

The Terminal Group Effect on Solution Properties of Linear Macromolecules : Preliminary Results*

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The terminal group effect on thermodynamical properties of polymer solutions has been studied for polystyrene carrying carboxyl groups at the ends. The samples have been prepared by polymerization of styrene in the presence of γ,γ' -azobis(γ -cyanovaleric acid) as initiator, and by subsequent fractionation.

Cyclohexane solutions of these samples exhibit higher precipitation temperature than those of thermally polymerized or benzoyl peroxide initiated polystyrenes. The theta temperature of cyclohexane solutions, at which the second virial coefficient is zero, is found to be higher than 34.5°C, and is remarkably increased as the molecular weight decreases. These anomalies disappear when terminal carboxyl groups are esterified with diazomethane.

INTRODUCTION

In addition polymerization, it has been known that the resulting polymer bears various terminal groups, depending on the methods and conditions employed for polymerization. Relatively little attention has been paid to the possible effect on physical properties due to the difference in terminal groups, because it is natural to assume that the effect must be of the order of the reciprocal of molecular weight and, hence, is negligible in most cases. However, for polymers having quite bulky or polar terminal groups, it is expected that these influences may become significant. In fact, several studies have revealed that terminal groups may influence the properties of polymers such as viscosity^{1,2,3}, glass temperature⁴, apparent specific volume^{5,6}, and osmotic second virial coefficient^{7,8}, especially for low molecular weight polymers.

In this study, a detailed investigation of the terminal group effect has been attempted. For this purpose, it is necessary to prepare polymer samples in which the chemical structure of the terminal group is known with certainty. Fortunately, such a technique has become available by Bamford and Jenkins⁹. They have elucidated the condition of radical polymerization of styrene under which termination occurs mostly by combination of polymeric radicals and the chain transfer to monomers, solvents and polymers can be minimized. Consequently, the resulting polymer molecules bear the initiator fragments at both ends of each chain. Following their method, we synthesized polystyrene carrying terminal carboxyl groups by using γ,γ' -azobis-(γ -cyanovaleric acid) as the initiator. If such small chemical changes in polymer structure may have any influence, the effect may conceivably be most pronounced in the vicinity of theta temperature. Hence, we have first

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studied the influence on the critical precipitation temperature and the theta temperature of this polymer in cyclohexane. The results will be fully discussed below.

EXPERIMENTAL

Materials.

Commercial styrene was washed three times with 10% NaOH solution to remove the stabilizer and then several times with water. It was dried over calcium chloride over night, filtered and then distilled twice under nitrogen stream at a pressure of 10-20 mm Hg just before use.

N,N'-dimethylformamide (hereafter referred to as DMF) used as a polymerization solvent, was purified by treatments with phosphorus pentoxide followed by distillation *in vacuo*.

γ,γ' -azobis-(γ -cyanovaleric acid) (referred to as ACVA) was prepared by the modified Haines and Waters's procedure^{9,10}.

All other solvents. *i. e.*, benzene, cyclohexane, and p-dioxane, were carefully purified according to standard procedures.

Preparation of Polymer Samples.

Three polystyrene samples with terminal carboxyl groups and with different molecular weights (PSC I, II, and III) were prepared by the procedure proposed by Bamford *et al.*⁹ and Misra *et al.*¹¹ by using ACVA as an initiator. As the initiator is almost insoluble in styrene, DMF was used as a polymerization solvent, in which the initiator was soluble. An advantage of using this solvent is that it has been known to have a low chain transfer constant with styrene (for styrene radicals at 100°C it is 1.08×10^{-4})¹¹. In each polymerization reaction, a mixture consisting of 1 part styrene to 1 part DMF with a certain amount of the initiator was kept at 100°C for a prescribed period. The reaction mixture was poured into a large excess of methanol at the end of the reaction. The whole polymers were purified by repeating reprecipitation into methanol from benzene solutions for three or four times, and finally dried *in vacuo*. The molecular weights were determined by limiting viscosity numbers in benzene at 30°C and by alkaline titration experiments employing the method described below. Table 1 lists the polymerization conditions, the conversions to polymer, the viscosity data etc. for these whole polymers.

Each of these polymers was fractionated into nine to twelve fractions by evaporating benzene from benzene-n-butanol mixture at 30°C. All the fractions were carefully dried at 50°C *in vacuo*.

For the sake of comparison, two low molecular weight fractions from thermally polymerized polystyrene were also used in this study.

Osmotic Pressure Measurements.

Osmotic pressure measurements for higher molecular weight fractions were made in benzene at 37°C with modified Zimm-Meyerson Osmometers¹² and a Mechrolab High Speed Membrane Osmometer (Model 502). For lower molecular weight fractions, a Mechrolab Vapour Pressure Osmometer (Model 301A) was used.

For thermally polymerized fractions, osmotic pressure measurements were made in toluene at 25°C with modified Zimm-Meyerson Osmometers. The mem-

branes were Ultracellafilter "Allerfeinst" (Göttingen).

Viscosity Measurements.

Viscosity measurements were carried out in benzene at $30 \pm 0.01^\circ\text{C}$ with either one of two Ubberohe dilution viscometers, whose efflux times were 277.3 ± 0.1 and 733.8 ± 0.1 sec. for benzene. Corrections for kinetic energy were found to be negligible. Concentrations are given in grams per 100 ml for all viscosity measurements. The viscosity average molecular weights are calculated by using the following relationship⁹⁾.

$$[\eta]_{\text{Benzene}}^{30^\circ\text{C}} = 1.72 \times 10^{-3} M_v^{0.715} \quad (1)$$

Light Scattering Measurements.

Light scattering (L.S.) measurements were carried out in a Shimadzu (modified Brice type) light scattering photometer equipped with a constant temperature jacket ($\pm 0.1^\circ\text{C}$). Scattering intensities were measured at various angles from 30° to 150° using vertically polarized light of $436 \text{ m}\mu$ or $546 \text{ m}\mu$ wave length. A cylindrical cell was used throughout the work. Calibration procedures of the apparatus were described elsewhere¹³⁾.

To evaluate the theta temperature of cyclohexane solutions for some fractions, measurements were made at three different temperatures near 40° , 50° and 60°C . The second virial coefficient A_2 was determined according to the following equation,

$$Kc/R_0 = 1/M_w + 2A_2c \quad (2)$$

where, c is the polymer concentration in grams per ml, R_0 is Rayleigh's ratio at zero angle, and K is the optical constant. For a few fractions, *p*-dioxane was used as a solvent and molecular weights were determined by the well-known method of the Zimm plot¹⁴⁾. All the measurements in *p*-dioxane were carried out at 30°C . The solutions were clarified by filtration through two round pieces of "Mittel" grade Cellafilter (Göttingen).

Refractive index increments were determined in a thermostated Shimadzu (Debye type) differential refractometer using $436 \text{ m}\mu$ for cyclohexane solutions at 40°C , and using $436 \text{ m}\mu$ and $546 \text{ m}\mu$ for *p*-dioxane solutions at 30°C . There was found substantially no difference in the refractive index increments between the polystyrenes with terminal carboxyl groups and other polystyrenes. Values for other temperatures were calculated by the empirical rule of Gladstone and Dale¹⁵⁾.

Terminal Carboxyl Group Analysis.

i) Alkaline Titration Method.

Terminal group analysis for the lower molecular weight fractions was carried out by the alkaline titration method. The polymer samples were dissolved in benzene, and titrated with 0.01-0.02 N sodium hydroxide in ethanol by using phenolphthalein as an indicator. The end point was reproducible to within at least 0.1 mls. In a typical example, 150 mg of polymer dissolved in 25 ml benzene was taken to give a titer of about 3 mls so that the error was about 3.3%. Because of the limitation in the amount of each fraction available for the test and of the error involved, this method was applied only to the fractions with molecular weight below 40,000. For the whole polymers, 1 g. of polymer in 50 ml benzene

was subjected to the test. By assuming that each polymer chain has two carboxyl groups at the both ends, number average molecular weights were calculated from the titration data. The results are shown in Tables 1 and 2.

Table 1. Polymerization conditions and molecular weights of the whole polymers.

Samples	PSC I	PSC II	PSC III
Concentration of initiator (m-mole/l)	4.04	0.553	1.10
Time of polymerization (min.)	13	80	30
Conversion (%)	9.51	9.16	6.35
$[\eta]_{\text{benzene}}^{30^\circ\text{C}}$	0.224	0.725	—
$M_v \times 10^4$	2.27	11.7	—
$M_n \times 10^4$ (titration)	2.05	10.1	—

ii) Palit's Dye Interaction Method.

Terminal group analysis for the higher molecular weight fractions was carried out by Palit's dye interaction method¹⁶⁾. This method is based on the fact that an extract of certain basic dyes by benzene (or similar nonpolar solvents) from an alkaline, properly buffered aqueous solution produces a color change upon addition to benzene solutions of either inorganic or organic acids. This method is extremely sensitive for detecting quantitatively a trace amount of acids in nonpolar solvents, and in fact, the presence of acids as low as 10^{-6} N in benzene can be easily detected. The method seemed to be quite promising for detecting the terminal carboxyl groups of higher molecular weight fractions.

As a reagent, the benzene extract of rhodamine 6Gx was employed. The rhodamine reagent was prepared as follows. About 5 mg of rhodamine 6Gx was dissolved into 4 ml of 0.4 M sodium-phosphate buffer (pH 10), immediately extracted by mixing the buffer solution with 50 ml benzene, shaking, and recovering the benzene phase. The benzene extract was further diluted with benzene to make a final solution so that the optical density (O. D.) of 1:1 (by volume) mixture of the final solution and pure benzene was 0.4 ± 0.01 at $515 m\mu$ against pure benzene. The solution was used as the reagent. Since the reagent easily deteriorated with prolonged storage, it was always freshly prepared just before use.

On performing the analysis, the rhodamine reagent was mixed with an equal volume of a benzene solution of a polymer which was to be tested, and with an equal volume of pure benzene as a control. Fig. 1 shows a typical example of absorption spectra of a test solution (1:1 mixture of the reagent and a 0.128 mg/ml benzene solution of PSC I-7) and of the control (1:1 mixture of the reagent and pure benzene). It is seen from Fig. 1 that the spectrum of the test solution differs markedly from that of the control and has a maximum at $515 m\mu$. The O. D. change at $515 m\mu$ could be a very good measure for the analysis. Fig. 2 shows an O. D. versus polymer concentration curve at $515 m\mu$ for the fraction PSC I-7 ($M_n = 15,800$ as determined by alkaline titration), in which the Beer law holds fairly well over a considerable range of concentration. The linear portion of the curve for PSC I-7 was used as a standard calibration curve for the later analysis.

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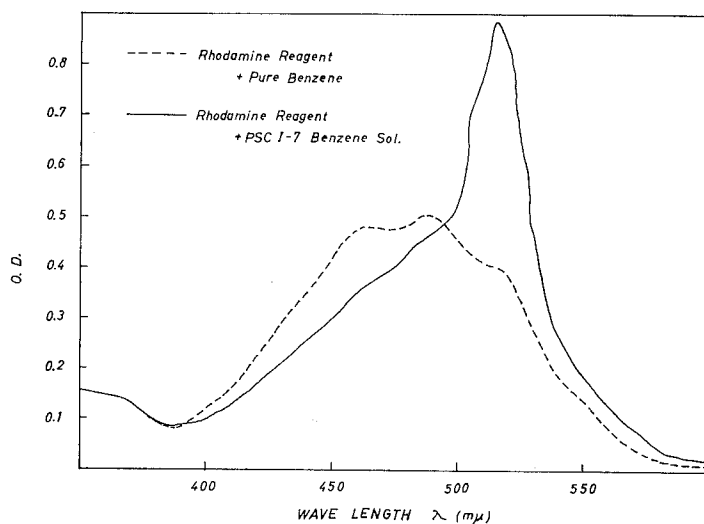


Fig. 1 Absorption spectra of the rhodamine reagent in the absence and presence of carboxylic acid.

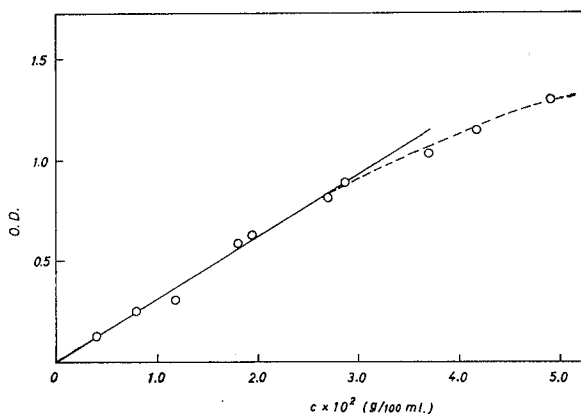


Fig. 2 O.D. versus polymer concentration curve at 515 $m\mu$ for PSC I-7.

The number average molecular weights of other fractions were evaluated from O.D.-values at 515 $m\mu$ of test solutions over the control by using this calibration curve and assuming M_n for PSC I-7 is 15,800. The results are all listed in Table 2.

All the optical measurements were made in a Hitachi model EPU-2 spectrophotometer with an 1-cm path length cell.

Phase Equilibria Measurements.

The apparatus and procedure for the determination of the critical precipitation temperatures were essentially the same as those described by Shultz and Flory¹⁷. In this work, the temperature was lowered at a rate of 0.1°C/min. until the solution became sufficiently cloudy.

Esterification of Terminal Carboxyl Groups with Diazomethane.

The terminal carboxyl groups were esterified with diazomethane for two of the fractions. In each experiment, three grams of polymer were dissolved in 100 ml

Table 2 Summary of the viscometry, osmometry and terminal-group analysis for PSC-fractions.

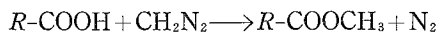
Fractions	viscosity data ^{a)}			osmotic pressure ^{b)}		terminal-group analysis ^{c)}	
	[η]	k'	$M_n \times 10^{-4}$	$M_n \times 10^{-4}$	$M_e \times 10^{-4}$	COOH-content	
PSC I							
I-2	0.354	0.66	4.30	—	(4.11)	2.09	
I-3	0.287	0.60	3.21	4.72(H)	—	—	
I-4	0.256	0.86	2.73	—	(2.10)	2.60	
I-5	0.224	0.82	2.27	2.34(V)	2.01(2.46)	1.85-2.35	
I-6	0.188	0.82	1.77	1.91(V)	—	—	
I-7	0.153	1.28	1.33	1.41(V)	(1.58)	1.68-1.79	
I-8	0.109	2.40	0.83	1.07(V)	1.11(0.991)	1.50-2.16	
PSC II							
II-2	1.468	0.33	31.5	30.1 (H)	—	—	
II-3	1.303	0.45	26.7	28.6 (O)	27.0	1.98-2.12	
II-4	1.156	0.38	22.5	26.9 (H)	—	—	
II-5	1.029	0.38	19.2	—	—	—	
II-6	0.911	0.36	16.2	21.0 (H)	—	—	
II-7	0.764	0.46	12.6	—	—	—	
II-8	0.769	0.31	12.7	—	—	—	
II-9	0.591	0.52	8.81	13.9 (H)	10.6	1.66-2.62	
II-10	0.510	0.36	7.19	—	—	—	
II-11	0.382	0.39	4.80	6.59(H)	6.49	1.48-2.03	
PSC III							
III-2	0.762	0.47	12.6	—	9.95	2.53	
III-3	0.693	0.31	11.0	14.6 (O)	12.5	1.76-2.34	
III-4	0.593	0.55	8.86	13.6 (O)	—	—	
III-5	0.541	0.45	7.80	13.9 (O)	12.2	1.28-2.28	
III-6	0.535	0.31	7.67	11.0(O) 10.0(H)	10.1	1.52-2.18	
III-7	0.468	0.36	6.36	8.85(O)	6.95	1.83-2.54	
III-8	0.371	0.44	4.60	7.75(H)	6.50	1.42-2.39	
III-9	0.359	0.40	4.39	—	—	—	
III-10	0.243	0.34	2.61	4.34(H)	2.89	1.81-3.00	
III-11	0.200	0.60	1.93	3.30(H)	1.74	2.22-3.79	

a) measured in benzene solution at 30°C. k' is the Huggins constant.

b) (H), (O), and (V) denote values determined by a High Speed Membrane Osmometer, Zimm-Meyerson type osmometers and a Vapour Pressure Osmometer, respectively.

c) Number average molecular weights evaluated from terminal group analysis. Values in parentheses are determined by alkaline titration. Others are determined by dye interaction test.

benzene containing 2.8 g (excess) diazomethane. The flask was occasionally shaken and stood for about 30 minutes at 5°C. The esterified polymer was precipitated by methanol, redissolved in benzene, reprecipitated with methanol, and dried *in vacuo* at 50°C. The terminal carboxyl groups of polymer are supposed to be converted into methyl ester by the following reaction with diazomethane.



The terminal group analysis indicated that more than 95% carboxyl groups were esterified by this procedure. The preparation of benzene solution of diazomethane has been described elsewhere¹⁸⁾.

RESULTS AND DISCUSSION

Carboxyl Group Content per Chain.

i) Evidence from the kinetics of polymerization.

Under the condition of polymerization mentioned above, there is a possibility that the sample may be contaminated with thermally polymerized polystyrene, i.e., polymer chains without terminal carboxyl groups. To estimate the possible extent

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of contamination, a blank test for the polymerization was carried out under the similar conditions as described before except by using a polymerization mixture consisting of the total mixture less the initiator. The result of blank test turned out that the conversion was less than 0.01%, so that the ACVA-initiated polystyrene would contain thermal-polystyrene less than 0.1%. In addition, since DMF has a low chain transfer constant to styrene¹¹⁾ and the termination in radical polymerization of styrene occurs predominantly by combination of polymer radicals⁹⁾, it is expected that most of the polymer chains would have two carboxyl groups at both ends.

ii) Evidence from the terminal group analysis.

The last column of Table 2 shows the average numbers of terminal carboxyl groups per chain. These values were evaluated by comparing the number average molecular weights determined by the terminal group analysis and those by the viscometry and osmometry. It is to be noted that the molecular weights determined by the osmometry are always higher than those by other methods, and these discrepancies are particularly larger for the lower molecular weight fractions. This may be due partly to an artifact in the osmometry such as the permeation of solutes through the membrane and due partly to some other unknown reasons. Although the values of carboxyl group contents are scattering, all the data suggest that each polymer chain has two carboxyl groups, one at each end. This is consistent with the consideration on the basis of the polymerization kinetics.

Critical Precipitation Temperature.

Liquid-liquid phase diagrams were determined in the vicinity of the critical precipitation temperature in cyclohexane for some of the fractions. Fig. 3 shows

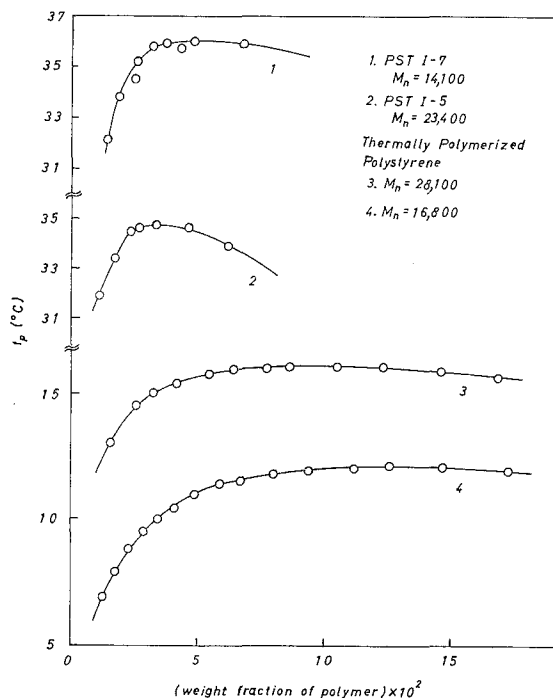


Fig. 3 Typical example of binary phase diagrams for PSC-fractions.

a few examples of the phase diagrams, where precipitation temperatures were plotted against the polymer concentration.

The reciprocal of the critical precipitation temperature, $1/T_c$, which is the temperature corresponding to the maximum of each phase diagram, is plotted against $[m^{1/2} + (1/2)m^{-1}]$ according to the relation¹⁹⁾.

$$\frac{1}{T_c} = \frac{1}{\Theta} \left[1 + \frac{1}{\psi_1} \left(\frac{1}{m^{1/2}} + \frac{1}{2m} \right) \right] \quad (3)$$

Here Θ and ψ_1 and the Flory's Θ -temperature and the entropy parameter, respectively, and m is the (number average) degree of polymerization. Fig. 4 shows the plot for the PSC-fractions and also those for benzoyl peroxide (BPO)-initiated polystyrenes by Shultz and Flory¹⁷⁾ and for thermally polymerized ones. It is seen

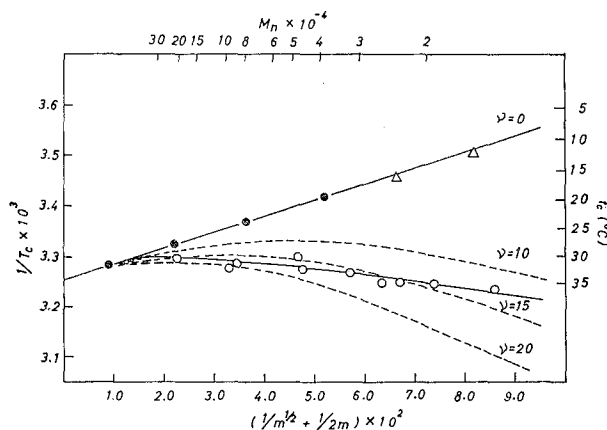


Fig. 4 Molecular weight dependence of the critical precipitation temperature for PSC-fractions (○), BPO-initiated polystyrenes (●) and thermally polymerized polystyrenes (▲) in cyclohexane. Theoretical curves are shown for various values of ν by dotted lines.

that there is no difference between the plots for BPO-polystyrenes and for thermal-polystyrenes. On the other hand, the plot for the PSC-fractions differs markedly from those of the above two. For example, the critical temperature, T_c , for the PSC-fractions is 25 degree higher at the molecular weight of 1.5×10^4 and 3 degree higher even at the molecular weight as high as 20×10^4 .

According to the theory of Flory¹⁹⁾, the plot of $1/T_c$ against $[m^{1/2} + (1/2)m^{-1}]$ should give a straight line in a given polymer-solvent system, so that the values of Θ and ψ_1 may be evaluated from the slope and the intercept of the plot, respectively. In this sense, the plot for the PSC-fractions extrapolates to 28°C and yields a negative value of ψ_1 . However, as will be shown later, the temperature at which the light scattering second virial coefficient vanishes is always much higher than 28°C and even higher than 34.5°C which has been known as the Θ -temperature for ordinarily polystyrenes in cyclohexane. The linear extrapolation according to equation (3) seems to be inapplicable to the PSC-fractions.

A possible explanation is that this anomaly might be resulted from the difference in solubility between the styrene unit and the terminal-group for cyclohexane. If such is the case, the van Laar-Scatchard type²⁰⁾ expression for the heat of mixing should be modified to include the contribution of the terminal groups. As

the simplest approximation, the modification for the solvent-polymer interaction parameter χ_1 may be written as

$$\chi_1 = \chi_1^0 + \frac{\nu}{m}, \quad (4)$$

where χ_1^0 and ν/m are the contributions to χ_1 of the styrene part and the terminal group, respectively. Further we assume that at the limit of infinitely large molecular weight, the relation for ordinary polystyrenes

$$\chi_1^0 = 1/2 - \psi_1 \left(1 - \frac{\theta}{T}\right) \quad (5)$$

should hold for the PSC-fractions as well, by using the same θ ($=34.5^\circ\text{C}$) and ψ_1 values. Finally we obtain

$$\frac{1}{T_c} = \frac{1}{\theta} \left[1 + \frac{1}{\psi_1} \left(\frac{1}{m^{1/2}} + \frac{1}{2m} - \frac{\nu}{2m} \right) \right] \quad (6)$$

Fig. 4 shows the plots of $1/T_c$ against $[m^{1/2} + (1/2)m^{-1}]$, calculated according to equation (6) for the several values of ν as indicated. In spite of the crudest assumptions adopted, these curves seem to represent fairly well the qualitative feature of the experimental curve.

The Theta Temperature.

In Fig. 5, the second virial coefficients A_2 from the light scattering measurements are plotted as functions of temperature for cyclohexane solutions of six PSC-fractions. From these plots, the theta temperature, defined as the temperature at

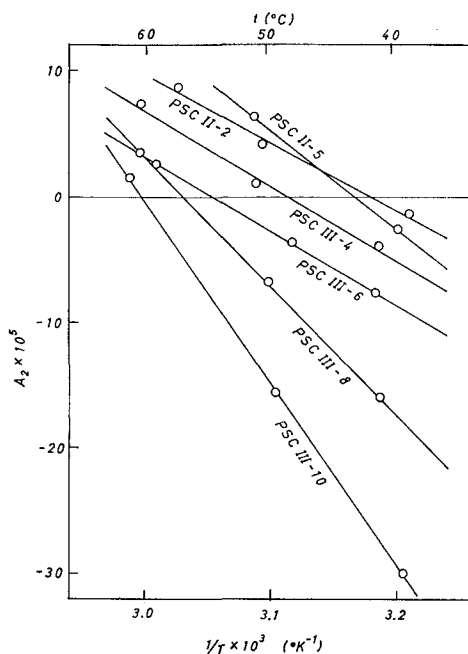


Fig. 5 Second virial coefficient (A_2) of PSC-fractions in cyclohexane as a function of temperature.

which A_2 vanishes, is determined for each fraction. The results are shown in Table 3, together with the weight average molecular weights determined by the L.S. measurements. In Table 3 the values determined for two of the fractions in

p-dioxane solutions at 30°C are also shown. As seen in Table 3, the theta temperatures of PSC-fractions are higher than 34.5°C especially for the low molecular weight fractions.

Table 3 The molecular weights and theta temperatures in cyclohexane solutions.

Samples	$M_w \times 10^{-4}$	θ (°C)
PSC II-2	56.8	42
PSC II-5	41.2	43
PSC III-4	21.8	48
PSC III-6	15.8 (16.6 ^a)	54
PSC III-8	11.5	57
PSC III-10	6.42(5.12 ^b)	60

a) measured in *p*-dioxane solution at 546 m μ .

b) measured in *p*-dioxane solution at 436 m μ .

In order to ensure whether these anomalies in thermodynamical properties are solely due to the presence of terminal carboxyl groups or not, the esterification of terminal carboxyl groups were carried out with diazomethane for two of the PSC-fractions, and L.S. measurements were made for cyclohexane solutions of the products in the vicinity of 35°C. The results of the L.S. measurements and of the viscosity for the fractions before and after esterification are summarized in Table 4. It is noticeable that the theta temperature is reduced to the same value as the

Table 4 Light scattering and viscometric data for the fractions before and after esterification.

Samples	before esterification			after esterification			
	$M_w \times 10^{-4}$ (dioxane)	[η]		$M_w \times 10^{-4}$ (cyclohexane)	[η]		$A_2 \times 10^4$ (cyclohexane)
		benzene at 30°C	dioxane at 30°C		benzene at 30°C	dioxane at 30°C	
PSC III-2	29.0	0.762	0.681	34.8	0.792	0.732	(35.4°C) 0.05
PSC III-9	8.40	0.359	0.321	9.52	0.353	0.318	(35.6°C) 0.13

thermally polymerized polystyrene after esterification of carboxylic acid, and the terminal group effect disappears. In Table 4, it is further noticed that the molecular weights after esterification become slightly higher than those of before. This may be resulted from the loss of lower molecular weight portions in the fractions during the reprecipitation processes after the esterification reaction.

In various articles^{3,7,8)}, the anomalous behavior of polystyrene with polar terminal groups have been reported, in some of which the anomalies are attributed to the association of polymer molecules through the terminal groups. We also looked for the evidence of the intermolecular association of the PSC-fractions. However, at the moment we have failed in finding any positive evidence. For example, examining the data in Table 3 and 4, we note the followings: (i) The light scatter-

ing molecular weights for the PSC-fractions are almost same in cyclohexane and in *p*-dioxane (Table 3), the latter solvent should diminish the polymer association if any is present. (ii) The esterification of terminal carboxyl groups does not result in any appreciable difference in the molecular weights and the viscometric data before and after esterification (Table 4). These evidences deny the presence of the polymer association. On the other hand, we have observed the anomalously high values of the osmotic pressure molecular weight fractions (Table 2), which have also been reported in various articles^{2,3)} and attributed to the polymer association. A more extensive study would be necessary for elucidating the anomalous features observed in the polystyrenes with terminal carboxyl groups.

CONCLUSIONS

The present study on the properties of polystyrene with terminal carboxyl groups may be summarized as follows:

- (i) The terminal group effect on the thermodynamical properties appears for the polymers having polar terminal groups even with molecular weights as high as 50×10^4 , which is surprisingly higher than one would anticipate.
- (ii) When the polar groups are shielded by any procedure such as, for example, esterification of carboxyl groups, the effect remarkably diminishes or even disappears.
- (iii) We have observed a sharp increase of the Huggins constant with decreasing molecular weight. The increase has been attributed by various other authors^{2,3)} to the polymer association.
- (iv) However, we could not find any other positive evidences for the polymer association. Rather the anomalies in thermodynamical behavior may be qualitatively explained by modification of the solvent-polymer interaction parameter χ_1 .

A more extensive study, particularly on the chain configuration in dilute solution is now in progress in our laboratory.

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