Here in an attempt to demonstrate occurrence of a monomer transfer reaction, the intrinsic viscosity—molecular weight relationship was determined by molecular weight determination on polystyrene formed by

cationic polymerization in dichloroethane. Jordan et al.[12] investigated in detail the molecular weight distribution of polystyrene obtained by cationic polymerization. In our laboratory, polystyrene obtained in a non-polar solvent was fractionated by Spencer's method, leading to the conclusion that the monomer transfer reaction controls the molecular weight of polystyrene.[1] Now, the following reactions were considered,

$$\text{Propagation} \qquad M_r^* + M \xrightarrow{k_p} M_{r+1}^* \qquad (8\text{-}6)$$

$$\text{Transfer and termination free from monomer} \qquad M_r^* \xrightarrow{k_t'} P_r \qquad (8\text{-}7)$$

$$\text{Monomer transfer} \qquad M_r^* + M \xrightarrow{k_{tm}} P_r + M^* \qquad (8\text{-}8)$$

For $k_t \gg k_{tm}$, the weight fraction of polymer having a chain length of $r(W_r)$, the number average degree of polymerization $(\bar{\bar{P}}_n)$, the weight average degree of polymerization $(\bar{\bar{P}}_w)$ and their ratio $(\bar{\bar{P}}_w/\bar{\bar{P}}_n)$ are given by,

$$W_r \simeq \left[(k_t'/k_p)/[M]\left\{1+(k_t'/k_p)\cdot 1/[M]\right\}^r\right]^{[M]_o}_{[M]_f} \qquad (8\text{-}9)$$

$$\bar{\bar{P}}_n = \frac{[M]_f - [M]_o}{\ln[M]_f - \ln[M]_o} \cdot \frac{k_p}{k_t'} \qquad (8\text{-}10)$$

$$\bar{\bar{P}}_w = ([M]_f + [M]_o)\frac{k_p}{k_t'} \qquad (8\text{-}11)$$

$$\bar{\bar{P}}_w/\bar{\bar{P}}_n = \frac{[M]_o + [M]_f}{[M]_o - [M]_f} \cdot \ln\frac{[M]_o}{[M]_f} \qquad (8\text{-}12)$$

On the other hand, with $k_t \ll k_{tm}$,

$$w_r \simeq r(\frac{k_{tm}}{k_p})^2/(1 + k_{tm}/k_p)^{r+1} \qquad (8\text{-}13)$$

$$\bar{\bar{P}}_n = k_p/k_{tm} \qquad (8\text{-}14)$$

$$\bar{\bar{P}}_w = 2\ k_p/k_{tm} \qquad (8\text{-}15)$$

$$\bar{\bar{P}}_w/\bar{\bar{P}}_n = 2 \qquad (8\text{-}16)$$

Focussing attention on the $\bar{\bar{P}}_w/\bar{\bar{P}}_n$ ratio, it is found that in equation (8-16) it is always two, and that even for $k_t' \gg k_{tm}$ it is, according to equation (8-12) 2.1 at less than 50% conversion, and 2.26 at 70%, 2.41 at 80% and 2.82 at 90% conversions. Therefore, it can safely be said that when polymerization does not lead to chain branching, $\bar{\bar{P}}_w/\bar{\bar{P}}_n$ for polymer obtained in cationic polymerization is about 2, save at extremely high conversion.

That the intrinsic viscosity—molecular weight equation for unfractionated polystyrene differs from that for fractionated polystyrene only in respect of the experimental

error is seen in Fig. 8-9. This is partly due to the incompleteness of the fractionation. Assuming $\bar{\bar{M}}_w/\bar{\bar{M}}_n$ to be 2 for those polystyrenes, equations (8-17) and (8-18) will be obtained instead respectively of equations (8-2) and (8-2'):—

$$[\eta]^{30^\circ C}_{\text{Benzene}} = 3.60 \times 10^{-4} \times \bar{\bar{M}}_n^{0.65} \qquad (8\text{-}17)$$

$$[\eta]^{30^\circ C}_{\text{Benzene}} = 1.65 \times 10^{-4} \times \bar{\bar{M}}_n^{0.72} \qquad (8\text{-}18)$$

Pepper[13] first gave the intrinsic viscosity—molecular weight equation (8-19) for unfractionated polystyrene obtained by cationic polymerization, and later[14] gave equation (8-20) as a better one,

$$[\eta] = 2.27 \times 10^{-4} \times \bar{\bar{M}}_n^{0.72} \qquad (8\text{-}19)$$

$$[\eta] = 4.37 \times 10^{-4} \times \bar{\bar{M}}_n^{0.66} \qquad (8\text{-}20)$$

All of the intrinsic viscosity—molecular weight equations for polystyrene so far reported are shown in Fig. 8-12. Equations (8-17) and (8-18), in which $\bar{\bar{M}}_w/\bar{\bar{M}}_n$ was assumed to be 2, give a molecular weight 1.5 times larger as that obtained by Pepper's equation

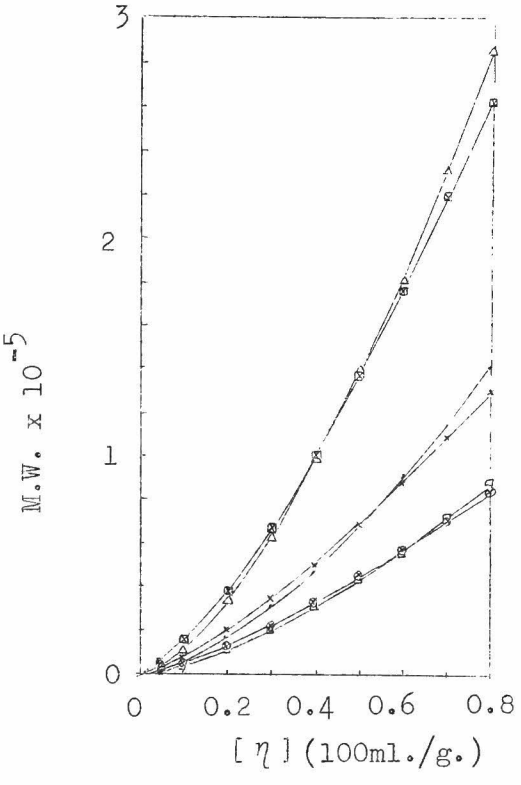

Fig. 8-12 Comparison between the intrinsic viscosity—molecular weight equations reported for polystyrene obtained in cationic polymerization ($[\eta]$ in benzene)

a(●) : eq. (8-17) $[\eta]^{30^\circ C} = 3.60 \times 10^{-4} \times \bar{M}_n^{0.65}$

b(×) : eq. (8-18) $[\eta]^{30^\circ C} = 1.65 \times 10^{-4} \times \bar{M}_n^{0.72}$

c(⊘) : eq. (8-19) $[\eta]^{25^\circ C} = 2.27 \times 10^{-4} \times \bar{M}_n^{0.72}$

d(□) : eq. (8-20) $[\eta]^{30^\circ C} = 4.37 \times 10^{-4} \times \bar{M}_n^{0.66}$

e(△) : eq. (8-2) $[\eta]^{30^\circ C} = 2.27 \times 10^{-4} \times \bar{M}_w^{0.65}$

f(⊠) : eq. (8-2') $[\eta]^{30^\circ C} = 1.0 \times 10^{-4} \times \bar{M}_w^{0.72}$

(8-20). Though a decisive conclusion cannot at present be reached, with polystyrene free from chain branching equation (8-2) here obtained well described the relationship between intrinsic viscosity and weight average molecular weight, and Pepper's equation (8-20) gave a good description of the relationship between the intrinsic viscosity and number average molecular weight. Equation (8-18) obtained here may hold for polystyrene produced at low conversion and with a distribution $\bar{\bar{M}}_w/\bar{\bar{M}}_n \simeq 2$. However more data are required to confirm this conclusion.

Next, the molecular weight distributions for polystyrenes obtained under various conditions were determined, and $\bar{\bar{M}}_w/\bar{\bar{M}}_n$ ratios were calculated from the distribution curves. From equations (8-12) and (8-16), the monomer transfer reaction should obtain if $\bar{\bar{M}}_w/\bar{\bar{M}}_n$ is 2, even at high conversion.

The fractionation of polymer was carried out just as for Table 8-1, that is, by the addition of methanol to a benzene solution of the polymer. The results are summarized in Table 8-6. As is seen in Table 8-6, $\bar{\bar{M}}_w$ from the distribution curve is in close agreement with observed value but $\bar{\bar{M}}_w/\bar{\bar{M}}_n$ is considerably smaller than expected. It is not at present clear, and remains to be

explained, why this is the case, whether it is due to loss of low molecular weight polystyrene during fractionation, or on recovery of polymer from the polymerization solution, or whether it is an essential characteristic of the polymerization. Since in some cases $\bar{\bar{M}}_w/\bar{\bar{M}}_n$ was considerably less than 2, the fact that $\bar{\bar{M}}_w/\bar{\bar{M}}_n$ for polystyrene obtained at high conversion was near 2 does not necessarily imply importance of the monomer transfer reaction.

3. Discussion

Though there is some ambiguity about the molecular weight distribution, the following can be said from the present experimental results:—

Taking into consideration the relationship between the intrinsic viscosity and the molecular weight for fractionated and unfractionated polystyrene, the polymer produced in dichloroethane is free from chain branching. On the other hand polystyrene produced in nitrobenzene — carbon tetrachloride has a molecular weight higher than would be expected from the intrinsic viscosity, suggesting occurrence of chain branching.

This is reflected in the relationship between con-

version and polymer molecular weight, i.e., the intrinsic viscosity of polystyrene produced in dichloroethane decreases with increasing conversion as would be expected of there was more than one transfer constant ratio, while with polymerization in nitrobenzene or nitrobenzene—carbon tetrachloride, the intrinsic viscosity is unchanged with conversion suggesting an increase of molecular weight due to the polymer transfer reaction.

From the above experimental results, it is quite clear that polystyrene produced in solvent containing nitrobenzene has a branched chain structure as was reported by Atkins et al. and by Overberger et al.[4] quite unlike what obtains for polystyrene produced in dichloroethane. It was reported[13] that hydrogen is extracted from the back-bone of polystyrene by a Friedel-Crafts catalyst such as aluminum chloride in nitrobenzene, leading to chain branching, and it is probable that nitrobenzene favors such chain branching. Hence it could be concluded that polystyrene generally produced by cationic polymerization does not always exhibit chain branching, but that it arises under the stated polymerization condition, and that disagreements between experimental results are due, ultimately, to the polymerization solvent

used.

In polymerization in dichloroethane, the experimental results (Table 8-5) are well explained by the monomer transfer reaction as the molecular weight controlling reaction, thus confirming occurrence of a monomer transfer reaction. However, when an attempt is made to check the occurrence of the monomer transfer reaction from the $\bar{M}_w/\bar{M}_n$ ratio an unexpectedly low value is obtained, and no conclusion can be drawn. With low-conversion, low-temperature polymerization polystyrene particularly, the ratio is considerably lower than two, which cannot be explained by loss of low molecular weight polystyrene during fractionation and remains to be investigated.

Table 8-6 $\bar{M}_w/\bar{M}_n$ ratio of polystyrene obtained under some conditions
Dichloroethane, $SnCl_4$

Sample No.	Polymn. temp.(°C)	Conversion (%)	Observed $\bar{M}_w \times 10^{-4}$		Molecular weight from distribution curve		
			From	Observed[a]	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$
HB	30	89.5	3.54	3.4(A)	1.45	3.26	2.25
LA'	-20	32.6	14.6	14.7(LS)	8.9	13.7	1.54
LB'	-20	96.7	9.6	10.3(LS)	5.4	10.5	1.95

a): A means Archibald method.
LS means light scattering method.

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Chapter 9 Poly-ortho-methoxystyrene and Poly-para-methoxystyrene

1. Introduction

Chapter 3 describes the carrying out of cationic polymerizations of ortho- and pare-methoxystyrene to clarify the mechanism of the monomer transfer reaction in polymerization of styrene derivatives, and there, the monomer transfer constant ratio was calculated from the degree of polymerization of the polymer and discussed. At that time, however, little had been reported on the intrinsic viscosity—molecular weight equations for those polymers. There was only an intrinsic viscosity—molecular weight equation reported by Saito et al.[1] for poly-p-methoxystyrene obtained using a light scattering method of molecular weight determination. In this Chapter the molecular weights of poly-ortho-methoxystyrene and poly-para-methoxystyrene were determined with precision by a light scattering method.

To calculate the rate constant ratios from the degree of polymerization of the polymers, the number average molecular weight $\bar{M}_n$ must be known. Since deter-

mination of $\bar{\bar{M}}_n$ is very difficult, rate constant ratios were calculated using the viscosity average molecular weight $\bar{\bar{M}}_v$, calculated by introducing the intrinsic viscosity of unfractionated polymer into the intrinsic viscosity—molecular weight equation for the fractionated sample. This gave the apparent rate constant ratio, which is $\bar{\bar{M}}_n/\bar{\bar{M}}_v$ times as large as the true rate constant ratio. Since $\bar{\bar{M}}_v$ is considered to close to $\bar{\bar{M}}_w$, the weight average molecular weight, it is very important in discussing the rate constant ratio to know the molecular weight distribution. In general, $\bar{\bar{M}}_w/\bar{\bar{M}}_n$ is 2 when the monomer transfer reaction controls the degree of polymerization[2], but it rises above 2 when polymerization involves either a unimolecular termination reaction or a solvent transfer reaction. For the discussion of the rate constant ratio it is also important to know about variation of the molecular weight distribution with extent of polymerization[3]. In this Cahpter, poly-p-methoxystyrenes prepared under the different conditions were fractionated, and $\bar{\bar{M}}_w$ and and $\bar{\bar{M}}_n$ were calculated, affording some information about the relationship between the molecular weight distribution and the conversion. The molecular weight distribution calculated using the transfer and the termination constant

ratios was compared with the actual molecular weight distribution, and the effect of molecular weight distribution on estimation of the rate constant ratio is discussed.

In Chapter 3, steric repulsion due to the ortho-methoxy group was proposed to explain the experimental results for the propagation reaction with o-methoxystyrene. To obtain some information about the steric repulsion, a study was made of the effects of ortho- and para-methoxy groups on polymer chain expansion. To that end, θ-solvents was sought for both polymers, and the expansion of the polymer chain in a θ-solvent was discussed in the light of the relationship between $[\eta]_\theta$ and the molecular weight. This Chapter gives experimental results relating to the above.

2. Experimental and Results

2.1 Determination of the intrinsic viscosity—molecular weight equation

2.1.1 Preparation and fractionation of polymer

Poly-p-methoxystyrene for fractionation was prepared under the following conditions (catalyst boron trifluoride etherate).

Monomer ml.	$(CH_2Cl)_2$ ml.	Temperature °C	Conversion %	$[\eta]^{30°C}$ Toluene 100 ml./g.
10	90	30	88.7	0.588

Poly-p-methoxystyrene 8.872 g. was dissolved in benzene 1ℓ. and fractionated into ten fractions at 30°C using methanol as the precipitant (recovery 89.5%); molecular weights of five fractions were determined.

Poly-o-methoxystyrene thermally polymerized at about 80°C (intrinsic viscosity 0.336) was used for fractionation, and 48.5 g. was dissolved in benzene 5 l. and fractionated into seventeen fractions (recovery 94.7 %) and molecular weights of five fractions determined.

2.1.2 Light scattering

The weight average molecular weights $\bar{M}_w$ of fractionated poly- o-methoxystyrene and poly- p-methoxystyrene were determined by the light scattering method, the method being the same as in Chapter 8. Measurements were made on methyl ethyl ketone solutions at room temperature using a Brice-type light scattering photometer and a wave length of 436 mμ. The refractive index concentration gradient ($\partial n / \partial C$) was found to be 0.210 for poly-o-

methoxystyrene and 0.211 for poly- p-methoxystyrene .

$\bar{M}_w$ and the second virial coefficient A_2 thus obtained are summarized in Tables 9-1 and 9-2, respectively.

Table 9-1 The molecular weight and the second virial coefficient of poly-o-methoxystyrene in methyl ethyl ketone

No.	$[\eta]^{30^oC}_{Toluene}$	$[\eta]^{30^oC}_{MEK}$	$\bar{M}_w \times 10^{-5}$	$A_2 \times 10^4$(MEK)
2	0.516	0.310	3.01	0.67
3	0.469	0.283	2.55	0.56
5	0.417	0.260	2.20	0.90
8	0.345	0.220	1.66	0.79
10	0.287	0.190	1.31	0.77

The relationship between the intrinsic viscosity and $\bar{M}_w$ for the present polymer is plotted in Figs. 9-1 and 9-2, which are based on the data of Tables 9-1 and 9-2.

From the above Figures, equations (9-1), (9-2), (9-3) and (9-4) were obtained for the intrinsic viscosity —molecular weight relationship:—

Table 9-2 The molecular weight and the second virial coefficient of poly-p-methoxystyrene in methyl ethyl ketone

No.	$[\eta]^{30°C}_{Toluene}$	$[\eta]^{30°C}_{MEK}$	$\bar{M}_w \times 10^{-5}$	$A_2 \times 10^4$(MEK)
B.2	1.028	0.734	7.45	1.3
B.3	0.788	0.563	5.13	1.1
B.5	0.488	0.349	2.64	1.5
B.6	0.376	0.267	1.88	1.3
B.7	0.260	0.186	1.33	1.7

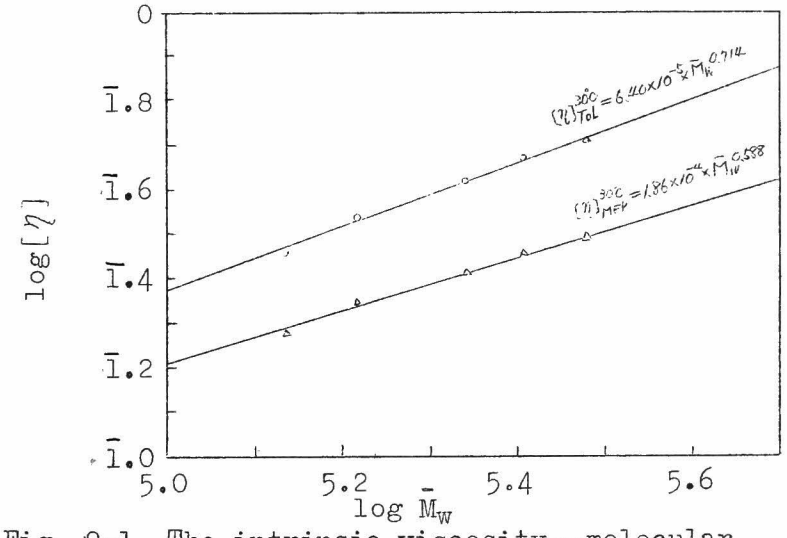

Fig. 9-1 The intrinsic viscosity—molecular weight relationship for poly-o-methoxystyrene
(o): Toluene 30°C
(Δ): MEK 30°C

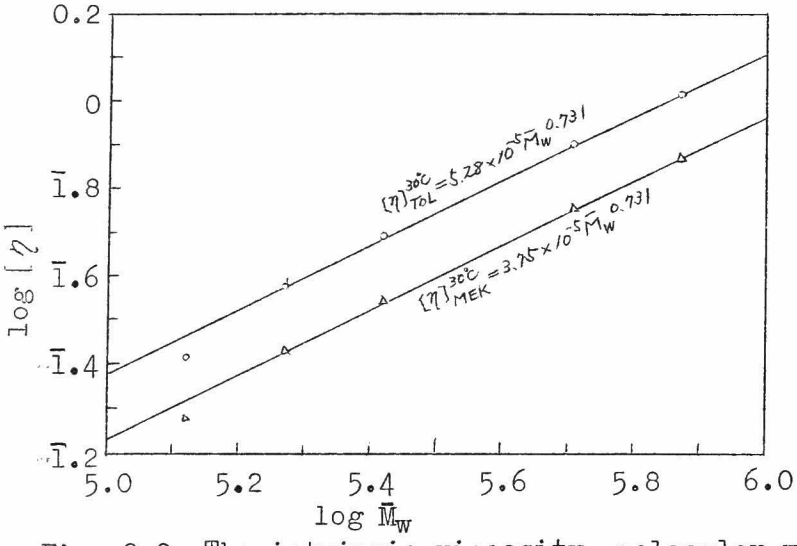

Fig. 9-2 The intrinsic viscosity—molecular weight relationship for poly-p-methoxystyrene
(○) : Toluene 30°C
(△): MEK 30°C

Poly-o-methoxystyrene $[\eta]^{30°C}_{\text{Toluene}} = 6.40 \times 10^{-5} \times \bar{M}_w^{0.71}$ (9-1)

$[\eta]^{30°C}_{\text{MEK}} = 1.86 \times 10^{-4} \times \bar{M}_w^{0.59}$ (9-2)

Poly-p-methoxystyrene $[\eta]^{30°C}_{\text{Toluene}} = 5.28 \times 10^{-5} \times \bar{M}_w^{0.73}$ (9-3)

$[\eta]^{30°C}_{\text{MEK}} = 3.75 \times 10^{-5} \times \bar{M}_w^{0.73}$ (9-4)

2.2 Variation of the polymer molecular weight distribution during the progress of polymerization

2.2.1 Fractionation of poly- p-methoxystyrene

As stated in the introduction, variation in polymer molecular weight distribution during polymerization is

very important when calculating the rate constant ratios. Consider the following elementary reactions:—

Propagation	$P_n^* + M \xrightarrow{k_p} P_{n+1}^*$	(9-5)
Monomer transfer reaction	$P_n^* + M \xrightarrow{k_{tm}} P_n + M^*$	(9-6)
Transfer and termination reaction	$P_n^* \xrightarrow{k_t'} P_n$	(9-7)

The rate constant ratios will be given by equation (9-8),

$$1/\bar{\bar{P}}_n = k_{tm}/k_p + k_t'/k_p \cdot 1/[M] \qquad (9\text{-}8)$$

where the notation used is that previously employed. Use of $\bar{\bar{P}}_v$ instead of $\bar{\bar{P}}_n$ in equation (9-8) makes the resultant rate constant ratio $\bar{\bar{P}}_n/\bar{\bar{P}}_v$ times lager than the true rate constant ratio (in Part 2 all calculations used $\bar{\bar{P}}_v$.). Hence to discuss the reaction mechanism in the light of the rate constant ratios estimated under the various conditions, it is very important to know how $\bar{\bar{P}}_v/\bar{\bar{P}}_n$ is related to the latter, estimated under the various conditions.

If $k_{tm} \gg k_t'$, the molecular weight distribution of the resultant polymer is constant for conversions (see

equation (8-16)),

$$\bar{\bar{P}}_w / \bar{\bar{P}}_n = 2 \qquad (9\text{-}9)$$

However, if $k_t' \gg k_{tm}$ (see equation (8-12)),

$$\bar{\bar{P}}_w/\bar{\bar{P}}_n = \frac{[M]_o + [M]_f}{[M]_o - [M]_f} \ln \frac{[M]_o}{[M]_f} \qquad (9\text{-}10)$$

the $\bar{\bar{P}}_w/\bar{\bar{P}}_n$ ratio is 2 at the beginning of the polymerization and increases gradually with increasing conversion (see Fig. 9-5). Equation (9-9) describes the case where the molecular weight distribution of polymer is narrowest for elementary reactions (9-5) - (9-7). On the other hand equation (9-10) describes the case where the molecular weight distribution is broadest under the same conditions. But even then, $\bar{\bar{P}}_w/\bar{\bar{P}}_n$ is as low as 2.41 at conversions as high as 80%. Generally in cationic polymerization of vinyl monomers, k_{tm} is nearly equal to or a little larger than k_t' as is seen in Part 2, suggesting that the actual $\bar{\bar{P}}_w/\bar{\bar{P}}_n$ ratio is usually 2.4 - 2.0. Since $\bar{\bar{P}}_v/\bar{\bar{P}}_n$ is found by experiment to be a little less than $\bar{\bar{P}}_w/\bar{\bar{P}}_n$, the error in the rate constant ratio due to different molecular weight distributions with different polymerization

conditions may be neglected. Comparison of a rate constant ratio calculated from $\bar{\bar{P}}_v$ with that from $\bar{\bar{P}}_v$ obtained under different polymerization conditions or at different conversions can reasonably be made.

To make this clear, the following experiment was carried out. p-Methoxystyrene was polymerized by boron trifluoride etherate under the two different conditions and the resultant poly-p-methoxystyrene was fractionated to determine the molecular weight distribution ($\bar{\bar{M}}_w/\bar{\bar{M}}_n$). Poly-p-methoxystyrene was prepared under the conditions shown in Table 9-3.

Table 9-3 Polymerization conditions of p-methoxystyrene used for fractionation

Sample	Monomer ml.	CCl_4 ml.	$(CH_2Cl)_2$ ml.	$BF_3 \cdot O(C_2H_5)_2$ m mole	Temp. °C	Resultant polymer Conv. %	$[\eta]^{30°C}_{TOL}$
S	10	90	—	1.2	-20	60.4	0.880
S'	10	90	—	1.5	-20	39.2	0.854
B	10	—	90	0.3	30	90.1	0.843

Samples S and S' were prepared at low conversion with $k_{tm} \gg k_t'$, and expected to have a $\bar{\bar{P}}_w/\bar{\bar{P}}_n$ ratio near

2 according to equation (9-10). Sample B was prepared with high conversion with $k_{tm} > k_t'$, and expected to have a broad molecular weight distribution.

Sample S' 3.5606 g. was dissolved in benzene 500 ml. and fractionated at 30°C using methanol as the precipitant. The results are shown in Table 9-4. The polymer recovery was 96.3% and $\bar{\bar{P}}_w/\bar{\bar{P}}_n$ was found to be 1.50.

Sample S 5.6236 g. was dissolved in benzene 600 ml. and fractionated at 30°C using methanol as the precipitant. The results are shown in Table 9-5. The recovery of polymer was 95.4% and $\bar{\bar{P}}_w/\bar{\bar{P}}_n$ was found to be 1.86.

Sample B 8.2041 g. was dissolved in benzene 1 l. and fractionated at 30°C using methanol as the precipitant. The results are shown in Table 9-6. The recovery of polymer was 97.7% and $\bar{\bar{P}}_w/\bar{\bar{P}}_n$ was found to be 2.61.

In general, the number average molecular weight $\bar{\bar{M}}_n$ and the weight average molecular weight $\bar{\bar{M}}_v$ are expressed as,[4]

$$\bar{\bar{M}}_n = 1/\Sigma(W_i/M_i) = \Sigma M_i N_i / \Sigma N_i \qquad (9\text{-}11)$$

$$\bar{\bar{M}}_w = \Sigma C_i M_i / C = \Sigma W_i M_i = \Sigma N_i M_i^2 / \Sigma N_i M_i \qquad (9\text{-}12)$$

Table 9-4 The fractionation of poly-p-methoxystyrene

Fraction	$[\eta]$ $30^{\circ}C$ TOL	Weight(g)	$[\eta]$ x g.	M.W.x10^{-5}	Wi	W_iM_i	$W_i/M_i \times 10^7$
Original	0.854	3.5606	3.0408	5.82			
1	1.567	0.3868	0.6061	13.35	0.1128	150590	0.8449
2	1.330	0.2700	0.3591	10.68	0.0787	84050	0.7369
3	1.207	0.2805	0.3386	9.36	0.0818	76560	0.8739
4	1.043	0.5386	0.5618	7.66	0.1570	120260	2.0496
5	0.882	0.3353	0.2957	6.07	0.0977	59300	1.6096
6	0.695	0.4528	0.3147	4.37	0.1320	57680	3.0206
7	0.584	0.6246	0.3648	3.45	0.1821	62820	5.2783
8	0.361	0.4644	0.1913	1.79	0.1354	24240	7.5642
9	0.331	0.0772	0.0256	1.59	0.0225	3580	1.4151
Total	0.859	3.4302	3.0577		1.0000	639080	23.3931

$(\bar{\bar{M}}_w)_{obs} = 6.39 \times 10^5$ $(\bar{\bar{P}}_w)_{obs} = 4769$

$(\bar{\bar{M}}_n)_{obs} = 4.28 \times 10^5$ $(\bar{\bar{P}}_n)_{obs} = 3190$

$(\bar{\bar{M}}_v)_{obs} = 5.82 \times 10^5$ $(\bar{\bar{P}}_v)_{obs} = 4343$

$(\bar{\bar{P}}_w/\bar{\bar{P}}_n)_{obs} = 1.50$ $(\bar{\bar{P}}_v/\bar{\bar{P}}_n)_{obs} = 1.36$

Table 9-5 The fractionation of poly-p-methoxystyrene

Fraction	$[\eta]$ $30^{\circ}C$ TOL	Weight(g.)	$[\eta]$ x g.	M.W.x10^{-5}	W_i	$W_i M_i$	$W_i/M_i \times 10^7$
Original	0.880	5.6236	4.9488	6.06			
1	2.130	0.2097	0.4467	20.39	0.0391	79720	0.1918
2	1.700	0.1822	0.3097	14.97	0.0340	50900	0.2271
3	1.484	0.2003	0.2972	12.42	0.0374	46450	0.3011
4	1.376	0.2589	0.3562	11.18	0.0483	54000	0.4320
5	1.264	0.4363	0.5514	9.95	0.0814	80990	0.8181
6	1.140	0.6210	0.7079	8.64	0.1154	99710	1.3356
7	0.916	0.7455	0.6829	6.41	0.1390	89100	2.1685
8	0.704	0.9235	0.6501	4.76	0.1722	81970	3.6176
9	0.512	0.7881	0.4035	2.89	0.1470	42480	5.0865
10	0.356	0.6520	0.2321	1.75	0.1216	21280	6.9486
11	0.210	0.3449	0.0714	0.85	0.0643	5470	7.5647
Total	0.878	5.3624	4.7094		1.001	652070	28.5916

$(\bar{\bar{M}}_w)_{obs} = 6.52 \times 10^5$ $\quad$ $(\bar{\bar{P}}_w)_{obs} = 4866$

$(\bar{\bar{M}}_n)_{obs} = 3.50 \times 10^5$ $\quad$ $(\bar{\bar{P}}_n)_{obs} = 2610$

$(\bar{\bar{M}}_v)_{obs} = 6.06 \times 10^5$ $\quad$ $(\bar{\bar{P}}_v)_{obs} = 4522$

$(\bar{\bar{P}}_w/\bar{\bar{P}}_n)_{obs} = 1.86$ $\quad$ $(\bar{\bar{P}}_v/\bar{\bar{P}}_n)_{obs} = 1.73$

Table 9-6 The fractionation of poly-p-methoxystyrene

Fraction	$[\eta]$ $30^{\circ}C$ TOL	Weight(g.)	$[\eta]$ x g.	M.W.x10^{-5}	W_i	W_iM_i	$W_i/M_i \times 10^7$
Original	0.843	8.2041	6.9161	5.70			
1	1.959	0.5381	1.0541	18.18	0.0671	121990	0.3691
2	1.762	0.3126	0.5508	15.72	0.0390	61310	0.2481
3	1.494	0.6600	0.9860	12.54	0.0823	103200	0.6563
4	1.211	0.8694	1.0528	9.38	0.1084	101680	1.1557
5	1.053	0.5799	0.6108	7.76	0.0723	56100	0.9317
6	0.888	0.7464	0.6628	6.15	0.0931	57260	1.5138
7	0.745	0.8602	0.6408	4.81	0.1073	51500	2.2354
8	0.583	0.6669	0.3888	3.43	0.0832	28540	2.4257
9	0.462	0.7597	0.3510	2.50	0.0948	23700	3.7920
10	0.338	0.7502	0.2536	1.54	0.0936	14410	6.0779
11	0.209	0.9205	0.1924	0.84	0.1148	9640	13.6667
12	0.151	0.3540	0.0535	0.54	0.0442	2390	8.1852
Total	0.848	8.0179	6.7972		1.0001	631720	41.2576

$(\bar{\bar{M}}_w)_{obs} = 6.32 \times 10^5$ $(\bar{\bar{P}}_w)_{obs} = 4714$

$(\bar{\bar{M}}_n)_{obs} = 2.42 \times 10^5$ $(\bar{\bar{P}}_n)_{obs} = 1809$

$(\bar{\bar{M}}_v)_{obs} = 5.70 \times 10^5$ $(\bar{\bar{P}}_v)_{obs} = 4254$

$(\bar{\bar{P}}_w/\bar{\bar{P}}_n)_{obs} = 2.61$ $(\bar{\bar{P}}_v/\bar{\bar{P}}_n)_{obs} = 2.35$

where M_i means the molecular weight of i-th kind of polymer, N_i denotes the number of polymer having a molecular weight M_i, C_i is the concentration of polymer having molecular weight M_i, and W_i is the weight fraction of polymer of molecular weight M_i.

Reactions (9-5), (9-6) and (9-7) were assumed to be the elementary reactions in cationic polymerization. The number average degree of polymerization and the weight average degree of polymerization of the instantaneously produced polymer are denoted by $\bar{P}_n$ and $\bar{P}_w$, respectively. Since during such a short period the concentrations of reagents remain constant, the polymer has the "most probable distribution"[2], i.e., $\bar{P}_w/\bar{P}_n$ is 2. $\bar{P}_n$ is given by equation (9-8). Starting the polymerization at the initial concentration $[M]_o$ and stopping the polymerization at the residual monomer concentration $[M]_f$, the molecular weight distribution of resultant polymer becomes broader than the "most probable distribution".[3] Putting the weight average molecular weight and the number average molecular weight of total polymer as $\bar{\bar{P}}_w$ and $\bar{\bar{P}}_w$ respectively, $\bar{\bar{P}}_w > 2\,\bar{\bar{P}}_n$. The value of α, which is defined as $\bar{\bar{P}}_w/\bar{\bar{P}}_n$ shows the broadness of the molecular weight distribution. $\bar{\bar{P}}_n$ and $\bar{\bar{P}}_w$ are given by:—

$$\bar{\bar{P}}_n = \int_{[M]_o}^{[M]_f} dM \Big/ \int_{[M]_o}^{[M]_f} 1/\bar{P}_n \, dM \qquad (9\text{-}13)$$

$$\bar{\bar{P}}_w = \int_{[M]_o}^{[M]_f} \bar{P}_w dM \Big/ \int_{[M]_o}^{[M]_f} dM = 2\int_{[M]_o}^{[M]_f} \bar{P}_n dM \Big/ \int_{[M]_o}^{[M]_f} dM \qquad (9\text{-}14)$$

Substituting equation (9-8) for $\bar{P}_n$ and integrating, the following equations were obtained:—

$$1/\bar{\bar{P}}_n = k_{tm}/k_p + \frac{1}{[M]_f - [M]_o} \frac{k_t'}{k_p} \ln \frac{[M]_f}{[M]_o} \qquad (9\text{-}15)$$

$$\bar{\bar{P}}_w = 2\frac{k_p}{k_{tm}} \left[1 - \frac{k_t'}{k_{tm}} \frac{1}{[M]_f - [M]_o} \ln \frac{1 + \frac{k_{tm}}{k_t'}[M]_f}{1 + \frac{k_{tm}}{k_t'}[M]_o} \right] \qquad (9\text{-}16)$$

Substituting the monomer transfer constant ratio and the unimolecular termination constant ratio for k_{tm}/k_p and k_t'/k_p in equation (9-16) gives the theoretical values of $\bar{\bar{P}}_n$ and $\bar{\bar{P}}_w$. For this purpose, the required rate constant ratios were estimated under polymerization conditions used for preparing samples S, S' and B and were found by using equation (9-8) as in Chapter 3.

The results are shown in Figs. 9-3 and 9-4.

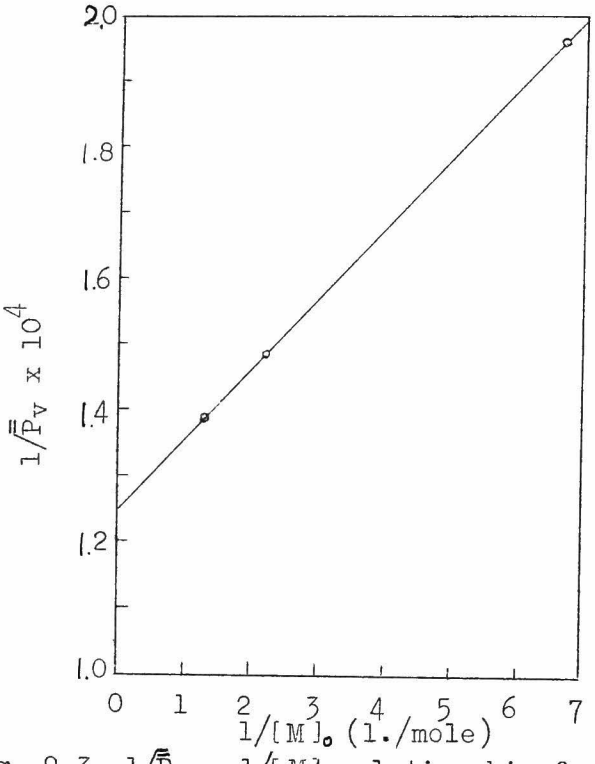

Fig. 9-3 $1/\bar{\bar{P}}_v$ —$1/[M]_o$ relationship for the cationic polymerization of p-methoxystyrene in carbon tetrachloride
$k_{tm}/k_p = 1.25 \times 10^{-4}$
$k_t'/k_p = 0.11 \times 10^{-4}$

Substituting the rate constant ratios thus obtained in equation (9-15) or (9-16), $\bar{\bar{P}}_w$ and $\bar{\bar{P}}_n$ can be calculated. The rate constant ratios estimated above were calculated from the degree of polymerization of polymer produced at low conversion. Since $\bar{\bar{P}}_w/\bar{\bar{P}}_n$ is about 2 at the beginning of the polymerization as is seen from equations

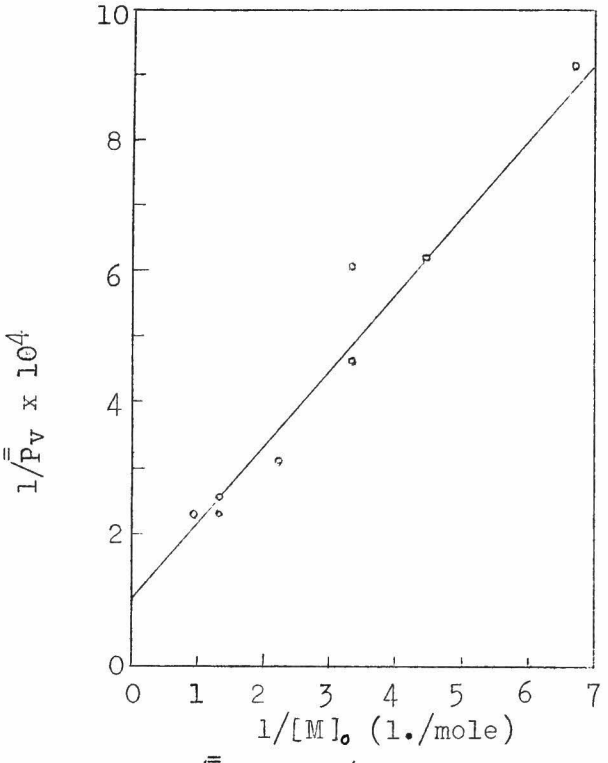

Fig. 9-4 $1/\bar{\bar{P}}_v$ — $1/[M]_o$ relationship for the cationic polymerization of p-methoxystyrene in dichloroethane
$k_{tm}/k_p = 1.00 \times 10^{-4}$
$k_t'/k_p = 1.17 \times 10^{-4}$

(9-15) and (9-16), the rate constant ratio obtained here is about one half as large as the true rate constant ratio! Then $\bar{\bar{P}}_w$ and $\bar{\bar{P}}_n$ calculated using the apparent rate constant ratio is about twice as large as the true molecular weight. The results of calculation are listed in Table 9-7.

The calculated molecular weight distribution and the actual molecular weight distribution are compared

Table 9-7 The observed and the calculated molecular weight distribution of poly-p-methoxystyrene

Sample	$[M]_o$ mole/l.	$[M]_f$ mole/l.	k_{tm}/k_p x 10^4	k_t'/k_p x 10^4	$\bar{\bar{P}}_n$ calculated using eq.(9-15)	$\bar{\bar{P}}_w$ calculated using eq.(9-16)	$\bar{\bar{P}}_w/\bar{\bar{P}}_n$ calc.
S	0.746	0.295	1.25	0.11	6744	13571	2.003
S'	0.746	0.454	1.25	0.11	6959	13922	2.001
B	0.746	0.074	1.00	1.17	1990	4958	2.49

$\bar{\bar{P}}_n$ observed by fractionation	$\bar{\bar{P}}_w$ observed by fractionation	$\bar{\bar{P}}_v$ obs.	$\bar{\bar{P}}_w/\bar{\bar{P}}_n$ obs.	$\bar{\bar{P}}_v/\bar{\bar{P}}_n$ obs.
2610	4866	4522	1.86	1.73
3190	4769	4343	1.50	1.36
1809	4714	4254	2.61	2.35

with each other in Fig. 9-5, where the broken line represents the theoretical case of $k_{tm} \gg k_t'$ and the unbroken line the the theoretical case of $k_{tm} \ll k_t'$.

2.3 The effect of the methoxy group on the expanded polymer chain

In investigation of the cationic polymerization of o-methoxystyrene described in Chapter 3, there was some evidence for a steric effect of o-methoxy group in the propagation reaction. Similar effects for an ortho-substituent were found in ionic polymerizations of ortho-substituted styrenes e.g., cationic polymerization of o-chlorostyrene, and anionic polymerization of o-methylstyrene and vinyl mesitylene[5] (see Chapter 10).

In order to estimate the steric interaction of the ortho-substituent in the propagation reaction and to compare the effect of an ortho-methoxy group on the comformation of the polymer in solution with that of a para-methoxy group, the molecular sizes of poly-o-methoxystyrene and poly-p-methoxystyrene were measured in a θ -solvent.

For this purpose, θ -solvents for both polymers were found. According to the method reported by Shultz[6], the composition of toluene—methanol θ -solvent at 30°C was determined. Poly-o-methoxystyrene of molecular weight 295970, 255820, 223320 and 168420 and poly-p-methoxystyrene of mole-

cular weight 926600, 659810, 420550, 399300 were used for measurements. For all polymers the phase separation temperature were determined in toluene—methanol of three different compositions and at four different polymer concentrations (0.4, 0.3, 0.2 and 0.1 g/100 ml.).

From these results the volume fraction of methanol in the critical consolute mixture at 30°C, when the polymer of infinite molecular weight begins to separate from solution, can be calculated. The θ-solvent compositions at 30°C were found to be methanol 25 vol%—toluene 75 vol.% for poly-o-methoxystyrene and methanol 28.1 vol.%—toluene 71.9 vol.% for poly-p-methoxystyrene. The θ-solvent determination for poly-p-methoxystyrene is shown in Fig. 9-6.

Intrinsic viscosities of four kinds of fractionated poly-o-methoxystyrene and of five kinds of fractionated poly-p-methoxystyrene were measured in θ-solvent at -30°C, and measurements were also made in toluene and methyl ethyl ketone at 30°C. The expansion coefficient α was calculated, and the results are shown in Tables 9-8 and 9-9.

In Figs. (9-7) and (9-8), molecular weights of poly- p-methoxystyrene calculated from the intrinsic viscosity in toluene at 30°C using equation (9-2) or equation (9-4) were plotted against $[\eta]_\theta$:—

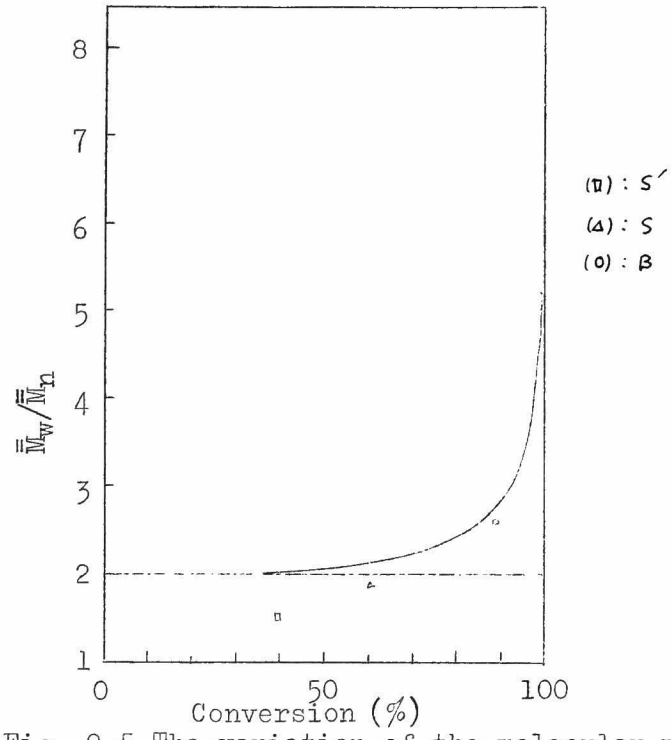

Fig. 9-5 The variation of the molecular weight distributions with conversion

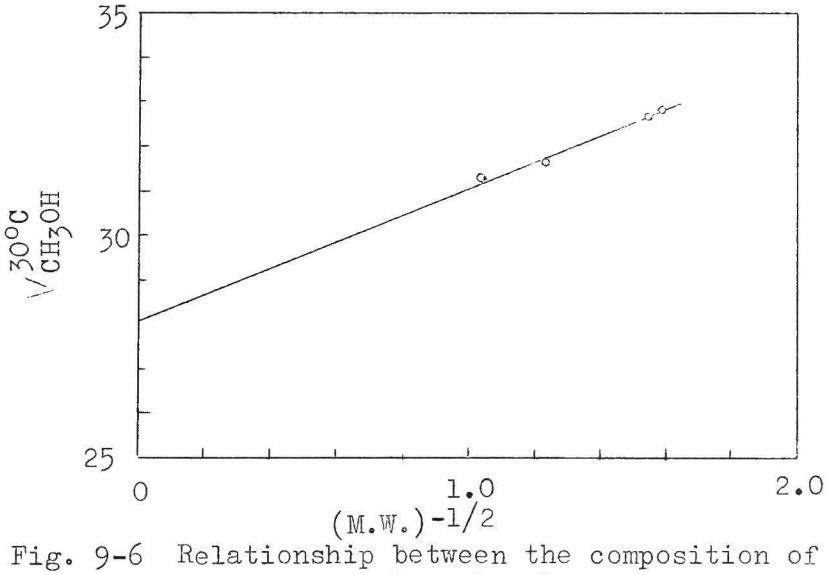

Fig. 9-6 Relationship between the composition of mixed solvent and the molecular weight of poly-p-methoxystyrene on the precipitation point at 30°C.

Table 9-8 The solution properties of poly-p-methoxystyrene

Sample	$[\eta]^{30^\circ C}_{TOL}$	$[\eta]^{30^\circ C}_{MEK}$	$[\eta]_\theta$	$[\eta]^{30^\circ C}_{TOL}/[\eta]_\theta$	$[\eta]^{30^\circ C}_{MEK}/[\eta]_\theta$	M.W.	$\alpha^{30^\circ C}_{TOL}$ *	$\alpha^{30^\circ C}_{MEK}$ *
4-1	1.936	1.359	0.803	2.41	1.69	1789000	1.44	1.24
4-3	1.486	1.004	0.658	2.26	1.53	1244000	1.40	1.19
4-5	1.046	0.761	0.548	1.91	1.39	768000	1.31	1.15
4-8	0.560	0.435	0.346	1.62	1.26	327000	1.22	1.10
4-11	0.198	0.175	0.160	1.24	1.09	78000	1.09	1.04

* Calculated using the equation $[\eta]/[\eta]_\theta = \alpha^{2.43}$.

Table 9-9 The solution properties of poly-o-methoxystyrene

Sample	$[\eta]^{30^\circ C}_{TOL}$	$[\eta]^{30^\circ C}_{MEK}$	$[\eta]_\theta$	$[\eta]^{30^\circ C}_{TOL}/[\eta]_\theta$	$[\eta]^{30^\circ C}_{MEK}/[\eta]_\theta$	M.W.	$\alpha^{30^\circ C}_{TOL}$*	$\alpha^{30^\circ C}_{MEK}$*	A_2 MEK x10^4	$\alpha^{30^\circ C}_{MEK}$**
2	0.516	0.338	0.310	1.66	1.09	295970	1.23	1.036	0.67	1.13
3	0.465	0.316	0.304	1.53	1.04	255820	1.19	1.016	0.56	1.09
5	0.422	0.292	0.259	1.63	1.13	223320	1.22	1.052	0.90	1.17
8	0.345	0.250	0.238	1.45	1.05	168420	1.17	1.020	0.79	1.12

* Calculated using the equation $[\eta]/[\eta]_\theta = \alpha^{2.43}$

** Calculated using Flory-Olofino equation $A_2[M]/[\eta] = 1.65 \log[1+4.50(\alpha^2-1)]$

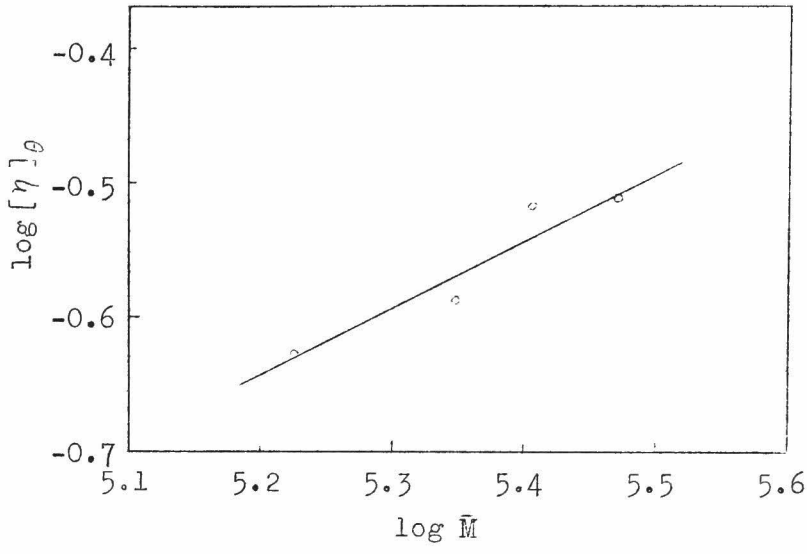

Fig. 9-7 The relationship between $\log[\eta]_\theta$ and $\log \bar{M}$ for poly-o-methoxystyrene

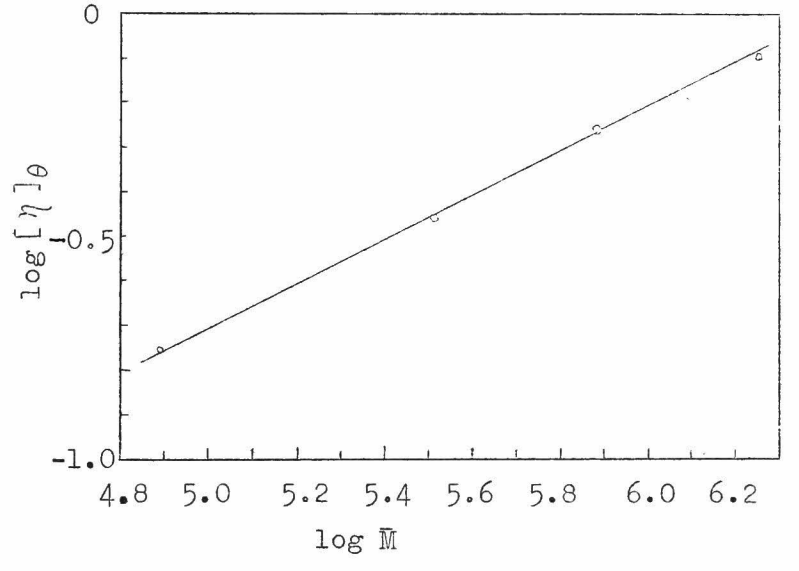

Fig. 9-8 The relationship between $\log[\eta]_\theta$ and $\log \bar{M}$ for poly-p-methoxystyrene

The straight lines in the Figure means that $[\eta]_\theta \propto \bar{M}^{0.50}$. In Figs. 9-7 and 9-8 the following equations were obtained for the intrinsic viscosity—molecular weight relationship in θ -solvent at 30°C:—

Poly- o-methoxystyrene $[\eta]_\theta = 5.75\times10^{-4} \times \bar{M}^{0.50}$ (9-17)

Poly- p-methoxystyrene $[\eta]_\theta = 6.21\times10^{-4} \times \bar{M}^{0.50}$ (9-18)

To estimate the effects of the ortho- and para-methoxy group in expanding the polystyrene chain, the molecular sizes of polymethoxystyrenes in θ -solvent were calculated. For poly-o-methoxystyrene, equation (9-17) gives $K = 5.75\times10^{-4}$. Equation (7-5) holds for K. By a calculation similar to that of Section 7.2, $(<\bar{r}_o^2>/M)^{1/2}=6.50\times10^{-9}$ was obtained. Assuming free rotation around a single bond, $(<\bar{r}_{of}^2>/M)^{1/2}=2.66\times10^{-9}$ was obtained, and $(<\bar{r}_o^2>/<\bar{r}_{of}^2>)^{1/2} = 2.44$.

On the other hand from equation (9-18) for poly-p-methoxystyrene, $K = 6.21\times10^{-4}$. Similarly, $(<\bar{r}_o^2>/M)^{1/2} = 6.66 \times 10^{-9}$ and $(<\bar{r}_{of}^2>/M)^{1/2} = 2.66\times10^{-9}$, and $(<\bar{r}_o^2>/<\bar{r}_{of}^2>)^{1/2}=2.50$.

3. Discussion

3.1 Discussions of the intrinsic viscosity—molecular weight relationship

In the present investigation, equations (9-1)-(9-4) were obtained for the intrinsic viscosity—molecular weight relationship. $\bar{M}_w$ of poly-p-methoxystyrene was previously studied by Saito et al.[1], and the following

equations reported:—

$$[\eta] = 2.40 \times 10^{-4} \times \bar{M}_w^{0.60} \quad \text{MEK, } 25^{\circ}C \qquad (9\text{-}19)$$

$$[\eta] = 1.80 \times 10^{-4} \times \bar{M}_w^{0.65} \quad \text{Toluene, } 30^{\circ}C \qquad (9\text{-}20)$$

To compare the intrinsic viscosity—molecular weight equations obtained here with those reported by Saito et al.,[1] the logarithmic plot of the equations are given in Fig. 9-9. When Saito et al.[1] derived equations (9-19) and (9-20), they used $(\partial n/\partial C)$ 0.225 at 436 mμ in methyl ethyl ketone. On the other hand, 0.211 was here obtained for $(\partial n/\partial C)$; equations (9-19) and (9-20) was recalculated using 0.211 instead of 0.225, leading to equations (9-21) and (9-22):—

$$[\eta] = 2.22 \times 10^{-4} \times \bar{M}_w^{0.60} \quad \text{MEK} \quad 25^{\circ}C \qquad (9\text{-}21)$$

$$[\eta] = 1.66 \times 10^{-4} \times \bar{M}_w^{0.65} \quad \text{Toluene} \quad 30^{\circ}C \qquad (9\text{-}22)$$

Equation (9-22) was used to calculate the rate constant ratios in Chapter 3. Fig. 9-9 shows equations (9-21) and (9-22) together.

Comparison of the intrinsic viscosity—molecular weight equations determined for poly-p-methoxystyrene under the same condition can be carried out with equations (9-3), (9-20) and (9-22) and with equations (9-4), (9-19)

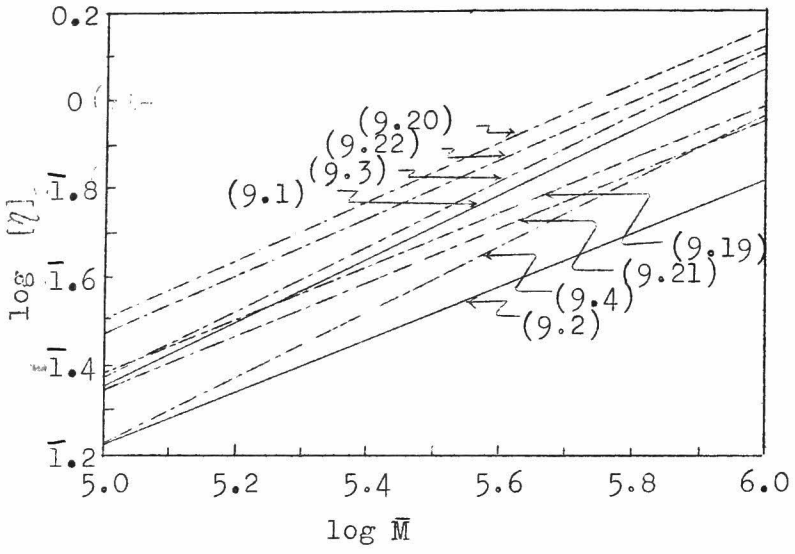

Fig. 9-9 The comparison between various intrinsic viscosity—molecular weight equations

and (9-21).

Regarding the intrinsic viscosity—molecular weight equation in toluene at 30°C, Saito's equation (9-20) is in poor agreement with the present equation (9-3). Saito's modified equation (9-22), used in Chapter 3, is intermediate between equations (9-3) and (9-20), and agrees well with equation (9-3) especially at high molecular weights.

Regarding the intrinsic viscosity—molecular weight equation in methyl ethyl ketone at 25°-30°C, Saito's

equation (9-19) is similarly in poor agreement with the present equation (9-4). Saito's modified equation (9-21) is intermediate between equations (9-4) and (9-21), and agreemes well with equation (9-4) especially at high molecular weights.

When the intrinsic viscosity—molecular weight equations for poly-o- and p-methoxystyrene are compared, it is seen that they behave differently in methyl ethyl ketone at 30°C (comparison between equation (9-2) and (9-4)). Since the methoxy group is a polar one, it might be suggested that when that group is introduced into the phenyl group of styrene, a dipole is induced in the polymer, and that this interacts with the dipole of the solvent, methyl ethyl ketone. However, in toluene at 30°C both behave very similarly (comparison of equation (9-1) with (9-3)). Saito et al.[1] studied the molecular weight dependency of the intrinsic viscosity for polystyrene, poly-p-chlorostyrene and poly-p-methoxystyrene and found no serious differences between them. They concluded that the major solution properties of polystyrene derivatives are decided by the phenyl group, and that introduction of para-chloro and para-methoxy groups in the phenyl nucleus has only a minor effect. It is

clear from the present investigation, that at least in non-polar solvent such as toluene the properties of the o-methoxy group exerts little effect upon the solution properties of the polymer.

Though it is interesting to note the relationship between A_2 and the molecular weight, the experimental errors in A_2 are such that detailed discussion is impossible. Saito[1] reported a value of A_2, 1.3-1.6 x 10^{-4}, for poly-p-methoxystyrene of molecular weight 2.2-9.0 x 10^5 in methyl ethyl ketone, in fairly good agreement with A_2 values reported here. Values of A_2 for poly-o-methoxystyrene are much smaller than those for poly-p-methoxystyrene. It is evident that poly-o-methoxystyrene is less soluble in methyl ethyl ketone than poly-p-methoxystyrene judging both by A_2 values as well as from the intrinsic viscosity—molecular weight equations.

3.2 Dependence of molecular weight distribution on polymerization conditions.

As is shown in Fig. 9-5, $\bar{\bar{M}}_w/\bar{\bar{M}}_n$ changes with the polymerization conversion, there the behavior for $\bar{\bar{M}}_w/\bar{\bar{M}}_n$ = 2 being shown by a broken line, while the behavior for

the case of the most widely distributed molecular weight distribution is shown by an unbroken one. A poly-p-methoxystyrene subjected to fractionation was prepared in a polymerization system giving the intermediate molecular weight distribution for the polymer. Of three samples, S and S' were theoretically expected to be near the dotted line. In practise $\bar{\bar{M}}_w/\bar{\bar{M}}_n$ for S and S' were found to be nearly 2. Furthermore as was expected on theroetical grounds the molecular weight distribution of S', which was prepared at low conversion, was sharper than that of S which was produced at high conversion. However, $\bar{\bar{M}}_w/\bar{\bar{M}}_n$ for both samples was unexpectedly less than 2. The reason for this is not known, but the same was observed in polymerization of styrene (see Chapter 8). These experimental results may well be ascribed to loss of low molecular weight polymer during fractionation or on removing polymer from the polymerization system. Taking into account the good recovery of polymer during fractionation and the good agreement between intrinsic viscosity of the original sample before fractionation and intrinsic viscosity calculated after fractionation, the loss of the low molecular weight polymer is supposed to be very small, though this would, however, be enough to

reduce $\bar{\bar{M}}_w/\bar{\bar{M}}_n$ below 2.

Sample B was expected theoretically to approximate to the continuous line, and this was confirmed experimentally, i.e., $\bar{\bar{M}}_w/\bar{\bar{M}}_n$ for B was very near the theoretical and its molecular weight distribution was much broader than that of S or S'.

In accordance with the foregoing, it is safely acceptable that the molecular weight distribution of polymer produced in an ordinary cationic polymerization is fixed by the rate constant ratios of the transfer and the termination reactions and the conversion in accordance with theoretical equations (9-15) or (9-16), though confirmatory experimental data are not adequate. $\bar{\bar{M}}_v$ can be calculated by inserting the intrinsic viscosity of unfractionated polymer into the intrinsic viscosity—molecular weight equation for fractionated polymer. It is evident from the above experimental findings that the ratio of $\bar{\bar{M}}_v$ (practically obtainable) to $\bar{\bar{M}}_n$ (necessary for calculation of the rate constant ratio) is about 2, independent of polymerization conditions, unless the conversion is greatly increased. The rate constant ratio calculated from $\bar{\bar{M}}_v$ is, therefore, about one-half as large as the true rate constant ratio, independent of the

polymerization conditions, consequently all the rate constant ratios obtained in Part 2 should be doubled. However, since only relative comparisons are being made, it is not necessary to correct these numbers.

3.3 The effect of substituent on polymer chain expansion

The experimental results shown in Table 9-8, will now be discussed. The expansion coefficient of the polymer chain, α, is larger in toluene than that in methyl ethyl ketone for both poly-p-methoxystyrene and poly-o-methoxystyrene. This suggests that toluene is a better solvent for both polymers than is methyl ethyl ketone. Saito et al.[1] reported however that there was no difference between the effects of toluene and methyl ethyl ketone on the molecular weight dependency of the end-to-end distance for the poly-p-methoxystyrene chain, and the discrepancy has not yet been explained.

For poly-o-methoxystyrene, α calculated from $[\eta]/[\eta]_\theta = \alpha^{2.43}$[7] agreed well with calculated from the Flory-Olofino equation.[8]

The effect of the substituent on the end-to-end distance of the polymer chain will next be discussed. $(<\bar{r}_o^2>/<\bar{r}_{of}^2>)^{1/2}$ was 2.50 for poly-p-methoxystyrene and 2.44 for poly-o-methoxystyrene at 30°C. And it was

2.73 for poly-α-methylstyrene at 30°C (Section 7.2). While for polystyrene it was 2.35 at 30°C.[9] On these values, the effect of the substituent on the free rotation of a single bond in back-bone chain of polymethoxystyrenes lies between the effects for polystyrene and poly-α-methylstyrene. This conclusion differs slightly from that reached by Saito et al.[1], that a methoxy group attached to phenyl group has a neglegible effect on the free rotation. The difference between the effects of ortho- and para-methoxy groups was fairly small, but the latter group had a slightly larger effect than the former. This means that the segment-segment and the segment-solvent interactions induced by a polar methoxy group are slightly larger with the para-substituent than with the ortho-one. Consequently an attempt to discuss the steric effect of the ortho- methoxy group on the propagation reaction for o-methoxystyrene, in terms of the steric effect of ortho-methoxy group on the solution properties of poly-o-methoxystyrene (assuming that the activation state of the propagation reaction resembles that of the final state) failed.

To sum up, the present investigation yielded the

following results:—

Using a light scattering method, the intrinsic viscosity—molecular weight equations (9-1)-(9-4) for poly-p-methoxystyrene and poly-o-methoxystyrene at 30°C in toluene and methyl ethyl ketone were obtained. These equations made possible study of the relationship between cationic polymerization conditions of p-methoxystyrene and the molecular weight distribution in poly-p-methoxystyrene, and it was established that $\bar{M}_v/\bar{M}_n$ was always about 2, independent of the polymerization condition, and that the true rate constant ratio is twice that reported in Part 2. The effect of the methoxy group on the expansion of the polymer chain was studied, and it was confirmed that due to the methoxy group polymethoxystyrene is more expanded than polystyrene, and further that poly-p-methoxystyrene is more expanded than poly-o-methoxystyrene.

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Part 4 The Reactivity of the Growing Ion in Ionic Polymerization

Chapter 10 Estimation of the Growing Ion Reactivity in Cationic Polymerization from the Chain Transfer Reaction

Section 10.1 Theoretical Considerations

1. Introduction

The mechanisms of monomer transfer and unimolecular termination reactions in the cationic polymerization of vinyl monomers were discussed in Part 2, where it was recognized that the reactivity of both monomer and growing ion must be considered to discuss the reactivity of the vinyl monomer in the propagation, transfer, and termination reactions (cf. Chapters 3 and 4). There have been many investigations of the reactivity of a monomer towards a radical or ion in copolymerization. In radical copolymerization the reactivity may be considered in terms of Q/e values. Alfrey and Price[1] showed that the propagation rate constant can be expressed as

$$k_p = PQ \exp (- e_r e_m) \qquad (10\text{-}1)$$

where Q and e_m represent respectively the reactivity and electronic character of the monomer, P and e_r ralating to the adduct radical. Okamura et al.[2] reconsidered the experimental results hitherto reported and found that the following relationship held between P and Q:—

$$\log P = kQ + a \qquad k < 0 \qquad (10\text{-}2)$$

From equation (10-2), it is seen that the reactivity of the radical produced from monomer with a greater reactivity is generally smaller.

On the other hand there have been few discussions of reactivities of growing ions produced from various kinds of monomers. Since the monomer reactivity ratio, r_1, is approximately equal to $1/r_2$ in ionic copolymerization, it has been considered that the relative reactivities of the two monomers towards different growing ions are about the same.[3] The difference in reactivity of the different kinds of ions towards a certain monomer has not been discussed.

In the present Section, the relation between the reactivity of monomer and that of the growing ion is investigated theoretically. Further, an outline of procedures for determining the reactivity of a growing

ion will be discussed.

2. Propagation rate constants and the reactivities of polymer ions

2.1 Cationic polymerization

In order to determine the reactivity of a growing ion, the propagation rate constant (k_p) and the monomer reactivity ratio (r_1, r_2) must be decided as in radical polymerization. However, for a long time there were not any methods for determining k_p in ionic polymerization, but recently a method of determining k_p for an iodine-catalyzed system has been reported from our laboratory.[4] According to it, k_p and (r_1, r_2) were determined for vinyl isobutyl ether (VIBE) and vinyl 2-chloroethyl ether (VCEE). The polymerization in dichloroethane by iodine at 30°C gave the following results: $r_1 = 2.0 \pm 0.1$, $r_2 = 0.5 \pm 0.1$ (M_1 is VIBE and M_2 is VCEE). On the other hand, k_{11} and k_{22} are considered to be equal to the values of k_p of the respective monomers under the same polymerization conditions. Thus it was found that $k_{11} = 390$ and $k_{22} = 260$ l/mole/min. and substituting these values in r_1 and r_2 gives k_{12} and k_{21}. The results are shown in Table 1. (All these values have been reported:[5] results are given here for convenience.)

Table 10-1 Propagation rate constants (l/mole/min.) in the copolymerization of vinyl isobutyl ether (M_1) and vinyl 2-chloroethyl ether (M_2) Catalyst: iodine, Solvent: dichloroethane Polymerization temperature: 30°C

k_{11}	k_{12}	k_{21}	k_{22}
390	195	520	260

It is seen from Table 10-1 that the reaction rate constants in ionic copolymerization decreases in the order:

$$k_{21} > k_{11} > k_{22} > k_{12}$$

which obviously indicates that a possible set of conditions, $k_{11} = k_{21}$ and $k_{22} = k_{12}$, making $r_1 = 1/r_2$, is not satisfied. It also means that addition is easiest between more reactive monomer (M_1) and the growing ion produced from the less reactive monomer (M_2) and is most difficult between the less reactive monomer and the ion from the more reactive monomer. Hence it may be concluded that the ion from the reactive monomer is not so reactive as that from the less reactive monomer.

To relate quantitatively the reactivities of the two ions in the ionic polymerization, it was tentatively

assumed that the rate constant $k_{p_{ij}}$ in the propagation step may be taken as:—

$$k_{p_{ij}} = R_{I_i} \times R_{M_j} \qquad (10\text{-}3)$$

where R_{I_i} is the reactivity of the growing ion i and R_{M_j} is the reactivity of the monomer j. Equation (10-3) may reasonably be applied to treat the rate constant in ionic copolymerization where the relation $r_1 = 1/r_2$ holds, but it is an equation which is open to criticism. At the present stage, it is doubtful whether $r_1 = 1/r_2$ always holds, and there is no definite explanation of why the intermolecular term can be ignored in the rate constant. But equation (10-3) which was derived with the simplest assumption, was used in this investigation.

Using equation (10-3), the following relations are easily derived:—

$$k_{11}/k_{12} = k_{21}/k_{22} = R_{M_1}/R_{M_2}$$

$$k_{11}/k_{21} = k_{12}/k_{22} = R_{I_1}/R_{I_2}$$

Inserting the rate constants from Table 10-1,

$$R_{M_1}/R_{M_2} = 2.0 \qquad R_{I_1}/R_{I_2} = 1/1.3$$

whence monomer 1 is twice as reactive as monomer 2, but ion 2 1.3 times as reactive as ion 1. This tendency is the same as in radical polymerization,[2] and is expected from the reaction mechanism.

However, the above relationship does not hold in the cationic polymerization of styrene derivatives. In the cationic polymerizations of p-chlorostyrene (M_1) and styrene (M_2) induced by iodine in dichloroethane at 30°C the propagation rate constants k_{11} and k_{22} were 0.071 and 0.22 l/mole/min., respectivety.[6] In cationic copolymerization of both monomers with the same polymerization condition as for homopolymerizations, the monomer reactivity ratios were found to be $r_1 = 0.45$ $r_2 = 2.5$.[6] Inserting the propagation rate constants in the monomer reactivity ratio, the rate constants k_{12} and k_{21} were calculated. The results of the calculations are shown in Table 10-2.

Table 10-2 gives the following sequences for rate constants in cationic copolymerization:—

$$k_{21} > k_{11} \qquad\qquad k_{22} > k_{12}$$

This order means that the reactivity of cation 2 is greater than that of cation 1. Using equation (10-3), the relative reactivities of monomers and cations were cal-

culated as:—

$$R_{M_1}/R_{M_2} = 0.40\text{-}0.45 \qquad R_{I_1}/R_{I_2} = 0.73\text{-}0.81$$

Table 10-2 Propagation rate constants (l/mole/min.) in the copolymerization of p-chlorostyrene (M_1) and styrene(M_2).
Catalyst: I_2, Solvent: dichloroethane, Polymerization temperature: 30°C

k_{11}	k_{12}	k_{21}	k_{22}
0.071	0.16	0.088	0.22

It was observed that monomer 2 is about twice as reactive as monomer 1, and that cation 1 is about three quarters as reactive as cation 2. This tendency is the reverse of that observed in radical polymerization[2] or in cationic polymerization of vinyl alkyl ether.

The reversal of the relationship between the reactivities of monomer and cation for vinyl alkyl ether and styrene derivatives is explained as follows.[7] In the cationic polymerization of vinyl alkyl ether by iodine, the formation of a new bond between the growing cation and the β carbon atom of the monomer is important. From

this point of view, the cation produced from a reactive monomer is stabilized by the action of a substituent attached to the cation which makes the monomer reactive, and which is itself consequently unreactive. On the other hand, in cationic polymerization of styrene derivatives by iodine, dissociation of the growing ion-pair into free ions is necessary prior to addition of monomer to the cation. In this connection, the stable ion produced from the reactive monomer can dissociate easily from the counter anion, and is consequently reactive. The peculiarity of the propagation reaction of styrene derivatives lies in an ion-pair being present and dissociation into free ions being necessary.

The above relationship was observed for polymerization induced by iodine, and it is doubtful whether the same holds in polymerization induced by a Friedel-Crafts catalyst. In the ion-pair derived from iodine, the counter anion is considered to be very near the carbonium ion. On the other hand, in the ion-pair from a Friedel-Crafts catalyst, the counter anion is considered to be somewhat distant from

the carbonium ion, and it is difficult to believe that dissociation into free ions is the rate determining step. For anionic polymerization in a high dielectric constant solvent such as tetrahydrofuran deseribed below, this was confirmed.

2.2 Anionic polymerization

It has been reported for styrene—methyl methacrylate copolymerization[8] that the growing anion produced from styrene, which is the less reactive monomer, can initiate the polymerization of styrene and methyl methacrylate, but that the growing anion produced from the more reactive monomer, methyl methacrylate, cannot initiate the polymerization of styrene. This result may indicate that the reactivity of the anion produced from the more reactive monomer is lower, as in cationic polymerization.

With suitable conditions, anionic polymerization proceeds without any transfer and termination reactions, to give a so-called living polymer. Using the living polymer system, the propagation rate cons-

tant can be estimated. Szwarc[9] determined the propagation rate constant in the anionic polymerization of vinyl monomers at 25°C in tetrahydrofuran with accompanying sodium cation as the counter cation. The experimental results for the propagation reaction, where the steric effect of the substituent can be neglected, were as follows:—

rate constant of the addition of vinyl monomers onto styrene anion

2-vinylpyridine > styrene > p-methylstyrene > p-methoxystyrene

rate constant of the addition of styrene onto anions of various kinds of vinyl monomers

2-vinylpyridine < styrene < p-methylstyrene < p-methoxystyrene

There too, the more reactive monomer gives the less reactive anion.

3. A molecular orbital treatment

In the foregoing, experimental evidence was chosen to demonstrate that the growing ion produced from the

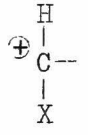
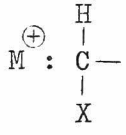
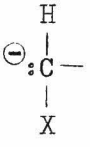
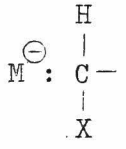
reactive monomer is not so reactive in cationic polymerization or anionic polymerization. However, it is not clear whether this tendency is found with other substances, since few experimental results are available. Hence a molecular orbital approach, to clarify this point, will now be made.

Regarding radical polymerizations, the reactivity of a monomer and a radical have been discussed in terms of the radical localization energy of a monomer L_M^R and the localization energy of a radical L_R[10]. Such investigation showed, generally, that the radical from the more reactive monomer is less reactive. In a like manner, L_M^C and L_M^A, the cationic and the anionic localization energies of the monomer, respectively, are now calculated, using the transition state model shown below.—

Type of reaction	Reagent monomer	Transition state	Localization energy
Electrophilic addition	$R^{\oplus}+CH_2=\underset{\displaystyle X}{\underset{\vert}{C}}H$	$R:\ \overset{\displaystyle H}{\underset{\displaystyle H}{\overset{\vert}{\underset{\vert}{C}}}}-\overset{\displaystyle H}{\underset{\displaystyle X}{\overset{\vert}{\underset{\vert}{C}}}}^{\oplus}$	L_M^C
Nucleophilic addition	$R^{\ominus}+CH_2=\underset{\displaystyle X}{\underset{\vert}{C}}H$	$R:\ \overset{\displaystyle H}{\underset{\displaystyle H}{\overset{\vert}{\underset{\vert}{C}}}}-\overset{\displaystyle H}{\underset{\displaystyle X}{\overset{\vert}{\underset{\vert}{C}}}}^{\ominus}:$	L_M^A

The effect of the counter ion is here neglected.

L_C and L_A, the localization energies of cation and anion respectively, are found in a similar way.

Attacking reagent		Reaction Reagent to be attacked	Transition state	Localization energy
M:	+			L_C
M	+			L_A

Parameters (Coulomb integral and resonance integral) used in these calculations are the same as those in the previous paper from our laboratory. For the methyl groups in isobutene and propylene, however, parameters which are approximately equal to the values given by Coulson[11], who treated the methyl group as $-\underset{a}{C} \equiv \underset{b}{H_3}$ were used:—

$$\alpha_a = \alpha - 0.1\beta$$

$$\alpha_b = \alpha - 0.5\beta$$

$$\beta_{C\equiv H_3} = 2.5\beta$$

where α and β are the values of the Coulomb integral of the carbon atom and of the resonance integral of the C-C double bond in benzene respectively.

From the definition of localization energy[12], it can be considered that a low localization energy value means a low value of the activation energy, i.e., high reactivity in an addition reaction. Solvents affect the propagation reaction, but this is neglected here. In Fig. 10-1, L_M^C is plotted against L_C.

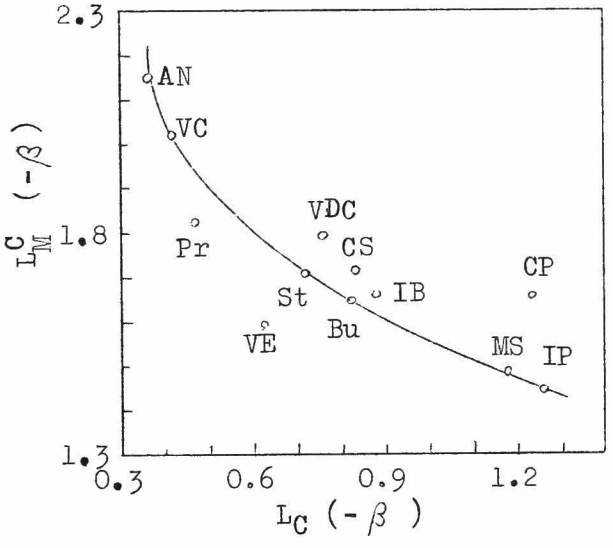


Fig.10-1 The relationship between the reactivity of a monomer and the reactivity of the cation produced from the monomer, calculated from the localization energies.
AN: Acrylonitrile, VC: Vinyl chloride Pr: Propylene,
VDC: Vinylidene chloride VE: Vinyl ether,
St: Styrene Bu: Butadiene, CS: Chlorostyrene
IB: Isobutene, MS: α-Methylstyrene CP: Chloroprene,
IP: Isoprene

Fig. 10-1 shows that the easily polymerizable monomers (α-methylstyrene, etc.) have smaller L_M^C and larger L_C, and that the less easily polymerizable monomers (acrylonitrile etc.) have the larger L_M^C and smaller L_C. It can therefore be understood that the carbonium ion of the more reactive monomer will have low reactivity, in agreement with experiments.

The localization energies of monomers and ions in anionic polymerization were calculated and the results plotted in Fig. 10-2. Again, it can be seen that the

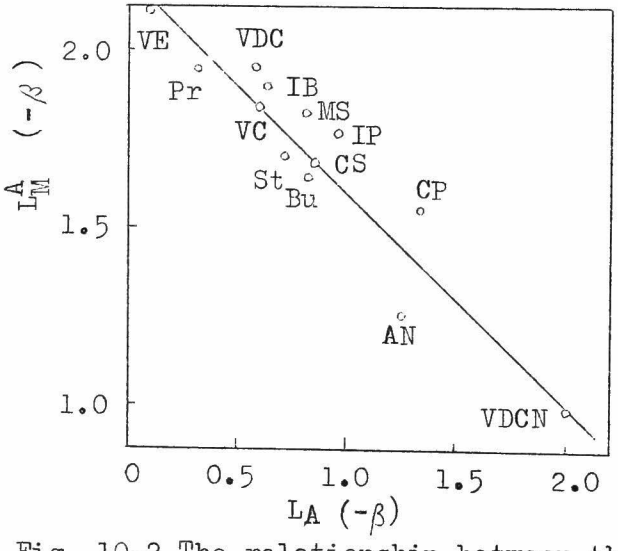


Fig. 10-2 The relationship between the reactivity of the anion produced from the monomer, calculated from the localization energies.
VDCN: Vinylidene cyanide
other symbols as used in Fig. 1

reactive monomer produces the unreactive adduct anion in anionic polymerization.

4. Reactivities of ions as estimated by the chain transfer constant

It was pointed out above that a satisfactory basis for discussion on reactivities of growing ions will be afforded by values of propagation rate constants and monomer reactivity ratios when available. Unfortunately, however, there are only a few cases where k_p is known. Hence an attempt is next made to determine the range of the reactivity ratios of two polymer ions by measuring the chain transfer constant ratio and the monomer reactivity ratio.

4.1 Method of estimation

If the reactivity of a certain chain transfer reagent towards different kinds of ions is constant, the value of the chain trnasfer constant (k_r) of the growing ions towards a certain substance affords a measure of their reactivities. Corresponding to equation (10-3) for the propagation reaction, equation (10-4) will hold for the chain transfer reaction:—

$$k_{r_{ij}} = R_I'_i \cdot R_{r_j} \qquad (10\text{-}4)$$

Then, on the growing ions k and i

$$R_I'_i/R_I'_k = k_{r_{ij}}/k_{r_{kj}} \qquad (10\text{-}5)$$

Bamford et al.[13] investigated radical reactivity by this procedure.

Two kinds of monomers are designated as M_1 and M_2, respectively, and it is assumed that M_1 is more reactive than M_2. From the definitions of r_1 and r_2:—

$$(r_1/r_2)^{\frac{1}{2}} = (k_{11}/k_{12})^{\frac{1}{2}}.(k_{21}/k_{22})^{\frac{1}{2}} = (k_{11}/k_{22})^{\frac{1}{2}}.(k_{21}/k_{12})^{\frac{1}{2}} \qquad (10\text{-}6)$$

In the case of the vinyl alkyl ether type of propagation;—[6]

$$k_{11}/k_{22} \leq k_{21}/k_{22} \qquad (10\text{-}7)$$

In the case of the styrene derivative type of propagation:—[6]

$$k_{11}/k_{22} \geq k_{21}/k_{12} \qquad (10\text{-}8)$$

Then, in all cases:—

$$k_{21}/k_{12} \geq k_{11}/k_{22} \geq k_{21}/k_{12} \qquad (10\text{-}9)$$

The precise position of k_{11}/k_{22} is not known at the present stage. However, it can safely be assumed that k_{11}/k_{22} does not differ seriously from k_{21}/k_{12}, giving equation (10-10):—

$$(r_1/r_2)^{\frac{1}{2}} \simeq (k_{11}/k_{22}) = (k_p)_A/(k_p)_B \qquad (10\text{-}10)$$

In Table 10-1 with VIBE (M_1) and VCEE (M_2), $(r_1/r_2)^{\frac{1}{2}}$ is equal to 2.0 and k_{11}/k_{22} is equal to 1.5, so equation (10-10) holds. In Table 10-2 with p-chlorostyrene (M_1) and styrene (M_2), $(r_1/r_2)^{\frac{1}{2}}$ is equal to 0.42 and k_{11}/k_{22} is equal to 0.32, so equation (10-10) again holds. As is seen from these two examples equation (10-10) holds fairly well, especially when $r_1 . r_2 \simeq 1$.

When the reactivity of the growing ion is discussed in terms of the chain transfer reaction, equation (10-7) will hold, because in the chain transfer reaction bond formation between a growing ion and a chain transfer reagent is important, as in the case of the vinyl alkyl ether type of propagation[7] (this was confirmed in Section 10-3). Hence equation (10-11) will hold instead of equation (10-10):—

$$(r_1/r_2)^{\frac{1}{2}} \geq k_{11}/k_{22} \qquad (10\text{-}11)$$

If δ is the ratio of the chain transfer constants ratio measured, δ is given by equation (10-12):—

$$\delta = (k_{r_2}/k_{22})/(k_{r_1}/k_{11}) = (k_{r_2}/k_{r_1}).(k_{11}/k_{22}) \quad (10\text{-}12)$$

Equation (10-13) was obtained using the reactivity ratio of the ions from equation (10-11) and (10-12).

The reactivity ratio of the ions $\simeq k_{r_2}/k_{r_1}$

$$= \delta \cdot k_{22}/k_{11} \geq \delta \cdot (r_2/r_1)^{\frac{1}{2}} \quad (10\text{-}13)$$

If, using the same polymerization conditions, the chain transfer constant ratios for more than two monomers and the monomer reactivity ratios for these monomer pairs are obtained, the lowest limit of the ratio of the ion reactivity will be given by equation (10-13). The next section will use equation (10-13) to discuss the experimental results.

4.2 Comparison with experimental results

Scarcely any chain transfer constant ratios for more than two monomers towards a certain transfer reagent under the same conditions have been reported in the literature. The only example to be found is that reported by Haas et al.[14], who measured the chain transfer constant ratios of styrene and p-methoxystyrene towards p-

methylanisole. Both monomers were polymerized by stannic chloride at 0°C. The chain transfer constant ratios for p-methylanisole in styrene polymerization $(k_r/k_p)_{St}$ and in p-methoxystyrene polymerization $(k_r/k_p)_{PMS}$ were 1.08 and 2.7×10^{-3}, respectively.

Using equation (10-13), the ratio of the ion reactivity was calculated from these values and the results are tabulated together with the relevant data. However, as the monomer reactivity ratio is not known accurately[15] the relative reactivities of the two ions, 4.0, is only approximate.

To check the validity of equation (10-13), an experiment was carried out with styrene and p-chlorostyrene as the monomer pair. The details of the experimental results will be described in Section 10.2. p-Chlorostyrene was polymerized by stannic chloride—trichloroacetic acid at 30°C, and the chain transfer constant ratio towards toluene was determined, the method used being the same as for styrene polymerization,[16] where polymerization was effected changing the mole ratio of monomer to toluene, and the chain transfer constant ratio was calculated by measuring the degree of polymerization of the resultant polymer. Many results for monomer reactivity ratio in

the styrene—p-chlorostyrene system have been published; $r_1 = 2.5 \pm 0.4$ and $r_2 = 0.3 \pm 0.03$ were used,[17] where styrene was M_1 and p-chlorostyrene was M_2. Table 10-2 gives the ion reactivity ratio along with some related data.

Values in the last column in Table 10-2 show the lowest limit of the ion reactivity as calculated from equation (10-13). The true ion reactivity ratio is considered to be larger than that given in Table 10-2. For the styrene—p-methoxystyrene pair, the monomer reactivity of p-methoxystyrene is 100 times greater than that of styrene, while the ion reactivity of styrene is 4 times greater than that of p-methoxystyrene. Moreover, the ion reactivity of p-chlorostyrene is about 5 times greater than that of styrene, while the monomer reactivity of styrene is greater than that of p-chlorostyrene. In either case k_{r_2} / k_{r_1} which is considered to give the ratio of the ion reactivities, is considerably greater than unity, monomer 1 having the greater reactivity. The author is interested in this fact and experimental results for other kinds of monomer pairs will be given later.

The present investigation can be summed up as

Table 10-3 Reactivities of ions estimated by chain transfer constant

Monomer	Transfer reagent, polymerization temp., Cat.	Chain transfer constant ratio (k_r/k_p)	Ratio of (k_r/k_p) $(k_r/k_p)_2/(k_r/k_p)_1$	Monomer reactivity ratio (r_1, r_2)	$(r_2/r_1)^{\frac{1}{2}}$ or (R_{M_2}/R_{M_1})	Lower limit of k_{r_2}/k_{r_1} or $(R_{I_2'}/R_{I_1'})$
Styrene(M_2) p-Methoxy-styrene(M_1)	p-Methyl-anisole, 0^oC, $SnCl_4$	1.08 2.7×10^{-3}	400	$r_1 = 100$ $r_2 = 0.01$	0.01	4.0
p-Choro-styrene(M_2) Styrene(M_1)	Toluene 30^oC $SnCl_4 \cdot CCl_3COOH$	4.0×10^{-2} 2.8×10^{-3}	14.3	$r_1 = 2.5 \pm 0.4$ $r_2 = 0.3 \pm 0.03$	0.35	5.0

follows: With a view to discussing reactivity in the propagation reaction of ionic polymerization, reactivities of both vinyl monomers and growing ions were investigated, and in this Section, three methods of comparing the reactivities of ions have been proposed: (1) direct measurement of the propagation rate constant, (2) comparison between chain transfer constant ratios, and (3) a molecular orbital approach. From these experimental and theoretical investigations, it has been found that the ion produced from the more reactive monomer is stable and less reactive, analogous to radical polymerization.

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Section 10.2 Ortho- and Para- Chlorostyrene

1. Introduction

In the previous Section it was mentioned how difference in reactivity of growing species should be taken into consideration in the cationic polymerization as well as in the radical polymerization, where the reactivity of growing ion was discussed in connection to the reactivity of monomer. The following three for determining the reactivity of growing ion were proposed; (1) direct comparison of the propagation rate constants, (2) comparison of the chain transfer constant ratios, and (3) comparison of the localization energies calculated by the molecular orbital method. In the present investigation, the reactivities of growing ion made from styrene were estimated by comparing the chain transfer constant ratios towards toluene found for constant polymerization conditions and they were discussed in connection with the reactivities of those monomers, though the reactivity of the growing ion could be changed with changing the kind of chain transfer reagent, the polymerization condition, and so on.

In this Section, the reactivities of growing ions made from styrene, p- and o-chlorostyrene were compared

with each other, and the electronic and the steric effects of the chlorine atom on the reactivities of the growing ion and monomer were discussed.

2. Experimental

2.1 Reagent

The method of synthesizing chlorostyrenes was described in Chapter 4. Styrene was purified as described there. The purifications of benzene, toluene, chloroform and dichloroethane as solvent, stannic chloride as catalyst, and trichloroacetic acid as co-catalyst were carried out as described in Chapter 4, special care being taken to remove water.

2.2 Procedure

Polymerization and molecular weight determinations were carried out as described in Chapter 4.

Copolymerization of styrene and o-chlorostyrene was carried out at 30°C in benzene or in dichloroethane. The polymerization was stopped at a conversion below 10%. The copolymer composition was determined by chlorine analysis.

3. Results

3.1 Comparison of the reactivity of the monomers by copolymerization

As seen from the description of Section 10.1, the monomer reactivity ratio is necessary to compare the reactivities of two kinds of growing ions or of monomers.

A large number of copolymerizations have been studied for the styrene—p-chlorostyrene syttem, and the monomer reactivity ratio has been found to be roughly independent of polymerization conditions, especially when stannic chloride is the catalyst. The results reported by Alfrey and Wechsler,[1] $r_1 = 2.7 \pm 0.3$ and $r_2 = 0.35 \pm 0.05$ (M_1: styrene, M_2: p-chlorostyrene, catalyst: stannic chloride, temperature: 30°C), was therefore available during the present investigation.

On the other hand, there have been only a few investigations of copolymerization of styrene with o-chlorostyrene. Here copolymerization of styrene (M_1) and o-chlorostyrene (M_2) was carried out at 30°C using stannic chloride—trichloroacetic acid as the catalyst. Results are shown in Fig. 10-3.

Fig. 10-4 shows determination of monomer reactivity ratio by the cross-section method, leading to $r_1 = 1.6 \pm 0.2$

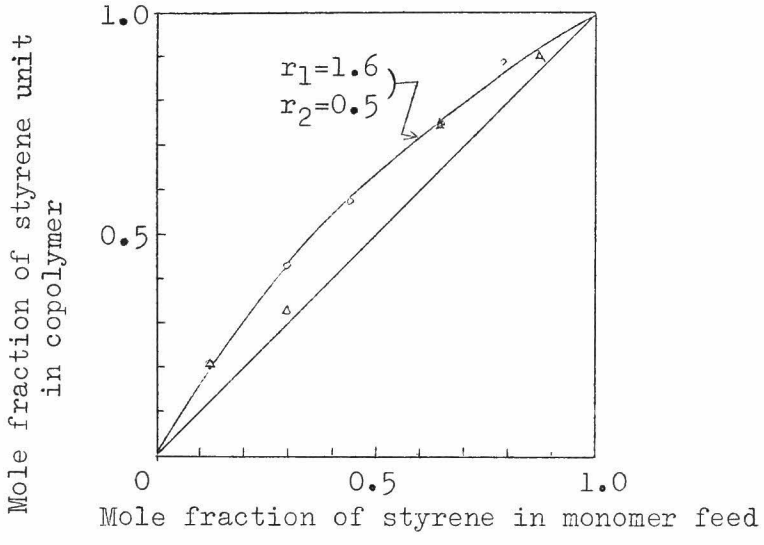


Fig. 10-3 Copolymerization of styrene (M_1) and o-chlorostyrene (M_2) at 30°C by $SnCl_4 \cdot CCl_3COOH$

(○):data in benzene
(△):data in dichloroethane

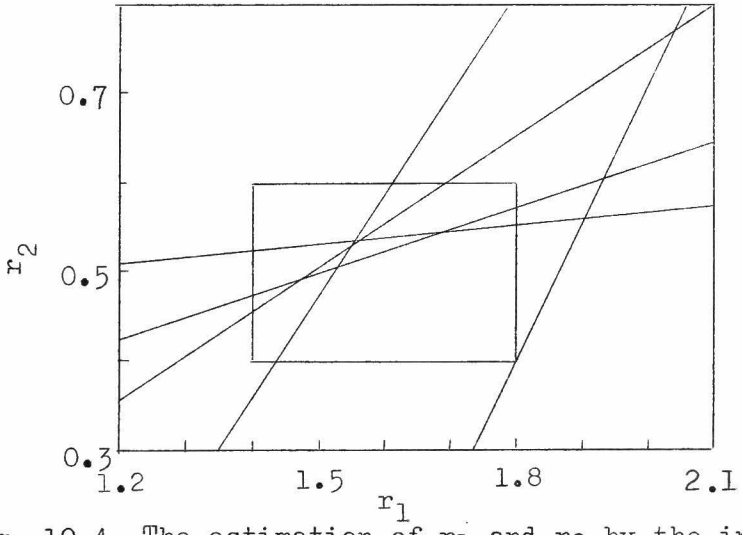


Fig. 10-4 The estimation of r_1 and r_2 by the intersection method. Copopymerization of styrene (M_1) and o-chlorostyrene (M_2) by $SnCl_4.CCl_3COOH$ at 30°C

and r_2 = 0.5 + 0.1 (lit.[2] r_1= 4 and r_2 = 0.5).

Monomer reactivity was considered with regard to monomer reactivity ratio thus obtained, and shown in Table 10-4 where r_2-value or reciprocal of r_1 were taken for the reactivity ratio of monomer 1 against monomer 2.

Table 10-4 The comparison of the reactivity of monomer

Monomer		Comparison of reactivity	
M_1	M_2	Reactivity of M_1	: Reactivity of M_2
Styrene	p-Chlorostyrene	1	: 0.35-0.37
Styrene	o-Chlorostyrene	1	: 0.50-0.63
o-Chlorostyrene	p-Chlorostyrene	1	: 0.56-0.74

Monomer reactivities could be placed in the following decreasing order:

styrene > o-chlorostyrene > p-chlorostyrene.

3.2 Estimation of the rate constant ratio

As is seen from the description in Section 10.1, for the chain transfer constant ratio towards a certain transfer reagent (toluene in this case) is necessary to compare growing ion reactivity. Here estimation of the chain

transfer constant ratio for toluene will be described.

3.2.1 The p-chlorostyrene termination and transfer constant ratios

To estimate the chain transfer constant ratio of the p-chlorostyrene cation to toluene, p-chlorostyrene has to be polymerized in toluene at various monomer concentrations. However the present catalyst polymerized p-chlorostyrene in toluene at only a low rate (cf. Chapter 4), so polymerization was carried out in toluene—benzene mixture with change of the ratio of these solvents while keeping the monomer concentration constant. Then equation (10-14) connects the degree of polymerization of the polymer and the concentrations of the reagents:—

$$1/\bar{P} = (k_{tm}/k_p + ak_{ts}/k_p \cdot 1/[M]) + (k_r/k_p - bk_{ts}/k_p)[r]/[M] \qquad (10\text{-}14)$$

where r and s represent respectively toluene and benzene, and the other symbols are defined elsewhere in this thesis. In equation (10-14) $a = 1000\ (V_r + V_s)\ d_s/d_w$ and $b = d_s W_r/d_r W_s$ where V, d and W denote respectively the volume fraction, density, and the molecular weight, and suffixes r and s stand for toluene and benzene respectively.

Since all of the polymerizations were carried out in a system consisting of monomer 5 ml. and mixed solvents 25 ml. (approximate dielectric constant = 2.5), the unimolecular termination reaction was neglected.[3)]

In order to find the chain transfer constant ratio towards toluene (k_r/k_p) using equation (10-14), the chain transfer constant ratio towards benzene (k_{ts}/k_p) must be known. A k_{ts}/k_p value of 1.22×10^{-3} estimated in Chapter 4 was available for this calculation. In Fig.10-5 $1/\bar{P}$ was plotted against [r]/[M]. k_r/k_p could be calculated, by adding $b \cdot k_{ts}/k_p$ to the slope of the straight

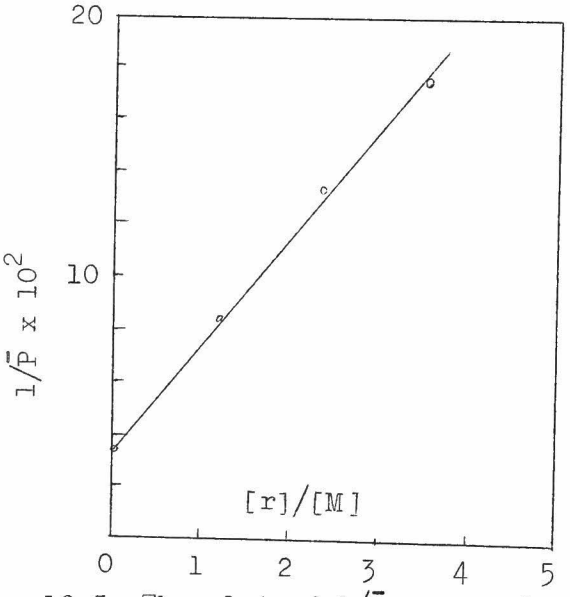


Fig. 10-5 The plot of $1/\bar{P}$ versus [r]/[M]
p-Chlorostyrene—benzene—toluene—30°C—
$SnCl_4 \cdot CCl_3COOH$ $k_r/k_p = 4.00 \times 10^{-2}$
$k_{tm}/k_p = 2.34 \times 10^{-2}$

line, as 4.00×10^{-2}, and k_{tm}/k_p could be calculated by deducing $a \cdot k_{ts}/k_p \cdot 1/[M]$ from the intercept of the straight line, as 2.34×10^{-2}. k_{tm}/k_p was previsouly found in Chapter 4, using a different method, to be 2.36×10^{-2}. The two values are in good agreement.

The present author assumed applicability of k_{ts}/k_p found for polymerization in benzene solution (cf. Chapter 4, section 3.2.1) to the polymerization in benzene—toluene mixed solvent, as the structures and properties of both solvents are almost the same. The validity of the assumption was confirmed by the fact that, the k_{tm}/k_p's found independently in different way, using only the above assumption, were in good agreement.

3.2.2 Termination and transfer constant ratios for o-chlorostyrene

As o-chlorostyrene undergoes polymerization at an extremely low rate even in benzene solution, it was carried out with a monomer concentration as high as monomer 12 ml. and benzene—toluene 18 ml. As in the case of p-chlorostyrene, the rate constant ratios were estimated from the degree of polymerization obtained with polymerization at different solvent compositions. However, in the present system the unimolecular termination reaction

can no longer be neglected[3], because the approximate dielectric constant of the system is as high as 3.5. So equation (10-15) would apply:—

$$1/\bar{P} = \left\{ k_{tm}/k_p + (k_t/k_p + ak_{ts}/k_p)1/[M] \right\} + (k_r/k_p - bk_{ts}/k_p)\,[r]/[M] \qquad (10\text{-}15)$$

Plotting $1/\bar{P}$ against [r]/[M], the slope gave $(k_r/k_p - bk_{ts}/k_p)$ as 8.8×10^{-2}, and the intercept gave $\left\{ k_{tm}/k_p + (k_t/k_p + ak_{ts}/k_p) \right\} 1/[M]$ as 6.5×10^{-2}. a and b have the same meanings as in 3.2.1. To calculate k_r/k_p from these values the following algebraic treatment

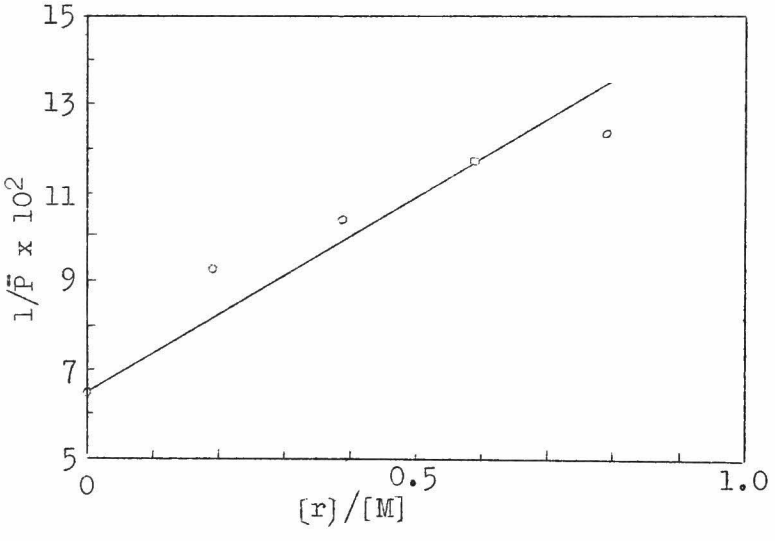


Fig. 10-6 The plot of $1/\bar{P}$ versus [r]/[M]
o-chlorostyrene—benzene—toluene—30°C—
$SnCl_4 \cdot CCl_3COOH$ $k_r/k_p = 9.46 \times 10^{-2}$
$k_{ts}/k_p = 5.55 \times 10^{-3}$

is needed. In Chapter 4, k_{tm}/k_p and $(k_{ts}/k_p + k_t/k_p \cdot 1/[M])$ were found to be 4.80×10^{-2} and 0.72×10^{-2} respectively for polymerization of o-chlorostyrene at 30°C by stannic chloride—trichloroacetic acid in monomer 12 ml. plus benzene 18 ml. It can be safely assumed that the mechanism of each elementary reaction is not seriously affected by change of solvent from benzene to benzene—toluene. This was true for the k_{tm}/k_p of p-chlorostyrene and it can be expected to hold for k_{ts}/k_p and k_t/k_p of o-chlorostyrene. Then, k_r/k_p is calculated using the rate constants obtained in Fig. 10-6, and those obtained in Chapter 4. k_r/k_p, k_{ts}/k_p and k_t/k_p thus calculated are 9.46×10^{-2}, 5.55×10^{-3} and 1.05×10^{-2}, respectively.

3.2.3 Termination and transfer constant ratios for styrene

k_r/k_p of styrene was previously found, in Chapter 4, to be 2.80×10^{-3}, and can be used here. Though the value employed is smaller than that obtained in polymerization by stannic chloride (without trichloroacetic acid) (1.10×10^{-2}), it may be ascribed to the nature of the counter ion.

The chain transfer constant ratios to benzene (k_{ts}/k_p) and toluene (k_r/k_p) for these three monomers are listed

in Table 10-5.

Table 10-5 The rate constant ratios

Rate constant ratios	DC* of the system	o-Chloro-styrene	p-Chloro-styrene	Styrene
$k_{ts}/k_p \times 10^3$	2.5	low conversion	1.22	—
(transfer to benzene)	3.5	5.55	—	—
$k_r/k_p \times 10^2$	2.5	low conversion	4.00	0.28
(transfer to toluene)	3.5	9.46	—	—

* Approximate values of dielectric constants of the polymerization systems, assuming that $\bar{\varepsilon} = \Sigma_i v_i \varepsilon_i$, where $\bar{\varepsilon}$ is the approximate value, ε_i is dielectric constant of i th component and v_i is volume fraction of i th component.

3.3 Estimation of the reactivity of growing ion

Estimation of the relative reactivity of the growing ion using the chain transfer constant ratio to toluene, k_r/k_p, listed in Table 3-10, will be described. In the following discussion, suffixes 1 and 2 represent the values for monomer 1 and monomer 2, respectively. If the reactivity of monomer 1 is larger than that of monomer 2 the relative reactivity of growing ion:—

$$k_{r_2}/k_{r_1} = \delta(k_{22}/k_{11}) \geq \delta(r_2/r_1)^{\frac{1}{2}} \qquad (10\text{-}16)$$

where δ is $(k_{r_2}/k_{22})/(k_{r_1}/k_{11})$ and k_{r_2}/k_{22} is the ratio of k_{r_2}, the chain transfer constant to toluene for the growing ion 2, to k_{22}, the propagation constant of monomer 2. k_{r_2}/k_{22} here is equivalent to k_r/k_p in the previous Section. The rate constant ratio k_{r_1}/k_{11} is for monomer 1 and otherwise the symbols are just as for k_{r_2}/k_{22}. Both k_{r_1}/k_{11} and k_{r_2}/k_{22} are obtainable experimentally, so δ is determined experimentally. r_1 and r_2 are the monomer reactivity ratio as determined under the same conditions as for determination of k_r/k_p. The lower limit of the reactivity ratio of the growing ions may be found from equation (10-16). However, since the value calculated from equation (10-16) is considered to be closely correlated with the true reactivity ratio of the growing ion, the discussion of reactivity of the growing ion given below is based on values calculated by equation (10-16).

M_1 being the monomer of higher reactivity in equation (10-3), for the pair of styrene (M_1) and p-chlorostyrene (M_2);—

$$(r_2/r_1)^{\frac{1}{2}} = 0.32 - 0.41 \qquad \delta = 14.3$$

$$\therefore\ k_{r_2}/k_{r_1} = 4.6 - 5.9$$

For the pair of styrene (M_1) and o-chlorostyrene (M_2),

$$(r_2/r_1)^{\frac{1}{2}} = 0.47 - 0.65 \qquad \delta = 33.8$$

$$\therefore \quad k_{r_2}/k_{r_1} = 15.9 - 22.0$$

For the pair of o-chlorostyrene (M_1) and p-chloro-styrene (M_2),

$$k_{r_2}/k_{r_1} = 0.21 - 0.37$$

The results of calculation are shown in Table 10-6.

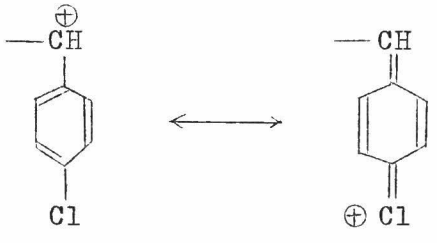
Table 10-6 The comparison of the reactivity of the growing ion

Monomer		Comparison of reactivity		
M_1	M_2	Reactivity of growing ion produced from M_1	:	Reactivity of growing ion produced from M_2
Styrene	p-Chloro-styrene	1	:	4.6 - 5.9
Styrene	o-Chloro styrene	1	:	15.9 - 22.0
o-Chloro-styrene	p-Chloro-styrene	1	:	0.21 - 0.37

4. Discussion

Table 10-4 showed that monomer reactivities in the propagation reaction could be arranged in the decreasing

order: styrene > o-chlorostyrene > p-chlorostyrene, and Table 10-6 that growing ion reactivities in the chain transfer reaction could be arranged in the decreasing order: o-chlorostyrene > p-chlorostyrene > styrene. Then comparing styrene with chlorostyrenes, the latter with less reactivity in the propagation reaction, could give a growing ion of larger reactivity in the transfer reaction, which is what has been found in radical polymerization.[4] This may be ascribed to the inductive effect of the chlorine atom, e.g. in p-chlorostyrene stabilization of the growing ion by contribution of the resonance structure:—



is negligible small,[5] and instead the reactivity of the growing ion is enhanced by the electron deficiency induced by chlorine atom. This would hold good for o-chlorostyrene, too.

On the other hand, o-chlorostyrene, which is more reactive than p-chlorostyrene, was found to give a more

reactive ion, a tendency opposite to that was found in radical polymerization. This may be interpreted in terms of the inductive and steric effects of the o-chloro substituent, that is, in the o-chlorostyrene cation the steric repulsion between the carbonium ion and chlorine atom at ortho-position is large enough to destroy the coplanarity, and hence resonance stabilization, between carbonium ion and phenyl group, and the inductive effect from chlorine atom at ortho-position affects the electron deficiency of the carbonium ion more than from chlorine atom at para-position.

Same experimental results reported by Szwarc[6] are relevant to the ortho effect. He investigated the rate constant of the addition of styrene monomer to several kinds of living ends, consisting of carbanion and sodium cation in tetrahydrofuran at 25°C, and found that the rate constants for addition to α-methylstyrene anion or 1,1-diphenyl ethylene anion were extremely small, and ascribed this to the steric effect of the bulky phenyl and methyl substituents. A similar phenomenon was found for the reaction of the vinyl mesitylene anion.[6] Though there are two ortho-substituents in the vinyl mesitylene anion, the carbanion can enter into resonance

stabilization with the phenyl neucleus. When styrene adds to this anion, the steric repulsion caused by the methyl groups gives the vinyl mesitylene anion an apparently low reactivity.

The writer proposed deviation of the growing end from coplanarity to explain the greater reactivity of o-chlorostyrene cation as compared with the p-chlorostyrene cation, while Szwarc suggested that the ortho-substituent does not destroy the coplanarity but lowers the reactivity of the anion because of steric repulsion between the substituent and the attacking monomer. It is not clear at the present stage how the anomaly can be explained. But it may usefully be mentioned in this connection that the rate of polymerization of o-chlorostyrene is much less than that of p-chlorostyrene, though the reactivity of o-chlorostyrene in copolymerization with styrene is greater than that of p-chlorostyrene. The greater reactivity of o-chlorostyrene in copolymerization is in accordance with the resonance stabilization energy and the localization energy terms in LCAO-MO investigation of the cationic copolymerization.[7] Hence the low rate of polymerization of o-chlorostyrene is considered to be abnormal.

Szwarc[6] found a similar thing in anionic polymeriz-

ation. He carried out anionic polymerizations of o-methylstyrene and p-methylstyrene in tetrahydrofuran at 25°C, using sodium cation as a counter ion, and found that the k_p's (l/mole/sec.) of o-methylstyrene and p-methylstyrene were 127-168 and 166-264 respectively. This suggests, with a high degree of probability, that the rate of polymerization of p-methylstyrene is greater than that of o-methylstyrene under the same conditions. However, in the reaction of these two monomers with living polystyrene, the rate constants for o-methylstyrene and p-methylstyrene were 530 and 180 respectively. Szwarc did not give any explanation of these results, but his experimental facts are very interesting when considered in connection with the present author's results.

The comparisons of growing ion reactivities are, in the present investigation, based on the chain transfer reaction to toluene. If one takes the chain transfer reaction to benzene as the standard, the differences between the growing cation reactivities will be much larger. Hence it is to be expected that the absolute value of the growing ion reactivity will change with the kind of standard reaction chosen, but at the same time it is not to be expected that inversion of relative reactivity will

occur for the chain transfer reaction (to aromatic compound).

To summarize, this investigation made clear the following:—

When the method for determining the reactivity of the growing ion by using a chain transfer reaction to a certain transfer agent (toluene here) was applied to styrene, o- and p-chlorostyrene. Growing ion reactivities were found to be in the decreasing order o-chlorostyrene ≥ p-chlorostyrene > styrene, while that of sequence of monomer reactivities was styrene > o-chlorostyrene > p-chlorostyrene. These experimental facts are interpreted in terms of the steric and electronic effects of the chlorine atom.

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Section 10.3 Styrene Derivatives

1. Introduction

In the previous Section, the reactivities of the growing cations produced from styrene, o- and p-chlorostyrene were compared with one other on the basis of the chain transfer constant ratio for toluene, and the electronic and steric effects of the negative inductive (-I) substituent was discussed.

In the present Section, a similar investigations were carried out for p-methylstyrene, p- and o-methoxystyrene, and the effect of the resonance electron donating (+M) substituent on growing cation reactivity was studied. The effect of catalyst was investigated for boron trifuloride etherate and stannic chloride—trichloroacetic acid, too.

2. Experimental

Purification of the solvents (toluene and chloroform) and catalysts ($SnCl_4$, $BF_3{\cdot}O(C_2H_5)_2$, CCl_3COOH) was described previously. The monomers used were p-methylstyrene, p- and o-methoxystyrene: the syntheses of o- and p-methoxystyrene were described in Chapter 3. p-Methylstyrene was synthesized using Overberger's method.[1] The

physical properties of the monomer are listed in Table 10-7.

Table 10-7 The physical properties of p-methylstyrene

Boiling point	68.5°C (9.5 mm) 82-83°C (27 mm)	obs. lit.
Refractive index	$n_D^{21} = 1.5412$ $n_D^{25} = 1.5395$	obs. lit.
Specific gravity	$d^{30} = 0.891$	obs.

The polymerization and the copolymerization procedures were just the same as described in the previous Section.

The polymer molecular weight was calculated from the intrinsic viscosity—molecular weight equation. For polystyrene Pepper's equation (4-3)[2] was used, while for poly-o- and p-methoxystyrenes equations (3-1) and (3-2) were used. No equation has been reported for poly-p-methylstyrene, but since the intrinsic viscosity—degree of polymerization relationships reported for various kinds of polystyrene derivatives are almost independent of the kind of substituent in the phenyl group[3], Pepper's

equation was used for poly-p-methylstyrene, too.

3. Results

3.1 Comparison of monomer reactivities by the copolymerization method

As stated previously, the monomer reactivity ratio must be known in order to discuss the reactivity of monomer or the reactivity of growing ion.

Copolymerizations of p-methoxystyrene (M_1) and o-methoxystyrene (M_2) were carried out in chloroform, using boron trifluoride etherate catalyst, at 30°, -20°, and -78°C, and the monomer reactivity ratios (r_1, r_2) were determined. The composition of the copolymer was found from the ratio of the optical densities of the absorptions at 825 cm^{-1} (p-substituted benzene) and 2800 cm^{-1} appearing in the infrared spectra measured in 5% carbon disulfide solution. Assuming that copolymer and the mixed polymers behave similarly in infrared spectroscopy, a calibration graph was obtained using the D-ratios for various mixtures of the separate polymers, as shown in Fig. 10-7, and this enabled the copolymer composition to be determined. Results where copolymerization is performed at -78°C are shown in Fig. 10-8.

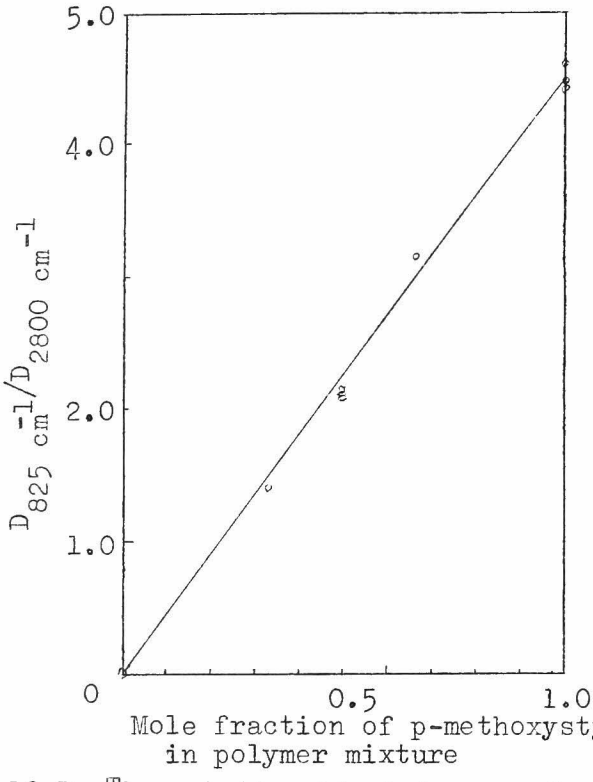


Fig. 10-7 The relationship between mole fraction of p-methoxystyrene and $D_{825\ cm^{-1}}/D_{2800\ cm^{-1}}$ of infrared spectrum. Mixtures of poly-p-methoxystyrene and poly-o-methoxystyrene

(r_1, r_2) value was determined by the cross-section method as shown in Fig. 10-9.

(r_1, r_2) values for copolymerizations at -20° and 30°C were found in the same way. Copolymerization by stannic chloride—trichloroacetic acid was not carried out.

Copolymerizations of o-methoxystyrene (M_1) and styrene (M_2) were carried out at 30°C using stannic chloride—trichloroacetic acid, and at -20°C by boron

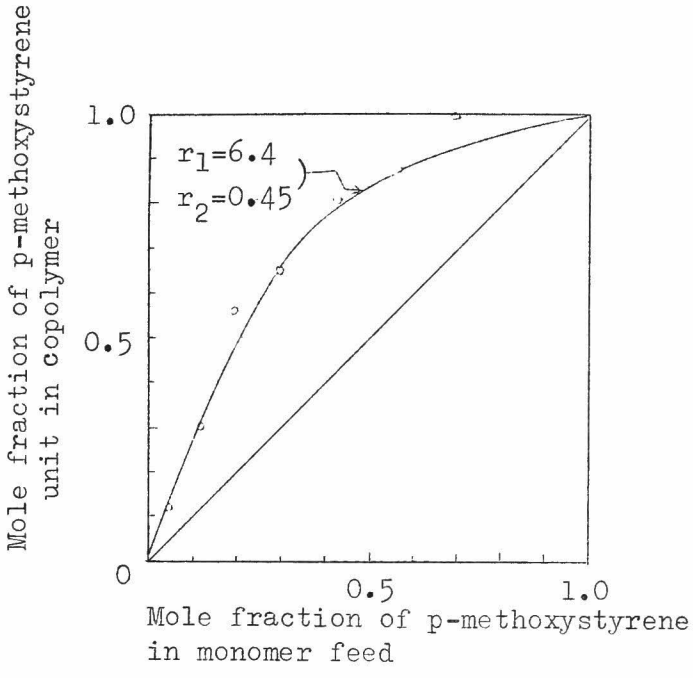


Fig. 10-8 The copolymer composition curve for the copolymerization of p-methoxystyrene (M_1) and o-methoxystyrene (M_2) by $BF_3.O(C_2H_5)_2$ in chloroform at -78°C

trifluoride etherate, the copolymer composition being analyzed by the elementary analysis. The experimental results for the former are shown in Fig. 10-10.

All of the experimental results for the copolymerizations are given in Table 10-8, where experimental data on the copolymerization of styrene and chlorostyrenes are shown. It is clear that the product of r_1 and r_2 is nearly equal to unity for these pairs of monomer. If

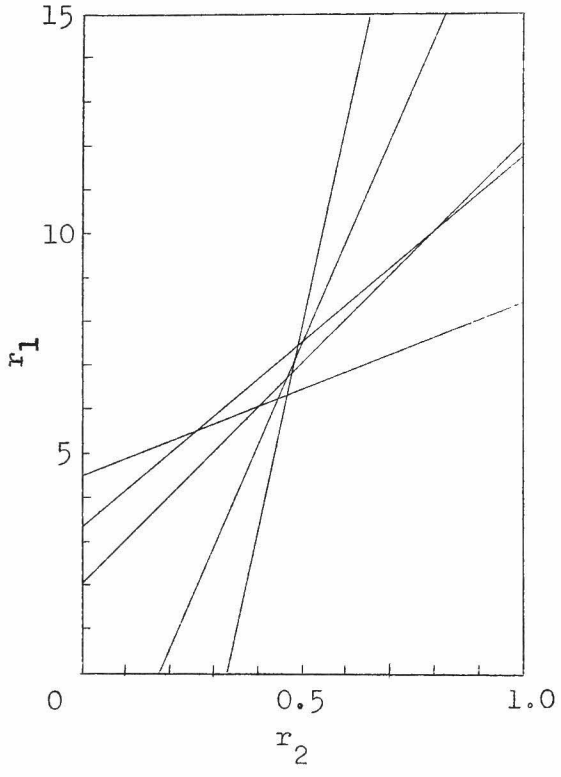


Fig. 10-9 The estimation of r_1 and r_2 by the intersection method. Copolymerization of p-methoxystyrene (M_1)—o-methoxystyrene (M_2) by $BF_3 \cdot O(C_2H_5)_2$ in Chloroform at -78°C

$r_1 = 6.4 \pm 0.4$ $r_2 = 0.45 \pm 0.05$

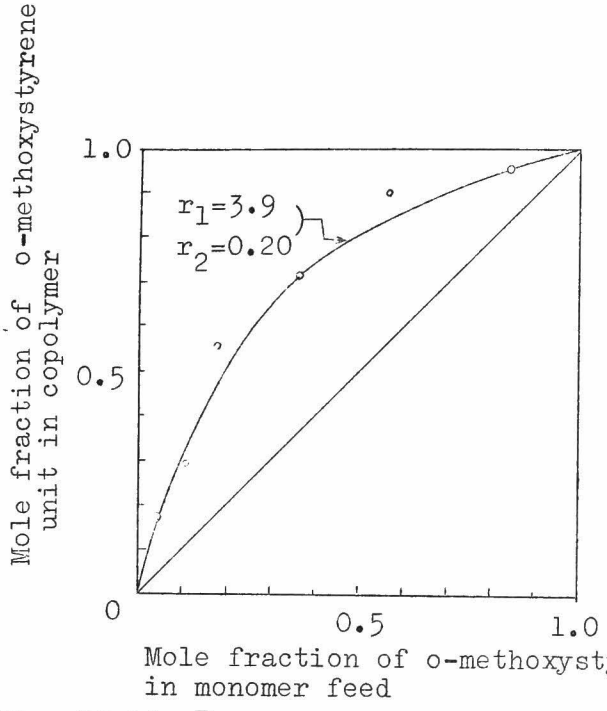


Fig. 10-10 The copolymer composition curve for the copolymerization of o-methoxystyrene (M_1) and styrene (M_2) by $SnCl_4 \cdot CCl_3COOH$ in chloroform at 30°C

$$r_1 = 3.9 \pm 0.7 \qquad r_2 = 0.20 \pm 0.02$$

the propagation rate constants for polymerization of monomer 1 and monomer 2 are taken as k_{p_1} and k_{p_2} respectively, k_{p_1}/k_{p_2} is equal to k_{11}/k_{22} using the symbols for copolymerization. Since (Section 10-1) $k_{11}/k_{22} \simeq (r_1/r_2)^{\frac{1}{2}} k_{p_1}/k_{p_2} = k_{11}/k_{22} \simeq (r_1/r_2)^{\frac{1}{2}}$. As will be shown in later, k_{p_1}/k_{p_2} is necessary for calculating k_{r_1}/k_{r_2} from k_{r_1}/k_{p_2} and k_{r_2}/k_{p_2}, and k_{tm_1}/k_{tm_2} from k_{tm_1}/k_{p_1} and k_{tm_2}/k_{p_2}. k_{p_1}/k_{p_2} values which calculated from $k_{p_1}/k_{p_2} \approx (r_1/r_2)^{\frac{1}{2}}$ are listed in Table 10-8.

Table 10-8 The monomer reactivity ratios in copolymerization and the propagation rate constant ratios

Catalyst	Temp. (°C)	M_1	M_2	r_1	r_2	$k_{p_1}/k_{p_2} \leq (r_1/r_2)^{\frac{1}{2}}$
$SnCl_4$ · CCl_3COOH	30	p-Chlorostyrene	Styrene	0.35±0.05	2.7±0.3	0.32-0.41
		o-Chlorostyrene	Styrene	0.5 ±0.1	1.6±0.2	0.47-0.65
		p-Methylstyrene	Styrene	—	—	1.09-2.27
		o-Methoxystyrene	Styrene	3.9 ±0.7	0.20±0.02	3.81-5.06
$BF_3 \cdot O(C_2H_5)_2$	30	p-Methoxystyrene	o-Methoxystyrene	2.9±0.7	0.35±0.03	2.41-3.36
	-20	o-Methoxystyrene	Styrene	3.6±0.8	0.11±0.04	4.32-7.93
	-20	p-Methoxystyrene	o-Methoxystyrene	3.9±1	0.35±0.09	2.57-4.34
	-78	p-Methoxystyrene	o-Methoxystyrene	6.4±0.4	0.45±0.5	3.46-4.12

As (r_1, r_2) values for p-methylstyrene (M_1)—styrene (M_2) copolymerization have not been obtained, k_{p_1}/k_{p_2} for that system shown in Table 10-8 was calculated by the procedure described below. From the (r_1, r_2) value ($r_1 = 2.5 \pm 0.4$, $r_2 = 0.30 \pm 0.05$)[1] for copolymerization of styrene (M_1) and p-chlorostyrene (M_2) by stannic chloride:—

$$k_{p_2}/k_{p_1} \simeq (r_2/r_1)^{\frac{1}{2}} = 0.29 - 0.41$$

and from the (r_1, r_2) value ($r_1 = 0.22 \pm 0.05$, $r_2 = 4.5 \pm 0.7$)[1] for copolymerization of p-chlorostyrene (M_1) and p-methylstyrene (M_2) by stannic chloride:—

$$k_{p_2}/k_{p_1} \simeq (r_2/r_1)^{\frac{1}{2}} = 3.75 - 5.53$$

hence, for the pair p-methylstyrene (M_1) and styrene (M_2):—

$$k_{p_1}/k_{p_2} = 1.09 - 2.27$$

These two sets of (r_1, r_2) values were determined by Overberger under the same conditions.

Taking the reactivity of styrene monomer as the standard, the relative reactivity of other monomers could be represented by r_1 or $1/r_2$; for a summary see

Table 10-9.

The relative reactivity of p-methylstyrene compared with styrene shown in Table 10-9 was calculated just as when calculating the k_p-ratio for that monomer pair. From the (r_1, r_2)[1] value for copolymerization of styrene (M_1) with p-chlorostyrene (M_2):—

Reactivity of p-chlorostyrene/Reactivity of styrene = 0.30 - 0.40,

and for the (r_1, r_2)[1] value for copolymerization of p-chlorostyrene (M_1) with p-methylstyrene (M_2):—

Reactivity of p-methylstyrene/Reactivity of p-chlorostyrene $\simeq$ 4.5,

hence, for the pair p-methylstyrene—styrene:—

Reactivity of p-methylstyrene/Reactivity of styrene = 1.4 - 1.8

(Reactivity of p-methoxystyrene/Reactivity of styrene) was calculated by multiplying (Reactivity of p-methoxystyrene/Reactivity of o-methoxystyrene) by (Reactivity of o-methoxystyrene/Reactivity of styrene). (Reactivity of p-methoxystyrene/Reactivity of styrene) could be calculated directly from the (r_1, r_2) value (r_1 = 38, r_2 =

Table 10-9 The comparison of the reactivity of monomer

Catalyst	Temp. (°C)	p-Chloro-styrene	o-Chloro-styrene	Styrene	p-Methyl-styrene	o-Methoxy-styrene	p-Methoxy-styrene
$SnCl_4 \cdot CCl_3COOH$	30	0.35-0.37	0.50-0.63	1	1.4-1.8	3.9-5.0	11.3-14.5
$BF_3 \cdot O(C_2H_5)_2$	-20	—	—	1	—	3.6-9.1	10.4-35.5

0.5) for the copolymerization of p-methoxystyrene (M_1) with styrene (M_2) using boron trifluoride etherate at 30°C (see Chapter 3). However, the (r_1, r_2) value for that system was less accurate because of the large difference between the reactivities of two monomers. Hence the reactivity of p-methoxystyrene relative to that of styrene was calculated indirectly with the aid of o-methoxystyrene, which has intermediate reactivity. Copolymerization of p-methoxystyrene and o-methoxystyrene by stannic chloride–trichloroacetic acid was not practically carried out, and the (r_1, r_2) value for this monomer pair with boron trifluoride etherate catalyst was used for calculating the relative monomer reactivity in polymerization with stannic chloride–trichloroacetic acid.

3.2 Determination of the transfer constant ratio

To compare growing ion reactivities the chain transfer constant ratio for a certain transfer agent must be known. The chain transfer constant ratios for toluene in cationic polymerization of styrene derivatives were determined as follows:—

As o- and p-methoxystyrene have almostly the same dielectric constant as chloroform, variation of con-

centration of monomer in toluene will cause change in the dielectric constant of the polymerization solution. To avoid this, the right amount of chloroform was added to the system with decrease in monomer concentration. The polymerization solution comprised toluene 90 vol.% and (monomer plus chloroform) 10 vol.%. Plotting the reciprocal of the degree of polymerization of the resultant polymer against the reciprocal of the monomer concentration, the chain transfer constant ratio for toluene (k_r/k_p) and the monomer transfer constant ratio (k_{tm}/k_p) were determined from the slope and intercept of the straight line, respectively, in accordance with equation (10-17):—

$$1/\bar{P} = k_{tm}/k_p + k_r/k_p \cdot [r] / [M] \qquad (10\text{-}17)$$

where [r] is the concentration of toluene, and the unimolecular termination reaction was neglected. One lot of experimental results is shown in Fig. 10-11.

As both p-methylstyrene and styrene have almostly the same dielectric constant as toluene, the monomer concentration could freely be changed in toluene without affecting dielectric constant of the solution. Plotting in accordance with equation (10-7) the reciprocal of the

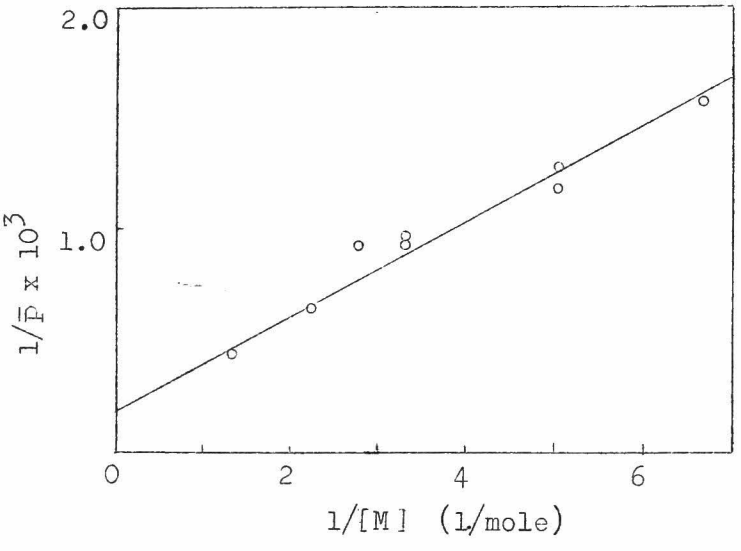


Fig. 10-11 The plot of $1/\bar{P}$ versus $1/[M]$ polymerization of p-methoxystyrene by $SnCl_4.CCl_3COOH$ in toluene at 30°C $k_{tm}/k_p = 1.80 \times 10^{-4}$, $k_r/k_p = 2.50 \times 10^{-5}$

degree of polymerization of the polymer, k_r/k_p and k_{tm}/k_p were derived. Results are shown in Figs. 10-12 and 10-13.

Experimentally-based results for k_r/k_p and k_{tm}/k_p are listed in Table 10-10.

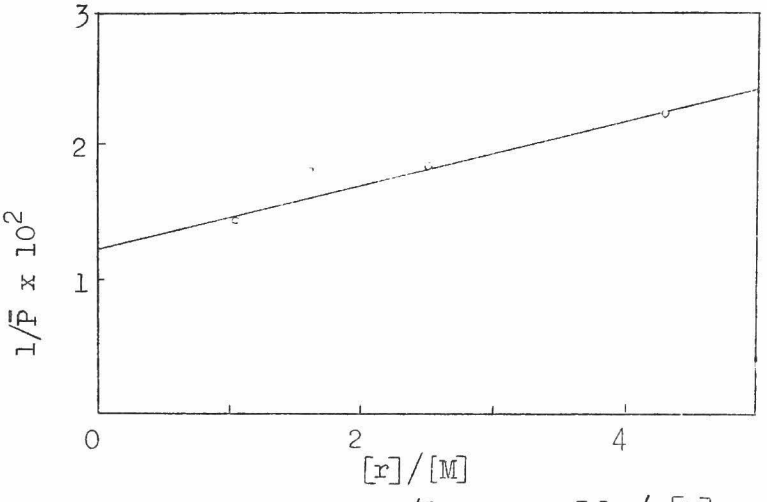


Fig. 10-12 The plot of $1/\bar{P}$ versus [r] / [M]
Polymerization of styrene by $BF_3 \cdot O(C_2H_5)_2$ at toluene at -20°C
$k_{tm}/k_p = 1.22 \times 10^{-2}$, $k_r/k_p = 2.43 \times 10^{-3}$

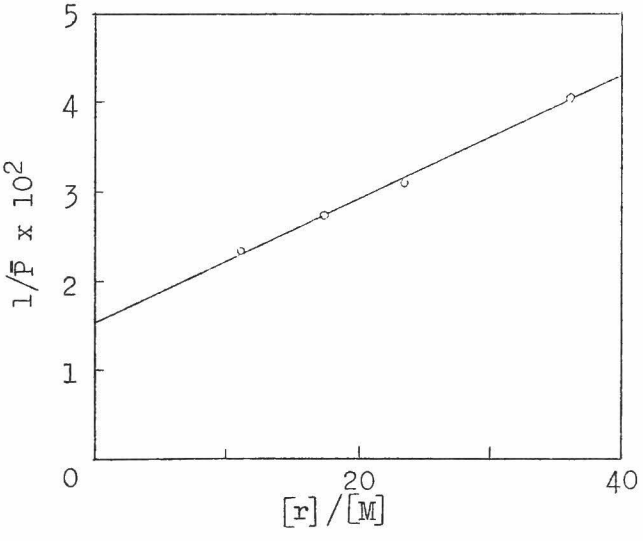


Fig. 10-13 The plot of $1/\bar{P}$ versus [r]/[M]
Polymerization of p-methylstyrene by $SnCl_4 \cdot CCl_3COOH$ in toluene at 30°C.
$k_{tm}/k_p = 1.54 \times 10^{-2}$, $k_r/k_p = 6.95 \times 10^{-4}$

Table 10-10 The rate constant ratios

Catalyst	Rate constant ratio	Temp. (°C)	Styrene	p-Methyl-styrene	o-Methoxy-styrene	p-Methoxy-styrene
$SnCl_4$· CCl_3COOH	k_r/k_p	30	2.80×10^{-3}	6.95×10^{-4}	1.10×10^{-4}	2.50×10^{-5}
	k_{tm}/k_p		5.35×10^{-2}	1.54×10^{-2}	9.20×10^{-3}	1.80×10^{-4}
$BF_3\cdot O(C_2H_5)_2$	k_r/k_p	-20	2.43×10^{-3}	—	9.69×10^{-5}	3.36×10^{-6}
	k_{tm}/k_p		1.22×10^{-2}	—	3.60×10^{-3}	0.70×10^{-4}

Table 10-11 The comparison of the reactivity of growing ion

Catalyst	Temp. (°C)	p-Chloro-styrene	o-Chloro-styrene	styrene	p-Methyl-styrene	o-Methoxy-styrene	p-Methoxy-styrene
$SnCl_4\cdot CCl_3COOH$	30	4.6-5.9	15.9-22.0	1	0.27-0.56	0.15-0.20	0.082-0.15
$BF_3\cdot O(C_2H_5)_2$	-20	—	—	1	—	0.17-0.32	0.015-0.047

3.3 Comparison of growing ion reactivities and of monomer transfer constants

The relative reactivity of growing ion in the transfer reaction (R_I') was calculated using equation (10-13), the results being shown in Table 10-11.

There the relative reactivity of the p-methoxystyrene cation was calculated with the aid of o-methoxystyrene as in Table 10-8, that is, the k_p-ratio, calculated as follows:—

$$k_p \text{ p-methoxystyrene}/k_p \text{ styrene}$$
$$=(k_p \text{ p-methoxystyrene}/k_p \text{ o-methoxystyrene}) \times (k_p \text{ o-methoxystyrene}/k_p \text{ styrene})$$

was introduced into equation (10-11). Also, in the case of polymerization by stannic chloride—trichloroacetic acid, the (k_p p-methoxystyrene/k_p o-methoxystyrene) value for boron trifluoride etherate polymerization was used.

The relative value of k_{tm} was calculated using equation (10-13). The relative reactivity of monomer in the monomer transfer reaction (R_M') was calculated from the k_{tm}-ratio and R_I' in Table 10-10. There it was assumed that equation (10-18) which was assumed for the

propagation reaction (see equation (10-3) also holds in the monomer transfer reaction,

$$k_{tm_{ii}} = k_{I_i}' \cdot R_{M_i}' \qquad (10\text{-}18)$$

For monomers i and j,

$$R_{M_i}'/R_{M_j}' = (k_{tm_{ii}}/k_{tm_{jj}}) \cdot (R_{I_j}'/R_{I_i}') \qquad (10\text{-}19)$$

The results are shown in Table 10-12.

4. Discussion

4.1 Considerations regarding monomer and ion reactivities

It is well known that the introduction of electron donating substituent at the phenyl group of monomer increases the reactivity of monomer in the cationic polymerization. Table 10-9 shows that clearly. The relationship between log R_M and the Hammett substituent constant (σ-value) was studied on p-chlorostyrene, styrene, p-methylstyrene and p-methoxystyrene in Fig. 10-14.

R_M means the reactivity of monomer in the propagation reaction and is the approximate value of (rate constant for the addition of styrene derivative to styrene cation)/(the rate constant for the addition of styrene to

Table 10-12 The comparison of monomer transfer constant

Catalyst	Temp. (°C)		p-Chloro-styrene	o-Chloro-styrene	Styrene	p-Methyl-styrene	o-Methoxy-styrene	p-Methoxy-styrene
$SnCl_4$·	30	Ratio of k_{tm}	0.14-0.8	1.56-2.15	1	0.32-0.65	0.66-0.87	0.031-0.057
CCl_3COOH		Ratio of R_M'	0.03	0.10	1	1.2	4.3	0.38
BF_3·	-20	Ratio of k_{tm}	—	—	1	—	1.27-2.34	0.064-0.20
$O(C_2H_5)_2$		Ratio of R_M'	—	—	1	—	7.2	4.2

styrene cation). In the present investigation, R_M for the polymerization by stannic chloride—trichloroacetic acid was plotted. Okamoto-Brown's σ^+ [4] value was used for the electron withdrawing substituent constant. Tobolsky[5] and Marvel[6] reported that σ^+ value is more suitable to the present purpose than Hammett's σ value. From the slope of the straight line of Fig. 10-14, $\rho = -1.8$ was obtained, which is in close agreement with $\rho = -2.34$ reported by Overberger[1] for the rate constant of the addition of styrene derivative to α-methylstyrene cation, and with $\rho = -1.44$ reported by Marvel[6] for the rate constant of the addition of styrene derivative to 2-chloroethyl vinyl ether cation.

Next, a Hammett plot was made for R_I' determined at 30° C by stannic chloride — trichloroacetic acid. log R_I' — σ^+ plots was made for the same four of monomers as in Fig. 10-14.

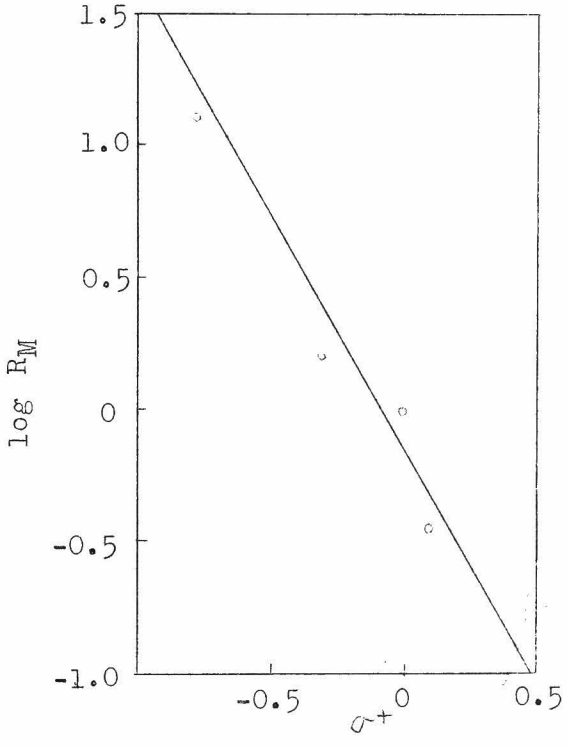


Fig. 10-14 The relationship between log R_M and Okamoto-Brown's σ^+ constant

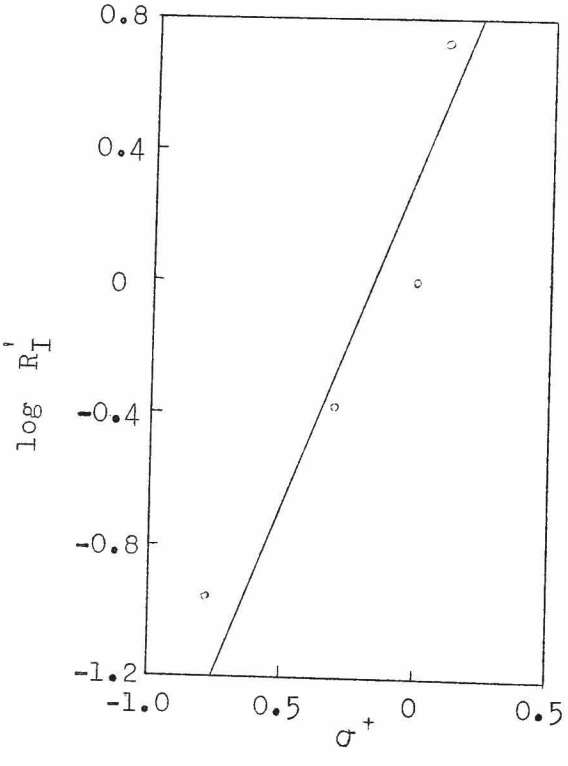
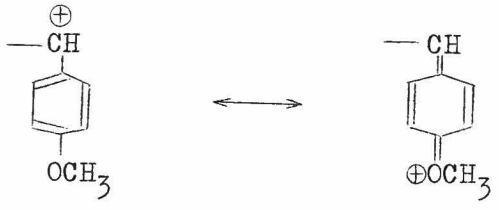


Fig. 10-15 The relationship between log R_I' and O
Okamoto-Brown's σ^+ constant

R_I' means the ratio of (transfer constant of the styrene derivative cation for toluene)/(the transfer constant of the styrene cation for toluene). From Fig. 10-15 ρ = 2.1 was obtained. The sign of ρ was opposite to that in Fig. 10-14, which means that the electron donating substituent decreases the reactivity of the growing ion. In other words, the larger the reactivity of monomer, the smaller the reactivity of growing ion. This confirms that the relationship observed for chlorostyrenes holds also in the styrene derivatives having a resonance electron donating substituent.

On p-substituted styrene the reactivities of monomer and growing ion are determined mainly by the electronic effect of the substituent. Let us consider o-methoxystyrene, where the large steric effect could be expected, and investigate the correlation with o-chlorostyrene. Even in the monomer having a resonance electron donating methoxy group, the reactivity of growing cation made from the ortho isomer was found to be larger than that from the para isomer, analogously to what obtains with chlorostyrenes. However, the monomer reactivity of the para isomer was found to be larger than that of the ortho isomer, contrarily to what holds for the chlorostyrenes.

In p-methoxystyrene the resonance stabilization due to contribution of structure (II) is supposed to be very large[1], while in o-methoxystyrene that kind of resonance stabilization will be decreased by deviation of the carbonium ion from coplanarity with the phenyl group, leading to larger ortho-isomer reactivity.

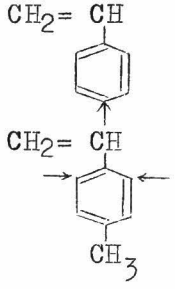


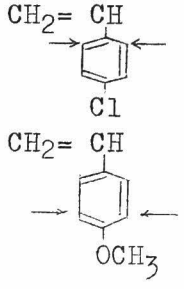
(I) (II)

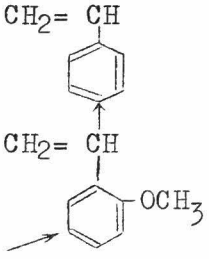
The reason why the effect of o-substituent on the reactivity of monomer was opposite for chlorostyrene and methoxystyrene is not at present clear.

4.2 The mechanism of the monomer transfer reaction R_M' will now be discussed. From the experimental results it has been suggested that the phenyl group of a styrene derivative participates the monomer transfer reaction. The reaction site of the monomer transfer reaction was deduced from the electron density calculated by the molecular orbital method for the six kinds of monomers used in this investigation, and is indicated

below by an arrow[7]:—







Since the reaction site is not constant relative to the vinyl group and the σ^+-value for vinyl group is not given, quantitative treatment of R_M' (cf. section 4.1) was not possible.

R_M' for o-methoxystyrene and p-methylstyrene, where the steric effect of the substituent on the reaction site of monomer transfer reaction may be less important, are larger than R_M' for styrene. Furthermore, R_M' for p-methoxystyrene, where the monomer transfer reaction will occur in the neighbourhood of a large substituent, is not so large as would be expected from the R_M value, and is sometimes smaller than R_M' for styrene. These observations suggest a steric effect as well as an electronic effect of substituent on the monomer transfer reaction, and such have also been observed in the chain transfer

reaction for aromatic compounds[8),9)]. The experimental results described here support the view that the monomer transfer reaction takes place at the phenyl group of the monomer.

Since the monomer transfer reaction is a reaction between a carbonium ion and a phenyl group, it is virtually the same reaction as the chain transfer reaction to aromatic compound. So it is worth comparing k_{tm}/k_p, k_r/k_p and k_{ts}/k_p obtained in cationic polymerization of a particular monomer with each other to estimate of the reactivity of the phenyl group of the monomer in an electrophilic substitution reaction. In Table 10-13, k_{tm} was was taken for the standard and k_{r1} and k_{ts} were compared

Table 10-13 The comparison of k_{tm}/k_p, k_r/k_p and k_{ts}/k_p Polymerization by $SnCl_4 \cdot CCl_3COOH$ at 30°C

	k_{tm}/k_r	k_{tm}/k_{ts}
Styrene	19.1	—
p-Methylstyrene	22.2	—
o-Methoxystyrene	83.6	—
p-Methoxystyrene	7.2	—
p-Chlorostyrene	0.59	19.3
o-Chlorostyrene	0.51	8.6

k_{tm} : chain transfer constant to monomer
k_r : chain transfer constant to toluene
k_{ts} : chain transfer constant to benzene

with k_{tm}. It was clear that the phenyl group of a monomer with chlorine substituent is less nucleophilic than toluene, and that the phenyl group of monomer with electron donating substituent is more reactive than toluene, and that the p-methoxy group has some steric effect in the monomer transfer reaction. These kinds of electronic and steric effects of the substituent are in good agreement with those expected from the mechanism of monomer transfer reaction proposed in Chapters 3 and 4.

To sum up the following could be concluded from the present investigation:—

Styrene derivatives having a resonance electron donating substituent, viz. p-methylstyrene, o-methoxystyrene and p-methoxystyrene, were polymerized by stannic chloride—trichloroacetic acid at 30°C, and the effects of substituent on the reactivities of the monomer and growing ion were investigated. Using in addition experimental results for chlorostyrenes, log R_M-σ^+ and log R_I'—σ^+ plots were constructed for the three kinds of p-substituted styrenes and for styrene itself, leading to ρ = - 1.8 and 2.1, respectively. It can be concluded that increase of electron donation by the

substituent increases the reactivity of monomer but decreases that of growing ion.

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Chapter 11 The Cross-transfer Reaction in the Copolymerization

Section 11.1 Lowering of Degree of Polymerization of Copolymer

1. Introduction

It has generally been recognized that in cationic polymerization the degree of polymerization of a copolymer is very much lower than those of the homopolymers used. Imoto,[1] Medvedev,[2] Sigwalt[3] and Abkin[4] reported on this, but the reason for the lowering is not clear. In this laboratory, copolymerization of isobutene with sytrene or α-methylstyrene has been investigated, the degree of polymerization of the copolymer studied kinetically, and the lowering of the degree of polymerization of the copolymer was explained kinetically by introducing the idea of cross-transfer reactions from cation 1 to monomer 2 (equation (11-4))and from cation 2 to monomer 1 (equation (11-5))[5]. In this kinetic scheme the degree of polymerization of the copolymer ($\bar{P}$) was given by equation (11-7) allowing for the transfer and termination reactions (equations (11-1)-(11-6)).

Termination $P_1^{\oplus} \longrightarrow$ stabilization k_{t_1}' (11-1)

$P_2^{\oplus} \longrightarrow$ stabilization k_{t_2}' (11-2)

Transfer $P_1^{\oplus} + M_1 \longrightarrow P_1 + M_1^{\oplus}$ $k_{tm_{11}}$ (11-3)

$P_1^{\oplus} + M_2 \longrightarrow P_1 + M_2^{\oplus}$ $k_{tm_{12}}$ (11-4)

$P_2^{\oplus} + M_1 \longrightarrow P_2 + M_1^{\oplus}$ $k_{tm_{21}}$ (11-5)

$P_2^{\oplus} + M_2 \longrightarrow P_2 + M_2^{\oplus}$ $k_{tm_{22}}$ (11-6)

$$\bar{P} = \frac{r_1[M_1]^2 + 2[M_1][M_2] + r_2[M_2]^2}{\frac{k_{t_1}' + k_{tm_{11}}[M_1]}{k_{p_{11}}} r_1[M_1] + \left(\frac{k_{tm_{12}}}{k_{p_{12}}} + \frac{k_{tm_{21}}}{k_{p_{21}}}\right)[M_1][M_2] + \frac{k_{t_2}' + k_{tm_{22}}[M_2]}{k_{p_{22}}} r_2[M_2]} \qquad (11\text{-}7)$$

Calling $(k_{tm_{12}}/k_{p_{12}} + k_{tm_{21}}/k_{p_{21}})$ in equation (11-7) A, A explains the cross-transfer reaction term, and depends on the polymerization conditions. The value of A determines the degree of lowering of the degree of polymerization of the copolymer.

A few experimental values for A have been reported,[5] but it is quantity which has been little discussed. In

the present investigation A was found for several copolymerization systems, and using the information about monomer transfer reaction obtained in Part 2 a substantial study was made of the reaction leading to low molecular weight copolymer.

2. Experimental

2.1 The polymerization procedure and the reagent

Copolymerizations of styrene and α-methylstyrene were carried out using titanium tetrachloride—trichloroacetic acid as the catalyst at -78°C in toluene and in methylene chloride. The polymerization procedure and the purification of reagents were previously described.

Of the monomer reactivity ratios (r_1, r_2) in the copolymerization of isobutene with styrene and isobutene with α-methylstyrene, some were obtained in the present investigation and others have been reported from this laboratory. Though these monomer reactivity ratios were determined for copolymerization by titanium tetrachloride (co-catalyst possibly water), the effect of co-catalyst on monomer reactivity ratio is considered to be small.

Commercial methanol for the Karl-Fischer apparatus (Mitsubishi Chemical Co., water content 2 mg/ml. was used

as chain transfer agent.

2.2 Determination of the molecular weight of copolymer and of copolymer composition

For three kinds of homopolymers produced here, the intrinsic viscosity—molecular weight equations are reported. However no equations are reported for copolymers of many compositions. Rehner[6] found that the intrinsic viscosity—molecular weight equations for toluene solutions of polyisobutene and polystyrene were very similar, and considered that when the molecular weight of ibobutene—styrene copolymer is calculated from an equation for a homopolymer, the error will not exceed 10 %. In accordance with view, molecular weights for copolymer were calculated from the intrinsic viscosity at 30°C in toluene, (which is a good solvent common for all three homopolymers) using equations (11-8), (11-9), and (11-10):—

Polystyrene[7] $[\eta] = 1.22 \times 10^{-4} \times \bar{M}_n^{0.70}$ (11-8)

Polyisobutene[8] $[\eta] = 2.0 \times 10^{-4} \times \bar{M}_n^{0.67}$ (11-9)

Poly-α-methylstyrene[9] $[\eta] = 1.92 \times 10^{-4} \times \bar{M}^{0.66}$ (11-10)

For example, the molecular weights of isobutene—

styrene copolymers were calculated as the algebraic mean of molecular weights found by equations (11-8) and (11-9) from the intrinsic viscosity of copolymer at 30°C in toluene. The degree of polymerization of copolymer was calculated from the molecular weight of the latter and the hypothetical molecular weight of the hypothetical monomer, which depended on the copolymer composition.

The composition of styrene—α-methylstyrene copolymer was determined from the ratio of optical densities of the infrared absorptions at 2986 cm^{-1} and 2850 cm^{-1}, measurements being made in carbon tetrachloride solution.[10)]

3. Results

3.1 The determination of monomer reactivity ratio (r_1, r_2) and A-value in the copolymerization, and the resolution of A into its components

3.1.1 Determination of monomer reactivity ratio

Since copolymerizations of isobutene with styrene[11)] and isobutene with α-methylstyrene[5)] have been carried out elsewhere, copolymerization of styrene and α-methylstyrene was carried out in toluene and in methylene chloride. The copolymer composition curves determined by the method described above are shown in Fig. 11-1. In both solvents,

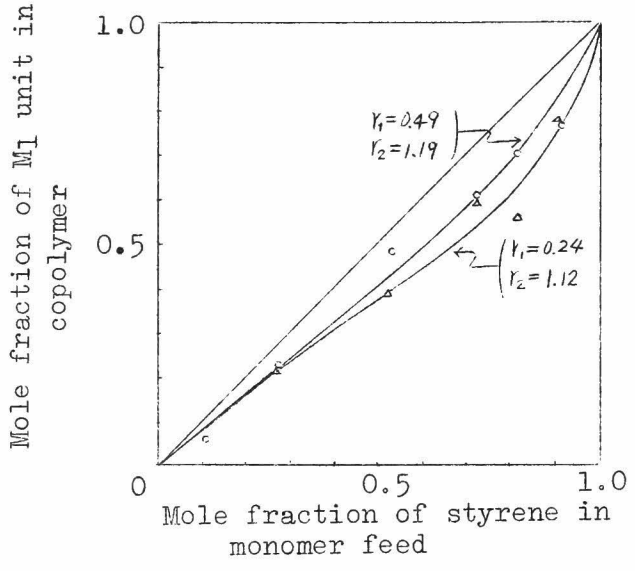


Fig. 11-1 Cationic copolymerization of styrene (M_1) and α-methylstyrene (M_2) at -78°C by $TiCl_4 \cdot CCl_3COOH$
Solvent, (○): toluene (△): methylene chloride

more reactive α-methylstyrene entered into the copolymer composition more than did styrene. Monomer reactivity ratio were determined by the cross-section method; see Fig. 11-1.

3.1.2 Relationship between composition of monomer feed and the degree of polymerization of copolymer

The degrees of polymerization of the copolymers obtained under the various conditions were calculated by the method described in section 2.2, and considered in relation to composition of monomer feed.

Fig. 11-2 a, b shows the relationship between the com-

position of monomer feed and the degree of polymerization of copolymer in the copolymerization of styrene and α-methylstyrene. Figs. 11-3 and 11-4 show for comparison the relationships for isobutene—α-methylstyrene and isobutene—styrene copolymerizations, previously reported.

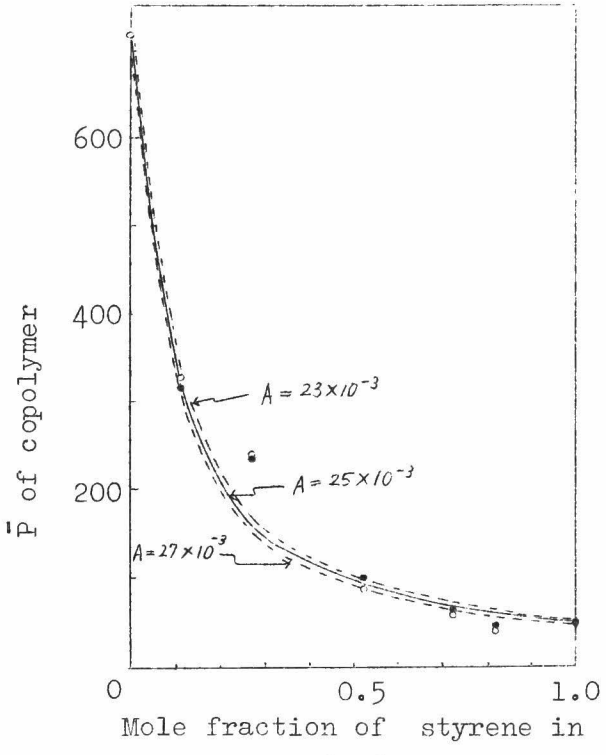


Fig. 11-2a

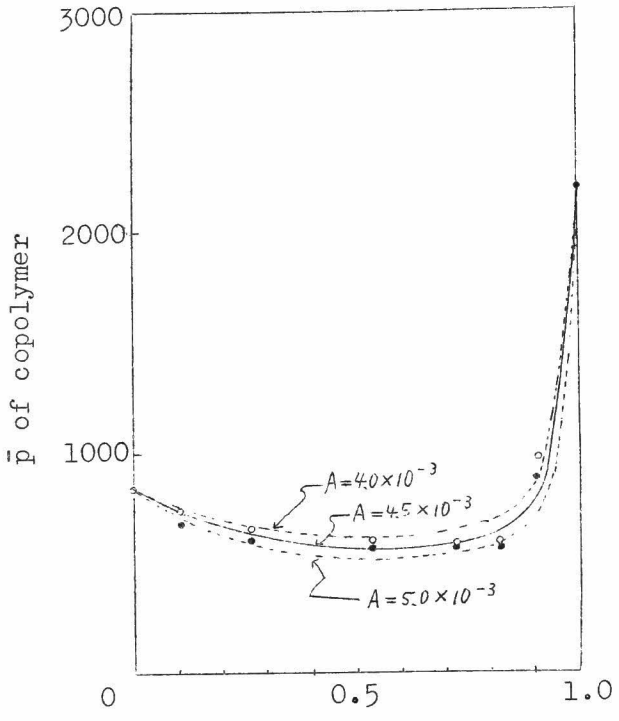


Fig. 11-2b

Fig. 11-2 $\bar{P}$ of copolymers of styrene (M_1) and α-methylstyrene (M_2) as a function of monomer composition. Copolymerization at -78°C by $TiCl_4 \cdot CCl_3COOH$.
a: Copolymerization in toluene
b: Copolymerization in methylene chloride
Curves were calculated from eq.(11-13) and the corresponding A values.
$\bar{P}$ (○ , ●) was determined with using $[\eta]$—molecular weight relationship for poly-α-methylstyrene (○) and for polystyrene (●).

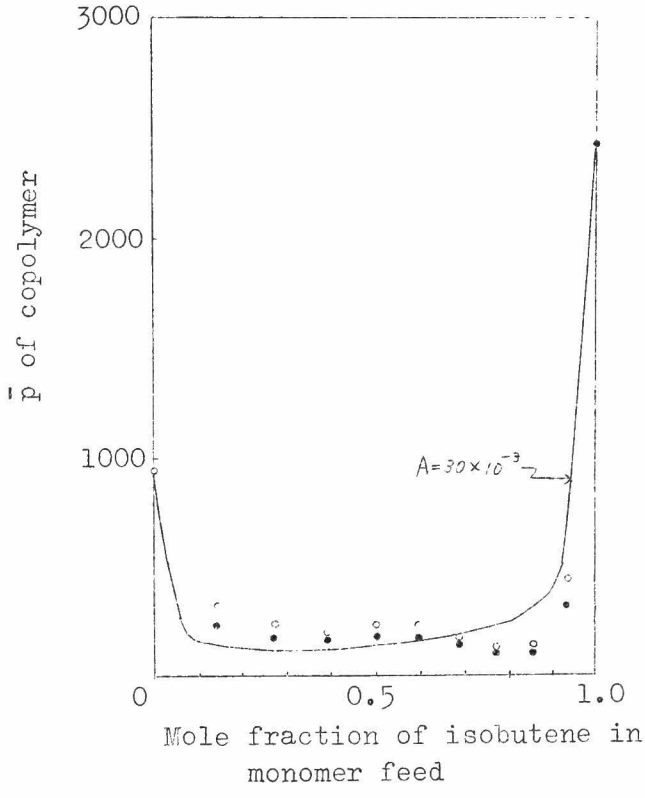


Fig. 11-3 $\bar{P}$ of copolymer of isobutene (M_1) and α-methylstyrene (M_2) as a function of monomer composition.
Copolymerization at -78°C by $TiCl_4$ in methylene chloride.

Curve corresponds to $A = 30 \times 10^{-3}$ (eq. (11-13).
(○)was determined by Eq. (11-10).
(●)was determined by Eq. (11- 9).

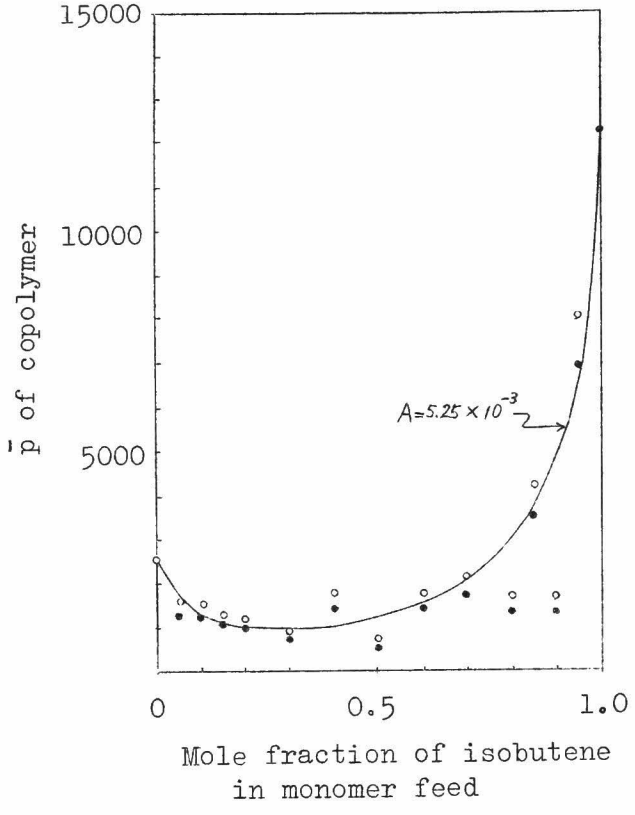


Fig. 11-4 $\bar{P}$ of copolymer of isobutene (M_1) and styrene (M_2) as a function of monomer composition
Copolymerization at -78°C by $TiCl_4$ in methylene chloride
Curve corresponds to $A = 5.25 \times 10^{-3}$ (eq. (11-13).
(○) was determined by Eq. (11-8).
(●) was determined by Eq. (11-9).

Comparing Figs. 11-2 b, 11-3 and 11-4, which relate to copolymerization in methylene chloride, it is clear that the lowering of the degree of polymerization of copolymer is most marked in copolymerization of isobutene with α-methylstyrene.

When calculating the value of A by equation (11-7), some of the monomer transfer reaction, the unimolecular termination reaction and the solvent transfer reaction must as a first approximation be taken to be the reaction determining the degree of polymerization. In the cationic polymerization of isobutene, styrene[12] and α-methylstyrene, the monomer transfer reaction predominates, especially in methylene chloride. If the degree of polymerization of homopolymer is assumed to be controlled by the monomer transfer reaction, equation (11-11) can be deduced:—

$$\bar{P} = \frac{r_1[M_1]^2 + 2[M_1][M_2] + r_2[M_2]^2}{\frac{k_{tm_{11}}}{k_{p_{11}}} r_1[M_1]^2 + A[M_1][M_2] + \frac{k_{tm_{22}}}{k_{p_{22}}} r_2[M_2]^2} \qquad (11\text{-}11)$$

The above assumption implies equation (11-12),

$$\bar{P}_1 = k_{p_{11}}/k_{tm_{11}}, \quad \bar{P}_2 = k_{p_{22}}/k_{tm_{22}} \qquad (11\text{-}12)$$

giving equation (11-13):—

$$\bar{P} = \frac{r_1[M_1]^2 + 2[M_1][M_2] + r_2[M_2]^2}{\frac{r_1}{P_1}[M_1]^2 + A[M_1][M_2] + \frac{r_2}{P_2}[M_2]^2} \qquad (11\text{-}13)$$

r_1, r_2, $\bar{P}_1$ and $\bar{P}_2$ are for a particular copolymerization system. If the concentrations of monomer 1 and 2 and the degree of polymerization of copolymer produced from the monomer feed are known, the value of A can be calculated by equation (11-13) for each monomer feed. Averaging A values over various monomer feeds, the mean value of A for the copolymerization system is obtained. Figs. 11-2, 11-3 and 11-4 show values of A thus calculated and the calculated curve of the degree of polymerization of copolymer corresponding to them. The calculated curve is in close agreement with the observed degree of polymerization of copolymer. Thus, the value of A can satisfactorily explain the lowering of the degree of polymerization of copolymer. In Fig. 2 a and b the accuracies of the values of A are shown.

Monomer reactivity ratios and A values thus obtained are summarized in Table 11-1.

The literature values are also given in Table 11-1. This Table shows that the A value for isobutene—α-methylstyrene copolymerization is essentially large, and this corresponds to the extremely low degree of polymerization of copolymer in that system.

Table 11-1 Monomer reactivity ratio and A.

Monomer pair		Solvent	Monomer reactivity ratio		A x 10^3
M_1	M_2		r_1	r_2	
Isobutene	Styrene	CH_2Cl_2	4.48[11-a)]	1.08[11-a)]	5.29[11-a)]
		$C_6H_5CH_3$	1.78[11-b)]	1.20[11-b)]	(28)*[11-b)]
Isobutene	α-Methylstyrene	CH_2Cl_2	0.3 [5)]	1.7 [5)]	30[5)]
		$C_6H_5CH_3$	1.2 [5)]	5.5 [5)]	90[5)]
Styrene	α-Methylstyrene	CH_2Cl_2	0.24	1.12	4.5
		$C_6H_5CH_3$	0.49	1.19	(2.5)*

* In these polymerization systems, transfer reaction to toluene can not be neglected compared with monomer transfer reaction. Therefore, the reliability of A is low.

3.1.3 Resolution of A

To investigate A value in more detail, it must be solved into its components. For this purpose, the assumption that the rate constant can be expressed as the product of the values of the ion and the monomer reactivities was again made. Applying equation (10-1) to k_p and equation (10-18) to k_{tm}, equation (11-14) is obtained:—

$$\left.\begin{aligned} k_{tm_{12}} &= R_{I_1}' \cdot R_{M_2}' \\ k_{p_{12}} &= R_{I_1} \cdot R_{M_2} \end{aligned}\right\} \qquad (11\text{-}14)$$

where R_I and R_M are reactivity of ion and monomer respectively, the reactivities in the propagation and in transfer reactions are expressed without and with "'" respectively, and the suffix number denotes the kind of ion or monomer.

The transfer constant ratio can be expressed as follows:—

$$\frac{k_{tm_{11}}}{k_{p_{11}}} = \frac{R_{I_1}' \cdot R_{M_1}'}{R_{I_1} \cdot R_{M_1}} = p$$

$$\frac{k_{tm_{22}}}{k_{p_{22}}} = \frac{R_{I_2}' \cdot R_{M_2}'}{R_{I_2} \cdot R_{M_2}} = q \qquad (11\text{-}5)$$

If the degree of polymerization of polymer obtained starting with an initial monomer concentration of 20 vol.% is assumed to be equal to the reciprocal of the monomer transfer constant ($\bar{P} = k_p/k_{tm}$), because the monomer transfer reaction predominates in the cationic polymerization of isobutene, styrene[12], and α-methylstyrene as mentioned previously, p and q are known.

Therefore,

$$p \cdot q = \frac{R_{I_1}'.R_{M_1}'}{R_{I_1}.R_{M_1}} \cdot \frac{R_{I_2}'.R_{M_2}'}{R_{I_2}.R_{M_2}} = \frac{R_{I_1}'.R_{M_2}'}{R_{I_1}.R_{M_2}} \cdot \frac{R_{I_2}'.R_{M_1}'}{R_{I_2}.R_{M_1}}$$

$$= \frac{k_{tm_{12}}}{k_{p_{12}}} \cdot \frac{k_{tm_{21}}}{k_{p_{21}}} \qquad (11\text{-}16)$$

and the product p.q. is known.

If x is taken for $k_{tm_{12}}/k_{p_{12}}$ and y is taken for $k_{tm_{21}}/k_{p_{21}}$

$$x + y = A \qquad x.y = p.q \qquad (11\text{-}17)$$

From the simultaneous equations (11-17), x and y can be

estimated, since A, p and q are known. The results of calculating x and y are shown in Table 11-2.

Since x and y thus obtained are the conjugate root of the simultaneous equation (11-17), it is not known whether it is x or y which corresponds to $k_{tm_{12}}/k_{p_{12}}$. In Table 11-2, it was assumed that the larger was as x, and that the relative value of x and y did not change with variation in solvent dielectric constant.

The Table showed that the x/y ratio was very much greater than unity, and that though A was apparently determined by two components, it was in practice controlled by one of the two.

When x and y are investigated in greater detail, it is found that the predominant rate constant ratio x decreases with increasing solvent dielectric constant in copolymerization of isobutene with styrene or α-methylstyrene, and that y behaves oppositely. This means that the behavior of x corresponds to the styrene-type of monomer transfer reaction (in the cationic polymerization of styrene and its derivative, the monomer transfer constant ratio becomes smaller, the more polar the solvent), and that in copolymerizations of the above monomer-pairs the isobutene cation attacks the styrene or α-methylstyrene to bring

Table 11-2 Resolution of A into its components

Monomer pair	Isobutene—styrene		Isobutene—α-methylstyrene		Styrene—α-methylstyrene
Solvent	CH_2Cl_2	$C_6H_5CH_3$	CH_2Cl_2	$C_6H_5CH_3$	CH_2Cl_2
$x \times 10^3$	5.25	27.95	30	90	4.38
$y \times 10^3$	0.0015	0.055	0.013	0.001	0.12
x/y	3500	500	2300	90000	27.5

about a cross-transfer reaction leading to a large A value and an extremely low degree of polymerization of copolymer.

3.2 The estimation of the reactivity of growing ion in the transfer reaction

As the monomer transfer constant k_{tm} was considered to depend on the reactivities of the ion and monomer in the transfer reaction, these reactivities must be determined in order to clarify the mechanism of the cross-transfer reaction. In section 3.2, the reactivities of isobutene cation, styrene cation, and α-methylstyrene cation in the transfer reaction will be estimated.

3.2.1 The method

The method of the determining the reactivity of a growing ion was previously given in Section 10.1. Firstly, the chain transfer constant ratios of cation 1 (k_{r_1}/k_{p_1}) and cation 2 (k_{r_2}/k_{p_2}) towards a certain transfer reagent are determined. Secondly, the copolymerization of monomer 1 and monomer 2 is carried out to obtain (r_1, r_2) values under the same condition as for the determination of k_r/k_p, and the k_p-ratio is given by the relation $(r_1/r_2)^{\frac{1}{2}} \simeq k_{p_1}/k_{p_2}$. Thirdly, the relative ion reactivity δ, which is assumed to be equal to k_{r_1}/k_{r_2}, is calculated from equation (11-18).

$$\delta \equiv \frac{k_{r_1}}{k_{r_2}} \simeq \frac{k_{r_1}}{k_{p_1}} \cdot \frac{k_{p_2}}{k_{r_2}} \cdot (r_1/r_2)^{\frac{1}{2}} \qquad (11\text{-}18)$$

Methanol was used as the chain transfer agent, and the chain transfer constant ratio for it (k_r/k_p) was obtained from equation (11-19);—

$$1/\bar{P} = 1/\bar{P}_o + k_r/k_p \cdot [r]/[M] \qquad (11\text{-}19)$$

where $\bar{P}$ and $\bar{P}_o$ are the degree of polymerization of polymer produced in the presence or absence of methanol respectively, polymerization conditions otherwise being kept constant, and [r] is the concentration of methanol. In this investigation very small amounts of methanol were used. To avoid the complication from the co-catalytic action of methanol, an equivalent amount of trichloroacetic acid, a very strong co-catalyst, was complexed with titanium tetrachloride and this catalytic complex added to the polymerization solution containing methanol. To minimize the effect of adventitious water and to sequre reproducible results, each experiment was run at least in duplicate.

3.2.2 The transfer constant ratio to methanol (k_r/k_p)

Polymerizations were run keeping the monomer con-

centration constant (10 vol.%, 1.15 mole/l.) and changing the concentration of methanol. Values of k_r/k_p using equation (11-19) are shown in Figs. 11-5, 11-6, and 11-7. The slope of the straight line gives k_r/k_p, values of the latter being summarized in Table 11-3.

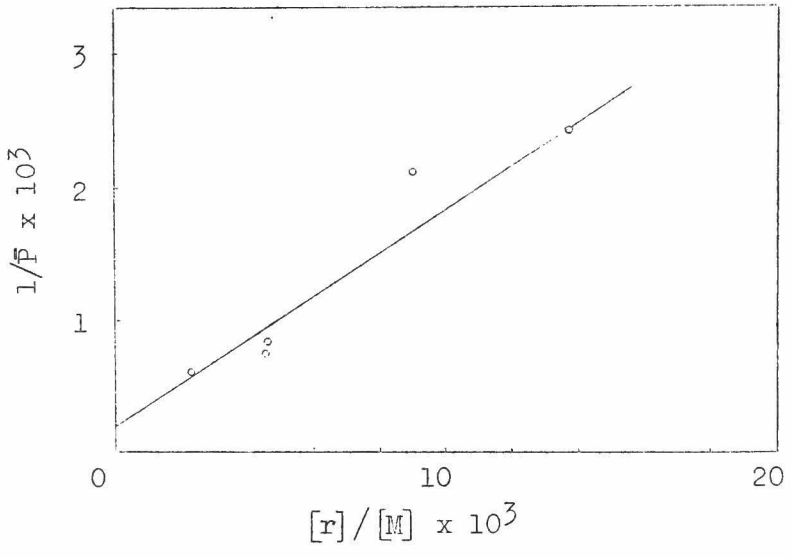


Fig. 11-5 The plot of $1/\bar{P}$ versus [r]/[M]. Polymerization of isobutene in CH_2Cl_2 at -78°C by $TiCl_4 \cdot CCl_3COOH$.
[r] : concentration of methanol
[M] : concentration of isobutene
k_r/k_p = 0.16

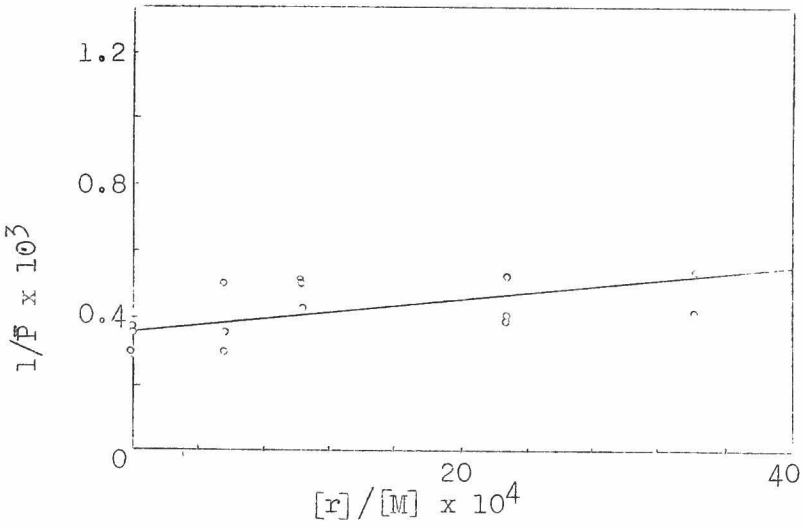


Fig. 11-6 The plot of $1/\bar{P}$ versus [r]/[M]. Polymerization of styrene in CH_2Cl_2 at -78°C by $TiCl_4 \cdot CCl_3COOH$
[r] : concentration of methanol
[M] : concentration of styrene
$k_r/k_p = 0.05$

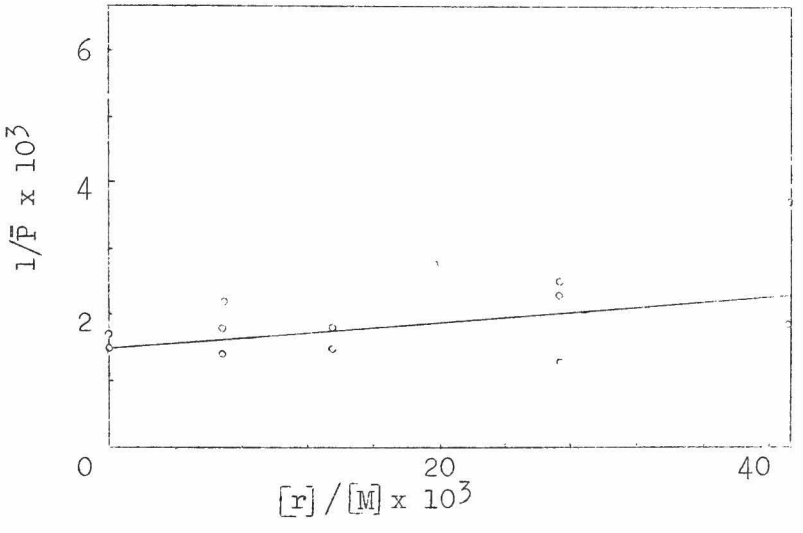


Fig. 11-7 The plot of $1/\bar{P}$ versus [r]/[M]. Polymerization of α-methylstyrene in toluene at -78°C by $TiCl_4 \cdot CCl_3COOH$
[r]: concentration of methanol
[M]: concentration of α-methylstyrene
k_r/k_p : 0.02

Table 11-3 Transfer constant ratio to methanol (k_r/k_p)

Cation		Isobutene	Styrene	α-Methylstyrene
Solvent	CH_2Cl_2	0.16	0.05	0.02
	$C_6H_5 \cdot CH_3$	0.075	—	0.02

3.2.3 The ratio of propagation constants (k_{p_1}/k_{p_2})

The propagation constant ratio can be calculated from (r_1, r_2) value as described in 3.2.1. The results of calculations using the data in Table 11-1 are shown in Table 11-4.

3.2.4 The ratio of the ion reactivities, "δ"

δ is calculated by introducing the data of Tables 11-3 and 11-4 into equation (11-18), and values of it are shown in Table 11-5.

The Table shows that growing ion reactivity can be arranged in a decreasing order isobutene > styrene > α-methylstyrene. Thus, it is evident that the isobutene cation reactivity is high enough to readily bring about a cross-transfer reaction with other monomers.

3.3 Reactivity of monomer in the transfer reaction

Next, the reactivities of these three monomers as

Table 11-4 Ratio of propagation constant (k_{p_1}/k_{p_2})

Ratio of k_p → / Solvent ↓	$\frac{k_p \text{ of isobutene}}{k_p \text{ of styrene}}$	$\frac{k_p \text{ of isobutene}}{k_p \text{ of } \alpha\text{-methylstyrene}}$	$\frac{k_p \text{ of styrene}}{k_p \text{ of } \alpha\text{-methylstyrene}}$
CH_2Cl_2	2.04	0.422	0.463
$C_6H_5 \cdot CH_3$	1.22	0.468	0.642

Table 11-5 Reactivity ratio of growing ion (δ)

$\delta = k_{r_1}/k_{r_2}$ → / Solvent ↓	$\frac{k_r \text{ of isobutene}}{k_r \text{ of styrene}}$	$\frac{k_r \text{ of isobutene}}{k_r \text{ of } \alpha\text{-methylstyrene}}$	$\frac{k_r \text{ of styrene}}{k_r \text{ of } \alpha\text{-methylstyrene}}$
CH_2Cl_2	6.53	3.38	1.16
$C_6H_5 \cdot CH_3$	—	1.76	—

transfer reagents were investigated.

3.3.1 Method

The degree of polymerization of copolymer in copolymerization of monomer 1 and monomer 2 is given by equation (11-13). If very small amount of styrene or α-methylstyrene (M_2) is added to the isobutene polymerization system (M_1), the reciprocal of the degree of polymerization is given by equation (11-20), obtained by modifying equation (11-13):—

$$1/\bar{P} \simeq \frac{\frac{1}{\bar{P}_1} r_1[M_1]^2 + A[M_1][M_2]}{r_1[M_1]^2 + 2[M_1][M_2]} \qquad (11\text{-}20)$$

Dividing both denominator and numerater by $r_1[M_1]^2$ gives equation (11-21):—

$$1/\bar{P} \simeq \frac{\frac{1}{\bar{P}_1} + A[M_2]/r_1[M_1]}{1 + 2[M_2]/r_1[M_1]} \qquad (11\text{-}21)$$

In equation (11-21), $2[M_2]/r_1[M_1]$ is very much smaller than unity, so substituting $(k_{tm_{12}}/k_{p_{12}} + k_{tm_{21}}/k_{p_{21}})$ for A and $k_{p_{11}}/k_{p_{12}}$ for r_1;—

$$1/\bar{P} = 1/\bar{P}_1 + (k_{tm_{12}}/k_{p_{11}} + k_{tm_{21}}/k_{p_{21}} \cdot 1/r_1 - 2/\bar{P}_1 \cdot r_1)[M_2]/[M_1] \quad (11\text{-}22)$$

Putting $(k_{tm_{12}}/k_{p_{11}} + k_{tm_{21}}/k_{p_{21}} \cdot 1/r_1 - 2/\bar{P}_1 \cdot r_1)$ equal to B,

$$1/\bar{P} = 1/\bar{P}_1 + B[M_2]/[M_1] \quad (11\text{-}23)$$

If $1/\bar{P}$ is plotted against $[M_2]/[M_1]$, a straight line will be obtained, the slope of which will give B. Of the components of B, $\bar{P}_1$ and r_1 are known, and $k_{tm_{21}}/k_{p_{11}}$ is obtainable by resolving A. So, $k_{tm_{12}}/k_{p_{11}}$ can be found. $k_{tm_{12}}/k_{p_{11}}$ is the ratio of the constant for the chain transfer reaction from isobutene cation (1) to styrene derivative monomer (2) to the propagation constant for isobutene. By using various kinds of monomer (2), the reactivities of monomers as a chain transfer reagents can be compared.

3.3.2 Determination of B and $k_{tm_{12}}/k_{p_{11}}$

A methylene chloride solution of isobutene (concentration: 1.15 mole/l., 10 vol.%) was polymerized in the presence of very small amounts of styrene and α-methylstyrene (concentration : 7×10^{-3} - 4.4×10^{-2} mole/l.), and the reactivity of the styrene derivative as a transfer agent

was examined. The plots according for equation (11-23) are shown in Figs. 11-8 and 11-9.

The $k_{tm_{12}}/k_{p_{11}}$'s thus obtained are summarized in Table 11-6, where the transfer constant ratios of isobutene cation to toluene and to isobutene monomer are also listed. The Table shows that the reactivities of those four kinds of compounds lie in the decreasing order: α-methylstyrene > styrene > isobutene > toluene. It was thus made clear that the isobutene cation very easily causes a cross-transfer reaction with α-methylstyrene.

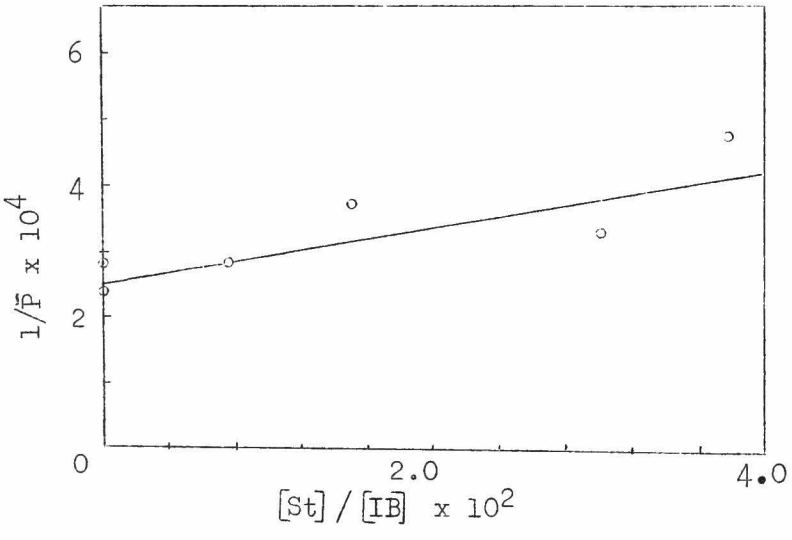


Fig. 11-8 The plot of $1/\bar{P}$ versus [styrene]/[isobutene]. Polymerization of isobutene in the presence of small quantity of styrene in the solution of CH_2Cl_2 at -78°C by $TiCl_4 \cdot CCl_3COOH$
B = 0.42 x 10^{-2}

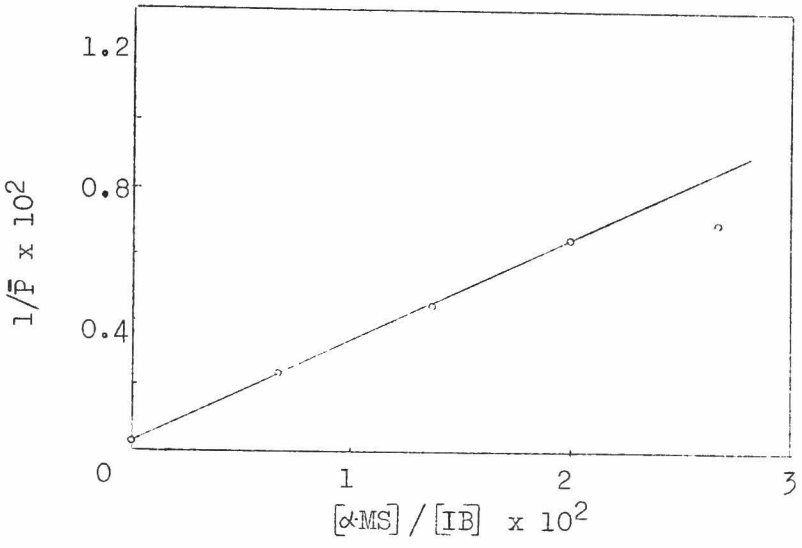


Fig. 11-9 The plot of $1/\bar{P}$ versus [α-methylstyrene]/[isobutene]. Polymerization of isobutene in the presence of small quantity of α-methylstyrene in the solution of CH_2Cl_2 at -78°C by $TiCl_4.CCl_3COOH$

$B = 29.6 \times 10^{-2}$

3.4 Copolymer structure

The infrared spectrum of the low molecular weight copolymer of isobutene and α-methylstyrene was investigated. Fig. 11-10 shows the infrared spectrum of an isobutene—α-methylstyrene copolymer produced at -78°C by titanium tetrachloride—trichloroacetic acid in methylene chloride.

Table 11-6 Estimation of B and $k_{r_{12}}/k_{p_{11}}$ in CH_2Cl_2

Cation $M_1^{\oplus}$	Transfer agent M_2	B x 10^2	$\frac{1}{r_1} \cdot \frac{k_{r_{21}}}{k_{p_{21}}} \times 10^6$	$\frac{1}{r_2} \cdot \frac{2}{\bar{P}_1} \times 10^4$	$\frac{k_{r_{12}}}{k_{p_{11}}} \times 10^2$	$\frac{(k_{r_{12}}/k_{p_{11}}) \text{ of } M_2}{(k_{r_{12}}/k_{p_{11}}) \text{ of toluene}}$
Isobutene	α-Methylstyrene	29.6	43	27.66	29.9	2151
	Styrene	0.42	0.3	0.365	0.42	30.2
	Isobutene	—	—	—	0.0244	1.76
	Toluene	—	—	—	0.0139	1

A weak absorption appears at 825 cm^{-1}, which is not found in polyisobutene of almostly the same degree of polymerization (Fig. 2-4) and is scarcely detectable in poly-α-methylstyrene of almostly the same degree of polymerization

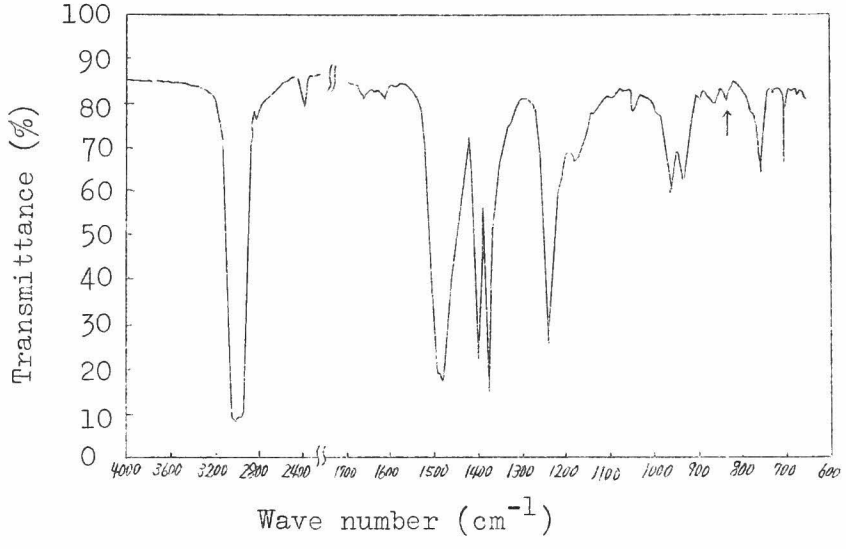
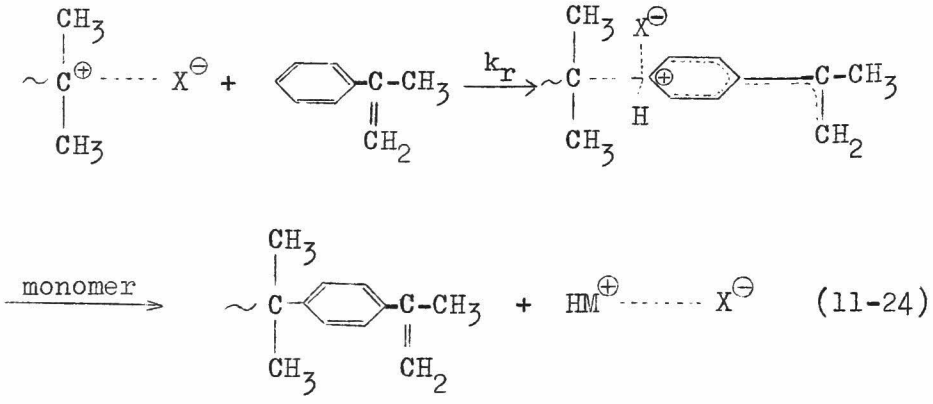


Fig. 11-10 Infrared spectrum of isobutene—α-methylstyrene copolymer obtained in CH_2Cl_2 by $TiCl_4 \cdot CCl_3COOH$ at $-78^{\circ}C$, $\bar{P}_v = 43$

(Fig. 2-5 A). This absorption may be assigned to the p-substituted phenyl group[13], suggesting the cross-transfer reaction of mechanism shown below:—



4. Discussion

The reactivities of growing ion and monomer in the transfer reaction, and copolymer infrared spectrum will here now be discussed.

Firstly, the decreasing order of the reactivity of growing cation: isobutene > styrene ≥ α-methylstyrene is due to the carbonium ion on the styrene cation or α-methylstyrene cation being conjugated with the phenyl group and resonance-stabilized, while with the isobutene cation the carbonium ion is less stabilized by resonance and is unstable. In copolymerization of styrene with α-methylstyrene, the lowering of the degree of polymerization of the copolymer is not so large as when copolymerizing with isobutene as a component (Fig. 11.2 a and b), because the styrene and α-methylstyrene cations are stable. In

section 3.2 the reactivity of growing ion was estimated using the chain transfer constant to methanol. As mentioned in the discussion of Section 10.2, the absolute value of the reactivity of the growing ion will change with change of transfer reagent (the relative order does not change). Refferinc to Section 10.2, the difference between the reactivities of chlorostyrene cations was greater when less reactive benzene was used as a chain transfer agent than when more reactive toluene was employed. On this basis, the difference between the reactivities of growing ions will be reduced when very reactive methanol is used as the chain transfer agent, but nevertheless, the reactivity of isobutene cation was then found to be five times as large as for the styrene and α-methylstyrene cations. Since the cross-transfer reaction is essentially a reaction with the phenyl group, which is less reactive than methanol, the difference between the reactities of isobutene and styrene derivative cations will be enhanced more in the reaction with phenyl.

Secondly, the decreasong order monomer reactivity in the monomer transfer reaction: α-methylstyrene $>$ styrene $>$ isobutene $>$ toluene, will now be discussed. The chain transfer reaction to three kinds of aromatic compounds

other than isobutene takes place at the phenyl group, taking into account the experimental results on the chain transfer reaction of styrene to aromatic compounds[14),15) 16)] and on the monomer transfer reaction of styrene derivative given in Part 2. From the $k_{r_{12}}/k_{p_{11}}$ values of Table 11-6, styrene and α-methylstyrene were more reactive as chain transfer reagent than toluene which is explicable in terms of a larger degree of resonance stabilization in the activated state of monomer transfer reaction with the styrene compounds. It was also found that α-methylstyrene showed larger reactivity in the monomer transfer reaction than styrene, which is explicalbe in terms of a larger contribution of resonance stabilization and the large positive inductive effect (+I) of the α-methyl group of α-methylstyrene. The experimental results stated here support the mechanisms of the cross-transfer (equation (11-18)) and the monomer transfer reactions for styrene compounds proposed in Part 2.

Thirdly, the results of infrared spectroscopy are supporting evidence for the kinetic conclusion about the cross-transfer reaction. In general, the monomer reactivity in the transfer reaction is parallel to that in the propagation reaction, leading to the relationship that a more

reactive monomer in the transfer reaction makes a less reactive cation. Hence in homopolymerization under mild conditions, the low molecular weight polymer which makes the end group analysis by infrared spectroscopy possible is hardly obtainable. However, in copolymerization the reactivities of two monomers are usually different, leading to production of growing ions of different reactivities. Hence, reactive monomer and reactive ion can exist simultaneously in the system, leading to an extremely low molecular weight copolymer, making end group analysis by infrared spectroscopy possible. Practical confirmation of reaction (11-24) was secured. That the A term involving mainly reaction (11-24) becomes smaller with increasing dielectric constant of the polymerization solution, falls well into line with the behavior of the styrene-type monomer transfer reaction related in Part 2.

As mentioned above, in cationic polymerization, especially in copolymerization of isobutene and styrene compounds, the reactive cation and reactive monomer can exist simultaneously. Lowering of the degree of polymerization of copolymer is, therefore, inevitable in cationic popolymerization. However, it can be stated from information obtained about the monomer transfer reaction, that if it is desired

to obtain copolymer having the highest possible molecular weight from a given monomer pair, polymerization must be performed under conditions such that the styrene-type monomer transfer reaction is suppressed, i.e., in a polar solvent and using a weaker catalyst. If one is seeking a monomer giving a copolymer of maximum molecular weight in copolymerization with isobutene for certain polymerization conditions, a monomer which exerts a large steric effect in the styrene-type monomer transfer reaction, e.g. p-methoxystyrene, will be suitable.

To sum up, the following emerged in the present investigation. When cationic copolymerizations of isobutene with α-methylstyrene, of isobutene with styrene, and of styrene with α-methylstyrene catalyzed by titanium tetrachloride—trichloroacetic acid were carried out at -78°C in toluene and methylene chloride, it was found that the degree of polymerization ($\bar{P}$) of the copolymer was usually lower than that of the homopolymer, and that the extent of lowering of $\bar{P}$ lay in the order: copolymer from isobutene—α-methylstyrene > isobutene—styrene > styrene—α-methylstyrene. To clarify these experimental facts, chain transfer constant ratios to methanol for these three growing cations

were determined to estimate their reactivities. They were found to lie in the sequence: isobutene cation > styrene cation > α -methylstyrene cation. Next, the reactivities of four kinds of chain transfer reagents towards isobutene cation were determined, and found to lie in the order: α -methylstyrene > styrene > isobutene > toluene. Thus, the lowering of $\bar{P}$ was shown kinetically to be largest for copolymerization of isobutene with α -methylstyrene. Infrared spectra of α -methylstyrene—isobutene copolymer showed an absorption band at 825 cm^{-1}, attributed to p-substituted benzene produced by reaction between isobutene cation and the phenyl group of α -methylstyrene.

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Section 11.2 The Solvent Effect in Cationic Copolymerization of Isobutene with Styrene in Mixed Solvents

1. Introduction

Since Landler's investigation[1] of ionic copolymerization, it has generally been accepted that the monomer reactivity ratio, r_1 and r_2, for ionic copolymerization for a set of monomers is independent of the polymerization condition, and that in most cases the product of r_1 and r_2 is around unity. However, it has recently been recognized that the above holds only for copolymerization between styrene derivatives,[2] that the monomer reactivity ratio is affected by the polymerization conditions and that $r_1 r_2$ deviates from unity in copolymerizations where two monomers of different structures,[3),4] and hence two ions of different reactivities, participate, or in copolymerization between two monomers with different steric requirement in the activated state.[5]

Overberger et al.[3] reported a change of monomer reactivity ratio depending on the polymerization conditions, in cationic copolymerization of isobutene and p-chloro-

styrene. Variation of monomer reactivity ratio depending on polymerization conditions in cationic copolymerization of isobutene and styrene has been reported from this laboratory.

This Section will describe experimental results for the cationic copolymerization of isobutene and styrene. Copolymerizations were carried out by titanium tetrachloride at -78°C in n-hexane (low dielectric constant), methylene chloride (high dielectric constant) and mixtures of them, and a dependency of monomer reactivity ratio on dielectric constant of solvent was observed. Section 11.1 noted a considerable difference between the stabilities of the isobutene and styrene cations. The experimental facts in the present Section were therefore discussed in terms of difference between the stabilities of isobutene and styrene cations and of effect of the solvent dielectric constant on growing ion stability.

Section 11.1 mentions a cross-transfer reaction between isobutene cation and styrene monomer, and here the effect of the solvent dielectric constant on the cross-transfer reaction will be discussed.

This Section will thus deal with the effect of solvent on the propagation and transfer reactions.

2. Experimental

2.1 Reagent

Purification of isobutene and styrene was described in Chapter 2 and Chapter 4, of n-hexane and methylene chloride in Section 1.1, and of titanium tetrachloride and stannic chloride catalysts in Chapter 2.

2.2 Procedure

Five kinds of solvent were used in the present investigation: 100 %-n-hexane, 75 %-n-hexane—25%-methylene chloride, 50 %-n-hexane—50%-methylene chloride, 25 %-n-hexane—75%-methylene chloride, and 100 %-methylene chloride (all volume percentages). All copolymerizations were effected at -78°C (dry ice—methanol) usually by titanium tetrachloride but sometimes by stannic chloride, adventitious water being regarded as the co-catalyst. The polymerization solution (total volume 50 ml.) comprised one of the above solvents (40 ml.), plus monomer mixture (10 ml.) containing varying ratios of isobutene and styrene.

Solvent and monomers were put in a 100 ml. falsk equipped with a long calcium chloride tube and a catalyst inlet (a syringe). The polymerization solution was cooled to -78°C and the polymerization started by addition

of precooled catalyst solution through the inlet. Polymerization was stopped by adding a large amount of methyl alcohol. Conversion was usually kept below 10 %. Polymer precipitated was repeatedly washed by methyl alcohol and dried in a vacuum at 40°C.

2.3 Determination of copolymer composition

Elementary analysis is not convenient for determining copolymer composition, since the elementary compositions of polystyrene (C % : 92.27) and polyisobutene (C % : 85.63) differ but little. In the present investigation, therefore, infrared spectroscopy was used for copolymer analysis. For this purpose, the calibration curve between optical density of the key band and copolymer composition has to be known, and it was assumed that the mole extinction coefficient of the key band in a copolymer is same as in a mixture of the corresponding homopolymers, though at present this has not been established experimentally. However, the optical densities ratio D_{3061} cm^{-1}/ D_{2923} cm^{-1}, for copolymer prepared at upto 100 % conversion using an initial monomer composition styrene 0.7 mole fraction and isobutene 0.3 mole fraction,

differs only by the experimental error from that of a mixture polystyrene 0.7 mole fraction and polyisobutene 0.3 mole fraction (D_{3061} cm^{-1}/D_{2923} cm^{-1} was 0.289 for the copolymer and 0.293 for the mixture.). This experimental finding suggests that the above assumption is reasonable.

Polyisobutene and polystyrene were prepared under the same conditions as in the copolymerization. A carbon disulfide solution of the mixture of polyisobutene and polystyrene (concentration was 25 g/l. solvent.) was made up for the infrared measurements. The absorption at 3061 cm^{-1}, which appears only in polystyrene and is ascribed to C-H stretching of the phenyl group, and that at 2923 cm^{-1}, which appears both in polystyrene and in polyisobutene and is ascribed to C-H stretching of the methylene group, were found to respectively correlate well with moles of styrene, and moles of styrene plus isobutene of the mixed polymer. Plotting the optical densities ratio, D_{3061} cm^{-1}/D_{2923} cm^{-1}, against mole fraction of styrene in the mixed polymer, the linear relationship shown in Fig. 11-11 was obtained. In the present investigation, copolymer composition was determined from the I.R.

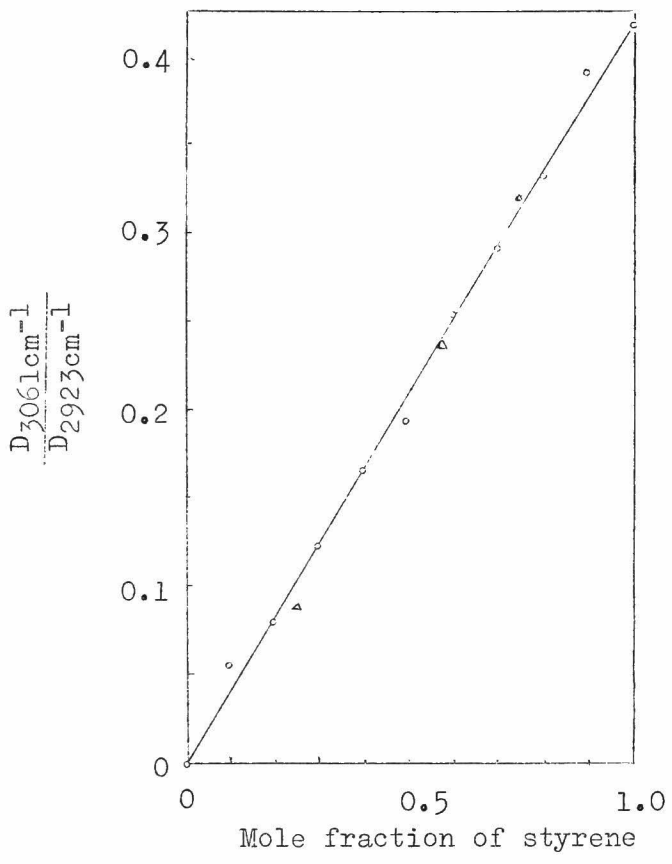

Fig. 11-11 The relationship between styrene-unit mole fraction in the polymer mixture and D_{3061} cm^{-1}/D_{2923} cm^{-1} of infrared spectrum

spectra optical densities ratio of the copolymers using Fig. 11-11. This method is based on the optical densities ratio (not on absolute optical density), affording the advantage that it is not necessary to prepare carbon disulfide solutions of accurately known concentration. The reproducibility obtainable by this

method is shown below:—

Table 11-7 Reproducibility for determining F_1 using infrared spectroscopy

F_1 in first run	0.123	0.175	0.272	0.492	0.830	0.924
F_1 in second run	0.135	0.187	0.314	0.455	0.810	0.939

2.4 Determination of the degree of polymerization of copolymer

The intrinsic viscosity—molecular weight relationship for isobutene—styrene copolymer of various compositions has never been reported. In the present investigation, the molecular weight of the copolymer was calculated from the intrinsic viscosity of the copolymer in toluene solution at 30°C, using equations (11-25) and (11-26), assuming that the copolymer is identical with polyisobutene or polystyrene.

$$[\eta] = 2.0 \times 10^{-4} \times \bar{M}_n^{0.67} \quad \text{for polyisobutene, } 30^\circ\text{C, toluene} \qquad (11\text{-}25)^{6)}$$

$$[\eta] = 1.22 \times 10^{-4} \times \bar{M}_n^{0.70} \quad \text{for polystyrene, } 30^\circ\text{C, toluene} \qquad (11\text{-}26)^{7)}$$

Since the true molecular weight of the copolymer is considered to lie between the molecular weights given by equations (11-25) and (11-26), an algebraic mean of the two was taken as the copolymer molecular weight. The degree of polymerization was calculated from the copolymer molecular weight and composition.

2.5 Measurement of solvent dielectric constant.

Dielectric constants of n-hexane and methylene chloride were obtained from the literature[8]. The dielectric constants of the solvent mixtures were measured in a stainless steel cell which was connected to a circuit comprising a frequency oscillator, a Wheatstone bridge and a multiplier at 1 KC./sec.

3. Results

3.1 Dielectric constant of mixed solvents

Dielectric constants of mixed solvents as measured by the method described in 2.5 are shown in Table 11-8.

3.2 Cationic copolymerization of isobutene and styrene in mixed solvents and determination of r_1 and r_2

Cationic copolymerization of isobutene (M_1) and styrene (M_2) was carried out in five different solvents. The copolymer was analyzed by infrared spectroscopy and the

Table 11-8 Dielectric constant of the polymerization solvent

Solvent composition	$n\text{-}C_6H_{14}$ 100%	$n\text{-}C_6H_{14}$ 75% — CH_2Cl_2 25%
D.C. at -78°C	2.046	3.95

$n\text{-}C_6H_{14}$ 50% — CH_2Cl_2 50%	$n\text{-}C_6H_{14}$ 25% — CH_2Cl_2 75%	CH_2Cl_2 100%
6.53	10.65	14.89

monomer reactivity ratio determined by the cross-section method. Typical experimental results obtained in n-hexane 25%—methylene chloride 75% are shown in Table 11-9, Figs. 11-12 and 11-13.

Monomer reactivity ratios in other solvents were obtained similarly. Copolymer composition curves are shown in Fig. 11-14 and monomer reactivity ratios are listed in Table 11-10.

Some of the copolymers obtained in three kinds of mixed solvent were submitted to elementary analysis and the results found to agree well with those of I.R. spectroscopy.

Table 11-9 Copolymerization in the solvent composed of n-hexane (25%)—methylene chloride (75%)

Run No.	Isobutene (ml.)	Styrene (ml.)	f_1 *	$TiCl_4$ (mg.)	Polym. time (sec.)	Yield (g.)	Conv. (%)	$R_p\left(\frac{\%}{g.\text{-cat.}\cdot sec.}\right)$	$\frac{D_{3061cm^{-1}}}{D_{2923cm^{-1}}}$	F_2 **	F_1 ***
53	0.0	10.0	0.000	30.1	120	3.4827	38.5	10.66	0.417	1.000	0.000
54	0.4	9.6	0.052	"	30	0.3312	3.7	4.10	0.387	0.929	0.071
55	0.8	9.2	0.103	"	37	0.6576	7.4	6.64	0.381	0.914	0.086
56	1.2	8.8	0.152	"	16	0.4159	4.7	9.76	0.369	0.885	0.115
57	1.6	8.4	0.201	"	16	0.5125	5.9	12.25	0.327	0.784	0.216
58	2.5	7.5	0.305	"	21	0.3243	3.9	6.17	0.265	0.635	0.365
59	3.4	6.6	0.404	"	16.5	0.3380	4.1	8.26	0.200	0.480	0.520
60	4.3	5.7	0.499	"	24	0.4241	5.4	7.48	0.149	0.357	0.643
61	5.4	4.6	0.607	"	60	0.1623	2.1	1.16	0.092	0.221	0.779
62	6.4	3.6	0.701	"	38.5	0.4267	5.8	5.00	0.057	0.137	0.863
63	7.5	2.5	0.798	"	120	0.1964	2.8	0.78	0.049	0.118	0.882
64	8.1	1.9	0.849	"	146	0.2073	3.0	0.68	0.048	0.117	0.883
65	8.7	1.3	0.898	"	46	0.1593	2.3	1.66	0.032	0.076	0.924
66	9.4	0.6	0.953	"	40	0.6665	10.1	8.39	0.020	0.048	0.952
67	10.0	0.0	1.000	"	71	0.3931	6.1	2.85	0.000	0.000	1.000

* f_1 = mole fraction of isobutene in monomer feed. ** F_2 = mole fraction of styrene unit in copolymer. *** F_1 = mole fraction of isobutene unit in copolymer.

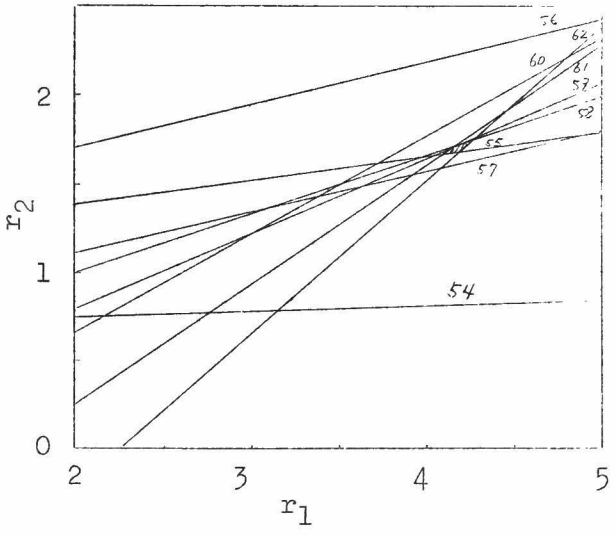

Fig. 11-12 The determination of r_1 and r_2 by the cross-section method, n-hexane 25%—methylene chloride 75%.

$r_1 = 4.11 \pm 0.19$ $r_2 = 1.70 \pm 0.07$

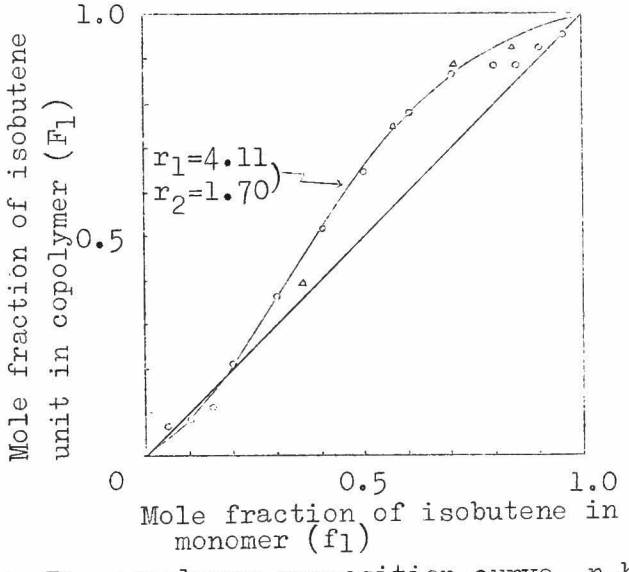

Fig. 11-13 The copolymer composition curve, n-hexane 25%-methylene chloride 75%

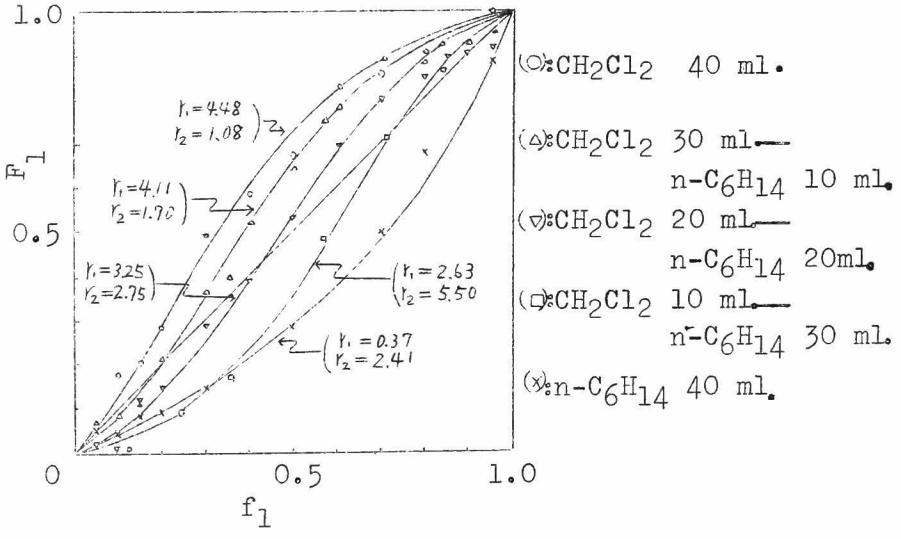

Fig. 11-14 The copolymer composition curves for isobutene (M_1)-styrene (M_2) copolymer obtained in various solvents at -78°C by $TiCl_4$ as catalyst

Table 11-10 The monomer reactivity ratios and the solvent composition

Solvent composition	$n\text{-}C_6H_{14}$ 100%	$n\text{-}C_6H_{14}$ 75% — CH_2Cl_2 25%
r_1	0.37±0.07	2.63 ± 0.52
r_2	2.41±0.12	5.50 ± 0.55

$n\text{-}C_6H_{14}$ 50% — CH_2Cl_2 50%	$n\text{-}C_6H_{14}$ 25% — CH_2Cl_2 75%	CH_2Cl_2 100%
3.25 ± 0.25	4.11 ± 0.19	4.48±0.28
2.75 ± 0.25	1.70 ± 0.07	1.08 ± 0.07

The effect of the nature of the counter ion on monomer reactivity ratio was also investigated. Copolymerizations using stannic chloride as the catalyst were carried out in n-hexane 25%—methylene chloride 75 %. Copolymer analysis as above gave for the monomer reactivity ratio $r_1 = 3.75 \pm 0.45$ $r_2 = 1.92 \pm 0.41$. Fig. 11-15 shows the copolymer composition curve. In Fig. 11-15 also shows for comparison the copolymer composition curve for copolymerization catalyzed by titanium tetrachloride in the same solvent.

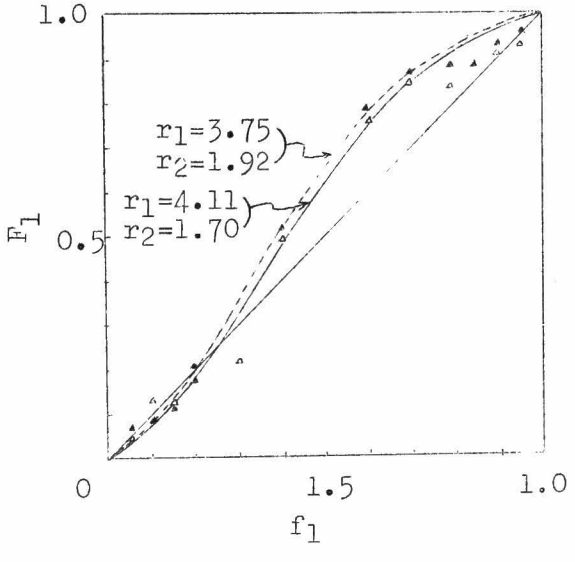

Fig. 11-15 The copolymer composition curve for the copolymerization of isobutene (M_1) and styrene (M_2) by $SnCl_4$ at -78°C

n-hexane 25%--methylene chloride 75%

(▲): $SnCl_4$ (△) : $TiCl_4$

The following points emerged clearly from the experimental results:—

(i) In copolymerization of isobutene and styrene the monomer reactivity ratio varies greatly with solvent and catalyst.

(ii) Isobutene has generally been considered to be more reactive than styrene in cationic polymerization. This obtains for polymerization in methylene chloride, but not in n-hexane.

(iii) In copolymerization in mixed solvents, a growing cation tends to add the same kind of monomer, leading to r_1 and r_2 larger than unity.

(iv) The greater the solvent dielectric constant, the greater the reactivity of isobutene.

(v) Slightly more styrene is incorporated into the copolymer in copolymerization by stannic chloride than in copolymerization by titanium tetrachloride.

3.3 The degree of polymerization of copolymer produced in mixed solvents and the determination of the A value

It was described in Section 11.1 how, in the cationic copolymerization of isobutene and styrene, the degree of polymerization of copolymer is considerably lower than for the corresponding homopolymers under the same conditions

because in the copolymerization system isobutene cation, which is very reactive in the transfer reaction, and styrene monomer, which is very reactive as transfer reagent coexist simultaneously and the cross-transfer reaction from isobutene cation to styrene monomer takes place very readily. The A value, which comprises the cross-transfer constant ratios, was used as a measure of the lowering of copolymer degree of polymerization. The method of calculating the A-value from the degree of polymerization of copolymer was explained in Section 11.1. The degree of polymerization of copolymer ($\bar{P}$) is given by equation (11-27);

$$\bar{P} \simeq \frac{r_1[M_1]^2 + 2[M_1][M_1] + r_2[M_2]^2}{\frac{1}{\bar{P}} r_1[M_1]^2 + A[M_1][M_2] + \frac{1}{\bar{P}} r_2[M_2]^2} \qquad (11\text{-}27)$$

$$A = k_{r_{12}}/k_{p_{12}} + k_{r_{21}}/k_{p_{21}}$$

where $\bar{P}_1$ and $\bar{P}_2$ are respectively the degrees of polymerization of homopolymer from monomers 1 and 2, and $[M_1]$ and $[M_2]$ are monomer concentrations (mole/l.) of monomer 1 and 2, respectively. k_r and k_p are the rate constant of the monomer transfer and the propagation reactions,

respectively. Suffix 12 means a reaction between cation 1 and monomer 2, and suffix 21 means the converse. With r_1, r_2 and $\bar{P}_1$, $\bar{P}_2$ given for a certain copolymerization system, and having determined the degree of copolymerization of copolymers obtained for various values of $[M_1]$ and $[M_2]$, A values can be calculated using equation (11-27).

In order to investigate the effect of solvent polarity on the monomer transfer reaction, A values in five kinds of solvent were calculated. Table 11-11 shows experimental results for n-hexane 50%—methylene chloride 50 %.

Fig. 11-16 shows the copolymer degree of polymerization and the claculated curve corresponding for the A value thus obtained.

A values were determined in other solvents by the same procedure as above, and are shown in Table 11-12.

Table 11-12 A values and the solvent composition

Solvent composition	$n\text{-}C_6H_{14}$ 100%	$n\text{-}C_6H_{14}$ 75%	CH_2Cl_2 25%
A ($\times 10^{-3}$)	25.0	10.2	

$n\text{-}C_6H_{14}$ 50%	CH_2Cl_2 50%	$n\text{-}C_6H_{14}$ 25%	CH_2Cl_2 75%	CH_2Cl_2 100%
6.93		4.48		5.25

Table 11-11 The molecular weight of copolymer and A value, n-hexane 50%—methylene chloride 50%

Run No.	f_1	F_1	$[\eta]$ 30°C, toluene	From eq.(11-25)		From eq.(11-26)		A x 10^4
				M.W.	$\bar{P}$	M.W.	$\bar{P}$	
68	0.000	0.000	0.648	—	—	209200	2009	—
69	0.052	0.021	0.585	148700	1442	180300	1748	78.11
70	0.103	0.012	0.673	183000	1769	221200	2138	—
71	0.152	0.119	0.420	90800	917	112800	1139	83.93
72	0.201	0.149	0.365	73900	751	92700	942	—
73	0.305	0.289	0.315	59400	658	75000	831	96.33
74	0.404	0.389	0.300	55200	646	70000	819	88.50
75	0.499	0.529	0.320	60800	772	76800	975	72.01
76	0.607	0.695	0.345	68000	961	85500	1208	—
77	0.701	0.799	0.408	87000	1323	108800	1655	52.73
78	0.798	0.852	0.476	109000	1724	136000	2151	53.38
79	0.849	0.892	0.522	125000	2039	153000	2496	55.85
80	0.898	0.899	0.583	148000	2428	180000	2953	61.14
81	0.953	0.918	0.754	216500	3606	260000	4330	51.25
82	1.000	1.000	0.953	308500	5499	—	—	—

Averaged value of A = 69.33 x 10^{-4}

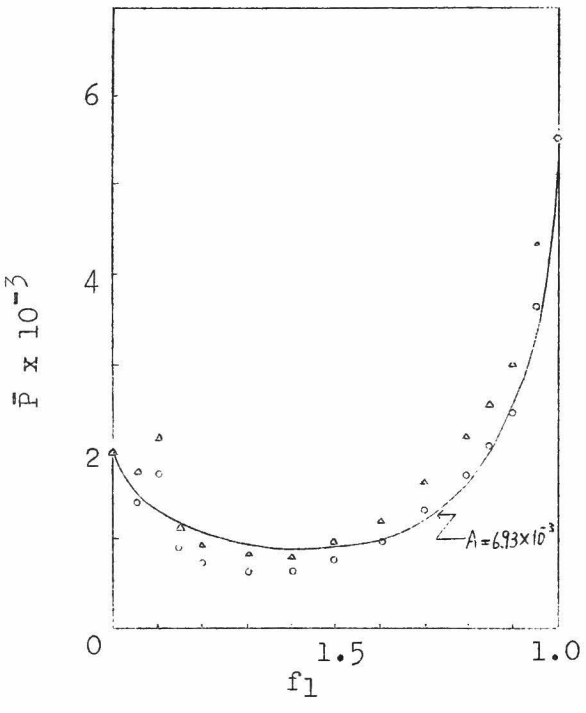

Fig. 11-16 The degree of polymerization of copolymer as a function of f_1

n-hexane 50%—methylene chloride 50%

(○): $\bar{P}$ from eq. (11-25)

(△): $\bar{P}$ from eq. (11-26)

Similarly in investigation of the monomer reactivity ratio, the effect of catalyst on A was studied. In the copolymerization by stannic chloride in the solvent of n-hexane 25%—methylene chloride 75 %, A was found to be 4.53×10^{-3}.

The following points were made clear:—

(i) The more polar the solvent, the less readily the cross-transfer reaction occurs. This is the same trend as in cationic polymerization of styrene.

(ii) The cross-transfer reaction is little affected by changing the catalyst, i.e., whether titanium tetrachloride or stannic chloride.

3.4 The effect of solvent composition on the reactivity of isobutene cation and the determination of B values

As is seen in equation (11-27) A is a combination of two kinds of transfer constant ratios. It is therefore difficult to use A to discuss the cross-transfer reaction, though it provides a good explanation for the lowering of the degree of polymerization of the copolymer. Section 11.1 proposed calculating $k_{r_{12}}/k_{p_{11}}$, the ratio of the chain transfer constant of isobutene cation to styrene to the propagation constant for isobutene, to enable the cross-transfer reaction to be discussed quantitatively. $k_{r_{12}}/k_{p_{11}}$ was determined according from equation (11-28) after calculating the degree of polymerization of polyisobutene obtained in a polymerization system consisting of solvent (45 ml.), isobutene (5 ml.) and a small amount of styrene. Introducing the relationship $[M_2] \ll [M_1]$

into equation (11-27) gives equation (11-28):—

$$\frac{1}{\bar{P}} = \frac{1}{\bar{P}_1} + B \cdot \frac{[M_2]}{[M_1]} \qquad (11\text{-}28)$$

$$B \equiv \frac{k_{r_{12}}}{k_{p_{11}}} + \frac{k_{r_{21}}}{k_{p_{21}}} \cdot \frac{1}{r_1} - \frac{2}{\bar{P}_1 \cdot r_1}$$

where $\bar{P}$ and $\bar{P}_1$ are the degree of polymerization of polyisobutene obtained in polymerization with and without styrene, respectively. Plotting $\bar{P}$ against $[M_2]/[M_1]$, the slope of the straight line gives the B value. As $k_{r_{21}}/k_{p_{11}}$, $\bar{P}_1$ and r_1 are known, $k_{r_{12}}/k_{p_{11}}$ can be calculated from B. Determination of $k_{r_{12}}/k_{p_{11}}$ for polymerization in n-hexane 75%—methylene chloride 25 % will be adduced below by way of example. Fig. 11-17 shows the determination of B.

In this system $\frac{k_{r_{21}}}{k_{p_{21}}} \cdot \frac{1}{r_2}$ and $\frac{2}{\bar{P}_1 \cdot r_1}$ were previously calculated to be 0.05×10^{-4} and 1.41×10^{-4}, respectively. Therefore, $k_{r_{21}}/k_{p_{11}}$ was found to be 2.21×10^{-2}. B values and $k_{r_{12}}/k_{p_{11}}$ were determined in other kinds of solvents, and the resultant values were shown in Table 11-13.

The following points emerged clearly from Table

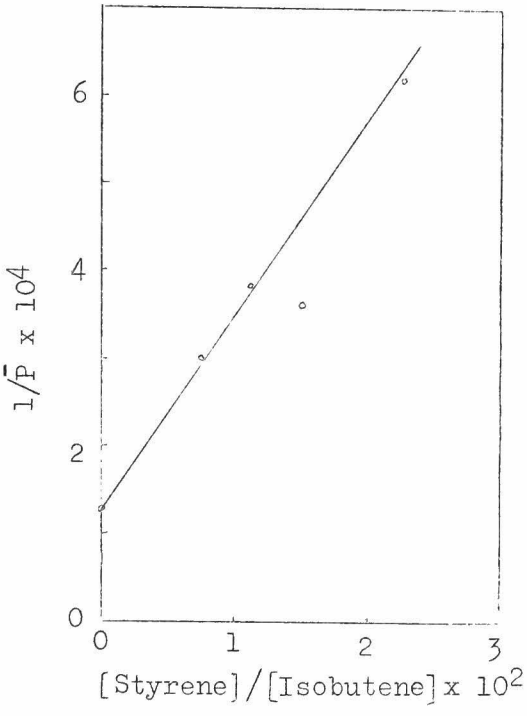

Fig. 11-17 The determination of B value
n-hexane 75%—methylene chloride 25%
$B = 2.2 \times 10^{-2}$

11-13:—

(i) B and $k_{r_{12}}/k_{p_{11}}$ are greatly affected by the nature of solvent.

(ii) $k_{r_{12}}/k_{p_{11}}$ decreases with an increase of solvent polarity, which is what was found for the monomer transfer constant ratio in cationic polymerization of styrene.

Table 11-13 B values, $k_{r_{12}}/k_{p_{11}}$'s and the solvent composition

Solvent composition	$n\text{-}C_6H_{14}$ 100%	$n\text{-}C_6H_{14}$ 75%	CH_2Cl_2 25%	$n\text{-}C_6H_{14}$ 50%	CH_2Cl_2 50%	$n\text{-}C_6H_{14}$ 25%	CH_2Cl_2 75%	CH_2Cl_2 100%
B x 10^3	47.0	22.0		13.4		2.48		4.55
$k_{r_{12}}/k_{p_{11}}$ x10^3	48.0	22.1		13.5		2.57		4.59

It is noticed that the change in A value with change in solvent composition runs pararell to that for $k_{r_{12}}/k_{p_{11}}$. Therefore, the lowering of the degree of polymerization of copolymer can be discussed in terms of the effect of solvent polarity on $k_{r_{12}}/k_{p_{11}}$.

3.5 Extraction of copolymer

As shown in Table 11-10, the monomer reactivity ratios, r_1 and r_2, obtained in the present investigation were mostly larger than unity. This suggests the possibility

that a mixture of the two homopolymers was obtained instead of the true copolymer. In order to elucidate this point, copolymers were subjected to solvent extraction.

The samples for the extraction were prepared by carrying out copolymerizations in five kinds of solvent. The feed monomer composition was controlled to give a copolymer having F_1 about 0.5. Table 11-14 shows this preparation. It is observed that these copolymers contain the isobutene unit, as expected from Fig. 11-14. Since the conversion rose to 100 % in polymerization No.1, the expected F_1 of copolymer No.1 is 0.3 which is same as the monomer composition of the feed.

Copolymer extraction was carried out by the method of Sparks et al.,[9] i.e., the copolymer was extracted by acetone, acetone--methyl ethyl ketone mixture, methyl ethyl ketone, and cyclohexanone in turn, and any final residue was recovered. The fraction of copolymer extracted by each solvent was submitted to infrared spectroscopy to determine its composition. It would be expected that the fractions extracted later would contain more isobutene units. The extraction results are shown in Table 11-15.

The copolymers obtained in methylene chloride, where

Table 11-14 The preparation of copolymer for the fractional extraction

Run No.	Isobutene (ml.)	Styrene (ml.)	f_1	Solvent composition	$TiCl_4$ (mg.)	Yield (g.)	Conv. (%)	$\frac{D_{3061\ cm^{-1}}}{D_{2923\ cm^{-1}}}$	F_1	F_1 expected from Fig.11-4
F-1	4.9	15.1	0.300	CH_2Cl_2 100%	93.7	—	100	0.289	0.310	0.300
F-2	7.7	12.3	0.452	CH_2Cl_2 75% $n\text{-}C_6H_{14}$ 25%	100.8	2.1884	13.6	0.174	0.584	0.590
F-3	8.6	11.4	0.498	CH_2Cl_2 50% $n\text{-}C_6H_{14}$ 50%	115.9	5.2617	33.1	0.222	0.470	0.550
F-4	10.4	9.6	0.588	CH_2Cl_2 25% $n\text{-}C_6H_{14}$ 75%	127.4	4.4383	28.9	0.212	0.494	0.493
F-5	12.1	7.9	0.669	$n\text{-}C_6H_{14}$ 100%	321.9	2.2007	14.7	0.194	0.537	0.446
F-6	12.1	7.9	0.669	$n\text{-}C_6H_{14}$ 100%	337.5	3.2000	21.4	0.194	0.537	0.446

r_1 is larger than unity and r_2 nearly unity, and in n-hexane, where r_1 is less than unity and r_2 larger than unity, were completely extracted by acetone-methyl ethyl ketone mixture, and considered to be true copolymers having the random and sharply distributed composition. On the other hand, copolymers obtained in mixed solvents, where both r_1 and r_2 are larger than unity, were extracted even by cyclohexanone, and considered to be copolymers of widely distributed composition. This is due to the somewhat longer sequence of same kind of monomer arising because both r_1 and r_2 are larger than unity. However, as traces of cyclohexanone soluble material and no residue were present in the copolymer, it appears that the sequence of the same kind of monomer is not so long. Hence, the copolymer obtained here may be considered to be a true copolymer to which the Mayo equation is applicable.

A considerable amount of copolymer was lost during extraction. But the weight average F_1 (mole fraction of isobutene unit in copolymer) of the sample calculated from F_1 of each fraction is approximately equal to F_1 of the original sample, hence discussions on extraction results are considered to be valid.

Table 11-15 The fractional extraction

Run No.	Original sample (g.)	Acetone soluble part			Acetone-MEK soluble part		
		g.	%	F_1	g.	%	F_1
F-1	10.0020	5.1495	51.5	0.297	4.0112	40.1	0.348
F-2	1.5318	0.3818	24.9	0.430	0.5761	37.6	0.497
F-3	4.0902	1.9470	47.6	0.388	1.3042	31.9	0.537
F-4	3.8817	0.7877	20.3	0.527	1.4124	36.4	0.530
F-5	1.6507	0.9315	56.4	0.431	0.5582	33.8	0.429
F-6	2.4577	1.3259	53.9	0.487	0.8037	32.7	0.536

of copolymer

MEK soluble part			Cyclohexanone soluble part			Residue	Loss		F_1 calculated $\sum_i \frac{F_i \cdot \%_i}{100}$
g.	%	F_1	g.	%	F_1	g.	g.	%	
0	0	—	0	0	—	0	0.8419	8.4	0.319
0.2294	15.0	0.638	0.0208	1.3	0.760	0	0.3237	21.1	0.507
0.3551	8.7	0.574	trace	0	—	0	0.4839	11.8	0.460
1.1593	30.0	0.563	trace	0	—	0	0.5223	13.5	0.541
0	0	—	0	0	—	0	0.1610	9.8	0.430
0	0	—	0	0	—	0	0.3281	13.3	0.505

4. Discussion

Here the effects of solvent dielectric constant and of catalyst on monomer reactivity ratio (the propagation reaction), A value, B value and $k_{r_{12}}/k_{p_{11}}$ (the transfer reaction) will be discussed. For this purpose, the experimental data are summarized in Table 11-16, and Figs. 11-18 and 11-19.

4.1 The effect of solvent of r_1 and r_2

Overberger et al.[3] proposed selective solvation of the growing ion-pair by one of two co-monomers in order to explain their experimental data on the copolymerizations of isobutene with p-chlorostyrene and of chloroprene with styrene. The results for methylene chloride and n-hexane in the present investigation can be satisfactorily explained on Overberger et al.'s theory. In order to explain the experimental results with mixed solvents, however, a new interprepation in addition to Overberger's theory is needed. The author considers all the experimental results explicable on the view that the solvent effect arises out of differences in structures of the monomers giving rise to differences in the cation reactivities, the isobutene cation and styrene cation being affected differently by

Table 11-16 The summary of the experimental data

Solvent composition	$n\text{-}C_6H_{14}$ 100%	$n\text{-}C_6H_{14}$ 75% — CH_2Cl_2 25%	$n\text{-}C_6H_{14}$ 50% — CH_2Cl_2 50%	$n\text{-}C_6H_{14}$ 25% — CH_2Cl_2 75%		CH_2Cl_2 100%
D.C. at -78°C	2.046	3.95	6.53	10.65		14.89
Catalyst	$TiCl_4$	$TiCl_4$	$TiCl_4$	$TiCl_4$	$SnCl_4$	$TiCl_4$
r_1	0.37±0.07	2.63±0.52	3.25±0.25	4.11±0.19	3.75±0.45	4.48±0.28
r_2	2.41±0.12	5.50±0.55	2.75±0.25	1.70±0.07	1.92±0.41	1.08±0.07
A x 10^3	25.0	10.2	6.93	4.48	4.53	5.25
$k_{r_{12}}/k_{p_{11}}$ x10^3	48.0	22.1	13.5	2.57	—	4.59

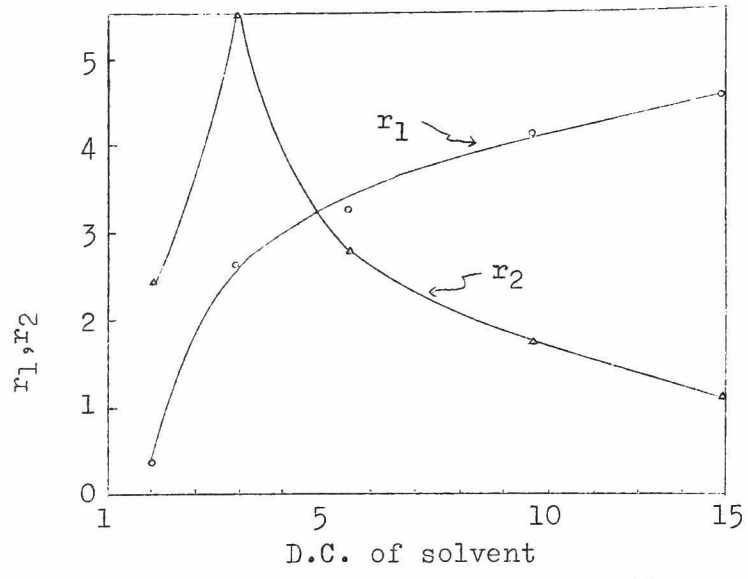

Fig. 11-18 The dependencies of r_1 and r_2 on the dielectric constant of solvent

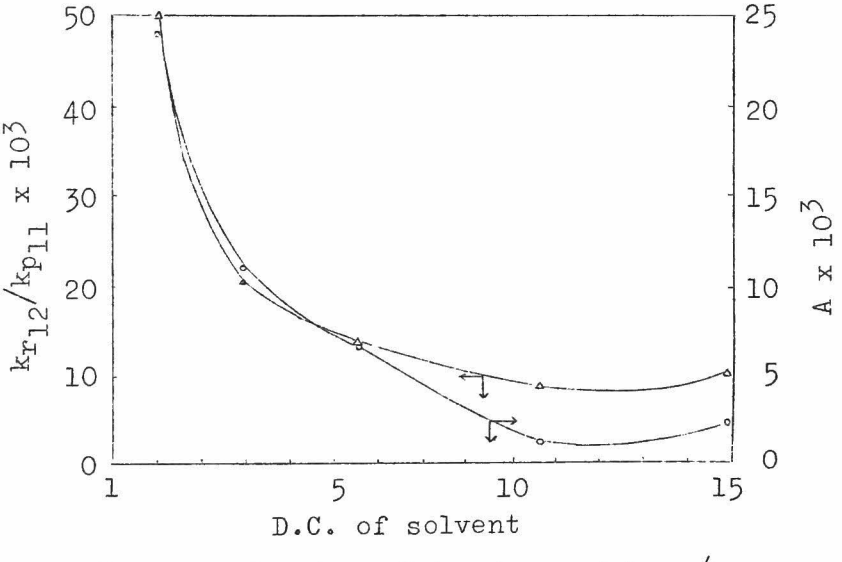

Fig. 11-19 The dependencies of A value and $k_{r_{12}}/k_{p_{11}}$ on the dielectric constant of solvent.

the solvent.

The following matters were considered in connection with explanation of the experimental results:—

(i) Four kinds of elementary reactions in copolymerization are divided into eight steps[10]:—

$$IB^{\oplus} + IB \overset{K_{1a}}{\rightleftharpoons} \text{complex of IB} \overset{K_{1b}}{\rightleftharpoons} IB^{\oplus} \qquad k_{11}$$

$$IB^{\oplus} + St \overset{K_{2a}}{\rightleftharpoons} \text{complex of St} \overset{K_{2b}}{\rightleftharpoons} St^{\oplus} \qquad k_{12}$$

$$St^{\oplus} + IB \overset{K_{3a}}{\rightleftharpoons} \text{complex of IB} \overset{K_{3b}}{\rightleftharpoons} IB^{\oplus} \qquad k_{21}$$

$$St^{\oplus} + St \overset{K_{4a}}{\rightleftharpoons} \text{complex of St} \overset{K_{4b}}{\rightleftharpoons} St^{\oplus} \qquad k_{22}$$

where $IB^{\oplus}$ and $St^{\oplus}$ represent respectively the growing isobutene and styrene cations, and IB and St denote respectively isobutene and styrene.

(ii) The cation of isobutene is less stable and consequently more reactive than the cation of styrene which is resonance-stabilized by phenyl group. Therefore, $K_{1a} > K_{3a}$, $K_{2a} > K_{4a}$, $K_{1b} > K_{3b}$ and $K_{2b} > K_{4b}$.

(iii) Isobutene is more nucleophilic than of styrene[11] (greater rate of π-complex formation) but forms a carbonium ion more difficultly.[12] Therefore,

$K_{1a} > K_{2a}$, $K_{3a} > K_{4a}$, $K_{2b} > K_{1b}$, $K_{4b} > K_{3b}$.

(iv) The ion-pair can hardly be solvated in a non-polar solvent such as n-hexane, so the stability of the resultant carbonium ion is an important determining factor in respect of reaction facility. This means that the magnitude of K_b is important, whence k_{11} is smaller than k_{12} and k_{21} is smaller than k_{22}. This leads to r_1 smaller than unity and r_2 larger than unity, which is actually the case. Moreover as Overberger et al.[3] proposed in a non-polar solvent selective solvation of the ion-pair by styrene is important. This effect tends to make r_1 (< 1) still smaller and r_2 (> 1) still larger than unity.

The instability of the isobutene cation is reflected in the rate of polymerization. The explosively fast polymerization of isobutene at -100°C by boron trifluoride[13] has been cited as an example of the rate of cationic polymerization being large even at low temperatures. However, this holds only for polymerization in polar solvents such as chlorinated hydrocarbons. The author compared the initial rate of polymerization (R_p) of isobutene with that of styrene. Expressing R_p as conversion (%) per g. of

catalyst per second, R_p in the polymerization at -78°C by titanium tetrachloride at a monomer concentration of 10 vol. % was 27.65 for isobutene and 9.03 for styrene in methylene chloride, and 1.70 for isobutene and 1.26 for styrene in n-hexane. Taking into account that in polymerization of isobutene in methylene chloride polyisobutene precipitates out and that occlusion of catalyst by polymer may occur, the R_p difference in methylene chloride must be much larger. Moreover, allowing for the fact that in polymerization of styrene in n-hexane the resultant polystyrene is insoluble and that the same precipitation effect as in the polymerization of isobutene in methylene chloride may obtain, the R_p difference in n-hexane must be much smaller. It is also possible that R_p for styrene in hexane is larger than for of isobutene. The greater decrease in R_p for isobutene than for styrene accompanying decrease of solvent dielectric constant suggests that stabilization by solvation is more important in the case of the unstable isobutene cation than with the stable styrene one. This leads to the conclusion that an unstable isobutene cation is formed less easily in a non-polar medium.

(v) In a polar solvent such as methylene chloride, both isobutene cation and styrene cation will be solvated almostly completely, so that the difference in stabilities of the growing ion-pairs is of minor importance in determining reaction rate, and consequently the magnitude of K_a is important. This results in $k_{11}>k_{12}$ and $k_{21}>k_{22}$, so in methylene chloride it is to be expected that r_1 will be larger than, and r_2 is smaller than, unity. However, in practice r_1 is larger than unity and r_2 is nearly equal to unity. This discrepancy can be explained satisfactorily on a basis that selective solvation[3] of the growing ion-pair by styrene obtains even in a polar medium to give higher concentration of styrene in the vicinity of the reaction site than in bulk. This enhances the tendency of r_1 to be larger than unity, and makes r_2 nearly equal unity.

(vi) In a solvent of intermediate polarity, the reaction between the olefinic double bond and a reactive cation such as isobutene cation is affected mainly by the equilibrium (a). On the other hand, the reaction of a stable cation such as styrene cation is affected mainly by equilibrium (b) (for the meanings of (a)

and (b) see p. 499). Hence $k_{11} > k_{12}$ and $k_{22} > k_{21}$, leading to r_1 larger than unity and r_2 larger than unity.

Passing from a 75% n-hexane mixture to 25% one stabilization of the growing ion-pair increases and the significance of step (a) gradually increases. This is why r_1 increases and r_2 decreases with increase of the polarity of mixed solvent with r_1 and r_2 remaining larger than unity.

To test the validity of the above ideas regarding growing ion-pair reactivity in mixed solvents, the effect of stannic chloride on copolymerization was studied in methylene chloride 75%—n-hexane 25 %. According to Chapter 2, a growing ion-pair including stannic chloride is less reactive than that including titanium tetrachloride. This means that the change from $IB^{\oplus}\ TiCl_4X^{\ominus}$ to $IB^{\oplus}\ SnCl_4X^{\ominus}$ is equivalent to change from $IB^{\oplus}\ TiCl_4X^{\ominus}$ to $St^{\oplus}\ TiCl_4X^{\ominus}$. Hence step (b) becomes to some extent important in the reaction of $IB^{\oplus}\ TiCl_4X^{\ominus}$, where step (a) dominates the reaction. This leads to r_1 ($SnCl_4$) smaller than r_1 ($TiCl_4$), with r_1 remaining larger than unity. On the other hand, the change from $St^{\oplus}\ TiCl_4X^{\ominus}$ to

$St^{\oplus}\ SnCl_4X^{\ominus}$ means, on the same basis, that step (b) dominates the reaction. This leads to the conclusion that $r_{2(SnCl_4)}$ is larger than $r_{2(TiCl_4)}$ with r_2 remaining larger than unity. Such actually obtains for copolymerization of isobutene with styrene by stannic chloride. Overberger et al.[3] reported that in the copolymerization of isobutene (M_1) and p-chlorostyrene (M_2) in nitrobenzene, $r_{1(AlBr_3)}$ was larger than $r_{1(SnCl_4)}$ and $r_{2(AlBr_3)}$ smaller than $r_{2(SnCl_4)}$. This is in good agreement with our experimental results and supports our views, if aluminum bromide forms an more reactive ion-pair than stannic chloride.

4.2 The effect of solvent on the A value and on $k_{r_{12}}/k_{p_{11}}$

As is seen from Fig. 11-19, both A and $k_{r_{12}}/k_{p_{11}}$ decrease with the increase of solvent dielectric constant. This is the same trend as was found for the monomer transfer reaction in cationic polymerization of styrene.[14] In cationic polymerization of isobutene[15] and styrene,[16] k_p increases with increasing solvent dielectric constant, which is ascribed to greater dissociation of the growing ion pair. On the other hand, the monomer transfer reaction

toward styrene monomer, which has been proved to be essentially a Friedel-Crafts alkylation, is not greatly accelerated by dissociation of growing ion-pair due increase of dielectric constant of solvent.[17] Here the cross-transfer reaction is substantially the same as the styrene type of monomer transfer reaction. Hence $k_{r_{12}}/k_{p_{11}}$ behaved as expected.

In Fig. 11-19, selective solvation by the solvent of greater polarity is seen to be absent in the present system. It is conceivable that the small change of $k_{r_{12}}/k_{p_{11}}$ in the solvents containing over 50% of methylene chloride is conditioned by dissociation of the growing ion-pair in such solvents gradually approaching its limiting value.

The present author has sometimes used mixed solvent to study the effect of solvent polarity on the monomer transfer reaction. In the present investigation it was found that selective solvation by one component of the mixed solvents is not important unless solvents of different structures are mixed. The mixing of solvents of analogous structure is considered to be a valid way of changing the polarity of the medium.

To sum up, the following can be stated:

Isobutene (M_1) was copolymerized with styrene (M_2) by titanium tetrachloride in n-hexane—methylene chloride. The monomer reactivity ratio was found to be greatly affected by the mixing ratio of solvent. r_1 was larger than unity and r_2 was nearly unity in methylene chloride, while r_1 was smaller and r_2 was larger than unity in h-hexane. Both r_1 and r_2 were larger than unity in mixed solvents. Furthermore, r_1 became larger with increasing solvent dielectric constant. These findings were interpreted in terms of the effect of solvent on stability of growing ion-pair.

The cross-transfer reaction from isobutene cation to styrene monomer was also affected by the ratio of solvents in a mixture and this was explained in terms of the effect of solvent on the styrene-type monomer transfer reaction.

No evidence for selective solvation by one of the components of the mixed solvent was detected in the n-hexane—methylene chloride system.

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Part 5 Summary

Investigations of transfer and termination reactions in cationic polymerization of vinyl monomers were described in Parts 2, 3 and 4. The experimental results will now be summarized.

Part 2 Kinetics of the transfer and termination reactions in cationic polymerization of vinyl monomers

To calrify the mechanism of the transfer and termination reactions in cationic polymerization, and the relationship between the polymerization condition and the polymer molecular weight, the typical ten vinyl monomers were polymerized using Friedel-Crafts catalysts, and the transfer and termination reactions were studied kinetically.

Chapter 1 α-Methylstyrene

α-Methylstyrene was polymerized using boron trifluoride etherate as the catalyst at -20°, -50° and -78°C. Polymerizations were carried out in n-hexane (non-solvent for the catalyst and polymer) mixed with toluene, or chloroform, or methylene chloride (good solvent for both), with the result that some interesting results were

obtained in polymerization at -78°C. The catalyst precipitates in n-hexane and the polymer formed around the catalyst also precipitates and covers the catalyst, leading to a low yield of low molecular weight polymer. On the other hand, mixed solvents facilitates monomer diffusion to the catalyst, leading to a high yield of high molecular weight polymer. Increasing ratio of good solvent in the mixed solvent causes polymerization rate and molecular weight to rise. Thus the polymer molecular weight could be widely varied simply by changing solvent composition.

With toluene—n-hexane mixed solvent, the polymer molecular weight rose to maximum when the volume ratio secured homogeneity of the polymerization system, and was not affected by increasing the amount of toluene. With chloroform—n-hexane, the polymerization system achieved homogeneity at the same mixing volumes, the polymer molecular weight continued to increase, and reached a maximum at chloroform—n-hexane 3:1, after which it decreased. In methylene chloride—n-hexane mixed solvent, the polymerization system became homogeneous at the ratio of solvents for which the polymer molecular weight became a maximum, and decreased with further increase of the proportion of methylene chloride.

To explain why the polymer molecular weight could widely be varied simply by changing the solvent composition, and why the effects of toluene, chloroform and methylene chloride on the polymer molecular weight in the homogeneous system were different, the rate constant ratios for the transfer and termination reactions were determined from the polymer molecular weight. It was found that, the monomer transfer reaction was most important in determining polymer molecular weight, so the effects of solvent on the monomer transfer constant ratio (k_{tm}/k_p) were interpreted in term of solvent dielectric constant. k_{tm}/k_p became a minimum at around dielectric constant 6 over a temperature range -20° to -78°C. Hence, it was kinetically proved that high molecular weight poly-α-methylstyrene could be produced by polymerization in a solvent of dielectric constant 6. This experimental fact corresponds to the results that poly-α-methylstyrene of the highest molecular weight could be produced in 3:1 chloroform—n-hexane or in 1:1 methylene chloride—n-hexane mixtures.

When the solvent dielectric constant was increased to 6, k_{tm}/k_p decreased, which was just what was found in styrene polymerization, suggesting that the monomer

transfer reaction mechanism is the same in both cases. However the increase of k_{tm}/k_p when the solvent dielectric constant is more than 6, which is opposite to what obtains with styrene, remains to be explained.

Chapter 2 Isobutene

The effects of polymerization temperature (-20°, -50° and $-78^{\circ}C$), solvent (n-hexane, chloroform, methylene chloride) and catalyst (stannic chloride—trichloroacetic acid, titanium tetrachloride—trichloroacetic acid, titanium tetrachloride) a cationic polymerization of isobutene were studied. It was found that the polymer molecular weight was higher, the lower the temperature, the lower the solvent dielectric constant, or the stronger the catalyst. The effects of catalyst and solvent on polymer molecular weight were just the opposite to what obtained with styrene. It was established kinetically that the monomer transfer reaction is important in determining polymer molecular weight; further, the effect of polymerization condition on k_{tm}/k_p was studied. It was found that the lower the temperature, the smaller the solvent dielectric constant, and the stronger the catalyst, the smaller k_{tm}/k_p. This, just opposite to what

obtains with styrene, explains kinetically the effect of polymerization condition on the polymer molecular weight.

Bromination showed the presence of double bonds in polyisobutene. From these experimental results it was considered that in isobutene polymerization the monomer transfer reaction is a proton extraction by monomer from a penultimate carbon atom, which is designated the isobutene-type monomer transfer reaction. Since in the isobutene-type monomer transfer reaction a proton is extracted and the ion-pair bonding of the growing end must be loosed, there the free ion form of the growing end is more important than the ion-pair form, and this view affords a satisfactory explanation of the effects of solvent and catalyst on k_{tm}/k_p.

Chapter 3 Methoxystyrenes

To clarify the mechanism of the monomer transfer reaction in cationic polymerization of styrene and its derivatives, cationic polymerizations of o- and p-methoxystyrenes using boron trifluoride etherate as catalyst were carried out in carbon tetrachloride, chloroform or methylene chloride over the temperature range 30°C to -50°C, and the electronic and steric effects of the sub-

stituent on k_{tm}/k_p were investigated.

The higher the solvent dielectric constant, the smaller k_{tm}/k_p for p-methoxystyrene, which is what is found for styrene polymerization. k_{tm}/k_p for o-methoxystyrene is independent of solvent dielectric constant. The k_{tm}'s of styrene, o- and p-methoxystyrene were compared with each other, and the reactivities of these three monomers in the monomer transfer reaction were considered. It was found that, due to the p-methoxy group, reactivity of p-methoxystyrene in the propagation step is ten times greater than that of styrene, but that in the monomer transfer reaction is only two to five times greater. On the other hand, stemming from the effect of the o-methoxy group, reactivity of o-methoxystyrene in the propagation reaction is only five times greater than that of styrene, but in the monomer transfer reaction it is ten times greater.

Since a substituent affects the propagation and monomer transfer reactions differently, the two reactions are thought to occur at the different places. As aromatic compounds act as chain transfer agents in cationic polymerization, it was assumed that the monomer transfer reaction of methoxystyrene occurs by the interaction between the growing end and the phenyl group of the monomer

(Friedel-Crafts reaction). The reaction site for the monomer transfer reaction was found, by molecular orbital calculations, to be ortho to the methoxy group for p-methoxystyrene and the para position to methoxy group for o-methoxystyrene. From the above it is evident that the monomer transfer reaction of p-methoxystyrene is sterically hindered more than that of o-methoxystyrene, and this condition is in good agreement with the experimental findings regarding the effect of the substituent on k_{tm}.

The infrared abosprption spectrum of polymethoxystyrene showed the presence of a terminal vinyl group in the polymer, which supports the view that a Friedel-Crafts reaction occurs between a monomer phenyl group and a growing cation, a reaction being named the styrene-type of monomer transfer reaction.

Chapter 4 Chlorostyrenes

To ascertain the validity of the mechanism of styrene-type monomer transfer reaction, o- and p-chlorostyrene, which are styrene derivatives with -I substituent, were polymerized using stannic chloride— trichloroacetic acid as catalyst at 30°C in benzene, toluene and dichloroethane, and effects of the substituent on k_{tm}/k_p were investigated.

k_{tm}/k_p's of both monomers decreased with increasing solvent dielectric constant, a tendency characteristic of the styrene-type monomer transfer reaction.

Using the method of Chapter 3, the monomer reactivities of styrene, o- and p-chlorostyrene in the monomer transfer reaction (R_M') were compared with each other, and it was found that R_M' of chlorostyrene was lower than that of styrene, due to the adverse influence of chlorine in respect of Friedel-Crafts reactions. Comparing the chlorostyrene isomers with one other, R_M' of the ortho isomer was larger than that of para isomer. As the monomer transfer reaction of chlorostyrene occurs at the monomer phenyl group, the reaction site was found by molecular orbital calculations. The reaction site of the monomer transfer reaction for o-chlorostyrene was found by calculation to be para to the vinyl group, which is less sterically hindered than is the position ortho to vinyl group in p-chlorostyrene where steric hindrance is large. Such is the reason for the difference in R_M' between the two isomers.

The infrared spectrum of the polymer showed the presence of a terminal vinyl group, suggesting reaction between a monomer phenyl group and a growing ion. Thus,

the monomer transfer reactions of methoxystyrene and chlorostyrene, which have +M and -I substituent respectively, were interpreted by the same mechanism. The effects of polymerization conditions on the styrene-type monomer transfer reaction are just opposite to those on the isobutene-type monomer transfer reaction, and consequently the ion-pair form would be expected to be important in the styrene-type monomer transfer reaction. The styrene-type monomer transfer reaction is essentially a Friedel-Crafts reaction, the latter being found to proceed without the dissociation of the ion-pair (Brown's result), but on the other hand, the propagation reaction is suppressed in the ion-pair form (Kanoh's result), so that ion-pair form is important in the styrene-type monomer transfer reaction.

The effect of solvent on k_{tm}/k_p of α-methylstyrene can conveniently be explained on the view that α-methylstyrene, the structure of which resembles either isobutene or styrene, undergoes the styrene-type monomer transfer reaction in solvent of dielectric constant below 6, but the isobutene-type monomer transfer reaction in the solvent of dielectric constant above 6.

Chapter 5 Methyl Vinyl Ether

To investigate the monomer transfer reaction in the cationic polymerization of a vinyl alkyl ether having ethereal oxygen of large carbonium ion affinity, methyl vinyl ether was polymerized at -20° and -50°C. The effects of solvent (carbon tetrachloride, chloroform, methylene chloride) and catalyst (stannic chloride—trichloroacetic acid, boron trifluoride etherate) on the degree of polymerization of polymer were investigated, and it was found that the lower the solvent dielectric constant and the milder the catalyst, the higher the degree of polymerization of the polymer. The effect of solvent was the same as was found in isobutene polymerization, while the effect of catalyst was the same as in styrene polymerization. The degree of polymerization of polymer was found to be determined mainly by the monomer transfer reaction. k_{tm}/k_p was smaller the lower the solvent dielectric constant (isobutene-type), and the milder the catalyst (styrene-type).

On the other hand, the unimolecular termination reaction constant ratio (k_t'/k_p) was affected by solvent and catalyst in the same way as was k_{tm}/k_p, suggesting

that both reactions are governed by a similar mechanism.

Bromination of polymer showed that the monomer transfer reaction resulted in a double bond at the end of the polymer, whereas the unimolecular termination reaction did not produce a double bond. Hydrolysing the polymer with hydrogen chloride, and analysing the resultant aldehyde with hydroxylamine, it was found that the monomer transfer reaction gives a polymer end group which affords two molecules of aldehyde, whereas the unimolecular termination reaction gives a polymer end group which cannot produce aldehyde.

These experimental results suggested that the monomer transfer reaction occurs by interaction between a growing ion and ethereal oxygen of the monomer, leading to the ether cleavage and the production of a methyl cation, and that the unimolecular termination reaction involves interactions between a growing ion and ethereal oxygen of the monomer unit penultimate with respect to the growing chain end, leading to ether cleavage and production of a tetrahydropyran ring.

Chapter 6 Butyl Vinyl Ether

To test the validity of the mechanism of the vinyl alkyl ether monomer transfer reaction proposed in Chapter 5, isobutyl and t-butyl vinyl ethers were polymerized by boron trifluoride etherate, and the effect of the alkyl substituent of k_{tm}/k_p considered. Polymerizations of isobutyl vinyl ether were run at -20° or $-50^\circ C$ or $-78^\circ C$. k_{tm}/k_p and k_t'/k_p for both kinds of monomers were larger, the higher the solvent dielectric constant and the higher the temperature, exactly as was found for polymerization of methyl vinyl ether. Regarding the difference between methyl vinyl ether and butyl vinyl ether, though the activation energies for k_{tm}/k_p and k_t'/k_p of methyl vinyl ether are fairly large, the rate constant for isobutyl vinyl ether is determined by solvent dielectric constant rather than by temperature, and the activation energies for both reactions are almost zero, especially in solvent of higher dielectric constant.

This experimental fact is explicable as follows in terms of the transfer and termination mechanisms proposed in Chapter 5: in the activated state for these reactions, an alkyl cation or alkyl cation-like state will appear, so formation of reactive methyl cation in the methyl vinyl

ether reaction needs more activation energy than formation of unreactive butyl cations (isobutyl and t-butyl cations) in the butyl vinyl ether reactions. Particularly in solvent of high dielectric constant, the activated complex of the butyl vinyl ether reactions is solvated enough to cut the activation energy to zero. Thus the same mechanism is proved to hold for the monomer transfer and unimolecular termination reactions of butyl vinyl ethers.

Part 3 Polymer molecular weight

To discuss the monomer transfer reaction and the unimolecular termination reaction on a basis of rate constant ratios calculated from the polymer molecular weight, it is necessary to have some information about the relationship between the polymer molecular weight and the intrinsic viscosity, the variation of polymer molecular weight distribution with the progress of polymerization, and the chain branching in the polymer. In the present Part the discussion will deal mainly with polymer molecular weight and partly with the stereospecificity of the polymer.

Chapter 7 Poly-α-methylstyrene

Of the poly-α-methylstyrenes produced at -78°C using boron trifluoride etherate as the catalyst, the polymers obtained in chloroform-rich chloroform—n-hexane mixed solvent (chloroform/n-hexane > 3) or in n-hexane-rich methylene chloride—n-hexane mixed solvent (methylene chloride/n-hexane ≃ 0.6) are partially insoluble in benzene at room temperature. This polymer dissolves in hot benzene (> 40°C), toluene, chloroform, methylene chloride and other organic solvents, so the crosslinking of the polymer chain cannot be responsible for the insolubility in cold benzene. The polymer was extracted with cold benzene, and it was found that the X-ray diagram of the extracted residue was sharper than that of the extractable part or of the total polymer, suggesting crystallinity of the polymer insoluble in cold benzene. This crystalline poly-α-methylstyrene could not be produced using catalysts other than boron trifluoride etherate (metal sodium, stannic chloride, aluminum chloride), or in solvent of dielectric constant other than 5-6 (toluene, methylene chloride), or at higher temperature (-20°C), indicating that some condition for a growing ion must be

fulfilled to obtain a crystalline polymer, and the effects of the polymerization conditions are possibly explained by the mechanism proposed from our laboratory for the stereospecific polymerization of alkyl vinyl ethers in a low temperature homogeneous cationic polymerization system.

However, once the polymer fraction insoluble in cold benzene was dissolved in benzene by heating, and re-precipitated, it became very soluble in cold benzene. Furthermore, the X-ray diagram of polymer film made from the fraction insoluble in cold benzene and afterwards stretched 5-6 times its original length showed some orientation, but it became diffuse when stretched more than 5-6 fold. The usual crystallyzing methods such as boiling the polymer film in non-solvent and thermal treatment did not lead to an oriented X-ray diagram. The polymer insoluble in cold benzene could be produced only at high polymerization conversion. Taking into account all of these facts, polymer entanglement was advanced as another reason for insolubility in cold benzene. What is more likely is the co-operation of crystallinity and entaglement.

The intrinsic viscosity of benzene solutions at 30°C and the number average molecular weight of the fractionated

poly-α-methylstyrene were determined, leading to an intrinsic viscosity—molecular weight equation:—

$$[\eta] = 2.49 \times 10^{-4} \times \bar{M}_n^{0.647}$$

There were no differences between the corresponding intrinsic viscosity—molecular weight relationships and A_2 —molecular weight relationships for the polymer insoluble and soluble in cold benzene, and hence it is concluded that there is no difference between the solution properties of the two types of poly-α-methylstyrene. The θ-solvent composition for poly-α-methylstyrene at 30°C (methanol 20.6 vol.%—benzene 79.4 vol.%) was determined, and $[\eta]_\theta$ was measured, leading to the equation below:

$$[\eta]_\theta = 9.68 \times 10^{-4} \times \bar{M}^{0.50}$$

Using $\Phi = 2.1 \times 10^{21}$, the ratio of root mean square of polymer end-to-end distance viz., $(\langle \bar{r}_o^2 \rangle / \langle \bar{r}_{of}^2 \rangle)^{1/2}$, was calculated to be 2.73 at 30°C. A steric effect of the α-methyl group on the free rotation of the polymer backbone chain is evident on comparing $(\langle \bar{r}_o^2 \rangle / \langle \bar{r}_{of}^2 \rangle)^{1/2}$ = 2.73 with the value 2.30 reported for polystyrene.

Chapter 8 Polystyrene

Styrene was polymerized in dichloroethane or carbon tetrachloride—nitrobenzene mixed solvent using boron trifluoride etherate or stannic chloride as the catalyst (30° or $0^{\circ}C$). The relationship between the conversion and the degree of polymerization of polymer was firstly investigated, and it was found that in polymerization in dichloroethane the degree of polymerization of polymer decreased with increasing conversion as expected from the decrease of monomer concentration, but that in polymerization in carbon tetrachloride—nitrobenzene the degree of polymerization of polymer was almost independent of, or increased with, increasing conversion. These results suggest that, due to the polymer chain transfer reaction, polymer of higher molecular weight than that expected from the decrease of monomer concentration was produced with the progress of polymerization.

Next, the weight average molecular weight ($\bar{\bar{M}}_w$) was measured for unfractionated polystyrene using an ultracentrifuge or light scattering. Plotting $\bar{\bar{M}}_w$ against intrinsic viscosity logarithmically, a certain straight line was obtained for polystyrene produced in dichloro-

ethane independent of conversion, but $\bar{M}_w$ of polystyrene produced in carbon tetrachloride—nitrobenzene deviated from the straight line to the higher molecular weight range. This again suggested the presence of chain branching due to polymer chain transfer in carbon tetrachloride—nitrobenzene.

Thirdly, the monomer transfer constant ratios (k_{tm}/k_p) and the unimolecular termination constant ratios (k_t'/k_p), determined when varying the initial monomer concentration, were compared with those calculated from the degree of polymerization—conversion, and it was found that the rate constant ratios for polymerization in dichloroethane agreed well, but that those for polymerization in carbon tetrachloride—nitrobenzene did not agree. So it can safely be said that in polymerization carried out in solvent containing nitrobenzene polymer chain branching due to the polymer transfer reaction is possible. This agrees well with the results reported by Overberger and Atkins.

Fourthly, to establish the occurrence of the monomer transfer reaction as an elementary reaction in cationic polymerization, the molecular weight distribution of poly-

styrene was considered. Polystyrene was synthesized in dichloroethane, fractionated, and the polymer molecular weight calculated. When the degree of polymerization of the polymer is controlled by the monomer transfer reaction only, $\bar{\bar{M}}_w/\bar{\bar{M}}_n$ is 2, independent of conversion, but when the unimolecular termination reaction or solvent transfer reaction occurs (as is usual), $\bar{\bar{M}}_w/\bar{\bar{M}}_n$ will be 2 at the beginning of polymerization and rise to over 2 as polymerization progresses. Actually it was found that $\bar{\bar{M}}_w/\bar{\bar{M}}_n$ was lower than 2 even for polystyrene produced with high conversion, and $\bar{\bar{M}}_w/\bar{\bar{M}}_n$ is not a useful criterion. However, why $\bar{\bar{M}}_w/\bar{\bar{M}}_n$ was lower than 2 is not at present clear.

Lastly, the following intrinsic viscosity—molecular weight equations were obtained for polystyrene without branching obtained in dichloroethane:

Unfractionated polystyrene

$$[\eta]^{30^\circ C}_{\text{Benzene}} = 1.0 \times 10^{-4} \times \bar{\bar{M}}_w^{0.72} \qquad (1)$$

Fractionated polystyrene

$$[\eta]^{30^\circ C}_{\text{MEK}} = 3.9 \times 10^{-4} \times \bar{M}_w^{0.56} \qquad (2)$$

$$[\eta]^{30^\circ C}_{\text{Benzene}} = 2.27 \times 10^{-4} \times \bar{M}_w^{0.65} \qquad (3)$$

Taking into consideration the intrinsic viscosity—molecular weight equations so far reported, Pepper's equation is best for unfractionated polystyrene (number average molecular weight):

$$[\eta]^{25^\circ C}_{\text{Benzene}} = 4.37 \times 10^{-4} \times \bar{M}_n^{0.66} \qquad (4)$$

and equation (3) for fractionated polystyrene (weight average molecular weight).

Chapter 9 Polymethoxystyrene

Poly-p-methoxystyrene obtained by cationic polymerization and poly-o-methoxystyrene obtained by thermal polymerization were fractionated, and $\bar{M}_w$ found by light scattering and intrinsic viscosity in toluene or methyl ethyl ketone solution at 30°C led to the following four equations:—

Poly-o-methoxystyrene

$$[\eta]^{30^\circ C}_{\text{Toluene}} = 6.40 \times 10^{-5} \times \bar{M}_w^{0.71} \qquad (1)$$

$$[\eta]^{30^\circ C}_{\text{MEK}} = 1.86 \times 10^{-4} \times \bar{M}_w^{0.59} \qquad (2)$$

Poly-p-methoxystyrene

$$[\eta]^{30^\circ C}_{\text{Toluene}} = 5.28 \times 10^{-5} \times \bar{M}_w^{0.73} \qquad (3)$$

$$[\eta]_{MEK}^{30^{\circ}C} = 3.75 \times 10^{-5} \times \bar{M}_w^{0.73} \qquad (4)$$

Saito et al. previously reported intrinsic viscosity—molecular weight equations for poly-p-methoxystyrene, but they do not agree well with equations (3) and (4). The relationship between intrinsic viscosity and molecular weight for poly-p-methoxystyrene is different from that for poly-o-methoxystyrene, especially in methyl ethyl ketone. This is not in accord with the conclusion of Saito et al. that the effect of substituting the phenyl group is not in evidence in the solution properties of the polymer because of the predominating effect of a large phenyl group.

p-Methoxystyrene was polymerized by boron trifluoride etherate in carbon tetrachloride, when $\bar{M}_w/\bar{M}_n$ was found to be in good agreement with that calculated using rate constant ratios determined in other experiments. This implies validity of the theoretical equation for molecular weight distribution, and from the latter it was found that the viscosity average molecular weight ($\bar{M}_v$), which is calculated by inserting intrinsic viscosity of unfractionated polymer into the intrinsic viscosity—molecular weight equation for fractionated polymer, is about twice $\bar{M}_n$, which is

needed to calculate the true rate constant. This means that it is valid to compare rate constant ratios obtained from the intrinsic viscosity of unfractionated polymer produced under various conditions.

The composition of θ-solvent at 30°C for poly-o-methoxystyrene (methanol 25 vol.%—toluene 75 vol.%) and for poly-p-methoxystyrene (methanol 28.1 vol.%—toluene 71.9 vol.%) were determined, and the effect of substituent on the polymer expansion was investigated. $(<\bar{r}_o^2>/<\bar{r}_{of}^2>)^{1/2}$ for poly-o-methoxystyrene was 2.44 and that for poly-p-methoxystyrene was 2.50. These values are slightly larger than 2.35 reported for polystyrene at 30°C, and it was found that the methoxy group substituting in the phenyl group exerts but little steric effect on free rotation of the back-bone chain.

Part 4 Growing ion reactivity

Recently it has been obvious that growing ion reactivity depends on the kind of monomer, on catalyst and on solvent. In Part 4, considerations were given to the method for evaluating the growing ion reactivity using chain transfer reaction. Some interesting results found in cationic popolymerization were interpreted in term of

the ion reactivity.

Chapter 10 Evaluation of ion reactivity using the chain transfer reaction

Three ways for evaluating the ion reactivity in ionic polymerization were proposed:—

Firstly, direct measurement of the propagation rate constant. For example, in the cationic polymerization of vinyl alkyl ethers catalyzed by iodine, Kanoh et al. reported homopolymerization propagation rate constants (l./mole/sec.) at 30°C in dichloroethane; k_{11} = 390 for isobutyl vinyl ether (M_1) and k_{22} = 260 for 2-chloroethyl vinyl ether (M_2). On the other hand, for the copolymerization carried out under the same condition, $r_1 = k_{11}/k_{12}$ = 2.0 and $r_2 = k_{22}/k_{21}$ = 0.5. These give k_{12}= 195 and k_{21}= 520, leading to the following sequence;—

$$k_{21} > k_{11} > k_{22} > k_{12}$$

This means that the more reactive monomer in the propagation reaction (M_1) gives the less reactive ion, the same trend as was found in radical polymerization.

Secondly, calculations using molecular orbital theory. The cation and anion localization energy of various monomers

(L_M^C and L_M^A) were calculated and plotted against calculated localization energy of various cation and anion (L_C and L_A), leading to an inverse propertionality between L_C and L_M^C and between L_A and L_M^A. Since the larger the localization energy the less readily the reaction occurs, the above relationship means that the more reactive monomer in cationic or anionic polymerization gives the less reactive cation or anion, the same trend as that found in radical polymerization. Thirdly, evaluation using the chain transfer reaction. For example, in cationic polymerization, chain transfer constant ratios to toluene of two kinds of cations (k_{r_1}/k_{p_1} and k_{r_2}/k_{p_2}) were determined. These two monomers were copolymerized under the same conditions as above, and r_1, r_2 were obtained. Assuming $k_{p_1}/k_{p_2} = (r_1/r_2)^{1/2}$ $k_{r_1}/k_{r_2} = (k_{r_1}/k_{p_1})/(k_{r_2}/k_{p_2})\ (r_1/r_2)^{1/2}$ was calculated. The reactivities of two cations were compared using k_{r_1}/k_{r_2}, assuming that the latter to be a good index of the ion reactivity ratio.

Styrene, o- and p-chlorostyrene, p-methylstyrene, o- and p-methoxystyrene were polymerized at 30°C using stannic chloride—trichloroacetic acid as the catalyst, and the ion reactivity was estimated using the method described above and was considered in relation to the

monomer reactivity. The order of monomer reactivity (R_M) found in copolymerization was:

p-methoxy > o-methoxy > p-methyl > p-H > o-chloro > p-chlorostyrene

The order of ion reactivity (R_I') found in chain transfer reaction to toluene was:

o-chloro > p-chloro > p-H > p-methyl > o-methoxy > p-methoxystyrene

A Hammett plot (log R_M— σ^+ and log R_I'— σ^+) was made with styrene and the three para-substituted styrenes, and straight lines were obtained, giving ρ = -1.8 for R_M and 2.1 for R_I'. This means that -I effect of chlorine caused decrease in monomer reactivity of chlorostyrenes and increase in ion reactivity, and that due to +M substituent methyl and methoxy the monomer reactivity was increased and the ion reactivity was decreased.

In both chlorostyrenes and methoxystyrenes, ortho isomers were found to give more reactive (less resonance-stabilized) cations than para isomers, due to effect of steric interaction of the ortho-substituent on the coplanarity of carbonium ion.

Chapter 11 The cross-transfer reaction in copolymerization

In cationic copolymerization the copolymer degree of polymerization is generally less than those of homopolymers used. In cationic copolymerization of isobutene with styrene derivatives at -78°C using titanium tetrachloride—trichloroacetic acid as the catalyst, the order of A-value which represents the degree of lowering of the copolymer degree of polymerization (the larger is A, the lower is the degree of polymerization of copolymer) was:—

Isobutene—α-methylstyrene > Isobutene—styrene> Styrene—α-methylstyrene

Reactivities of the above three cations were estimated using the chain transfer constant to methanol, the order of reactivity being as:—

Isobutene cation > Styrene cation ≃ α-Methylstyrene cation

Reactivities of the above three monomers as a chain transfer agent were determined, leading to the sequence:—

α-Methylstyrene > Styrene > Isobutene > Toluene

It was thus made clear that, particularly in cationic copolymerization of isobutene with α-methylstyrene, there

is coexistence of the most reactive cation (isobutene cation) and the most reactive chain transfer agent (α-methylstyrene), and that this is the reason for the marked occurrence of the cross-transfer reaction and formation of low molecular weight copolymer.

Low molecular weight copolymer from isobutene and α-methylstyrene showed an infrared absorption at 825 cm^{-1}, due to para-substituted benzene, which supports the styrene-type monomer transfer reaction between isobutene cation and phenyl group of α-methylstyrene.

Copolymerizations of isobutene (M_1) and styrene (M_2) were carried out at -78°C using titanium tetrachloride as the catalyst in n-hexane—methylene chloride mixed solvents with various compositions, and a great variation of r_1, r_2 was observed.

Solvent Composition	$n\text{-}C_6H_{14}$ 100%	$n\text{-}C_6H_{14}$—CH_2Cl_2 75% 25%	$n\text{-}C_6H_{14}$—CH_2Cl_2 50% 50%	$n\text{-}C_6H_{14}$—CH_2Cl_2 25% 75%	CH_2Cl_2 100%
r_1	0.37	2.63	3.25	4.11	4.48
r_2	2.41	5.50	2.75	1.70	1.08

As mentioned above, a large difference was observed between the reactivities of isobutene cation and styrene cation, and the less resonance stabilized isobutene cation was found to be very reactive or unstable. In the copolymerization in n-C_6H_{14}, there is a lack of solvation-stabilization of growing ion, and the stability of the growing ion controls the reaction. Under these circumstances the styrene cation is more easily formed than is the isobutene cation, leading to $r_1 < 1$ and $r_2 > 1$. With increasing proportion of methylene chloride in the mixed solvent, the isobutene cation can be increasingly solvated and stabilized. In methylene chloride both ions may be almost completely solvated, so the influence of ion stability on the reaction is small. Instead, the monomer reactivity is determined mainly by the nucleophilic nature of the vinyl double bond of the monomer, leading to $r_1 > 1$ and $r_2 \simeq 1$.

In mixed solvents, both r_1 and r_2 were greater than unity, and this was explained on the view that in the reaction concerning the isobutene cation, the nucleophilic nature of the monomer is important but that in the reaction involving the styrene cation, what is important is the stability of ion.

Regarding A-values in the present experiments, they were a maximum in n-hexane and decreased with increasing ratio of methylene chloride in the mixed solvent, which is characteristic of the styrene-type monomer transfer reaction.

Papers relevant to the present thesis

—art	Chapter	Section	Paper No.
2	1	1.1	1) Chem. High Polymers Japan, 16, 69(1959)
		1.2	2) Chem. High Polymers Japan, 17, 236(1960)
	2		3) Chem. High Polymers Japan, 18, 333(1961)
	3		4) Makromol.Chem., 70, 68 (1964)
	4		5) Chem. High Polymers Japan, 20, 49(1963) (a part)
	5		6) Chem. High Polymers Japan, 19, 154(1962)
	6		7) Chem. High Polymers Japan, 19, 565(1962)
3	7	7.1	8) J. Polymer Sci., 33, 491(1958)
			9) Chem. High Polymers Japan, 16, 129(1959)
		7.2	10) Chem. High Polymers Japan, 16, 244(1959)
	8		11) Sent to Chem. High Polymers Japan
	9		12) Sent to Chem. High Polymers Japan
4	10	10.1	13) Polymer, 3, 167(1962)
		10.2	5) (a part)
		10.3	14) Chem. High Polymers Japan, 20, 58(1963)
	11	11.1	15) Chem. High Polymers Japan, 20, 369(1963)
		11.2	16) Sent to J. Polymer Sci.

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