

SYNTHESES OF FUNCTIONAL POLYMERS BY CATIONIC POLYMERIZATION : LIVING POLYMERIZATION AND CONTROLLED CHAIN TRANSFER

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SYNTHESES OF FUNCTIONAL POLYMERS BY CATIONIC
POLYMERIZATION: LIVING POLYMERIZATION AND
CONTROLLED CHAIN TRANSFER

INTRODUCTION

New polymer materials with specific functions and high performance are the key to the advanced technology today and tomorrow. The synthesis of such polymers requires elaborate design and control of their molecular structure; i.e., at least the following factors should be controlled: (i) pendant substituents, (ii) terminal group(s), (iii) the steric structure of the main chain, and (iv) molecular weight and its distribution.

Approaches to the controlled polymer synthesis are divided, in principle, into controlled polymerizations reactions and chemical modification of existing (often commodity) polymers. As an approach of the first category, "living" polymerization is most useful and versatile, particularly for the control of terminal functionality (factor ii) and polymer molecular weight and its distribution (factor iv). Since the first discovery of the formation of living anionic poly(styrene) by Szwarc¹⁾ in 1956 and the following finding of living ring-opening polymerization of cyclic ethers²⁾ in 1965, the concept of living polymerization has been extended to other systems, and the advances in the last decade are impressive in quantity and quality. Even by an anionic mechanism, however, vinyl monomers having a polar substituent are still very difficult to polymerize into living polymers, unless the polar function is masked with a protective group.³⁾ This is because the polar pendants usually cause various side reactions, such as chain transfer, during the polymerization.

In contrast to the abundance of living anionic and ring-opening polymerizations, cationic polymerization of vinyl compounds⁴⁾ has been suffering the dearth of well-defined living processes that are useful for the syntheses of new polymers which

are otherwise impossible to obtain. The virtual absence of truly living cationic vinyl polymerizations is surprising in view of their unique potentialities, including the very large number and variety of cationically polymerizable monomers (as many as 500), low cost and high efficiency of acidic initiators, and modest investment required for industrial applications.⁵⁾ Based on these advantages, industrial processes that involve cationic polymerization are in fact very significant, producing, e.g., butyl rubbers, petroleum resins, etc.; these processes are not living at all, however. The difficulty in achieving living cationic polymerization stems from the involvement of carbocations as the propagating species, which are inherently so unstable as to undergo side reactions (chain transfer, termination, isomerization, etc.) in parallel with electrophilic addition (propagation) to a vinyl monomer.

Since around 1970, Higashimura et al. have systematically studied the nature of the propagating species in cationic polymerization and found that the elementary polymerization steps in general and chain transfer in particular can be controlled by selecting initiators (counteranions) and reaction conditions.⁶⁾ On the basis of these investigations, they established the existence of the propagating species with extremely different lifetime; i.e., a short-lived intermediate that can propagate only once, followed by chain transfer,⁷⁾ and a long-lived species that eventually leads to living polymers.⁶⁾ The key to the latter species is iodine employed as an initiator to depress chain transfer reactions.

Thus the iodine-initiated polymerization of p-methoxystyrene yields long-lived polymers.⁸⁾ More improved, perfectly living processes have recently been found by using a mixture of hydrogen iodide and iodine (HI/I₂) as an initiating system.⁹⁾ The HI/I₂ initiator, however, has so far been employed to only nonpolar alkyl vinyl ethers without polar functional groups; the range of

monomers, as well as initiators, for living cationic polymerization is thus limited.

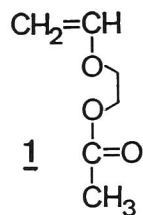
In order to synthesize well-defined functional polymers via cationic mechanisms, the author has started to examine the possibility of living cationic polymerization of vinyl monomers having a functional group. To this end, it is of particular significance to control or suppress reactions of the highly reactive carbocationic propagating species toward the functional groups in the monomer and polymer. The following part of this thesis shows examples in which the living technique has enabled synthesis of new tailor-made functional polymers.

Another method to synthesize functionalized polymers, as mentioned before, is chemical modification of commodity polymers.¹⁰⁾ This method is advantageous in industry, because of (i) easier control of the structure and molecular weight of precursor polymers, (ii) variety of functional groups to be introduced, and (iii) the facile manipulation and low cost. The most abundant uses of chemically modified polymers are found for ion-exchange resins,¹¹⁾ poly(vinyl alcohol) fibers,¹²⁾ and reformed rubbers.¹³⁾ On the other hand, few polymers obtained by cationic polymerization have been chemically modified so far. The limited examples include halogenation of butyl rubber¹⁴⁾ and transformation of the terminals of low molecular weight telechelic polyisobutylene.¹⁵⁾ The last part of this thesis (Part III) concerns the chemical modification of unsaturated polymers which can be prepared only by cationic techniques. An emphasis is placed on new methods of efficient functionalization of selected sites of the polymer.

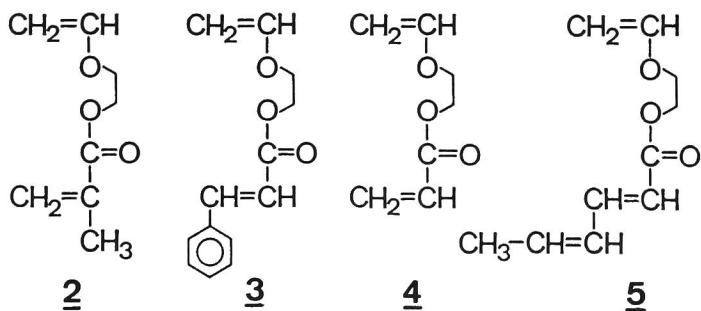
The present thesis consists of three parts. Part I deals with the living cationic polymerization of vinyl monomers having an ester pendant, which is of interest because of its facile conversion into other functional groups. As cationically polymerizable monomers, vinyl ethers were employed which are highly

polymerizable, contain an electron-donating alkoxy substituent, and thereby generate stable propagating species. The author also extensively studied chain transfer reactions in cationic polymerization of vinyl ethers, and developed a new class of living polymerization systems that in turn led to functional polymers with controlled structure, functionality, and molecular weight.

Chapter 1 describes the possibility of living cationic polymerization of 2-acetoxyethyl vinyl ether (1) having a saturated ester in the pendant. In spite of the presence of the polar ester pendant, which often disturbs cationic polymerization, the polymerization of vinyl ether 1 by HI/I_2 in nonpolar solvent was found to proceed without any side reactions, to yield a living polymer; the molecular weight distribution of the polymer was very narrow and close to monodisperse ($\bar{M}_w/\bar{M}_n \sim 1.1$), and its $\bar{M}_n$ could be controlled by regulating monomer conversion and the feed ratio of monomer to initiator. Poly(1) was readily hydrolyzed under basic conditions into a water-soluble polyalcohol, with a controlled molecular weight.



The following two chapters concern the extension of the use of HI/I_2 initiator to living cationic polymerization of vinyl ethers having unsaturated ester pendants. The ester pendants include methacrylate (2) and cinnamate (3) (Chapter 2) or acrylate (4) and sorbate (5) (Chapter 3). The cationic polymerizations of the four



vinyl ethers proceeded exclusively via their vinyloxy groups to give living polymers composed of a vinyl ether backbone and unsaturated ester pendants.

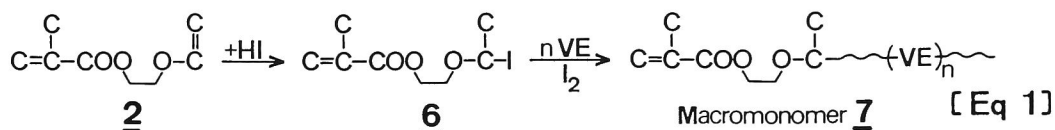
Chapter 4 delineates an exploration of new initiating systems for living cationic polymerization, other than HI/I_2 , which can be employed at higher temperatures ($0^\circ \sim +25^\circ\text{C}$) preferred in practical applications. EtAlCl_2 modified with Lewis bases (e.g., esters) was found to fulfill such requirement, and initiated living polymerizations of alkyl vinyl ethers even at ambient temperature. Similarly, living polymers were obtained from vinyl ethers with an ester pendant (1 - 5) using EtAlCl_2 alone as an initiator. To our knowledge, it is the first time that living polymers were obtained in the cationic polymerization by an organometallic halide.

Chapter 5 discusses in detail the mechanisms of chain transfer reactions in cationic polymerization of vinyl ethers. Detailed understanding of the chain-transfer mechanism is indispensable not only for developing living processes but for synthesizing well-defined oligomers as well. As models for vinyl ether polymerization, oligomerization was carried out at such a high temperature as chain transfer becomes dominant over propagation. On the basis of structural analysis of the produced oligomers, a new chain-transfer mechanism has been proposed which involves a successive dealcoholation from the growing chain.

Part II of this thesis, following the rather fundamental research directed toward "living" systems described in Part I, presents the application of the HI/I_2 -initiated living polymerization to the design and synthesis of new functional polymers. As typical examples, two chapters illustrate the syntheses of poly(vinyl ether) macromonomers and comb-like polyoxyethylenes.

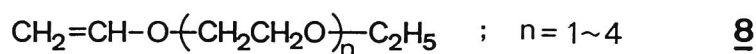
Chapter 6 is devoted to the syntheses of poly(vinyl ether) macromonomers. In general, macromonomers are a class of linear polymers having a polymerizable group at one chain end and are useful to prepare well-defined graft copolymers. As shown in eq 1,

6, an HI adduct of 2, initiated living polymerizations of alkyl vinyl ethers in the presence of iodine;



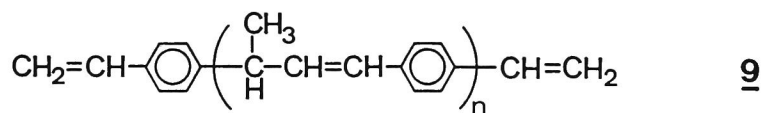
the products were of structure 7 consisting of a methacrylate terminal and a poly(vinyl ether) backbone with a narrow molecular weight distribution.

Chapter 7 treats the living cationic polymerization of polyether-containing vinyl ethers 8 and the synthesis of comb-like polymers with pendant oxyethylene chains thereby. These vinyl



ethers also formed living polymers when polymerized by HI/I₂ under the conditions similar to those for the ester-containing vinyl ethers (1 - 5). The polymers having two or more oxyethylene units in each pendant were soluble in water and formed complexes with alkali metal ions.

Part III concerns chemical modification of linear poly (divinylbenzene) [poly(DVB)] 9, an unsaturated polymer obtained via cationic polyaddition of DVB.¹⁶⁾ Since polymer 9 contains



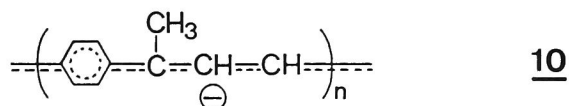
successively connected trans olefinic, allylic methine, and phenyl groups in the main chain capped with a vinyl group at each end, it is capable of undergoing various chemical reactions through these in-chain and terminal functions.

Chapter 8 demonstrates the usefulness of the terminal vinyl groups of 9 for the synthesis of α,ω -bifunctional ("telechelic")

poly(DVB). Linear poly(DVB)'s, having a variety of functional groups at both termini, were prepared by the polymerization of DVB initiated by oxo acids (e.g., acetyl perchlorate) in the presence of a substituted styrene. The terminal functions include acetoxyl, hydroxyl, and chloromethyl groups.

Chapter 9 shows that linear poly(DVB) 9 can be modified by the reactions on its terminal and in-chain unsaturations. Thus, hydration, epoxidation, and hydroxylation were performed to introduce hydroxyl groups into pendants or terminals or both, yielding fully hydrated poly(DVB), α,ω -dihydroxylated poly(DVB), etc.

Chapter 10 explores the application of polymeric delocalized polyanion (10) of linear poly(DVB) to polymer functionalization.



Polyanion 10 was obtained by the proton abstraction with alkyl lithium from the allylic methine moieties of 9. The obtained polyanion 10, despite its delocalized character, readily reacted with various electrophilic compounds in high yield to give poly(DVB) derivatives having functional pendants such as trimethylsilyl, vinyl, vinyloxy, hydroxyl, and carboxyl groups.

In conclusion, this research has provided new methods and strategies for the syntheses of various functional polymers which can be obtained exclusively by cationic methods. The author wishes that this thesis would contribute not only to the design and development of new advanced polymer materials but also to the study of related organic reactions mediated by carbocationic intermediates.

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PART I

LIVING CATIONIC POLYMERIZATION OF VINYL ETHERS WITH VARIOUS ESTER PENDANTS

CHAPTER 1

LIVING CATIONIC POLYMERIZATION OF 2-ACETOXYETHYL VINYL ETHER AND SYNTHESIS OF POLYALCOHOLS WITH NARROW MOLECULAR WEIGHT DISTRIBUTION

ABSTRACT

"Living" cationic polymerization of 2-acetoxyethyl vinyl ether (AcOVE, $\text{CH}_2=\text{CHOCH}_2\text{CH}_2\text{OCOCH}_3$) was achieved by the hydrogen iodide/iodine (HI/I₂) initiating system in toluene at -15° and -40°C to give polymers with a narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n \leq 1.2$). In spite of the presence of a polar ester group in the monomer, its cationic polymerization proceeded cleanly without any side reactions. The number-average molecular weight of poly(AcOVE) can be controlled by regulating the feed ratio of monomer to initiator (HI) and conversion. The BF₃OEt₂-initiated polymerization of AcOVE yielded polymers of high molecular weight and a broader molecular weight distribution. Base-catalyzed deacetylation (hydrolysis) of poly(AcOVE) quantitatively gave poly(2-hydroxyethyl vinyl ether), a polyalcohol more soluble in cold water than the corresponding poly(vinyl alcohol).

INTRODUCTION

Polymerization of vinyl monomers with a functional pendant group provides a simple one-pot method to prepare functionalized linear polymers. A difficulty often encountered in this approach is that side reactions (chain transfer, termination, and the like) induced by the polar functional group in the monomer disturb polymerization processes and thereby make control of the structure and molecular weight (distribution) of the target polymers very difficult. This is particularly the case in cationic vinyl polymerization in which the propagating carbocations are extremely susceptible to polar functional groups.

Recently Higashimura et al. started a systematic search of living cationic polymerization of vinyl ethers and related monomers¹⁾ and found that hydrogen iodide combined with iodine (HI/I₂ initiator) induces nearly perfect living polymerization of alkyl vinyl ethers to yield monodisperse polymers.^{2,3)} This series of studies is to extend the scope of the living systems to vinyl ethers ($\text{CH}_2=\text{CHOCH}_2\text{CH}_2\text{R}$) with a polar functional pendant (R) that may adversely affect their polymerization. Substituent R may include ester, alkoxycarbonyl, polyether, substituted phenoxy, and polymerizable olefinic groups. Although a number of such "functionalized" vinyl ether monomers have already been prepared,^{4,5)} most of them have eluded systematic investigations, except for 2-vinyloxyethyl cinnamates.⁵⁾ Living polymerization of the functionalized vinyl ethers, if achieved, will allow one to control the molecular weight, molecular weight distribution (MWD), and end-group structure of their polymers and thus to prepare poly(vinyl ethers) of interesting functions and/or properties.

This first chapter concerns the living cationic polymerization of 2-acetoxyethyl vinyl ether (AcOVE; 1) and the chemical modification of poly(AcOVE) 2 into poly(2-hydroxyethyl vinyl ether)

and thermometer were placed CEVE (240 ml, 2.4 mol), sodium acetate (82 g, 1.0 mol), and tetra-n-butylammonium iodide (2 g), and the mixture was stirred for 4 h under mild reflux and cooled to room temperature. The resulting sodium chloride was separated from the organic phase by filtration and extracted with 200 ml of ethyl ether. The ether extract was combined with the organic layer, and the ether and unreacted CEVE were removed from the mixture by distillation. The crude monomer was distilled twice over calcium hydride under reduced pressure to give AcOVE as a colorless oil, purity > 99 % by gas chromatography; the isolated yield was ca. 50 % based on the sodium acetate charge. The monomer was identified by infrared (IR) (Figure 8A) and ^1H and ^{13}C NMR spectroscopy: ^1H NMR (CDCl_3) δ 6.5 (q, 1H, =CH-O-), ~4 (m, 2H, $\text{CH}_2=$), 4.2 - 4.1 and 3.9 - 3.7 (m, 4H, $-\text{OCH}_2\text{CH}_2\text{O}-$), 2.1 (s, 3H, $-\text{CH}_3$); ^{13}C NMR(CDCl_3) δ 170.0 (C=O), 151.1 (=CH-O-), 86.5 ($\text{CH}_2=$), 65.5 and 62.1 ($-\text{OCH}_2\text{CH}_2\text{O}-$), 20.2 ($-\text{CH}_3$).

Polymerization. Cationic polymerization of AcOVE was carried out under dry nitrogen in a baked glass tube equipped with a three-way stopcock. The reaction was initiated by adding an initiator solution to a monomer solution and quenched with prechilled ammoniacal methanol. When the HI/I_2 initiating system was employed, hydrogen iodide and iodine solutions were added successively. The concentration of hydrogen iodide in a stock solution was determined by titration just before use.^{2,3}) AcOVE conversion was measured by gas chromatography with bromobenzene as internal standard. The quenched reaction mixture was washed with deionized water to remove the initiator residues and evaporated to dryness to give the product polymers. The polymerization solutions obtained with HI/I_2 or iodine were washed with 10 % aqueous sodium thiosulfate solution before the above-described workup.

Synthesis of Poly(HOVE). Polyalcohol 3 was prepared by base-catalyzed hydrolysis of poly(AcOVE) (eq 1). Thus, a solution of poly(AcOVE) in acetone (5% (w/v)) was mixed with 20 % aqueous sodium hydroxide solution (3 equiv. to the ester units in the polymer), and the mixture was stirred at room temperature for 3 h, during which period partially hydrolyzed polymers precipitated. After the water and acetone were removed by evaporation or decantation, the precipitate was dissolved in a large amount of water. The solution was stirred for 5 h at room temperature to complete the hydrolysis, neutralized to pH 7.0 with dilute hydrochloric acid, and concentrated by evaporation to a few milliliters. The concentrated solution was poured into a large amount of aqueous acetone (ca. 5 % (v/v) water) to remove sodium acetate and sodium chloride. The precipitated polymer was separated by decantation and dried in vacuo. The complete deacetylation was confirmed by IR and ^1H and ^{13}C NMR spectroscopy (see below).

Polymer Characterization. The molecular weight distribution (MWD) of poly(AcOVE) was determined by size exclusion chromatography (SEC) in chloroform on a JASCO Trirotar chromatograph equipped with polystyrene gel columns and ultraviolet/refractive index dual-mode detectors; column sets were Shodex A-802 and A-804 (x2) for the polymers (8.0 mm i.d. x 500 mm each) and JSP-101 for the oligomers (20 mm i.d. x 500 mm). The number-average molecular weight ($\bar{M}_n$) and polydispersity ratio ($\bar{M}_w/\bar{M}_n$) were calculated from SEC curves on the basis of a polystyrene calibration. ^1H and ^{13}C NMR spectra were recorded on a JEOL FX90Q spectrometer. IR spectra (KBr) were recorded on a Shimadzu IR-435 spectrophotometer.

RESULTS AND DISCUSSION

AcOVE Polymerization by Acid Initiators.

Orienting experiments with a variety of acid initiators were carried out in toluene at -15°C to examine whether the ester group of AcOVE affects its polymerization. The initiators employed include $\text{CF}_3\text{SO}_3\text{H}$ as a strong protonic acid, iodine as molecular halogen, and BF_3OEt_2 as a metal halide. Table I summarizes the results.

The polymerizations by $\text{CF}_3\text{SO}_3\text{H}$ and BF_3OEt_2 were almost completed within 10 min. The products obtained with $\text{CF}_3\text{SO}_3\text{H}$ were pale yellow, slightly viscous, liquid oligomers. BF_3OEt_2 , on the other hand, yielded rubbery high polymers and was found most effective for the synthesis of high-molecular-weight poly(AcOVE). The iodine-initiated polymerization was quantitative but slower than those by the other initiators and gave polymers with lower molecular weight. It is of interest that the polymers showed a rather narrow MWD (see below).

TABLE I
Polymerization of AcOVE by Acid Initiators
in Toluene at $-15^{\circ}\text{C}^{\text{a)}$

Initiator	[Initiator] ₀ (mM)	Time (h)	Conv. (%)	$\bar{M}_w^{\text{b)}$ $\times 10^{-3}$	$\bar{M}_n^{\text{b)}$ $\times 10^{-3}$
$\text{CF}_3\text{SO}_3\text{H}$	5.0	0.2	100	3.0	1.8
BF_3OEt_2	20	0.2	93	68	26
I_2	20	3.8	100	8.6	5.6

a) $[\text{M}]_0 = 10 \text{ vol\%}$ (0.76 M).

b) By SEC; polystyrene calibration.

The optimum conditions for the synthesis of high-molecular-weight poly(AcOVE) were studied with BF_3OEt_2 as the initiator, which was found best suited for this purpose. The molecular weight of poly(AcOVE), similarly to those of other poly(alkyl vinyl ethers), increased with decreasing polarity of polymerization solvent (hexane-toluene mixtures) and decreasing temperature from -15° to -78°C , indicating that chain transfer is suppressed in less polar media and at lower temperature. Thus, the highest molecular weight polymer, around 10^5 ($\bar{M}_w = 11.0 \times 10^4$, $\bar{M}_n = 5.0 \times 10^4$), was obtained at -78°C in a hexane-toluene (3:1 (v/v)) mixture.

The formation of high polymers by BF_3OEt_2 shows that, under suitable reaction conditions, the ester group in AcOVE neither inhibits nor disturbs cationic AcOVE polymerization. In fact, all the polymers obtained in this study exhibited ^1H and ^{13}C NMR spectra (see below) fully consistent with structure 2 (eq 1) in which all repeat units carry an ester pendant.

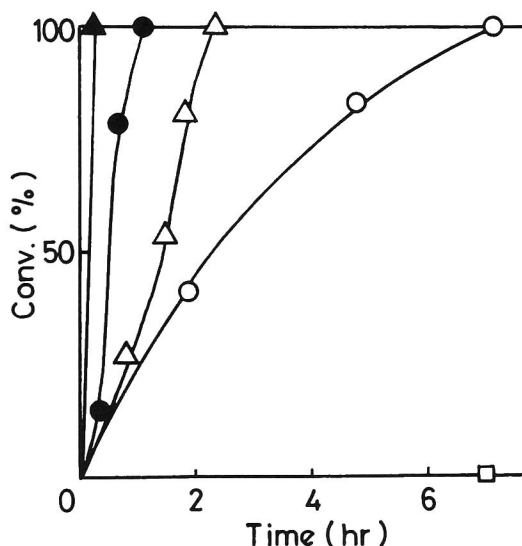


Figure 1. Time-conversion curves for the polymerization of AcOVE in toluene at -15°C and $[\text{M}]_0 = 5 \text{ vol}\%$ (0.38 M). Initiator and $[\text{Initiator}]_0$ (mM): (▲) BF_3OEt_2 , 4.0; (●) HI/I_2 , 10/10; (○) HI/I_2 , 10/10 (-40°C); (△) I_2 , 20; (□) HI , 10.

Living Polymerization by HI/I₂ Initiator.

The vinyl ethers thus far found to form living polymers with HI/I₂ initiator are all alkyl^{2,3)} and chloroalkyl⁸⁾ derivatives that have no polar functional pendant groups. Since the orienting experiments described above indicated that even a vinyl monomer with an ester substituent can be polymerized cationically into high polymers, the author studied the possibility of living polymerization of AcOVE with HI/I₂ and related initiators.

Thus the acetoxy monomer was polymerized in toluene at -15° or -40°C by HI/I₂ initiator; for comparison, iodine or hydrogen iodide alone and BF₃OEt₂ were also used as initiators. As shown in Figure 1, the polymerizations by HI/I₂ and iodine proceeded without an

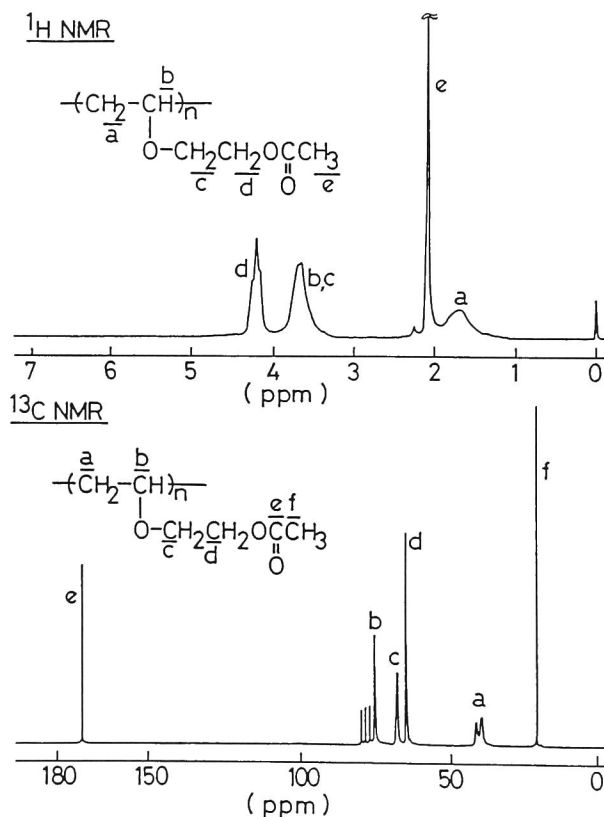


Figure 2. ¹H and ¹³C NMR spectra of poly(AcOVE) ($\bar{M}_n = 12300$) obtained with HI/I₂ in toluene at -40°C: $[M]_0 = 5 \text{ vol\% (0.38 M)}$; $[HI]_0 = 4.1 \text{ mM}$; $[I_2]_0 = 2.5 \text{ mM}$. Conversion was 100 %.

induction phase up to 100 % conversion, though slower than that by BF_3OEt_2 even when higher hydrogen iodide and iodine concentrations were employed. With HI/I_2 initiator, the higher the initial hydrogen iodide concentration, the greater the polymerization rate (data not shown). In contrast, no polymers formed within a week in the presence of hydrogen iodide alone.

Figure 2 shows typical ^1H and ^{13}C NMR spectra of poly(AcOVE) obtained with HI/I_2 initiator, along with peak assignments. The absence of the olefinic protons of AcOVE and the presence of main-chain methylene and methine groups and acetoxyl pendants all indicate the expected structure of poly(AcOVE) (2, eq 1): IR analysis of the polymer also supported structure 2 (cf. Figure 8B).

The MWD of poly(AcOVE) thus obtained depended clearly on initiators (Figure 3). HI/I_2 initiator gave a very narrow MWD

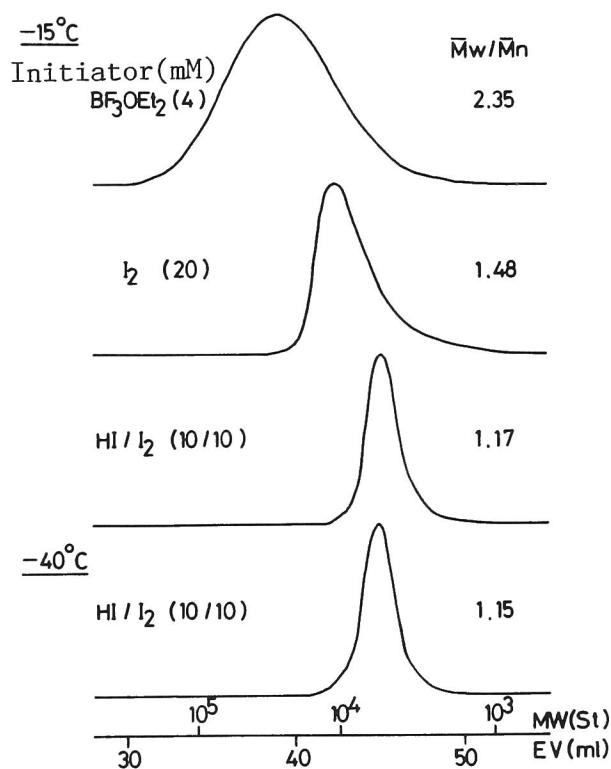


Figure 3. MWD of poly(AcOVE) obtained in toluene at -15° or -40°C : $[\text{M}]_0 = 5 \text{ vol\%}$ (0.38 M). Initiators and $\bar{M}_w/\bar{M}_n$ as indicated.

($\bar{M}_w/\bar{M}_n \leq 1.2$) at -15° and -40°C . The MWD with iodine was narrow ($\bar{M}_w/\bar{M}_n \sim 1.5$) but broader than that with HI/I₂. In contrast, the polymer obtained by BF₃OEt₂ exhibited a much broader MWD extending to molecular weight ca. 10^5 . Thus, HI/I₂ initiator was found to produce polymers with a narrow MWD not only from simple alkyl vinyl ethers^{2,3}) but from those with a polar functional group like AcOVE.

Figure 4 illustrates a typical relationship between monomer conversion and the $\bar{M}_n$ of the polymers formed by HI/I₂ in toluene at -40°C . In these so-called "monomer-addition" experiments, AcOVE was first polymerized, and then a new monomer charge (neat) was supplied to the reaction mixture. The second-stage polymerization was also quantitative. The MWDs of the polymers formed before and after the monomer addition were all very narrow ($\bar{M}_w/\bar{M}_n \leq 1.2$) at any conversion, and these MWDs shifted toward higher molecular weight with increasing conversion; no tailing appeared in the lower molecular weight region. Accordingly, the polymer molecular weight ($\bar{M}_n$) increased proportionally to conversion, and the linear $\bar{M}_n$ -conversion plot was maintained for the polymers obtained after the monomer addition. Such a proportionality of $\bar{M}_n$ to conversion was found at all concentrations of hydrogen iodide, iodine, and AcOVE employed, if hydrogen iodide was in excess over iodine. The smooth, linear increase of $\bar{M}_n$ after the monomer addition shows that all polymer chains formed in the first-stage polymerization can resume propagation when an additional monomer feed is supplied.

Figure 5 depicts the control of the $\bar{M}_n$ and MWD of poly(AcOVE) by regulating the monomer-to-initiator (HI) feed ratio ($[M]_0/[HI]_0$). Polymerization was carried out in toluene at -40°C at a constant monomer concentration $[M]_0$ (5 vol%; 0.38 M), while the initial hydrogen iodide concentration $[HI]_0$ was varied from 2.5 to 20 mM; conversion was 100 %. The $\bar{M}_n$ of the produced polymers was nearly proportional to the reciprocal of $[HI]_0$, and all the polymers had narrow MWDs.

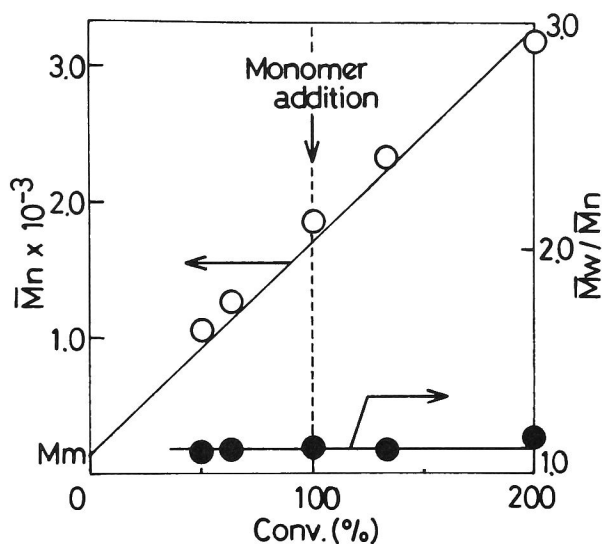


Figure 4. Relationship between conversion and $\bar{M}_n$ or $\bar{M}_w/\bar{M}_n$ ratio before and after the monomer addition in the AcOVE polymerization by HI/I₂ in toluene at -40°C: $[M]_0 = [M]_{\text{add}} = 0.20 \text{ M}$; $[HI]_0 = 24 \text{ mM}$; $[I_2]_0 = 20 \text{ mM}$. M_m indicates the molecular weight of AcOVE monomer.

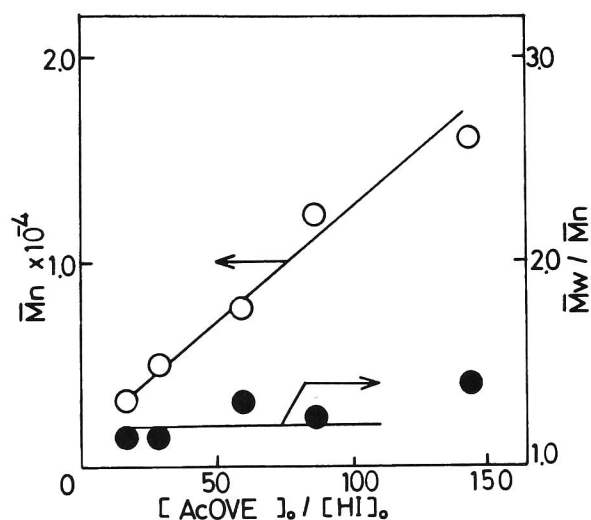


Figure 5. $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ ratio as functions of the monomer-to-initiator feed ratio $[M]_0/[HI]_0$ in the AcOVE polymerization by HI/I₂ in toluene at -40°C, conversion ~100 %.

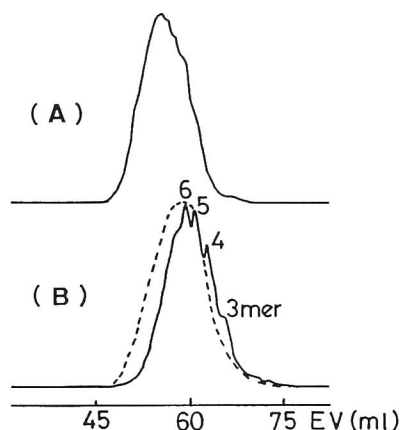


Figure 6. MWD of AcOVE oligomers obtained by HI/I₂ in toluene at -40°C: (A) [M]₀ = 0.20 M, [HI]₀ = 22 mM, [I₂]₀ = 20 mM, $\bar{M}_w/\bar{M}_n$ = 1.12; (B) [M]₀ = 0.10 M, [HI]₀ = 20 mM, [I₂]₀ = 20 mM, $\bar{M}_w/\bar{M}_n$ = 1.17. (----) Poisson distribution with the same peak molecular weight as that of oligomer B.

These results demonstrate the formation of "living"^{9,10} polymers from AcOVE by HI/I₂ initiator. It should be emphasized that living cationic polymerization is possible with HI/I₂ initiator even for a vinyl monomer with a polar ester group.

Living Oligomers and End-Group Analysis.

In the course of the study, the author found that HI/I₂-initiated polymerization of AcOVE cleanly gives living oligomers (DP ≤ 10) having a controlled molecular weight, which serve as model compounds for analysis of the MWD and end-group structure of living poly(AcOVE).

Figure 6 shows the MWD of such living oligomers prepared in toluene at -40°C at low [M]₀/[HI]₀ ratios (9.1 and 5.0). At the two ratios the polymerization was completed in 1 h to give oligomers A and B, the MWD of which was found to be very close to a Poisson distribution. Figure 6B exemplifies this agreement, where the broken-line curve indicates the calculated Poisson distribution.

Figure 7 presents the ¹H NMR spectrum of oligomer B quenched with methanol. It exhibits absorptions (a, g, and h) due to the terminal group that was not observable for higher living poly(AcOVE) (Figure 2). The doublet (a) at 1.2 ppm indicates the "head" methyl group ($\text{CH}_3\text{CH}(\text{OR}); \text{R}=\text{CH}_2\text{CH}_2\text{OCOCH}_3$); the triplet (g) at

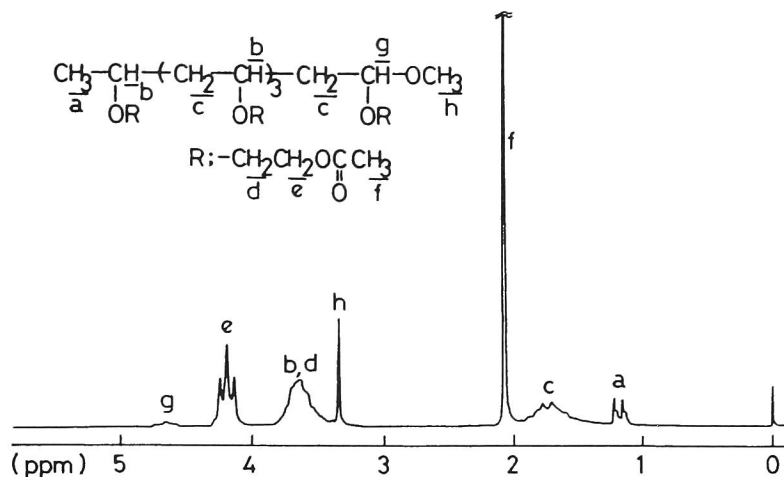
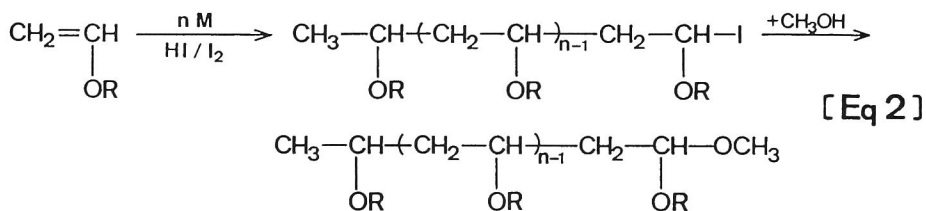


Figure 7. ^1H NMR spectrum of oligomer B shown in Figure 6B.

4.6 ppm and the singlet (h) at 3.3 ppm are assignable respectively to the methine and methoxyl units of the "tail" (terminal) acetal group ($\text{CH}_2\text{CH}(\text{OR})\text{OCH}_3$).

According to the recent mechanistic study on the HI/I_2 -initiated polymerization,¹¹⁾ the propagating living end consists of a $-\text{CH}(\text{OR}')-\text{I}$ bond activated by iodine. The NMR end-group analysis described above indicates, therefore, that the initiation is the addition of a proton derived from hydrogen iodide across the $\text{C}=\text{C}$ double bond of AcOVE to give a head methyl group and that the quenching with methanol proceeds via replacement of the terminal iodine with a methoxyl group to form an acetal unit (eq 2).



The signal intensity ratio of all protons of repeat units $[-\text{CH}_2\text{CH}(\text{OR})-]$ to the head methyl or tail methoxyl protons gave the number average degree of polymerization (P_n) of oligomer A ($= 8.5$), which was in good agreement with the $[\text{M}]_0/[\text{HI}]_0$ ratio employed ($= 9.1$).

Synthesis of Poly(2-hydroxyethyl vinyl ether).

Deacetylation (hydrolysis) of poly(AcOVE) will give poly(HOVE) 3 (eq 1). Thus a sample of high-molecular-weight poly(AcOVE) ($\bar{M}_w = 11.0 \times 10^4$) obtained with BF_3OEt_2 was hydrolyzed under basic conditions (see Experimental Section). Figure 8 compares the IR spectra of AcOVE monomer, the precursor poly(AcOVE), and its hydrolysis product. The carbonyl stretching band seen at 1700 cm^{-1} in Figure 8A, B completely disappeared upon hydrolysis, and the hydroxyl stretching band in turn appeared at 3400 cm^{-1} . The product gave ^1H and ^{13}C NMR spectra expected for poly(HOVE):

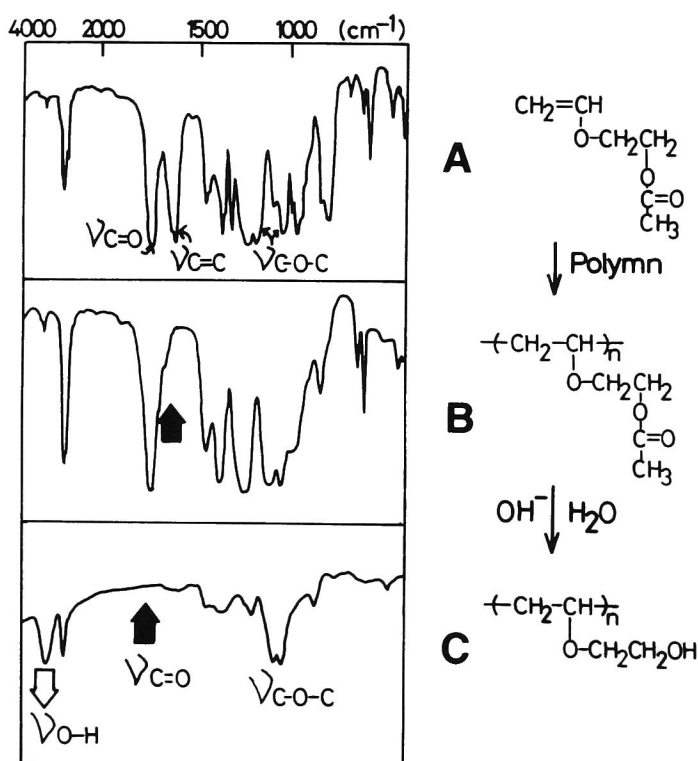


Figure 8. Hydrolysis of poly(AcOVE) monitored by IR spectroscopy: (A) AcOVE monomer; (B) poly(AcOVE) ($\bar{M}_w = 11.0 \times 10^4$) prepared with BF_3OEt_2 ; (C) hydrolysis product [poly(HOVE)] from sample B.

TABLE II

Solubility of Poly(2-hydroxyethyl vinyl ether) 3 and Related Polymers $\text{-(CH}_2\text{CHX)-}_n$

	X= OH ^{a)} <u>5</u> ^{b)}	X= O(CH ₂) ₂ OH <u>3</u>	X= CH(OH)CH ₃ ^{a)} <u>6</u> ^{c)}	X= O(CH ₂) ₂ OCOCH ₃ <u>2</u>
	<u>Repeat Unit</u>			
Formula	C ₂ H ₄ O	C ₄ H ₈ O ₂	C ₄ H ₈ O	C ₆ H ₁₀ O ₃
C/O	2/1	2/1	4/1	2/1
C/OH	2/1	4/1	4/1	6/0
	<u>Polymer Solubility</u> ^{d)}			
H ₂ O	○	○	X	X
CH ₃ OH	X	△	○	X
Dioxane	X	X	○	○
THF	X	X	○	○
Acetone	X	X	n.d.	○
CH ₂ Cl ₂	X	X	n.d.	○

a) Reference 12. b) Poly(vinyl alcohol). c) Poly(2-hydroxy-3-butene).

d) (○) soluble, (△) swelling, (X) insoluble. The solubilities of 2 and 3 were measured on 1 % (w/v) solutions at room temperature.

^1H NMR (D_2O) δ 3.9 (m, 5H, $-\text{CHOCH}_2\text{CH}_2\text{O}-$), 2.0 (m, 2H, $-\text{CCH}_2\text{C}-$); ^{13}C NMR (D_2O) δ 74.8 ($-\text{CH}-$), 70.2 ($-\text{CH}_2\text{OH}$), 61.6 ($-\text{OCH}_2-$), 40.7 and 39.1 ($-\text{CCH}_2\text{C}-$). The spectral analysis shows the quantitative removal of acetoxyl groups from the precursor and the formation of a new polyalcohol 3, having both ether and alcohol units in the pendant.

Similarly, hydrolysis of poly(AcOVE) obtained with HI/I_2 gave poly(HOVE) in a quantitative yield. Because no evidence for main-chain degradation during the hydrolysis was obtained, the resulting polyalcohol should inherit the narrow MWD of the precursor.

In Table II, the solubility characteristics of poly(HOVE) are compared with those of poly(AcOVE) and related polymeric alcohols.¹²⁾ Poly(HOVE) completely differed in solubility from poly(AcOVE), i.e., insoluble in good solvents for poly(AcOVE) [ethers (dioxane and THF) and aromatic (toluene) or chlorinated (CH_2Cl_2) hydrocarbons] while soluble (in water) and swelling (in methanol) in nonsolvents of poly(AcOVE) at room temperature. Although the apparent hydrophilicity of poly(HOVE), indicated by the carbon/oxygen (C/O) and carbon/hydroxy (C/OH) ratios (Table II), lies intermediate between those of poly(vinyl alcohol) (5, soluble in water) and poly(2-hydroxy-3-butene) (6, soluble in methanol but not in water), polyalcohol 3 was in fact more soluble in cold water than poly(vinyl alcohol).

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 - (9) In the following part of this chapter, the term "living" means that, because of the absence or suppression of termination and chain transfer, the propagating species has a very long lifetime to give polymers whose $\bar{M}_n$ is directly proportional to monomer conversion. In view of the successful sequential polymerizations under the conditions (monomer-addition experiments and block copolymerizations) and the resulting increase in polymer molecular weight, there is no doubt that almost all polymer chains carry an active propagating end. It has recently been pointed out, however, that such a proportionality of $\bar{M}_n$ does not necessarily prove the "complete absence" of termination and chain transfer required for "perfectly living" polymerization if the observed $\bar{M}_n$'s are less than 10000.¹⁰⁾
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CHAPTER 2

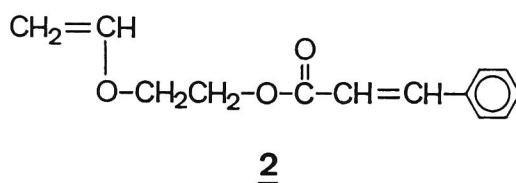
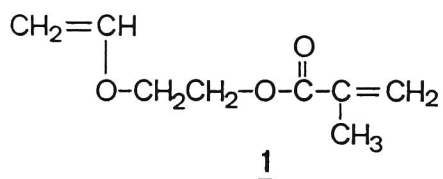
LIVING CATIONIC POLYMERIZATION OF VINYL ETHERS WITH AN UNSATURATED ESTER; METHACRYLATE AND CINNAMATE

ABSTRACT

"Living" polymerizations of 2-vinyloxyethyl methacrylate and 2-vinyloxyethyl cinnamate were successfully performed with a mixture of hydrogen iodide and iodine (HI/I₂) as an initiating system in toluene at -15° to -40°C. Although the two monomers have an unsaturated ester pendant group, their living polymerizations proceeded exclusively via the vinyloxy group without undesirable side reactions of the pendant group. The product polymers had a very narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n \sim 1.1$), and $\bar{M}_n$ directly proportional to monomer conversion. For both vinyloxyethyl monomers, the addition of a new feed of monomer to a polymerization mixture led to an increase in polymer molecular weight which was again proportional to the conversion.

INTRODUCTION

Following the recent discovery of the perfectly "living" cationic polymerization of alkyl vinyl ethers initiated by a mixture of hydrogen iodide and iodine (HI/I₂ initiator),^{1,2)} Chapter 1 of this thesis has shown that 2-acetoxyethyl vinyl ether (CH₂=CHOCH₂CH₂OCOCH₃), in spite of its polar ester pendant, can be cleanly polymerized by the same initiator to yield monodisperse living polymers.³⁾ Encouraged by this breakthrough, the author has now applied this HI/I₂-initiator to vinyl ethers having a reactive or polymerizable "unsaturated" ester group as pendant. This chapter describes the results on the HI/I₂-initiated living cationic polymerization of 2-vinyloxyethyl methacrylate (VEM; 1) and 2-vinyloxyethyl cinnamate (VEC; 2) in which, respectively, a methacryloyl and a cinnamoyl groups are connected to a vinyl ether moiety.



The methacryloyl group in VEM is, of course, radically or anionically polymerizable, whereas the cinnamoyl pendant in VEC readily undergoes four-centered photo-dimerization to form a cyclobutane ring. In view of the high cationic polymerizability of their vinyl ether moieties, these "functionalized" vinyl ethers are of interest as precursors of photoresists, curable coatings, etc. Besides these potential applications, they will provide, when cationically polymerized, an insight into the effects of polar and unsaturated ester groups on cationic vinyl polymerization in general and "living" cationic polymerization in particular where unsaturated ester pendants may deteriorate the initiation and

propagation processes.

VEM has been polymerized cationically (via the vinyloxy group) and anionically (via the methacryloyl group) to give soluble polymers.⁴⁾ The cationically obtained poly(VEM) retained the methacryloyl groups intact and readily crosslinked on exposure to heat, light, or X-ray⁵⁾. Extensive studies by Kato et al.⁶⁾ on the cationic polymerization of vinyloxyethyl cinnamates including VEC led to high-performance photo-resists now commercially available. The hitherto reported cationic polymerizations of VEM and VEC, however, are all non-living processes initiated by conventional Lewis-acid initiators, resulting in polymers with a broad, and uncontrolled molecular weight distribution (MWD). The author has succeeded in living cationic polymerization of VEM and VEC with HI/I₂ initiator to obtain monodisperse polymers, as described below.

EXPERIMENTAL SECTION

Materials. VEM and VEC were prepared by the phase transfer-catalyzed condensation of 2-chloroethyl vinyl ether with sodium methacrylate and cinnamate, respectively, in the presence of a catalytic amount of tetra-n-butylammonium iodide.⁶⁾ The monomers, solvents (toluene and n-hexane), initiators, and other chemicals were purified as described.^{1,3)}

Procedures. Polymerization by HI/I₂ was carried out under dry nitrogen. It was initiated by adding, successively, a hydrogen iodide solution in n-hexane and an iodine solution in toluene to a monomer solution in toluene, and terminated with prechilled methanol containing a small amount of ammonia. The quenched reaction mixture was washed with 10% aqueous sodium thiosulfate solution and then water to remove the initiator residues, followed

by evaporation under reduced pressure to give the products. The MWD of the polymers was measured by size exclusion chromatography on a JASCO Trirotar chromatograph equipped with three polystyrene gel columns [Shodex A-802 and A-804 (x 2)]. The $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ ratios were calculated from size exclusion chromatograms on the basis of a polystyrene calibration. ^1H and ^{13}C NMR spectra were recorded on a JEOL FX90Q spectrometer in CDCl_3 .

RESULTS AND DISCUSSION

Polymerization of 2-Vinyloxyethyl Methacrylate (VEM).

The possibility of living cationic polymerization of VEM was studied using HI/I_2 initiator in toluene at -15° to -40°C . For comparison, boron trifluoride etherate (BF_3OEt_2) was also employed as initiator.

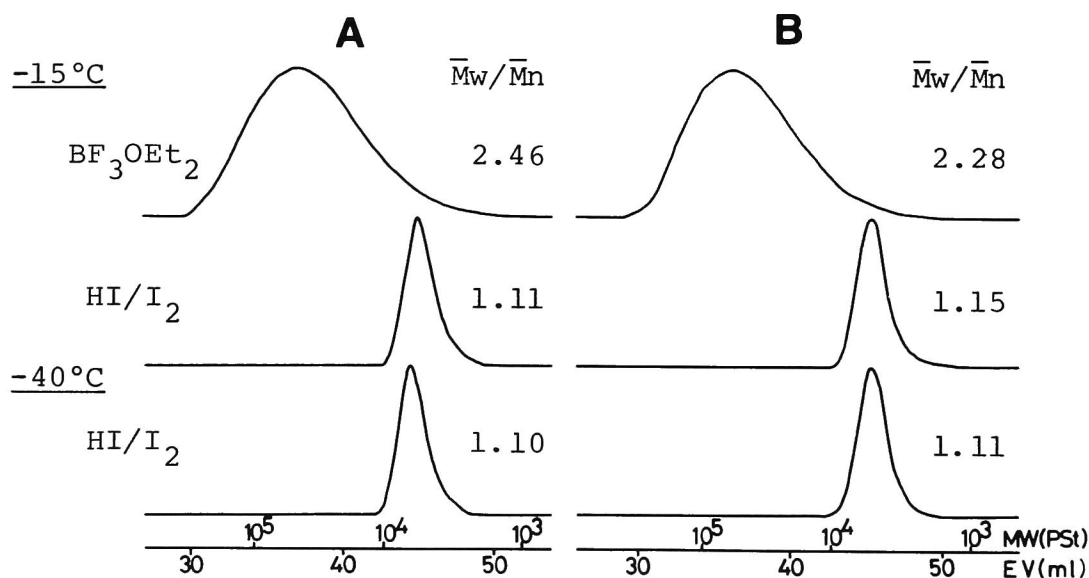


Figure 1. MWDs of poly(VEM) (A) and poly(VEC) (B) obtained in toluene at -15° and -40°C : A (from top), samples 1, 2, and 3, Table I; B (from top), samples 7, 8, and 9, Table I. See also Table I for reaction conditions.

With both initiators the methacrylate derivative readily polymerized quantitatively to give soluble polymers. Figure 1A shows the MWD of the produced polymers at a 100 % conversion. BF_3OEt_2 yielded poly(VEM) with a broad (normal) MWD ($\bar{M}_w/\bar{M}_n = 2.46$), whereas HI/I_2 initiator led to a very narrow MWD ($\bar{M}_w/\bar{M}_n = 1.11$), similar to that of living poly(2-acetoxyethyl vinyl ether) ($\bar{M}_w/\bar{M}_n = 1.15$) produced by the same initiator.³⁾

In addition to the monodisperse MWD, analysis of polymer molecular weight ($\bar{M}_n$) demonstrated the living character of the HI/I_2 -initiated polymerization of VEM (Table I and Figure 2). Thus, the $\bar{M}_n$ of obtained poly(VEM) increased proportionally to the monomer-to-initiator feed ratio ($[\text{M}]_0/[\text{HI}]_0$) (Table I, entries 3 - 6) and to monomer conversion (Figure 2). Addition of a fresh

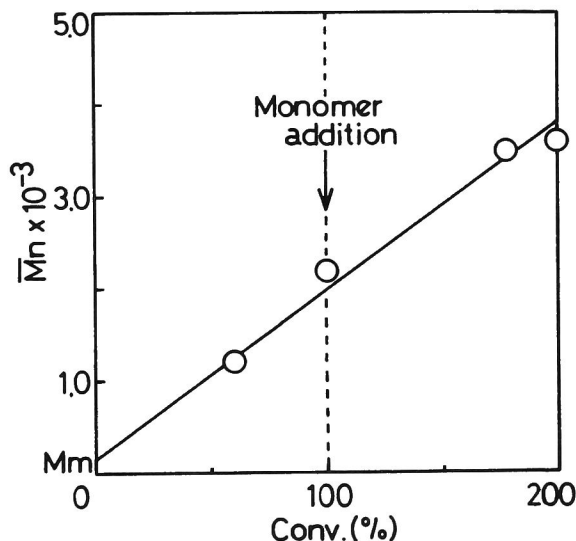


Figure 2. Relationship between conversion and $\bar{M}_n$ before and after the monomer addition in the VEM polymerization by HI/I_2 in toluene at -40°C : $[\text{M}]_0 = [\text{M}]_{\text{add}} = 0.16 \text{ M}$; $[\text{HI}]_0/[\text{I}_2]_0 = 21/20 \text{ (mM)}$. Mm indicates the molecular weight of VEM monomer.

TABLE I
Cationic Polymerization of VEM and VEC in Toluene^{a)}

No.	Monomer	Initiator(mM)	[M] ₀ (M)	Temp. (°C)	Time (h)	$\bar{M}_n$ ^{b)} x10 ⁻³	$\frac{\bar{M}_w}{\bar{M}_n}$
1	VEM	BF ₃ OEt ₂ (2.0)	0.32	-15	0.25	22	2.46
2	VEM	HI/I ₂ (11/10)	0.32	-15	2.5	5.0	1.11
3	VEM	HI/I ₂ (10/10)	0.32	-40	31.7	5.9	1.10
4	VEM	HI/I ₂ (5/5)	0.32	-40	233	9.9	1.16
5	VEM	HI/I ₂ (23/20)	0.32	-40	7.5	3.1	1.09
6	VEM	HI/I ₂ (5/5)	0.64	-40	650	14	1.17
7	VEC	BF ₃ OEt ₂ (4.0)	0.21	-15	0.50	29	2.28
8	VEC	HI/I ₂ (10/10)	0.21	-15	1.3	4.5	1.15
9	VEC	HI/I ₂ (11/10)	0.21	-40	9.7	4.8	1.11
10	VEC	HI/I ₂ (3/3)	0.21	-40	700	12	1.28
11	VEC	HI/I ₂ (20/20)	0.21	-40	1.5	2.9	1.11
11A ^{c)}	VEC	HI/I ₂ (20/20)	0.21	-40	7.0	5.6	1.18
			+0.21				

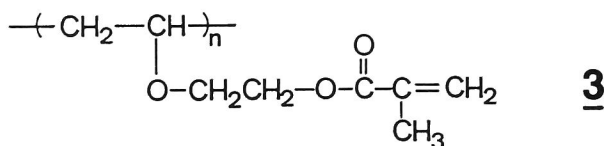
a) Conversion ~100 %.

b) Determined by size exclusion chromatography (polystyrene calibration).

c) Monomer addition experiment for run 11. To the completely polymerized reaction mixture of this run (1.5 h after initiation) was added the same molar amount of fresh VEC (neat) as in the first-stage polymerization. The second dose of VEC polymerized quantitatively after 5.5 h.

VEM feed to a polymerized solution led to a second stage polymerization in which the $\bar{M}_n$ of the polymers again increased with monomer conversion; the linear $\bar{M}_n$ -conversion plot passing the origin was retained before and after the monomer addition (Figure 2).

Figure 3 illustrates the ^1H and ^{13}C NMR spectra of VEM monomer and its polymer produced by HI/I_2 . Comparison of the spectra shows that the poly(VEM) is free from vinyloxy groups [^1H NMR: ca. 6.4 ppm ($=\text{CH}-\text{O}-$); ^{13}C NMR: 86.5 and 151.2 ppm ($\text{CH}_2=\text{CH}-\text{O}-$)] but retains methacryloyl functions [^1H NMR: 2.0 ppm ($=\text{C}(\text{CH}_3)-\text{CO}-$) 5.6 and 6.1 ppm ($\text{CH}_2=$); ^{13}C NMR: 17.7 ($-\text{CH}_3$), 125.2 ($=\text{C}-\text{CO}-$), and 135.7 ppm ($\text{CH}_2=$)]. The absence of signals assignable to poly(methacrylate) units (e.g., ^1H NMR, ca. 1 ppm for the methyl group) further excludes the possibility of side-reactions on the methacryloyl groups such as crosslinking, cyclization, and the addition of hydrogen iodide. All these facts show that the HI/I_2 -initiated polymerization of VEM proceeds exclusively via its vinyloxy (vinyl ether) group to yield polymer 3.



When heated, the monodisperse poly(VEM) readily crosslinked to form an insoluble network.

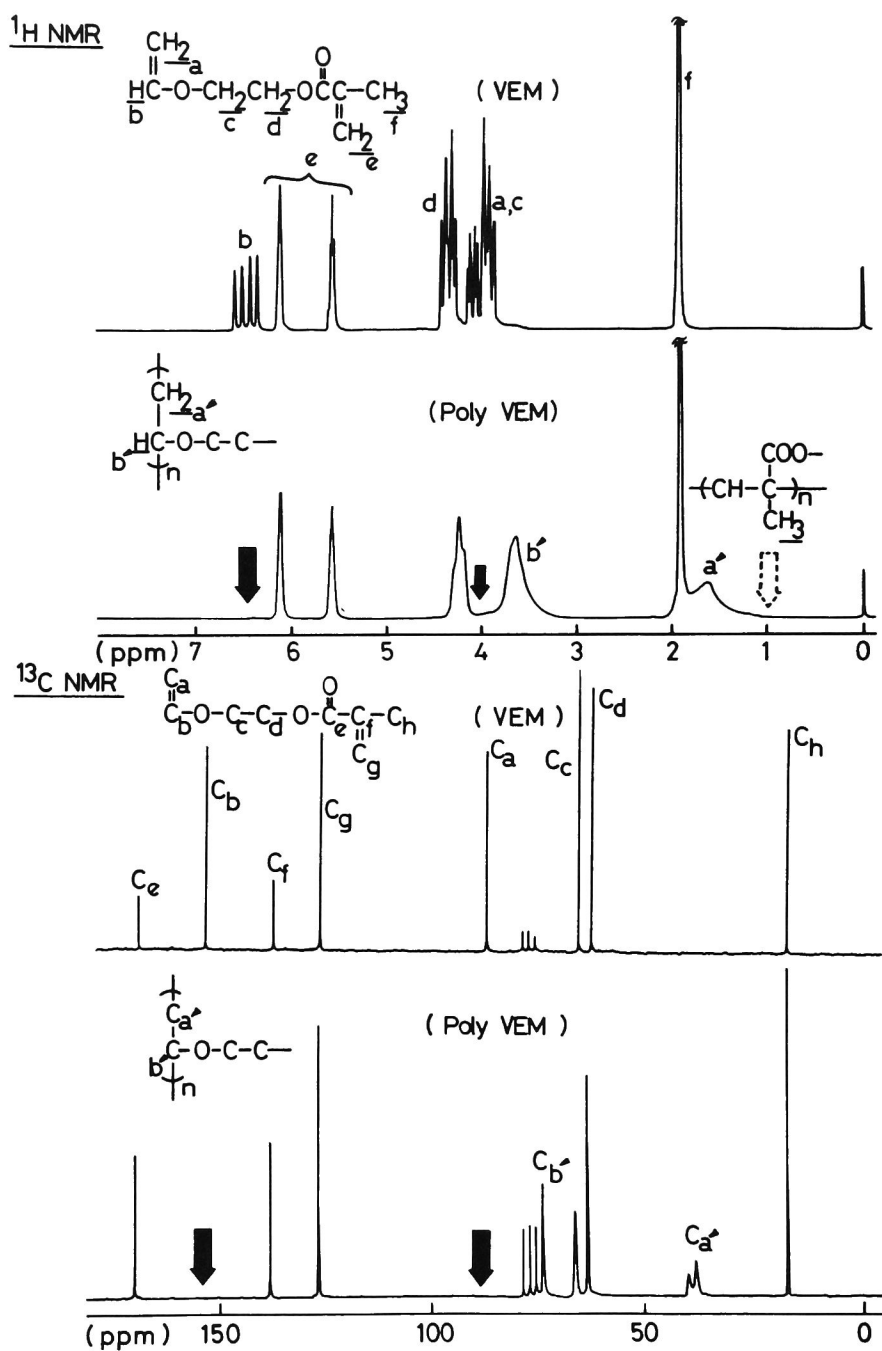


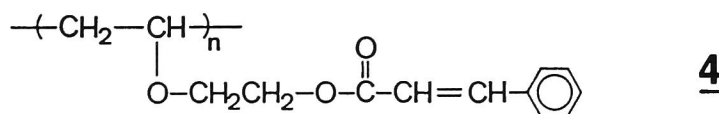
Figure 3. ¹H and ¹³C NMR spectra of VEM and poly(VEM) obtained with HI/I₂ in toluene at -40°C (sample 6, Table I).

Polymerization of 2-Vinyloxyethyl Cinnamate (VEC).

Under reaction conditions similar to those for VEM, this cinnamate monomer was polymerized in toluene at -15° to -40°C with HI/I_2 and BF_3OEt_2 as initiators. Figure 1B shows the MWD of the product polymers.

The polymerization by HI/I_2 initiator gave soluble polymers with a sharp MWD ($\bar{M}_w/\bar{M}_n = 1.11$). The $\bar{M}_n$ of the polymers increased proportionally to monomer conversion, and further increased on the addition of a fresh VEC feed to a polymerized reaction mixture (Table I, entries 11 and 11A); the monodisperse MWD was retained for the polymers formed after the monomer addition. The polymer molecular weight can also be controlled by regulating the $[\text{M}]_0/[\text{HI}]_0$ feed ratio (Table I, entries 9 - 11).

Figure 4 presents the ^1H and ^{13}C NMR spectra of VEC monomer and poly(VEC) obtained by HI/I_2 initiator, along with peak assignments. The spectra of the poly(VEC) lacked the signals due to vinyloxy groups but exhibited those of cinnamoyl groups; absorptions indicative of cyclobutane rings (^1H NMR, ca. 5 ppm)⁷⁾ were absent. Therefore, the VEC polymerization with HI/I_2 occurs exclusively on the vinyloxy unit to give polymer 4, in the absence of any side reactions such as the cyclodimerization of the cinnamoyl groups.



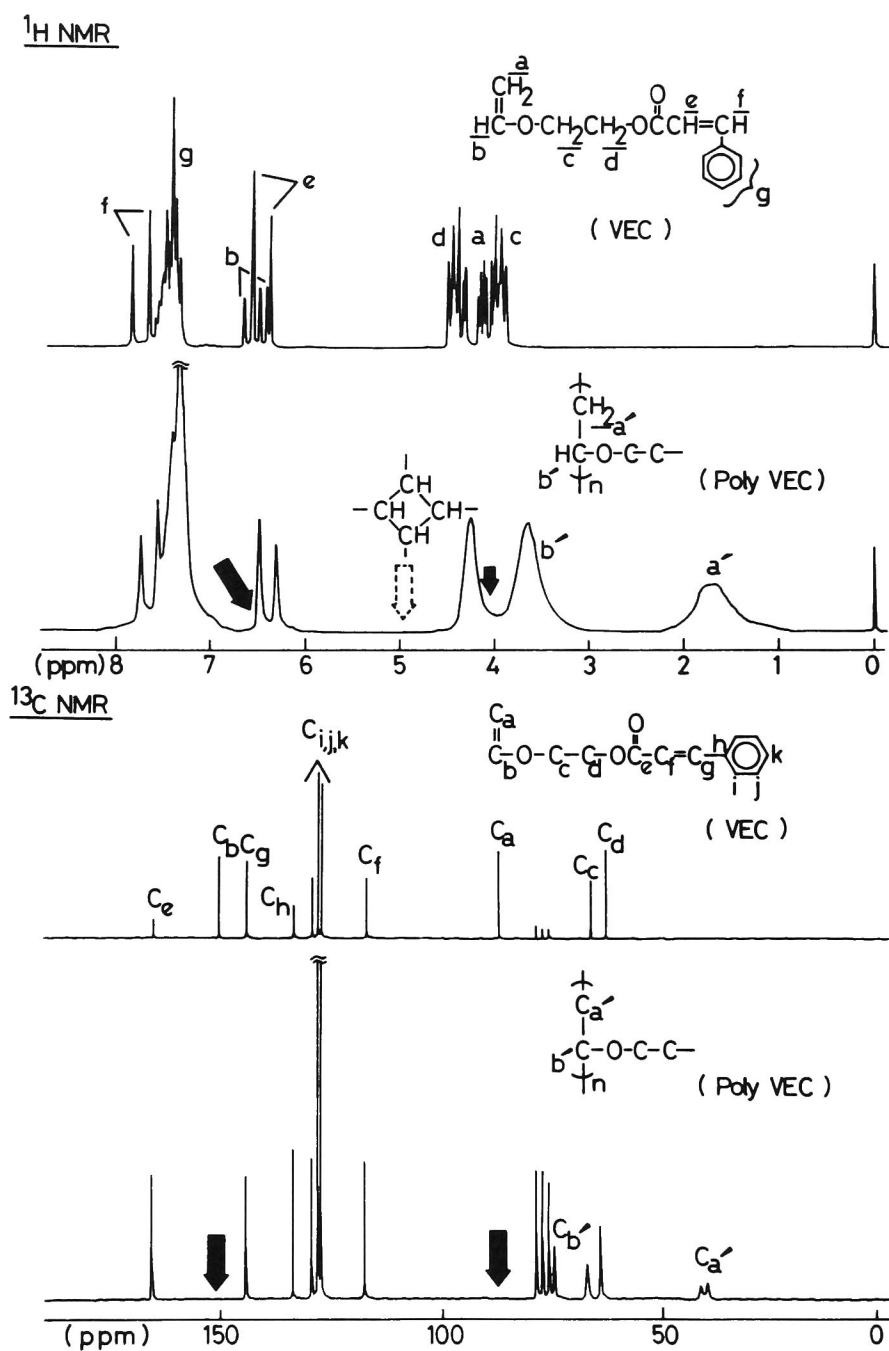


Figure 4. ^1H and ^{13}C NMR spectra of VEC and poly(VEC) obtained with HI/I_2 in toluene at -40°C (sample 10, Table I).

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CHAPTER 3

LIVING CATIONIC POLYMERIZATION OF VINYL ETHERS WITH AN UNSATURATED ESTER: ACRYLATE AND SORBATE

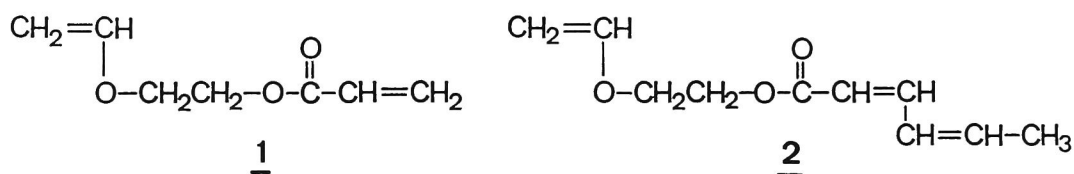
ABSTRACT

Two unsaturated ester-containing vinyl ethers, 2-vinyloxyethyl acrylate and sorbate, were polymerized by the hydrogen iodide/iodine (HI/I₂) initiating system in toluene at -15° or -40°C, to give "living" polymers, having a very narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n = 1.10 - 1.15$) and crosslinkable via their pendant C=C double bonds. The number-average molecular weight of the polymers increased in direct proportion to conversion, and further increased on addition of a new monomer feed to a polymerized reaction mixture. According to ¹H and ¹³C NMR structural analysis, the polymerization proceeds exclusively via the vinyloxy group of the potentially bifunctional monomers without undesirable side reactions of the unsaturated ester pendants.

INTRODUCTION

Recently, the author et al. have shown that the hydrogen iodide/iodine (HI/I₂) initiator, under appropriate conditions, induces living polymerization of vinyl ethers,¹⁾ including those with a variety of functional pendants such as ester, phenyl, and olefinic groups.^{2,3)} The HI/I₂-initiated living process thus provides new routes for the synthesis of functionalized polymers with a controlled molecular weight and structure, for the first time in the field of the cationic polymerization of vinyl compounds.

In this chapter, the author examined the possibility of the living cationic polymerization of two unsaturated ester-containing vinyl ethers, 2-vinyloxyethyl acrylate (VEA; 1) and 2-vinyloxyethyl sorbate (VES; 2) in which, respectively, the simplest unsaturated ester (acrylate) and a conjugated dienyl ester (sorbate) groups are connected to a vinyl ether moiety. The preceding chapter of this



thesis³⁾ described the living polymerization of 2-vinyloxyethyl methacrylate and cinnamate, both having a sterically hindered C=C double bond (due to the α-methyl or β-phenyl group) in the ester pendant. When compared with these monomers, VEA and VES have a less crowded or "naked" double bond in the ester pendant, which is, therefore, more accessible to the propagating species and may be detrimental to living cationic polymerization. In addition, the reactive diene unit involved in VES may cause other side reactions. The cationic polymerization of VEA and VES have been performed by

Nishikubo et al.⁴⁾ for the synthesis of resist materials crosslinkable by heat, light, or X-ray.⁵⁾ Since they employed a metal halide initiator (BF_3OEt_2), however, they were unable to prepare living polymers, with a narrow molecular weight distribution (MWD). Using HI/I_2 initiator, the author succeeded in the living cationic polymerization of VEA and VES and obtained poly(vinyl ethers) with a narrow MWD, controlled molecular weight, and unsaturated ester pendant.

EXPERIMENTAL SECTION

Materials. VEA and VES were prepared by the reaction of 2-chloroethyl vinyl ether with the sodium salts of the corresponding carboxylic acids in the presence of small amounts of tetra-n-butylammonium iodide as a phase-transfer catalyst and p-tert-butyl catecol as a radical inhibitor; isolated yield 30 - 50 %. The monomers, solvents, initiators, and other materials were purified and used as previously described.¹⁻³⁾

Procedures. Polymerization was carried out in a baked Shlenk tube equipped with a three-way stopcock under dry nitrogen. The reaction was initiated by adding an initiator solution with a syringe to a monomer solution and, after a certain period, quenched by adding ammoniacal methanol. Conversion to polymers was determined from the residual monomer concentration by gas chromatography. The $\bar{M}_n$ and MWD of the polymers were measured by size exclusion chromatography using a set of polystyrene gel columns calibrated against polystyrene standard samples.³⁾

RESULTS AND DISCUSSION

Cationic Polymerization of 2-Vinyloxyethyl Acrylate and Sorbate.

To examine whether the unsaturated substituent of VEA and VES affects "living" cationic polymerization of vinyl ethers, these vinyloxyethyl monomers were polymerized by HI/I₂ initiator in toluene at -15° or -40°C ([M]₀ = 5 vol%). For comparison, boron trifluoride etherate (BF₃OEt₂) and iodine (I₂) were also employed as initiators. BF₃OEt₂ is known to be effective for the synthesis of high-molecular-weight polymers in cationic polymerization; iodine is known to generate long-lived poly(vinyl ethers) but to initiate slowly vinyl ether polymerization.⁶⁾

With all the initiators, the polymerizations of both monomers proceeded quantitatively without an induction period, to give soluble products. Figure 1 shows the time-conversion curves for the polymerization of VEA as typical examples. Separate experiments showed that the rate of homopolymerization of

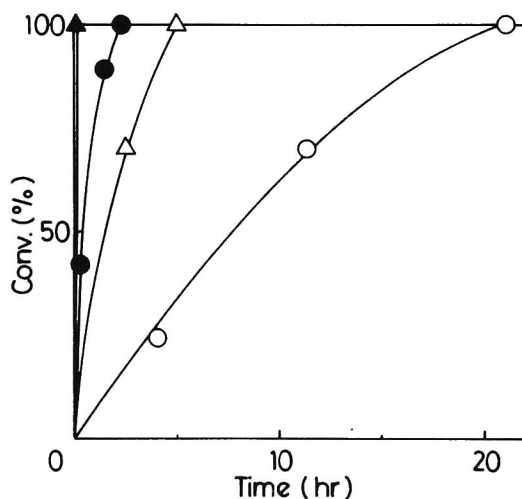


Figure 1. Time-conversion curves for the polymerization of VEA in toluene at -15°C and [M]₀ = 0.36 M (5 vol%). Initiator, mM: (▲) BF₃OEt₂, 2; (△) I₂, 20; (●) HI/I₂, 12/10; (○) HI/I₂, 12/10, (-40°C).

unsaturated ester-containing vinyl ethers by HI/I₂ initiator decreases in the order VES > VEA > 2-vinyloxyethyl methacrylate.

HI/I₂-Initiated Living Polymerization.

Figure 2 shows the MWDs of the polymers obtained by the three initiators at -15°C (conversion ~100 %; see also Table I for detailed data). BF₃OEt₂ gave higher molecular weight polymers with a broad MWD ($\bar{M}_w/\bar{M}_n \sim 2.5$). With iodine the MWD was narrower ($\bar{M}_w/\bar{M}_n = 1.3 - 1.6$) but consisted of a tailing in the lower molecular weight side. HI/I₂ initiator, in contrast, gave a very narrow MWD ($\bar{M}_w/\bar{M}_n = 1.10 - 1.15$); even at -40°C where the polymerization was so slow as to reach a 100 % conversion in 40-72 hrs, nearly monodisperse MWDs were obtained without undesired crosslinking of the unsaturated ester pendants.

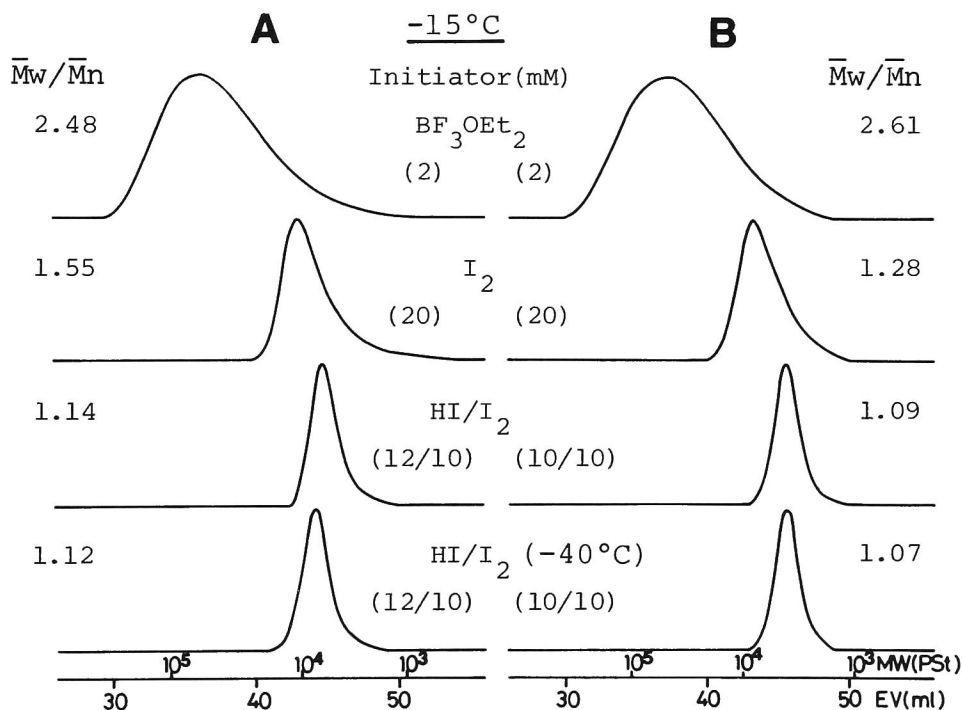


Figure 2. MWDs of poly(VEA) (A) and poly(VES) (B) obtained in toluene at -15° and -40°C: see Table I for the $\bar{M}_n$ data and reaction conditions.

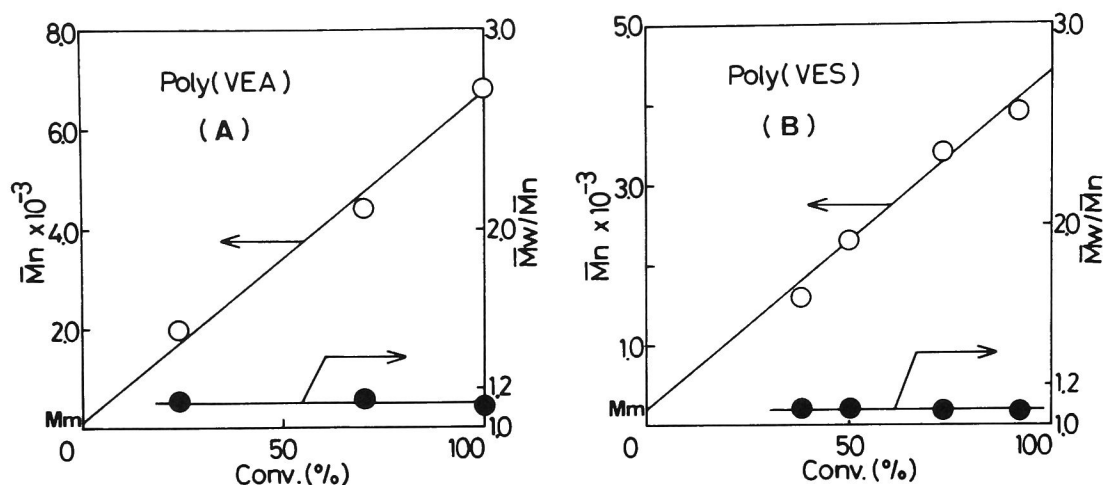


Figure 3. Relationships between conversion and $\bar{M}_n$ or $\bar{M}_w/\bar{M}_n$ ratio in the polymerization of VEA (A) and VES (B) by HI/I₂ in toluene at -40°C: A, [M]₀ = 0.36 M (5 vol%), [HI]₀/[I₂]₀ = 12/10 (mM); B, [M]₀ = 0.27 M (5 vol%), [HI]₀/[I₂]₀ = 10/10 (mM). M_m indicates the molecular weight of each monomer.

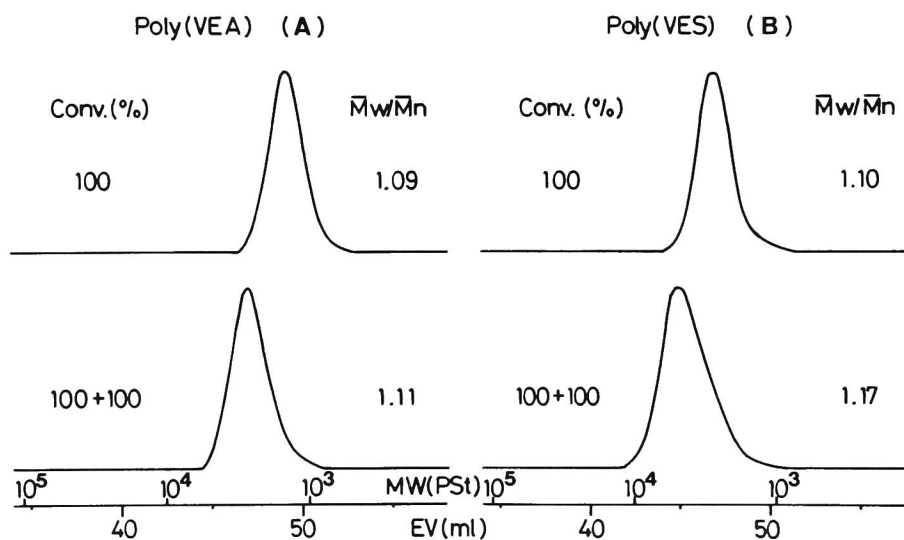


Figure 4. MWDs of poly(VEA) (A) and poly(VES) (B) obtained in monomer-addition experiments in the polymerization by HI/I₂ in toluene at -40°C: A, samples 7 and 7A, Table I; B, samples 15 and 15A, Table I; See also Table I for reaction conditions.

Figure 3 illustrates the $\bar{M}_n$ -conversion relationships for poly(VEA) and poly(VES) obtained with HI/I₂ initiator in toluene at -40°C. The $\bar{M}_n$ of the polymers linearly increased with the progress of the reaction, keeping the MWD very narrow. To obtain further evidence for the living nature of the HI/I₂-initiated processes, a new portion of VEA or VES (equimolar to the initial charge) was added to the polymerization mixture at a nearly 100 % conversion. Figure 4 compares the MWDs of the polymers thus obtained before and after the monomer addition. After the monomer addition, the polymer molecular weight was doubled without any broadening in MWD nor producing by-products due to inactivation of the living ends and/or initiation of new shorter chains.

Table I summarizes the effects of reaction conditions on the polymerizations of VEA and VES in toluene. With HI/I₂ initiator, the $\bar{M}_n$ of polymer can be readily controlled by regulating the feed ratio of monomer to HI ($[M]_0/[HI]_0$).

Polymer Structure.

Figure 5 compares the ¹H and ¹³C NMR spectra of VEA monomer and its polymer obtained by HI/I₂ initiator, along with peak assignments. After polymerization, the absorptions of the vinyloxy group of the monomer [¹H NMR: ca. 6.4 ppm (=CH-O-); ¹³C NMR: 86.8 and 151.2 ppm (CH₂=CH-O-)] completely disappeared and, in turn, those of the main-chain methylene and methine groups [¹H NMR: ~1.7 and ~3.7 ppm (-CH₂-CH-); ¹³C NMR: 39.0 and 40.6 (-CH₂-), 74.0 ppm (-CH-)] appeared. On the other hand, the absorptions of the acrylic olefin [¹H NMR: 5.8 - 6.6 ppm; ¹³C NMR: 127.9 and 130.5 ppm] remained unchanged. The two pendant methylene units (-O-CH₂CH₂-OCO-) are also observable in the polymer spectra with some broadening. Importantly, signals indicative of side reactions of the acrylate group (crosslinking, cyclization, and the addition of HI or I₂) are absent at all. These observations demonstrate

TABLE I

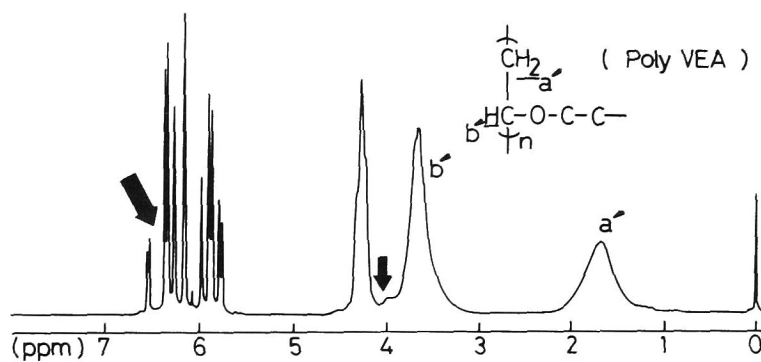
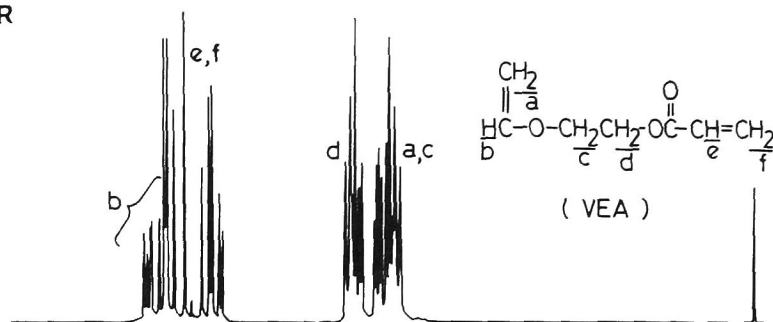
Cationic Polymerization of VEA and VES in Toluene^{a)}

No.	Monomer	Initiator(mM)	[M] ₀ (M)	Temp. (°C)	$\bar{M}_n$ ^{b)} x10 ⁻³	$\frac{\bar{M}_w}{\bar{M}_n}$
1	VEA	BF ₃ OEt ₂ (2.0)	0.36	-15	25	2.48
2	VEA	I ₂ (20)	0.36	-15	5.9	1.55
3	VEA	HI/I ₂ (12/10)	0.36	-15	5.3	1.14
4	VEA	HI/I ₂ (6/5)	0.71	-15	14	1.23
5	VEA	HI/I ₂ (5/5)	0.36	-40	9.2	1.15
6	VEA	HI/I ₂ (12/10)	0.36	-40	6.8	1.12
7	VEA	HI/I ₂ (21/20)	0.18	-40	1.4	1.09
7A	VEA	HI/I ₂ (21/20)	0.18 +0.18	-40	2.5	1.11
8	VES	BF ₃ OEt ₂ (2.0)	0.27	-15	22	2.61
9	VES	I ₂ (20)	0.27	-15	5.7	1.28
10	VES	HI/I ₂ (10/10)	0.27	-15	3.9	1.09
11	VES	HI/I ₂ (6/5)	0.54	-15	11	1.19
12	VES	HI/I ₂ (5/5)	0.27	-40	8.0	1.19
13	VES	HI/I ₂ (10/10)	0.27	-40	3.9	1.07
14	VES	HI/I ₂ (22/20)	0.27	-40	2.2	1.09
15	VES	HI/I ₂ (22/20)	0.27	-40	2.6	1.10
15A	VES	HI/I ₂ (22/20)	0.27 +0.27	-40	4.0	1.17

a) Conversion ~100 %.

b) Determined by size exclusion chromatography (polystyrene calibration).

^1H NMR



^{13}C NMR

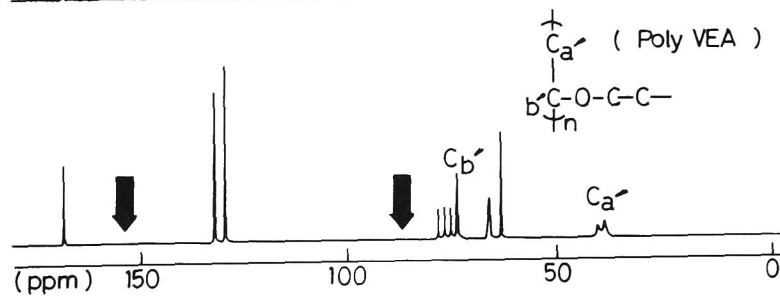
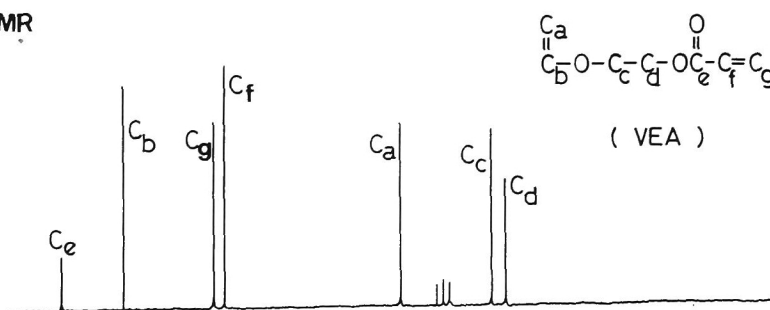


Figure 5. ^1H and ^{13}C NMR spectra of VEA and poly(VEA) obtained with HI/I_2 in toluene at -40°C (sample 5, Table I).

that the polymerization of VEA by HI/I₂ initiator proceeds exclusively via its vinyloxyl group to yield polymer 3.

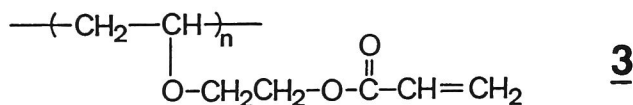
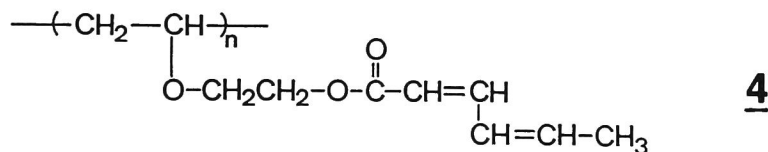


Figure 6 shows the ¹H and ¹³C NMR spectra of VES monomer and poly(VES) produced by HI/I₂ initiator. The spectra of the poly(VES) are free from vinyloxyl signals expected at ~6.4 ppm (¹H) and 86.9, 151.3 ppm (¹³C) but clearly exhibit the sorbate absorptions [¹H NMR: 1.8, 5.7 - 6.2 and 7.1 - 7.4 ppm; ¹³C NMR: 18.2, 118.4, 129.6, 139.1, 145.2, and 166.6 ppm], indicating the expected polymer structure 4. In the ¹³C NMR spectrum, however, small additional absorptions were detected in the aliphatic (13.7 ppm) and olefinic regions (120.2, 127.0, and 135.6 ppm). On the basis of the ¹³C NMR analysis on a mixture of poly(VES) or its model compound for side chain (methyl sorbate) and iodine, these signals were assigned to the pendant diene groups of poly(VES) (4) complexing with molecular iodine. The complexation most likely takes place during not the living polymerization but the workup of the polymer solution where iodine may be regenerated from the initiator residues.



These investigations demonstrate that vinyl ethers VEA and VES can be polymerized by HI/I₂ initiator without side reactions to yield linear living polymers with a poly(vinyl ether) backbone carrying radical-sensitive unsaturated pendants. These polymers readily crosslink into an insoluble network, on heating [poly(VEA)]

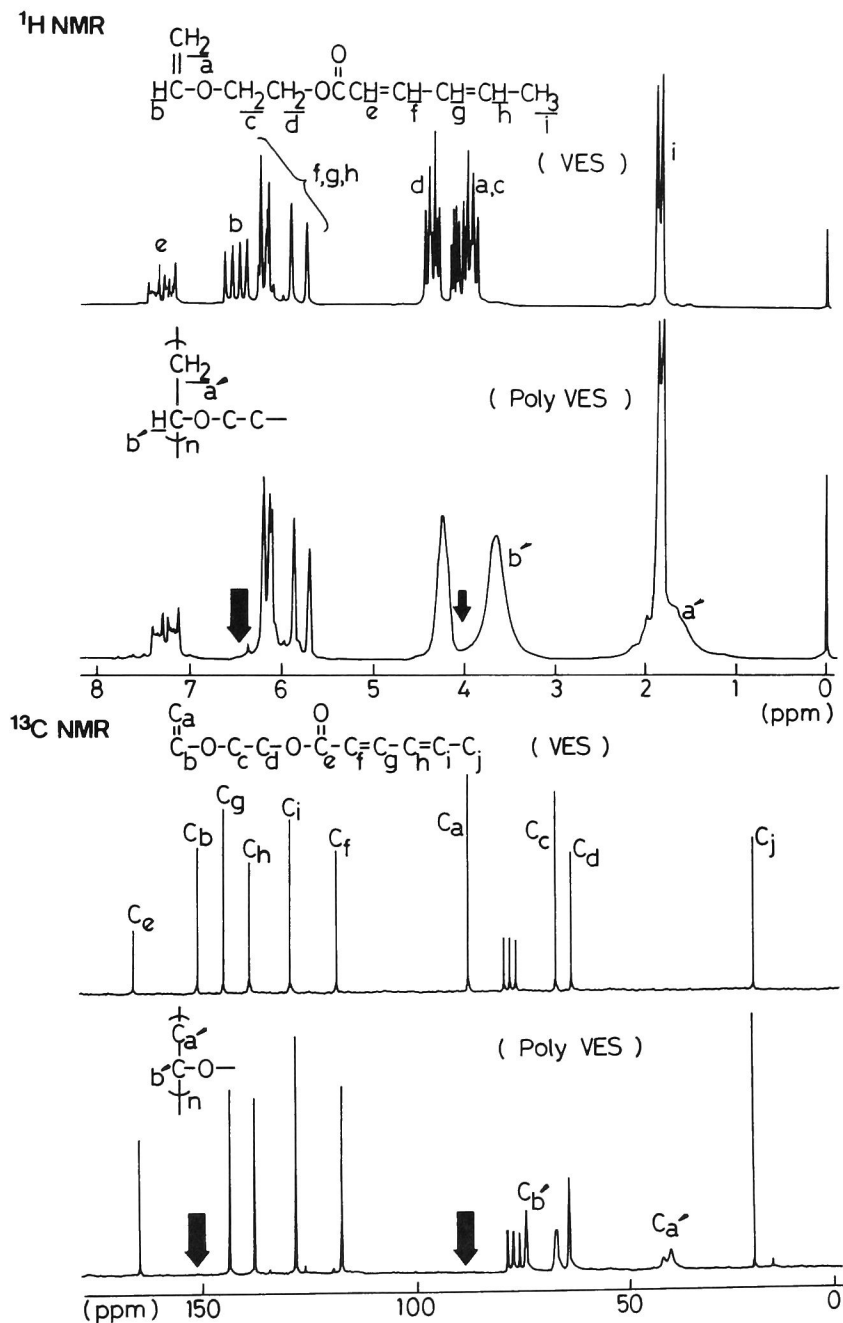


Figure 6. ^1H and ^{13}C NMR spectra of VES and poly(VES) obtained with HI/I_2 in toluene at -40°C (sample 12, Table I).

or even at room temperature [poly(VES)], without a radical initiator.

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CHAPTER 4

EtAlCl₂/ESTER INITIATING SYSTEMS FOR LIVING CATIONIC POLYMERIZATION OF VINYL ETHERS

ABSTRACT

Living cationic polymerization of isobutyl vinyl ether was achieved by EtAlCl₂ in the presence of ethyl acetate at rather high temperatures up to +25°C in toluene. In the absence of the ester additives, neither living nor long-lived propagating species were formed under these conditions. Similarly, living propagating species of vinyl ethers with an ester unit in the pendant (2-vinyloxyethyl benzoate and methacrylate) were obtained with EtAlCl₂ alone. The obtained polymers showed a very narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n < 1.2$) and the $\bar{M}_n$ directly proportional to the monomer conversion.

INTRODUCTION

Although a number of acidic compounds cationically polymerize vinyl monomers, few afford truly living cationic polymerization. Perhaps the best initiator for this purpose is, thus far, a combination of hydrogen iodide and iodine (HI/I_2) that gives monodisperse living polymers from vinyl ethers and related monomers.¹⁾ Metal halides (MX_n), most general, commodity initiators for cationic polymerization, lead to uncontrollable, transfer-dominant, non-living processes, except under special conditions.²⁻⁴⁾ The most recent example of the formation of living-like species by MX_n is the "quasi-living" polymerization developed by Kennedy et al.⁴⁾

The HI/I_2 initiating system, however, has also some disadvantages. It is rather mild as initiator and effective only for very reactive monomers (e.g., vinyl ethers). In addition, the HI/I_2 -initiated living polymerization has to be carried out at low temperatures below -15°C , which renders this otherwise useful process less attractive from practical viewpoints.

This study concerns the living cationic polymerization of vinyl compounds initiated by metal halides modified with Lewis bases (e.g., esters), as a new class of cationic initiators that overcome the drawbacks of not only metal halides but the HI/I_2 initiating system as well. According to the mechanism for the living polymerization by HI/I_2 ,¹⁾ the high nucleophilicity of the iodide counteranion plays a critical role in suppressing chain transfer and termination. Counteranions derived from metal halides, in contrast, are much less nucleophilic than the iodide ion and, for this reason, they cannot induce living cationic polymerization. It occurred to the author, therefore, that living propagation might be possible by controlling (modifying) the nucleophilicity of the metal halide-derived counteranions by the

use of nucleophilic additives which interact with metal halides.⁵⁾

In this study, the author employed esters (ethyl acetate and benzoate) as Lewis base modifiers for ethylaluminum dichloride. These $\text{EtAlCl}_2/\text{RCOOEt}$ initiating systems⁶⁾ eventually led to living cationic polymerization of isobutyl vinyl ether (IBVE) above -15°C up to $+25^\circ\text{C}$, rather high temperatures for cationic living processes.

EXPERIMENTAL SECTION

Materials. Commercial IBVE was washed with an aqueous alkaline solution and then with water. 2-Vinyloxyethyl benzoate (VEBz) and 2-vinyloxyethyl methacrylate (VEM) were prepared by the reactions of 2-chloroethyl vinyl ether with sodium benzoate and methacrylate, respectively⁹⁾. The three monomers were distilled twice over calcium hydride before use. EtAlCl_2 was commercially obtained as an *n*-hexane solution (Kanto Chemicals) or an *n*-heptane solution (Japan Alkyl Aluminium Co.) and used without further purification. BF_3OEt_2 was purified by distillation under reduced pressure. Ethyl acetate and benzoate (Wako Chemicals, both guaranteed reagents) were distilled over magnesium sulfate and calcium hydride, respectively. Toluene was purified by the usual methods and distilled over calcium hydride at least twice before use.

Procedures. Polymerization was carried out under dry nitrogen in a baked glass tube equipped with a three-way stopcock. The reaction was initiated by addition of an EtAlCl_2 solution into a monomer solution, and quenched with ammoniacal methanol. The ester additives, when employed for IBVE polymerization, were added to a monomer solution before the addition of EtAlCl_2 . The quenched reaction mixture was sequentially washed with a dilute aqueous acid

and water to remove the initiator residues, and the products were recovered by evaporating the organic layer under reduced pressure.

The molecular weight distribution (MWD) of the polymers was measured by size exclusion chromatography (SEC) using polystyrene gel columns.¹⁾ The $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ ratios were calculated from SEC curves on the basis of a polystyrene calibration. ^1H and ^{13}C NMR spectra (89.55 and 22.5 MHz, respectively) were recorded on a JEOL FX90Q spectrometer in CDCl_3 . The steric structure of the polymers was determined by ^{13}C NMR spectroscopy.¹⁰⁾

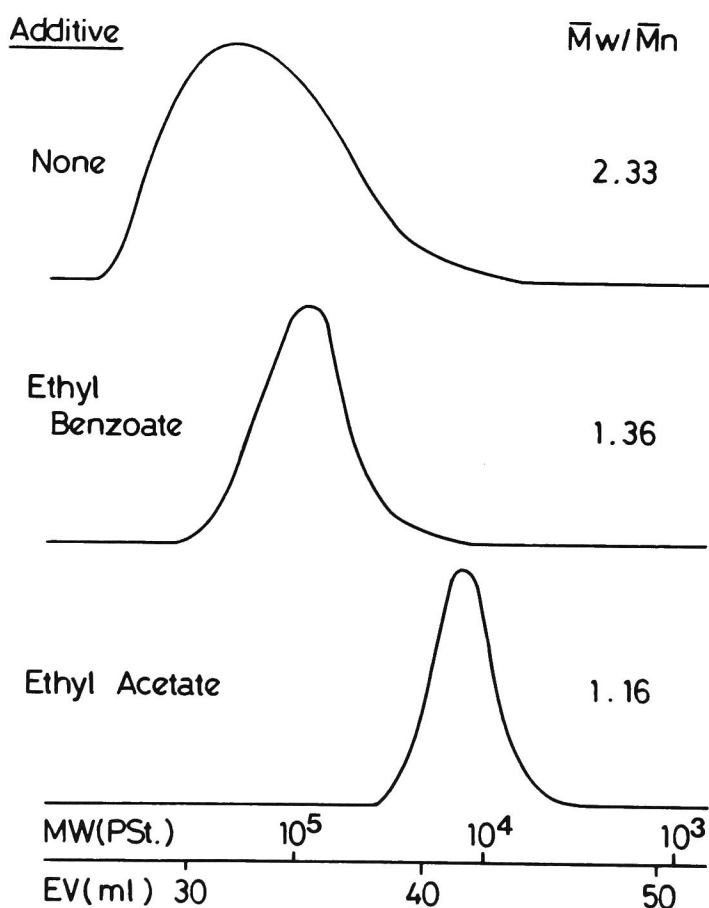


Figure 1. MWD of poly(IBVE) obtained by EtAlCl_2 in the presence and absence of esters in toluene at -40°C : $[\text{IBVE}]_0 = 10 \text{ vol\%}$ (0.76 M), $[\text{EtAlCl}_2]_0 = 20 \text{ mM}$, $[\text{ester}]_0 = 10 \text{ vol\%}$. Ester additives and $\bar{M}_w/\bar{M}_n$ as indicated.

RESULTS AND DISCUSSION

Living Cationic Polymerization of IBVE by the EtAlCl₂/Ester Systems.

IBVE was polymerized with EtAlCl₂ in the presence or absence of ethyl acetate or benzoate ($[\text{ester}]_0 = [\text{IBVE}]_0 = 10 \text{ vol\%}$; $[\text{EtAlCl}_2]_0 = 20 \text{ mM}$) in toluene at a low temperature (-40°C). These esters are known to form complexes with MX_n .⁵⁾ All the polymerizations proceeded smoothly up to 100 % conversion without an induction period. The additives remarkably retarded the polymerization; i.e., the half-life period of the monomer:

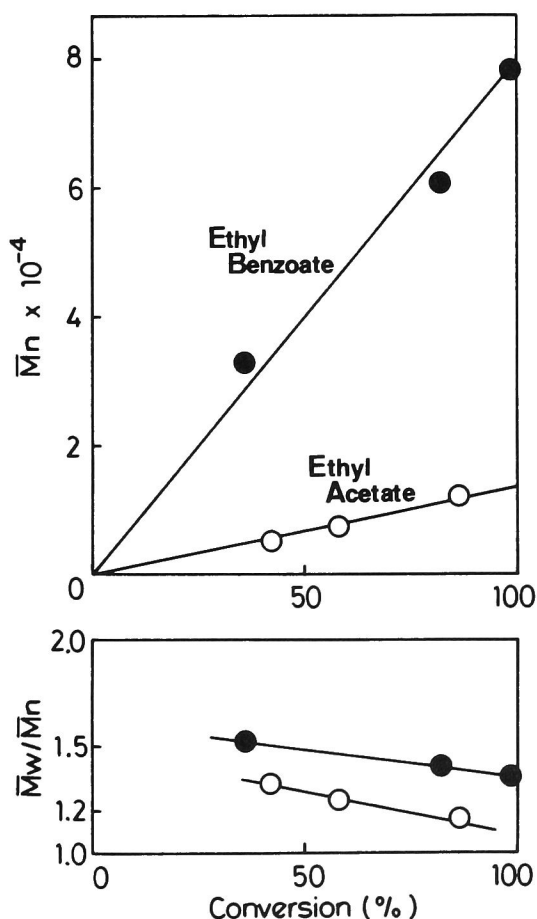


Figure 2. Relationships between conversion and $\bar{M}_n$ or $\bar{M}_w/\bar{M}_n$ ratio for poly(IBVE) obtained with EtAlCl₂ in the presence of ester at -40°C : $[\text{IBVE}]_0 = 10 \text{ vol\%}$ (0.76 M), $[\text{EtAlCl}_2]_0 = 20 \text{ mM}$, $[\text{ester}]_0 = 10 \text{ vol\%}$.

Additive: (●) ethyl benzoate
(○) ethyl acetate.

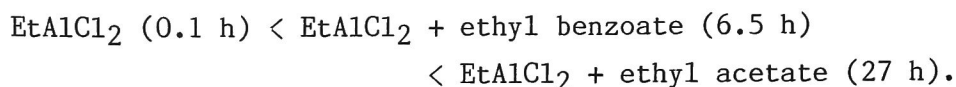


Figure 1 shows the MWD of the polymers obtained at high conversions (> 85 %). The dependence of their number-average molecular weights ($\bar{M}_n$) on conversion is shown in Figure 2. EtAlCl_2 alone, similarly to BF_3OEt_2 , gave high polymers ($\bar{M}_n \sim 10^5$) with a broad MWD ($\bar{M}_w/\bar{M}_n > 2$); the $\bar{M}_n$ decreased slightly with conversion. On the other hand, the MWDs with both EtAlCl_2 /ester systems were narrower, obviously shifting toward higher molecular weight as the polymerization proceeded. Ethyl acetate affected the polymer molecular weight, MWD, and polymerization rate much greater than ethyl benzoate. In particular, the acetate ester led to quite narrow MWD with $\bar{M}_w/\bar{M}_n = 1.1 - 1.3$.

The $\bar{M}_n$ of the polymers obtained with the EtAlCl_2 /ester systems was proportional to conversion (Figure 2). This, coupled with the narrow MWD, shows that living polymers are formed from IBVE by EtAlCl_2 in conjunction with esters. It is the first time that a living cationic polymerization has been achieved with typical metal halides.

The IBVE polymerizations at different EtAlCl_2 /ester molar ratios indicated that the esters should be added in excess over EtAlCl_2 to realize living propagation. For example, when an equimolar mixture of EtAlCl_2 and ethyl acetate or benzoate was used, the obtained polymers exhibited a broad MWD ($\bar{M}_w/\bar{M}_n > 2$) and $\bar{M}_n$'s unchanged with conversion. The polymerization rate, however, was smaller than that with EtAlCl_2 alone.

Living Polymerization at Higher Temperature.

The living cationic polymerization of vinyl ether was found to be possible at such a low temperature (-40°C), although the rate of polymerization was very low. In order to elucidate the effect of

temperature on the "long-lived" nature of propagating species and to increase the reaction rate, polymerizations were carried out at relatively high temperature.

Figure 3 shows the effect of temperature on the time-conversion curves for the polymerization of IBVE by the $\text{EtAlCl}_2/\text{CH}_3\text{COOEt}$ system in toluene. The polymerization at $+25^\circ\text{C}$ was rapid and completed within 2 h, whereas at -40°C it took about one week to reach ca. 90 % conversion.

At -15°C or above, the polymerization mixture with the $\text{EtAlCl}_2/\text{CH}_3\text{COOEt}$ system was colorless, whereas in the absence of the ester component, it intensely colored (green to dark violet). The strong color in the latter indicates the extensive occurrence of chain transfer, leading to conjugated olefin terminals.¹¹⁾

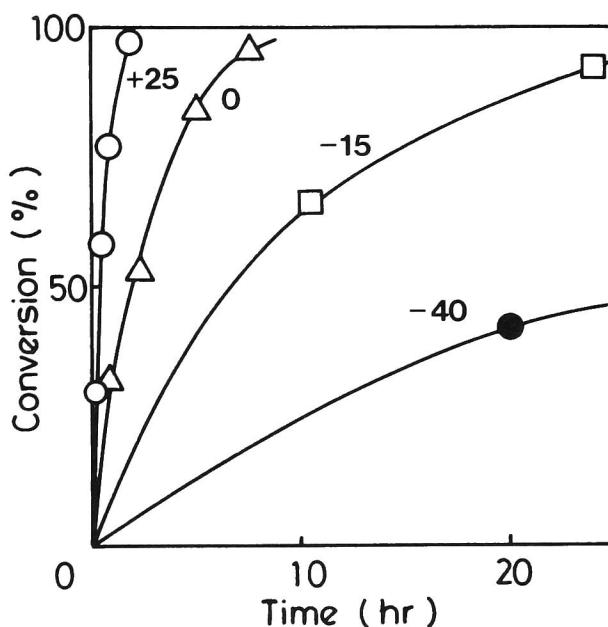


Figure 3. Effect of temperature on the time-conversion curves for the polymerization of IBVE by the $\text{EtAlCl}_2/\text{CH}_3\text{COOEt}$ system in toluene: $[\text{IBVE}]_0 = 10 \text{ vol\%}$ (0.76 M), $[\text{EtAlCl}_2]_0 = 20 \text{ mM}$, $[\text{CH}_3\text{COOEt}]_0 = 10 \text{ vol\%}$. Temperatures as indicated.

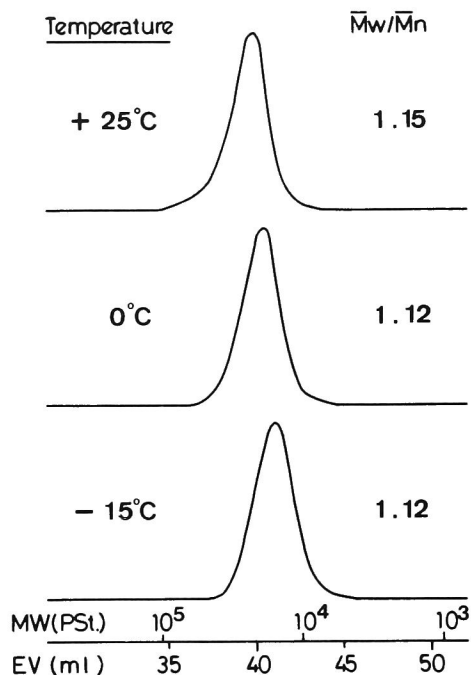


Figure 4. Effect of temperature on the MWD of poly(IBVE) obtained by the $\text{EtAlCl}_2/\text{CH}_3\text{COOEt}$ system in toluene: $[\text{IBVE}]_0 = 10 \text{ vol\%}$ (0.76 M), $[\text{EtAlCl}_2]_0 = 20 \text{ mM}$, $[\text{CH}_3\text{COOEt}]_0 = 10 \text{ vol\%}$; conversion > 90 %. Temperatures and $\bar{M}_w/\bar{M}_n$ as indicated.

Rather surprisingly, the polymerizations by the $\text{EtAlCl}_2/\text{CH}_3\text{COOEt}$ system remained "living" even at higher temperatures up to +25°C, as shown in Figures 4 and 5. The polymers obtained in the temperature range $-15^\circ \sim +25^\circ\text{C}$ (Figure 4) all exhibited very narrow MWDs ($\bar{M}_w/\bar{M}_n = 1.12 - 1.15$) without tailing. Their $\bar{M}_n$'s were directly proportional to conversion, irrespective of the change of polymerization temperatures (Figure 5). Over the whole range of conversion, the $\bar{M}_w/\bar{M}_n$ ratio stayed below 1.2, slightly decreasing at higher conversions. All these results confirm the living nature of the polymerizations.

Further inspection of Figure 5 shows that the polymer molecular weight is higher at higher temperatures, a trend quite opposite to that in conventional (transfer-dominant) cationic polymerization. In fact, the number of polymer chains produced per

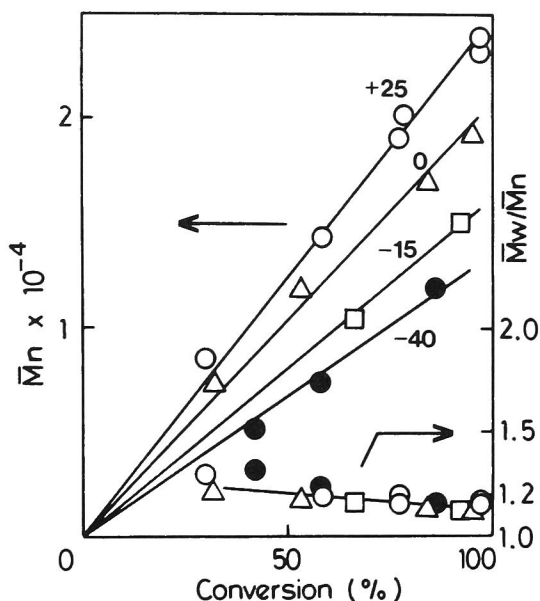


Figure 5. Effect of temperature on relationships between conversion and $\bar{M}_n$ or $\bar{M}_w/\bar{M}_n$ ratio in the polymerization of IBVE by the $\text{EtAlCl}_2/\text{CH}_3\text{COOEt}$ system in toluene: $[\text{IBVE}]_0 = 10 \text{ vol}\%$ (0.76 M), $[\text{EtAlCl}_2]_0 = 20 \text{ mM}$, $[\text{CH}_3\text{COOEt}]_0 = 10 \text{ vol}\%$. Temperature: (○) +25°C; (△) 0°C; (□) -15°C; (●) -40°C.

initiator (EtAlCl_2), calculated from the linear $\bar{M}_n$ -conversion plots, decreased at higher temperatures (-15°C, 0.24; 0°C, 0.18; +25°C, 0.15), while remained almost constant during the course of polymerization. Thus, in the $\text{EtAlCl}_2/\text{CH}_3\text{COOEt}$ -initiated polymerization, chain transfer is essentially absent even at temperatures as high as +25°C, although the initiation efficiency is not so high.

According to structural analysis of the polymers by ^1H and ^{13}C NMR spectroscopy, the IBVE polymerization by $\text{EtAlCl}_2/\text{CH}_3\text{COOEt}$ proceeds without any side reactions; the polymers were free of ester groups derived from CH_3COOEt , neither complexing nor bonded chemically. Their steric structure was almost the same as that obtained with EtAlCl_2 alone, consisting of 70% meso and 30% racemic diads (Table I).

TABLE I
Stereoregularity of Poly(IBVE)^{a)}

[AcOEt] ₀ (M)	Temp. (°C)	$\bar{M}_n$ x10 ⁻⁴	$\frac{\bar{M}_w}{\bar{M}_n}$	Diad (%) ^{b)}	
				racemo	meso
0	-15	11.2	2.2	30	70
1.0	-15	1.50	1.1	30	70
1.0	0	1.92	1.1	33	67

a) Obtained with EtAlCl₂ in the presence or absence of CH₃COOEt ([IBVE]₀ = 10 vol%, [EtAlCl₂]₀ = 20 mM).

b) Measured by ¹³C NMR.

Living Cationic Polymerization of Vinyl Ethers with an Ester Pendant.

The successful living polymerization of IBVE by EtAlCl₂ in the presence of esters prompted the author to polymerize vinyl ethers with an ester pendant using EtAlCl₂ alone as initiator. VEBz and VEM were employed as such vinyl ethers. In these cases, an ester modifier for the metal halide is "internally" incorporated in the monomer, rather than "externally" added as in the polymerization by the EtAlCl₂/ester systems. Note that VEBz, an aromatic ester, is similar in structure to ethyl benzoate, whereas VEM, an unsaturated aliphatic ester, to ethyl acetate. The author has already reported the living cationic polymerizations of these vinyl ethers initiated by HI/I₂ at low temperature.^{9,12)}

Figure 6 shows the MWD of the polymers of VEBz and VEM produced by EtAlCl₂ (and BF₃OEt₂ for comparison) in toluene at -15°C. Very narrow MWDs ($\bar{M}_w/\bar{M}_n \sim 1.2$) were obtained by EtAlCl₂, in contrast to the broad MWDs by BF₃OEt₂. The conversion dependence of the $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ of poly(VEBz) obtained with EtAlCl₂ is shown in Figure 7. The $\bar{M}_n$ increased proportionally to conversion. The MWD

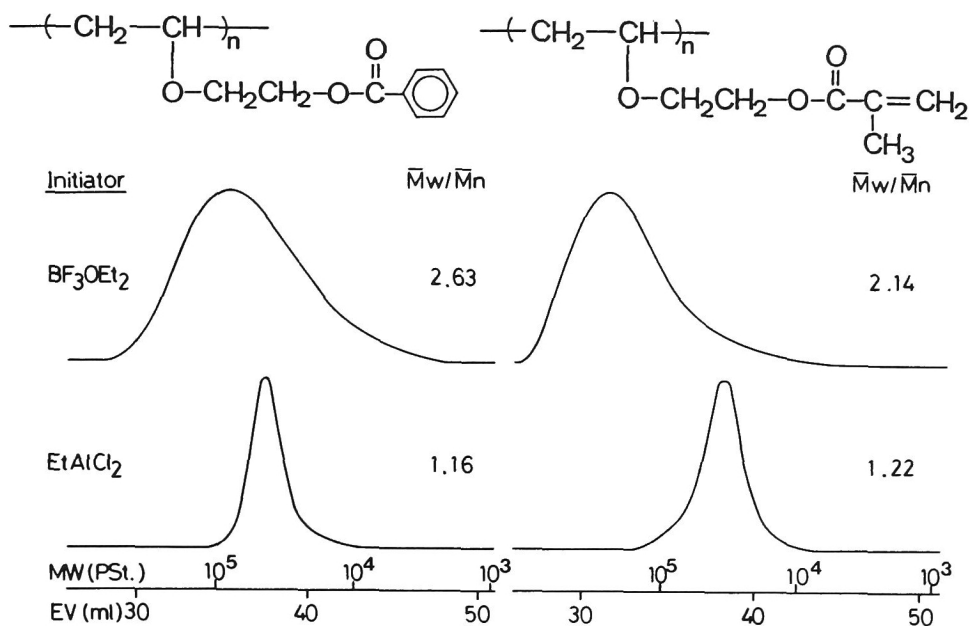


Figure 6. MWDs of poly(VEBz) and poly(VEM) obtained with EtAlCl_2 and BF_3OEt_2 (no ester additives) in toluene at -15°C : $[\text{VEBz}]_0 = 0.56 \text{ M}$; $[\text{VEM}]_0 = 0.64 \text{ M}$; $[\text{Initiator}]_0 = 20 \text{ mM}$.

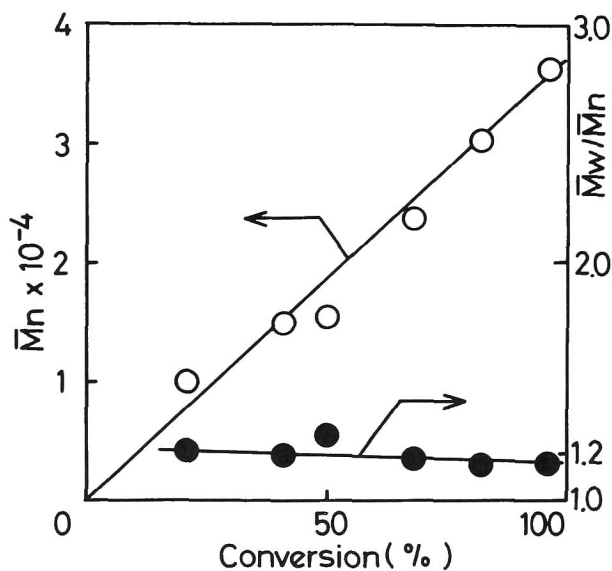


Figure 7. Relationships between conversion and $\bar{M}_n$ or $\bar{M}_w/\bar{M}_n$ ratio in the polymerization of VEBz by EtAlCl_2 in toluene at -15°C ; $[\text{VEBz}]_0 = 0.56 \text{ M}$, $[\text{EtAlCl}_2]_0 = 20 \text{ mM}$.

of the produced polymers remained very narrow ($\bar{M}_w/\bar{M}_n \sim 1.2$) at any conversion. Thus, EtAlCl_2 alone induced living polymerization of the ester-containing vinyl ethers.

In conclusion, this chapter has shown that EtAlCl_2 , in the presence of esters both as additives and as pendant groups in the monomer, initiates living polymerization of vinyl ethers in toluene, to give high molecular weight polymers with a very narrow MWD ($\bar{M}_n > 10^4$, $\bar{M}_w/\bar{M}_n \leq 1.2$). It is of interest that this living polymerization can be carried out at relatively high temperatures (-15° to $+25^\circ\text{C}$) where cationic polymerization of vinyl compounds cannot generally give high polymers.

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CHAPTER 5

CHAIN TRANSFER REACTIONS IN CATIONIC POLYMERIZATION OF VINYL ETHERS

ABSTRACT

Cationic oligomerizations of isobutyl vinyl ether (IBVE) and 2-chloroethyl vinyl ether (CEVE) were carried out with various initiators (BF_3OEt_2 , I_2 , $\text{CF}_3\text{SO}_3\text{H}$, $\text{CH}_3\text{SO}_3\text{H}$, and $\text{CH}_3\text{COCIO}_4$) in benzene at 70°C , and the structure and molecular weight distribution of the products were investigated. The obtained oligomers were constituted of oligo(vinyl ethers) with a conjugated polyene (I) or an acetal(II) terminal. To account for the formation of I and II, a new chain-transfer mechanism has been proposed, which involves successive dealcoholation from the growing chain to give polyene I and a reaction of the released alcohol with the growing vinyl ether cation to yield acetal-capped oligomers II. Oxo acid initiators ($\text{CH}_3\text{SO}_3\text{H}$, $\text{CF}_3\text{SO}_3\text{H}$, and $\text{CH}_3\text{COCIO}_4$) induced the dealcoholation more than BF_3OEt_2 or iodine, giving higher yields of I. It was also demonstrated that the polyene and acetal terminal are formed not only in the oligomerization at high temperatures but also in the polymerization at around 0°C . Thus the coloration of reaction mixtures in vinyl ether polymerization has now been interpreted by the formation of polyenes I.

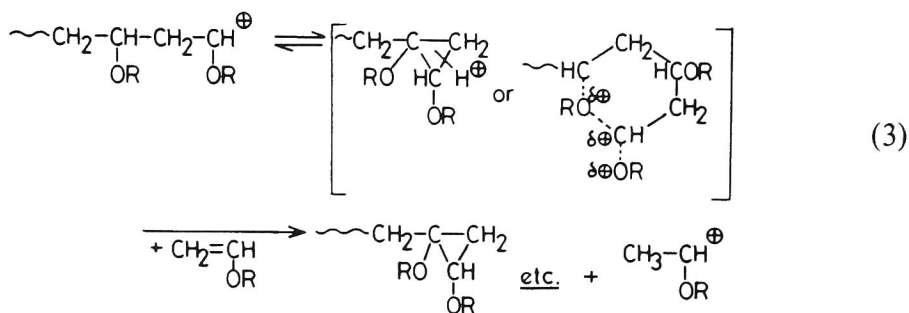
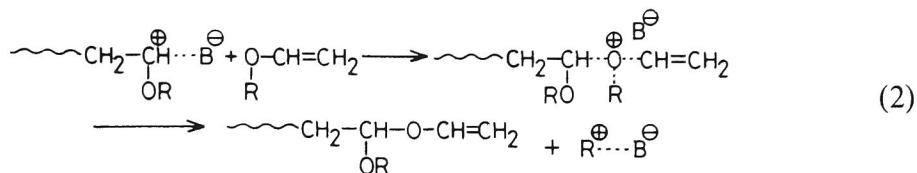
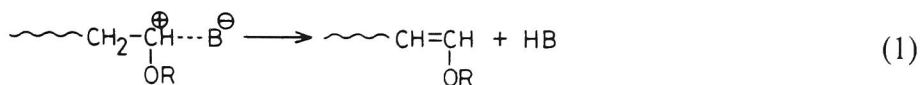
INTRODUCTION

Vinyl ethers are typical monomers cationically polymerizable by various acidic initiators.¹⁾ Their polymerization behavior has been investigated in detail; the classical studies by Eley et al.²⁾ (kinetics) and Schildknecht et al.³⁾ (stereochemistry) were performed as early as in 1940's. More recently, Higashimura et al. and the author have reported "living" vinyl ether polymerization that leads to nearly monodisperse polymers.⁴⁾

In spite of the accumulated studies, vinyl ether polymerization is known to show peculiar, still uninterpreted phenomena¹⁾ such as the coloration of reaction mixtures (typically starting from tint yellow through green to dark violet) and sometimes the polymers (yellowish) isolated therefrom. These phenomena are apparently related to chain-transfer and termination processes, but they have been studied much less than initiation and propagation reactions. In particular, few investigations have concerned the spectroscopic analysis of polymer endgroups that should directly reflect chain-transfer and termination mechanisms.

Equations 1 - 3 illustrate the three chain-transfer mechanisms thus far proposed for vinyl ether polymerization, including direct proton transfer from the growing chain (eq 1), cleavage of the terminal ether bond in the propagating species via an oxonium-ion intermediate (eq 2),⁵⁾ and a back-biting reaction via a cyclopropyl or six-membered cyclic intermediate (eq 3).⁶⁾ These proposals are based on rather indirect evidence such as relative transfer constants (k_{tr}/k_p) and the steric structure of polymers. Reaction 2 has been proposed to account for the presence of an olefinic endgroup (determined by bromination) and the formation of an aldehyde on hydrolysis of product polymers; the amount of them increased with increasing k_{tr}/k_p . None of the mechanisms, however, can explain consistently all the characteristics of vinyl ether

polymerization, particularly the coloration of reaction mixtures and resulting polymers.



This chapter aims to elucidate the chain-transfer reactions in cationic polymerization of vinyl ethers and in turn to synthesize new vinyl ether oligomers by controlled chain transfer. Thus, the oligomerizations of 2-chloroethyl and isobutyl vinyl ethers, as models for their polymerizations, were carried out at 70°C.

EXPERIMENTAL SECTION

Materials. Commercial isobutyl vinyl ether (IBVE) and 2-chloroethyl vinyl ether (CEVE) were washed with an aqueous alkaline solution and then with water, dried overnight with anhydrous sodium sulfate, and distilled twice over sodium metal (for IBVE) or calcium hydride (for CEVE) before use. Acetyl perchlorate (AcClO_4) was synthesized as described elsewhere.⁷⁾ BF_3OEt_2 and $\text{CH}_3\text{SO}_3\text{H}$ (Wako Chemicals) were purified by distillation

under reduced pressure. Iodine (Merck) and $\text{CF}_3\text{SO}_3\text{H}$ (Wako Chemicals), both guaranteed reagents, were used without further purification. Solvents and the internal standard ($\text{C}_6\text{H}_5\text{Cl}$) for gas chromatography were purified as reported⁸⁾ and were distilled over CaH_2 at least twice before use.

Acetaldehyde bis-2-chloroethyl and bis-isobutyl acetals, as model compounds for structural analysis, were prepared by the reaction of acetaldehyde with the corresponding alcohols (2 equiv. to the aldehyde) in the presence of hydrochloric acid and calcium chloride as the dehydrating agent.⁹⁾

Oligomerization. Oligomerization was carried out in an Erlenmeyer flask equipped with a three-way stop-cock under dry nitrogen. The concentration of water in the reaction mixture was smaller than 0.5 mM. The reaction was initiated by adding an initiator solution with a syringe to a monomer solution and, after a certain period, stopped by adding methanol containing a small amount of aqueous ammonia. Conversion was determined by measuring the residual monomer concentration by gas chromatography with chlorobenzene as the internal standard. The reaction solution after quenching was washed with a dilute aqueous alkaline solution (or with an aqueous sodium thiosulfate solution for iodine) to remove the initiator residue, and the products were recovered from the organic layer by evaporation of the unreacted monomer and solvent under reduced pressure.

Characterization. The apparent molecular weight distribution (MWD) of the product was determined by size exclusion chromatography (SEC; a JASCO Trirotar chromatograph with a JSP-101 polystyrene gel column, 20 mm i.d. x 500 mm; CHCl_3 eluent). A dual-mode [UV-visible and refractive index (RI)] detection was applied. The molecular weight of poly(vinyl ethers) was

approximately assessed from that of polystyrene of the same elution volume. When necessary, fractions containing dimers to octamers were separated from the product by preparative, recycling SEC on the same instrument. The structure of the product was determined by ^1H and ^{13}C NMR (JEOL FX90Q, CDCl_3) and UV-visible (Shimadzu UV 190) spectroscopy.

RESULTS AND DISCUSSION

Oligomerization of CEVE.

MWD of Products. CEVE was oligomerized with various acid initiators [oxo acids and their derivative ($\text{CF}_3\text{SO}_3\text{H}$, $\text{CH}_3\text{SO}_3\text{H}$, and AcClO_4), a halogen (I_2), and a metal halide (BF_3OEt_2)] in benzene at 70°C at a low monomer concentration (0.05 M). The oligomerizations by I_2 and $\text{CH}_3\text{SO}_3\text{H}$ proceeded at such a slow rate as to give ca. 80 % conversion in several hours, whereas those by the stronger initiators ($\text{CF}_3\text{SO}_3\text{H}$, AcClO_4 , and BF_3OEt_2) were completed within a few to several tens of min. In spite of this rate difference, yellow-brown oligomers ($\text{MW} = 2 \times 10^2 - 2 \times 10^3$) and a small amount of an insoluble product were obtained in all cases.

Figure 1 shows the SEC traces (MWD) of the oligomers (soluble part) obtained by these initiators. These traces do not show the actual MWD, because the refractive index of CEVE oligomers slightly increases with increasing molecular weights. The oxo-acid initiators formed the oligomers having a main peak (b) at elution volume ~ 93 ml ($\text{MW} \sim 200$; polystyrene calibration) coupled with a broad plateau (c) extending to $\text{MW} \sim 2 \times 10^3$ (Figures 1A - C). This main peak notably increased in intensity with $\text{CH}_3\text{SO}_3\text{H}$ (Figure 1A). On the other hand, I_2 and BF_3OEt_2 gave the oligomers with higher molecular weights ($\text{MW} = 1000 - 2000$; Figures 1D and E).

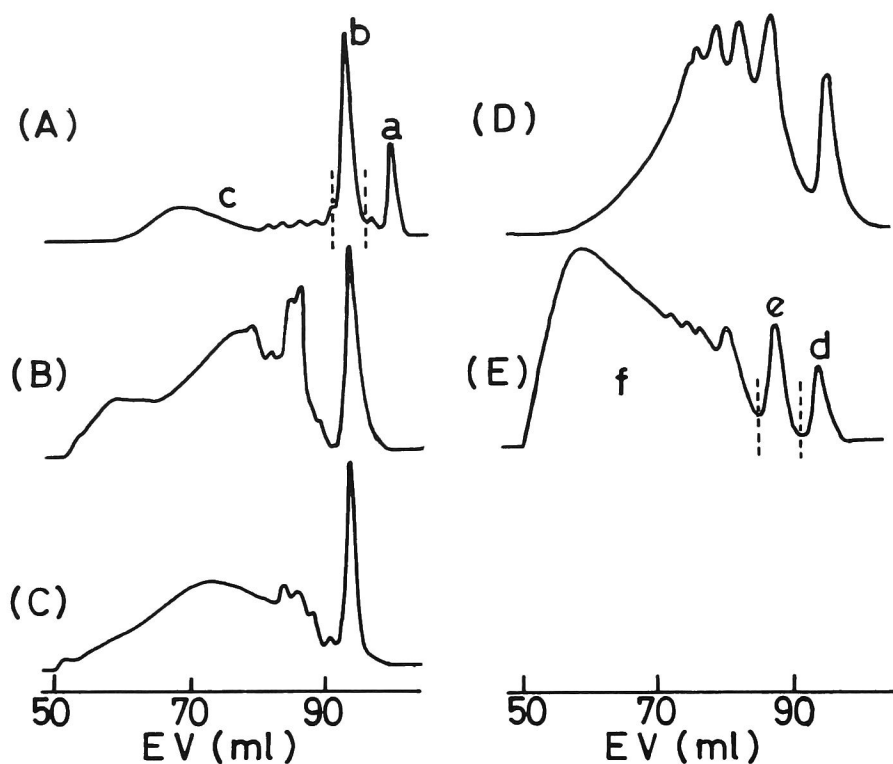


Figure 1. SEC curves for CEVE oligomers obtained in benzene at 70°C: $[M]_0 = 0.05$ M; initiator (mM). (A) $\text{CH}_3\text{SO}_3\text{H}$ (1.0); (B) AcClO_4 (0.05); (C) $\text{CF}_3\text{SO}_3\text{H}$ (0.1); (D) I_2 (5.0); (E) BF_3OEt_2 (0.2).

Structure of CEVE Oligomer Obtained with $\text{CH}_3\text{SO}_3\text{H}$.

(i) Characterization by NMR Spectroscopy. For structural analysis the oligomeric product obtained with $\text{CH}_3\text{SO}_3\text{H}$ was fractionated into three fractions a – c (shown in Figure 1A) by preparative SEC. The ^1H NMR spectra of these fractions are shown in Figure 2.

The spectrum of fraction a is featured by the split peaks in the $\delta = 5 - 7$ region, which are practically the same as those of trans-1-alkoxy-1,3-butadienes (methoxy, ethoxy and isopropoxy).¹⁰ Thus fraction a was assigned to a trans-butadiene derivative with one chloroethyl group. Peak assignments are as follows: δ (ppm) 3.7 ($-\text{CH}_2\text{Cl}$), 4.0 ($-\text{OCH}_2-$), and 4.8–6.7 ($\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-$; 4.9 (H_d), 5.0 (H_e), 5.6 (H_b), 6.2 (H_c), 6.6 (H_a); $J_{ab} = 13$ Hz, $J_{bc} = 11$ Hz,

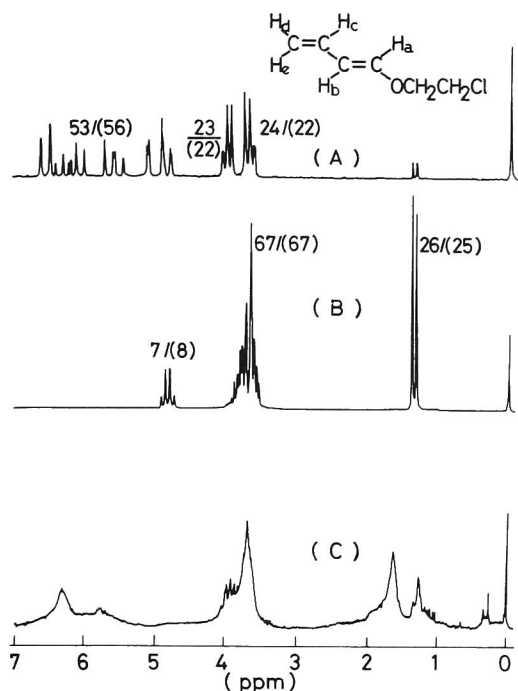


Figure 2. ^1H NMR spectra of fractions a - c shown in Figure 1A: A, fraction a; B, fraction b; C, fraction c.

$J_{\text{cd}} = 11 \text{ Hz}$, $J_{\text{ce}} = 17 \text{ Hz}$, $J_{\text{de}} = 2 \text{ Hz}$). Fraction b showed no unsaturated protons and its ^1H and ^{13}C NMR spectra were found identical with those of an acetal model, $\text{CH}_3\text{CH}(\text{OCH}_2\text{CH}_2\text{Cl})_2$. ^1H and ^{13}C NMR peak assignments are as follows: ^1H NMR δ (ppm) 1.4 (CH_3 -), 3.5 - 4.0 ($-\text{OCH}_2\text{CH}_2\text{Cl}$), and 4.9 ($-\text{CH}<$); ^{13}C NMR δ (ppm) 19.4 (q, CH_3 -), 43.1 (t, $-\text{CH}_2\text{Cl}$), 64.8 (t, $-\text{OCH}_2$ -), and 99.9 (d, $-\text{CH}<$), (d, t, and q indicate peak multiplicity on off-resonance decoupling). The numbers in Figure 2 indicate the relative signal intensities in percent determined from peak areas; those in parentheses show the corresponding values based on the assigned structures. The agreement between the calculated and observed values is satisfactory.

Comparison of Figure 2C with Figures 2A and B indicates that fraction c consists of oligomers with a conjugated diene (or higher polyene) terminal; namely, spectrum 2C exhibits a broad multiplet in the region δ 5.3 - 6.6 ppm, assignable to $-(\text{CH}=\text{CH})_n-$, but no signals of an acetal methine proton [$-\text{CH}(\text{OCH}_2\text{CH}_2\text{Cl})_2$] at δ 4.9 ppm.

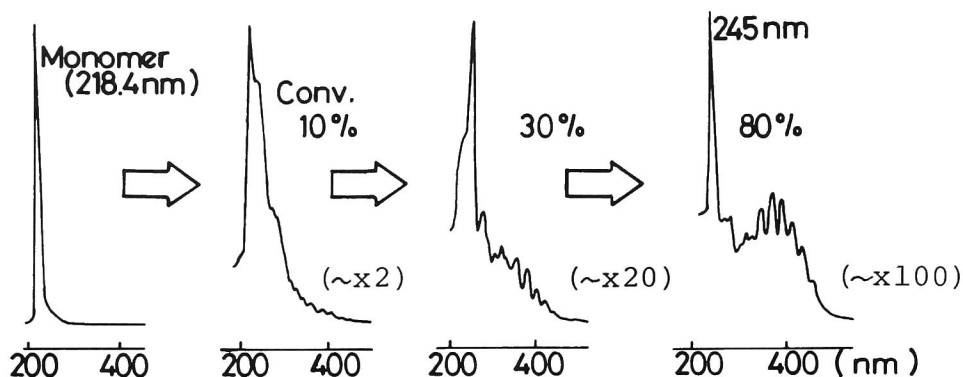


Figure 3. Conversion dependence of the UV-visible spectra of the CEVE oligomers obtained by $\text{CH}_3\text{SO}_3\text{H}$ in benzene at 70°C ($[\text{M}]_0 = 0.05 \text{ M}$).

Therefore, the author concluded that the CEVE oligomerization by $\text{CH}_3\text{SO}_3\text{H}$ leads to oligomers having a conjugated diene or higher conjugated polyene terminal (fractions a and c) together with an acetal, $\text{CH}_3\text{CH}(\text{OCH}_2\text{CH}_2\text{Cl})_2$ (fraction b), formed from the CEVE monomer.

(ii) Characterization by UV-Visible Spectroscopy. The formation of unsaturated (polyene) oligomers was confirmed by UV-visible spectroscopic analysis. Figure 3 shows the absorption spectra of a series of unfractionated oligomerization products obtained at different CEVE conversions. At each conversion, the product exhibited absorptions with a fine structure in the region 220 - 450 nm. Interestingly, with increasing conversion the absorbance increased remarkably (by a factor of 10^2 or more; see the magnification ratios indicated), and new bands emerged at longer wavelengths. Thus the product obtained at 100 % conversion absorbed intensely in the visible region up to ca. 500 nm.

Figure 4 illustrates the dual-mode [UV-RI] SEC traces for the oligomer obtained with $\text{CH}_3\text{SO}_3\text{H}$ (sample A in Figure 1). The RI-detector trace (Figure 4A) indicates the MWD of the whole product and is compared with a series of UV-detector traces

monitored at various wavelengths (Figures 4B - F). These SEC spectra indicate that each oligomer fraction can be detected only at a specific wavelength which is longer for a higher oligomer. For instance, fraction 2 is detectable only at 250 nm (Figure 4B), whereas higher oligomers 8 - 10 should be monitored above 445 nm (Figure 4F). Therefore, the complicated UV spectra shown in Figure 3 are not due to one chromophore showing an absorption with a fine structure (e.g., compounds having aromatic moieties) but to nine or more unsaturated compounds (2 - 10) exhibiting different absorption maxima depending on their molecular weight.

The specific UV-visible detection of CEVE oligomers according to their molecular weight, in turn, enabled the author to separate compounds 2 - 8 (Figure 4) by SEC using a UV detector; note that

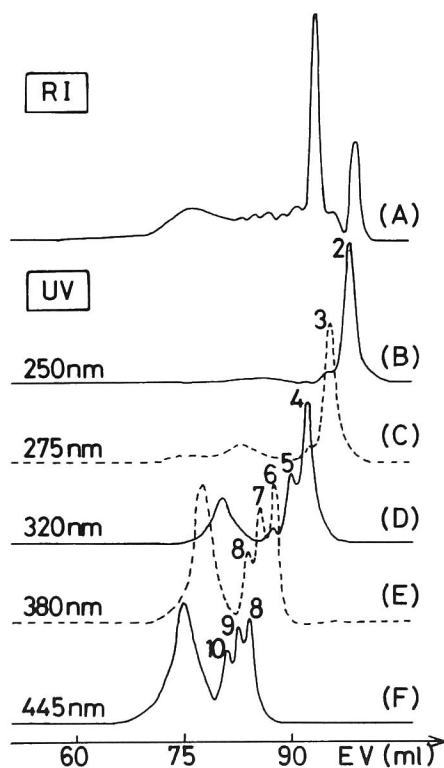
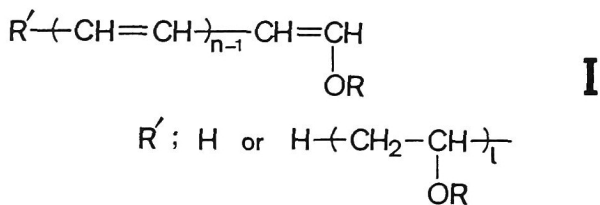


Figure 4. Dual-mode [UV-RI] SEC traces for the CEVE oligomers obtained by $\text{CH}_3\text{SO}_3\text{H}$ in benzene at 70°C ($[\text{M}]_0 = 0.05 \text{ M}$). UV traces were monitored at: (B) 250; (C) 275; (D) 320; (E) 380; (F) 445 nm.

this separation cannot be accomplished on a RI detector that will give only a poorly resolved eluogram (Figure 4A). Figure 5 shows the absorption spectra of fractions 2 - 8. Each fractionated product exhibits an absorption with a clear fine structure, the peak maximum of which increases progressively with increasing molecular weight. These phenomena are characteristic of conjugated polyenes (e.g., non-substituted, conjugated polyene; $H-(CH=CH)_n-H$).¹¹⁾ In addition, the spectrum of fraction 2 was the same as that of $CH_2=CH-CH=CH-OCH_2CH_2Cl$ (fraction a in Figure 1; see above). All these facts indicate that the unsaturated oligomers (e.g., 2 - 10) obtained by CH_3SO_3H are conjugated polyenes I ($R = CH_2CH_2Cl$, $R' = H$; $n = 2 - 10$).



Another proof for conjugated polyene structure I was obtained by plotting the square of the absorption maximum wavelength ($\lambda_{\max}^2$) for fractions 2 - 8 against the number of their expected conjugated double bonds (n) (Figure 6, line a). The plot gave a straight line. It is known, both empirically^{12,13)} and theoretically,^{12,14)} that such a linear $\lambda_{\max}^2$ - n relation holds for a homologous series of conjugated polyenes, e.g., $\text{C}_6\text{H}_5-(\text{CH}=\text{CH})_n\text{C}_6\text{H}_5$ (Figure 6, line b) and $\text{H}-(\text{CH}=\text{CH})_n\text{H}$ (Figure 6, line c).^{12,13)} Taking into account minor effects of the terminal alkoxy group, the close overlap of plots a and c further confirms structure I for the CEVE oligomers obtained with $\text{CH}_3\text{SO}_3\text{H}$.

(iii) Interpretation of the Coloration during Oligomerization.

When conjugated polyenes are protonated with an acid, their UV-visible absorptions exhibit a large bathochromic shift to the

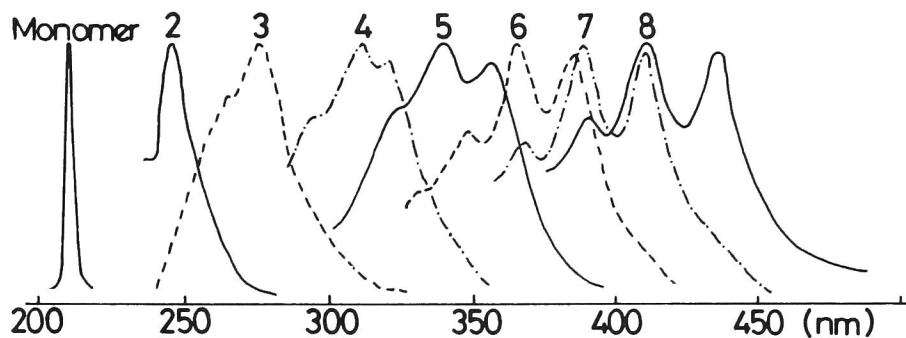


Figure 5. UV spectra of fractions 2 - 8 shown in Figure 4.

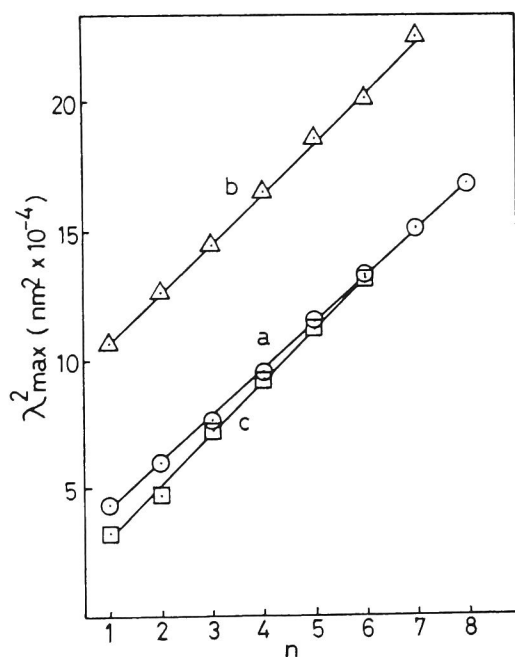


Figure 6. Relationships between λ_{max}^2 , the square of absorption maximum wavelength, and n , the number of conjugated double bonds: (○) $\text{H}-(\text{CH}=\text{CH})_n\text{OCH}_2\text{CH}_2\text{Cl}$ (2 - 8 in Figure 4); (Δ) $\text{C}_6\text{H}_5-(\text{CH}=\text{CH})_n-\text{C}_6\text{H}_5$; (□) $\text{H}-(\text{CH}=\text{CH})_n\text{H}$.^{10,11)}

visible region.¹⁵⁾ The author thus studied protonation (re-acidification) and subsequent neutralization of the CEVE oligomers to find out conclusive evidence for structure I (Figure 7). A CEVE oligomer solution obtained by $\text{CF}_3\text{SO}_3\text{H}$ in benzene shows absorptions extending from 300 to 400 nm (Figure 7A). When a small amount of $\text{CF}_3\text{SO}_3\text{H}$ was added to this yellow solution, it immediately turned black and, correspondingly, its absorption spectrum exhibited a new broad band in the visible region above 450 nm, while the peak near 350 nm in turn decreased in intensity (Figure 7B). Neutralization of this solution with ammoniacal methanol regenerated a yellow solution; the flat band around 600 nm completely disappeared and the 350 nm peak increased (Figure 7C). These series of color and spectral changes indicate that the coloration of a polymerizing solution of vinyl ethers, as often observed, is due to the protonation of the polyene terminals formed during the polymerization.

Separate experiments showed that, when brominated in CHCl_3 at room temperature, the yellowish CEVE oligomer turns colorless, again supporting its polyene structure.

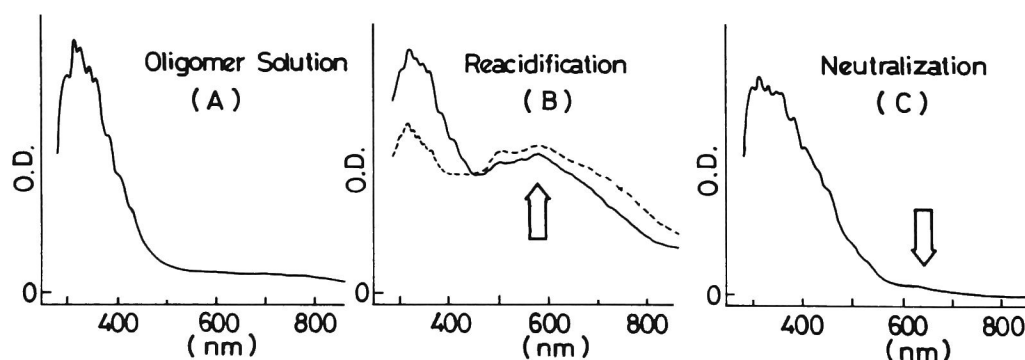
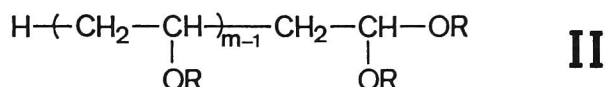


Figure 7. Changes in the UV-visible spectrum of the CEVE oligomers obtained by $\text{CF}_3\text{SO}_3\text{H}$ in benzene at room temperature ($[\text{CEVE}]_0 = 0.5$ mM; $[\text{CF}_3\text{SO}_3\text{H}] = 2.5$ μM). (A), oligomer solution, yellow; (B), after re-acidification to give $[\text{CF}_3\text{SO}_3\text{H}]/[\text{CEVE}]_0 = 0.03$ (—), 0.06 (---), black; (C), after neutralization with ammoniacal methanol, yellow.

Effects of Initiators on Oligomer Structure.

A sample of the CEVE oligomers obtained with a metal halide (BF_3OEt_2) was fractionated by SEC into fractions d to f shown in Figure 1E. With this initiator no insoluble material was formed. Typical ^1H NMR spectra of these fractions are shown in Figure 8. The lowest two fractions, d and e, were found to be acetal-type compounds II (d, $m = 1$; e, $m = 2$). Oligomer part f (Figure 8C)



showed signals of both polyene (δ 5 - 6.7 ppm) and acetal (δ 4.9 ppm) terminals. This indicates that BF_3OEt_2 produces not only polyenes I but acetal-terminated oligomers II ($m \geq 3$) which, in contrast, could not be detected in ^1H NMR of oligomers with

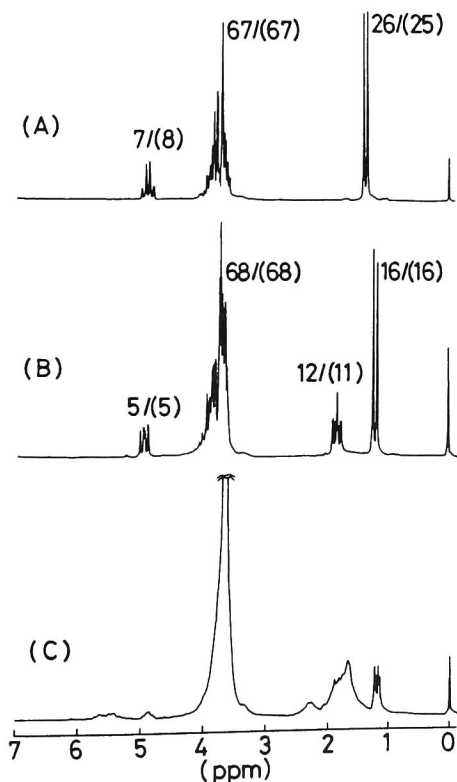


Figure 8. ^1H NMR spectra of (A) fraction d shown in Figure 1E; (B) fraction e; (C) fraction f.

CH₃SO₃H in Figure 2 (see above). Interestingly, the butadiene derivative CH₂=CH-CH=CH-OCH₂CH₂Cl (I, n = 2) did not form in the presence of BF₃OEt₂. A halogen (I₂) was also used, and it gave similar qualitative results as BF₃OEt₂.

Since BF₃OEt₂ gave the completely soluble product, the relative amounts of the polyene- and acetal-capped oligomers could be determined by ¹H NMR (Table I). Table I also lists the ratio of monomeric (m = 1) to oligomeric (m ≥ 2) homologs of II for CH₃SO₃H and CH₃COC10₄; the amount of polyene-capped oligomers could not be obtained, since these oxo acids yielded partly insoluble products.

Although the amount of polyenes I was not quantitatively determined, the oxo acid initiators (CH₃SO₃H, CF₃SO₃H, and AcC10₄) obviously led to much more polyenes I (n ≥ 2) than a metal halide (BF₃OEt₂) or a halogen (I₂). This suggests that these initiators

TABLE I

Structure of CEVE Oligomers Obtained with Different Initiators
in Benzene at 70°C^{a)}

Initiator	$\text{CH}_3-\text{CH} \begin{array}{l} \nearrow \text{OR} \\ \searrow \text{OR} \end{array}$	$\text{H}-(\text{CH}_2-\underset{\text{OR}}{\text{CH}})_{m-1}-\text{CH}_2-\text{CH} \begin{array}{l} \nearrow \text{OR} \\ \searrow \text{OR} \end{array}$	$-(\text{CH}=\text{CH})_n$
BF ₃ OEt ₂	~ 0.2	~ 0.3	~ 0.5
CH ₃ COC10 ₄	(~0.7)	(~0.3)	n.d. ^{b)}
CH ₃ SO ₃ H	(1.0)	(0)	n.d. ^{b)}

a) mol% determined by ¹H NMR.

b) The amount of polyene could not be obtained because of yielding partly insoluble (cross-linked) products.

promote the dealcoholation from the growing chain (see Scheme I below) by promoting the β -proton elimination or migration through their nucleophilic, oxygen-containing counteranions, as Higashimura et al. pointed out previously.¹⁶⁾

Oligomerization of IBVE.

As a vinyl ether other than CEVE and free of hetero atoms, IBVE was oligomerized with oxo acids ($\text{CF}_3\text{SO}_3\text{H}$ and $\text{CH}_3\text{SO}_3\text{H}$) in benzene at 70°C ($[\text{IBVE}]_0 = 0.050 - 1.0 \text{ M}$). Under these conditions, the reactions by the two initiators were completed within several min to yield a brown solid and a transparent yellowish liquid with a fragrance. The solid product was insoluble in all common organic solvents and presumably a crosslinked material formed from polyenes similar to I.

The liquid (soluble) part showed a single, sharp peak at MW 200 (polystyrene calibration) on SEC analysis. The ^1H and ^{13}C NMR spectra of this part were also identical with those of an authentic sample of an acetal [II, $m = 1$; $\text{R} = \text{CH}_2\text{CH}(\text{CH}_3)_2$, $(\text{CH}_3\text{CH}[\text{OCH}_2\text{CH}(\text{CH}_3)_2]_2)$, δ_{H} NMR (ppm); 0.9 (d, $-\text{CH}(\text{CH}_3)_2$), 1.2 (d, $\text{CH}_3-\text{CH}<$), 1.8 (m, $-\text{OCH}_2-\text{CH}<$), 3.2 (m, $-\text{O}-\text{CH}_2-$), 4.7 (q, $\text{CH}_3-\text{CH}<$)]. These data indicate that the oligomerizations of IBVE and CEVE by oxo acids are very similar in mechanism, both yielding monomeric acetals (II; $m = 1$) and conjugated polyenes (I).

Reaction of CEVE at low temperatures.

Polyene I and acetal-capped polymer II were found to form not only in oligomerization at high temperatures but also in polymerization of CEVE at low temperatures. The oligomerization was carried out with $\text{CF}_3\text{SO}_3\text{H}$ in benzene at 0°C and a high CEVE concentration (1.0 M). Nearly 90 % of the monomer was consumed within twenty minutes to give poly(CEVE) with $\bar{M}_w = 5.7 \times 10^3$, $\bar{M}_n = 2.2 \times 10^3$ (by SEC, polystyrene calibration).

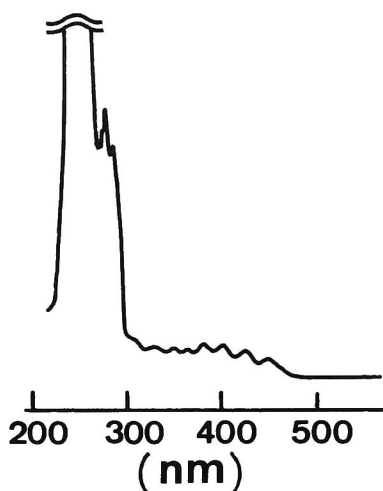


Figure 9. UV-visible spectrum of the CEVE polymer obtained by $\text{CF}_3\text{SO}_3\text{H}$ in benzene at 0°C ($[\text{M}]_0 = 1.0 \text{ M}$).

Figure 9 shows the UV spectrum of the polymer. The bands with a fine structure seen in the visible region indicate the formation of various conjugated polyenes similar to I. Because of its higher molecular weight, the poly(CEVE) showed weaker polyene absorptions than the corresponding oligomers.

Figure 10 shows the ^1H NMR spectrum of the same polymer along with peak assignments. Similarly to the CEVE oligomers (cf. Figure 8C), the polymer exhibited signals of both polyene (δ 5 - 6 ppm) and acetal (δ 4.9 ppm, triplet) endgroups, along with the doublet at δ 1.2 ppm due to the methyl "head" group ($\text{CH}_3\text{CH}(\text{OR})-$). These endgroup signals were not entirely due to oligomer fractions in the product, because its average molecular weight calculated on the basis of these peaks was in good agreement with the observed $\bar{M}_n$. The ratio of the terminal methine (acetal) to the head methyl groups ($-\text{CH}/\text{CH}_3-$) was 0.92, indicating that at least 90 % of the polymer is of acetal-capped structure II.

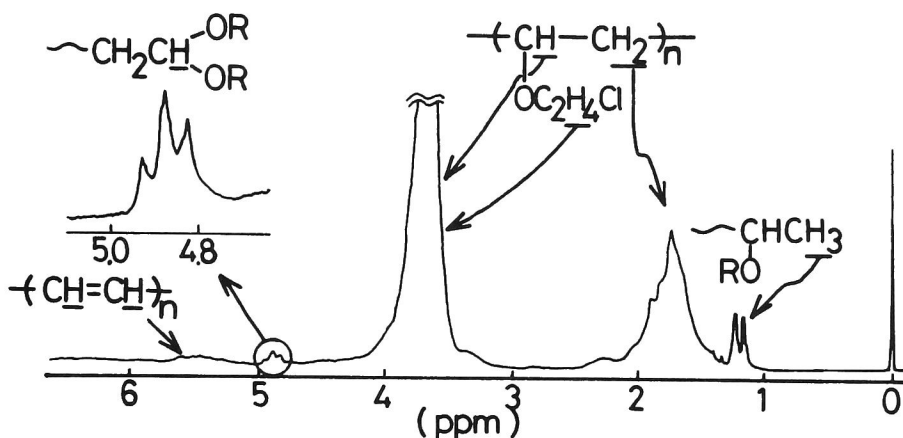
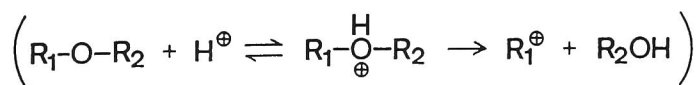


Figure 10. ^1H NMR spectrum of the CEVE polymer obtained by $\text{CF}_3\text{SO}_3\text{H}$ in benzene at 0°C ($[\text{M}]_0 = 1.0 \text{ M}$).

Reaction Mechanism.

To account for the formation of the conjugated polyenes (I) and saturated oligomers (II) with an acetal terminal, the author now proposes the mechanism shown in Scheme I. In the first step, the propagating species III rearranges into oxonium ion V either via the direct migration of the β -proton to the penultimate ether oxygen or via the β -proton abstraction by the counteranion (to give olefin IV) followed by protonation of the penultimate ether oxygen in IV. Intermediate V then releases an alcohol, resulting in conjugated carbocation VI. It is well-known that a protonated ether readily decomposes into an alcohol and a carbocation in an acidic medium.



The driving forces of this dealcoholation are a good leaving property of the alcohol and the generation of more delocalized



Conjugated polyenes similar to IX have been reported to form during chemical modification of polymers, e.g., dehydrochlorination of PVC¹⁷⁾ and dehydration of PVA.¹⁸⁾ Although the polyene formation during polymerization does occur in some cases, e.g., by dehydrogenation of polystyrene¹⁹⁾ and poly(vinylfuran),²⁰⁾ that by dealcoholation from the growing species has not been known, except in the polymerization of ketene acetal²¹⁾ where no details have been reported on the mechanism and product structure.

Scheme I also shows the pathway for acetal-capped polymer II. Thus the released alcohol ROH, an effective transfer agent, readily reacts with the growing chain, and deprotonation from the resulting oxonium ion yields polymer X (II) with an acetal endgroup. The formation of an alcohol during polymerization takes place in the system $\text{Et}_3\text{O}^+\text{SbCl}_6^-$ /alkyl vinyl ether/ CH_2Cl_2 as well, however, a different mechanism has been proposed.²²⁾

The chain-transfer mechanism proposed in Scheme I seems to be unique for vinyl ethers that have an alkoxy group, which is easy to be eliminated in an acidic environment. Such a pendant, a good leaving group, is not present in styrenes or alkenes.

Consequently, this chapter has shown that the color of produced polymers and reaction mixtures in vinyl ether polymerizations result from, respectively, conjugated polyene termini in the polymers and their protonated forms having different lengths.

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PART II

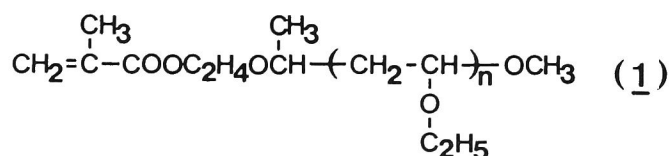
SYNTHESIS OF FUNCTIONAL POLYMERS BY LIVING CATIONIC POLYMERIZATION TECHNIQUE

CHAPTER 6

SYNTHESIS OF POLY(VINYL ETHER) MACROMONOMER WITH A METHACRYLATE HEAD

ABSTRACT

A new poly(vinyl ether) macromonomer (1) having a methacrylate group has been prepared. The adduct $[\text{CH}_2=\text{C}(\text{CH}_3)-\text{COOCH}_2\text{CH}_2-\text{O}-\text{CHI}-\text{CH}_3]$ obtained by the reaction of 2-vinyloxyethyl methacrylate with hydrogen iodide was employed as an initiator to induce living polymerization of ethyl vinyl ether in the presence of a small amount of iodine. According to ^1H and ^{13}C NMR analysis, the products were poly(ethyl vinyl ether) macromonomers 1 with a narrow molecular weight distribution having one methacrylate group at the chain end per molecule. The molecular weight of macromonomer 1 could be controlled by regulating the feed ratio of monomer to initiator.

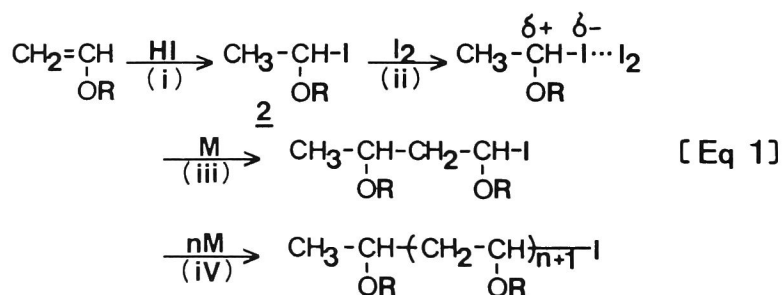


INTRODUCTION

Recently, the author et al. have found that not only alkyl vinyl ethers¹⁾ but vinyl ethers with a functional pendant²⁾ can be polymerized into living polymers by the HI/I₂ initiator under suitable conditions. Among a number of synthetic advantages offered by "living" polymerization, the elaborate control of polymer molecular weight distribution (MWD) and end functionality is of particular importance. The previous investigations on the HI/I₂-initiated living polymerization have concerned primarily the extension of the scope of the process and the control of polymer molecular weight and MWD (synthesis of monodisperse polymers). In this chapter, the author now turns the attention to the control of the end functionality of poly(vinyl ethers), focusing in particular on the synthesis of macromolecular monomers (or "macromonomers"³⁾) that have a radically polymerizable end-group attached to a monodisperse poly(vinyl ether) chain.

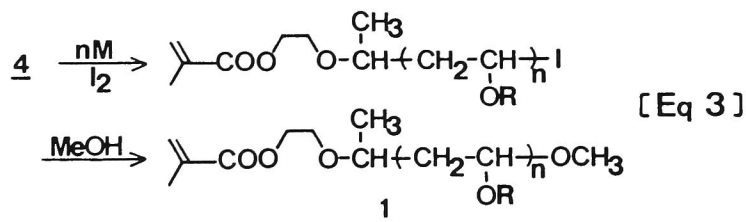
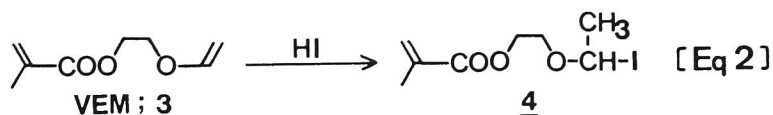
Principle of the Macromonomer Synthesis.

The HI/I₂-initiated living polymerization of alkyl vinyl ethers proceeds as eq 1⁴⁾: (i) addition of HI to vinyl ether monomer to form adduct 2; (ii) activation of the C-I bond of 2 by added iodine; (iii) insertion of a monomer molecule (propagation); (iv) repetition of reactions (ii) and (iii) to give living polymer. Importantly, vinyl ether-HI adduct 2 has been found to initiate, in



the presence of a small amount of iodine, a living polymerization that is essentially identical with that by the HI/I₂ initiator.⁵⁾

In usual homopolymerizations, adduct 2 comes from the monomer itself, so that the head group [CH₃-CH(OR)] and the main chain of the polymer have the same pendant group OR. The proposed mechanism (eq 1), however, implies that adduct 2 can polymerize vinyl ethers having an alkoxy pendant OR' different from that (OR) in it. If HI adduct 4 (eq 2) can be selectively prepared from vinyloxyethyl methacrylate (VEM) (3) and utilized as a "functionalized" initiator for living polymerization of vinyl ethers other than 3 (eq 3), then the resulting polymers (1) will have a methacrylate head group attached to a poly(vinyl ether) chain with a monodisperse MWD. Thus, eqs 2 and 3 provide a new simple method for preparing macromonomers via the living polymerization by the HI/I₂ initiator.



The present chapter describes preliminary results of the synthesis of a methacrylate macromonomer (1) having a poly(ethyl vinyl ether) pendant, based on the strategy shown above. Initiator 4 is potentially able to polymerize any vinyl ethers, but in this study the author employed ethyl vinyl ether, one of the simplest alkyl vinyl ethers, because of the easy structural characterization of its product.

EXPERIMENTAL SECTION

The monomers, solvents, and initiators were prepared and/or purified as reported.^{1,2)} Polymerizations were carried out under dry nitrogen.

A typical example of the synthesis of macromonomer 1 having 50 ethyl vinyl ether units was as follows. In a baked vessel equipped with a three-way cock, 0.046 ml (0.3 mmol) VEM in toluene (24.6 ml) was treated with an equimolar amount of HI in hexane (330 mM, 0.9 ml) at -78°C , to yield quantitatively adduct 4. To this initiator solution was added, successively, ethyl vinyl ether (1.43 ml, 15 mmol) and iodine in toluene (50 mM, 3 ml) and the mixture was then kept at -40°C . After 2 h, when the monomer had been consumed almost completely, the reaction was terminated with prechilled ammoniacal methanol. The quenched reaction mixture was washed with 10% sodium thiosulfate solution and then water to remove the iodine residues, and evaporated to dryness under reduced pressure to give the product macromonomer.

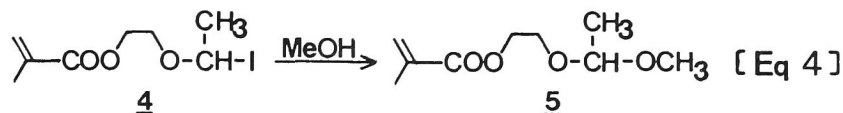
The MWD of the macromonomers was measured by size exclusion chromatography (SEC) using polystyrene gel columns.^{1,2)} The $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ ratios were calculated from SEC curves on the basis of a polystyrene calibration. The ^1H and ^{13}C NMR spectra of the polymers were recorded on a JEOL FX90Q spectrometer in CDCl_3 .

RESULTS AND DISCUSSION

Preparation of Initiator 4.

VEM-HI adduct 4 was prepared by the treatment of VEM with HI in toluene at -78°C under dry nitrogen (eq 2). The quantitative formation of 4 was proved as follows. Since adduct 4 was not stable enough to be isolated at room temperature, it was converted in situ into a more stable acetal form (5) by quenching with

methanol (eq 4). The size exclusion chromatogram of the product showed a sharp single peak; there was no peak assignable to VEM or polymeric by-products.



The ^1H NMR spectra of VEM and the acetalized product are shown in Figure 1, along with peak assignments. After the treatment of VEM with HI then with methanol, the absorption of the vinyloxy group [ca. 6.4 ppm (=CH-O-)] of VEM disappeared completely, and methyl [1.3 ppm], methine [4.7 ppm], and methoxy [3.3 ppm] peaks appeared. In contrast to these changes, the methacrylate moiety [5.6 and 6.1 ppm] remained intact. In addition, the spectrum does

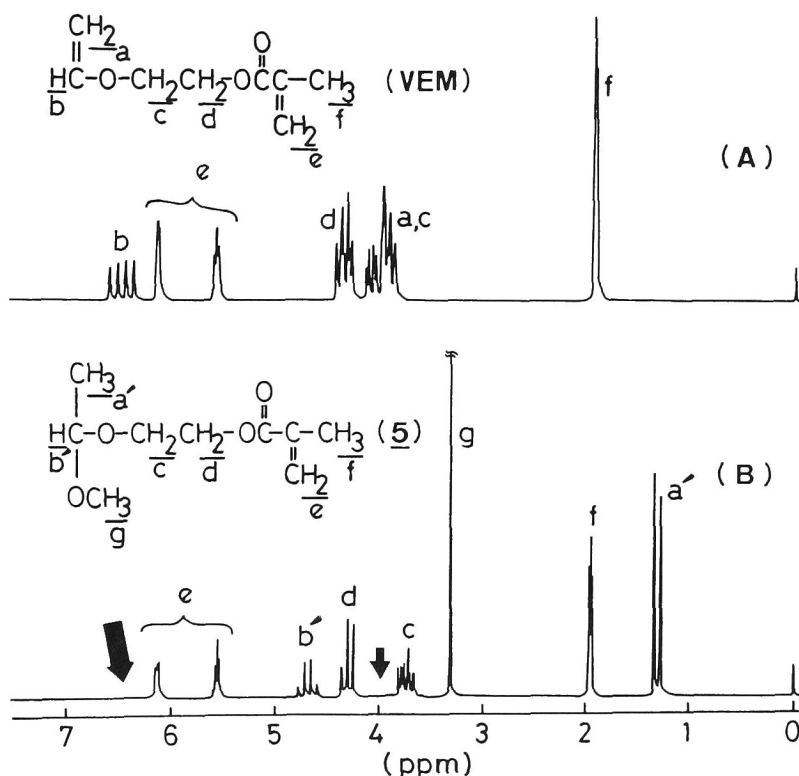


Figure 1. ^1H NMR spectra (A) VEM and (B) acetal 5 in CDCl_3 .

not exhibit signals indicative of undesirable side reactions, e.g., the addition of HI or I₂ to the methacrylate group or HI-initiated polymerization via the vinyloxy group. The formation of adduct 4 was also shown by ¹³C NMR analysis: [δ (ppm); 166.6 (s, -COO-), 135.8 (s, =C-CO-), 124.9 (t, CH₂=), 99.9 (d, -O-CH-O-), 63.5 and 62.1 (t, -O-CH₂CH₂-O-), 51.7 (q, -OCH₃), 18.5 (q, CH₃-CH-O-), 17.6 (q, =C(CH₃)-CO-)]. These results show the selective addition of HI to the vinyloxy group of VEM to form adduct 4.

Polymerization of Ethyl Vinyl Ether by $\underline{4}/\text{I}_2$ Initiator.

To a toluene solution of adduct 4 prepared at -78°C was added ethyl vinyl ether and iodine in this order, and then the temperature of the reaction mixture was raised to -40°C. The polymerization by the $\underline{4}/\text{I}_2$ system proceeded without an induction phase up to 100 % at a rate comparable to that by HI/I₂, as shown in Figure 2.

Figure 3 shows the MWDs of the products obtained at various feed ratios of ethyl vinyl ether to 4 ($[\text{M}]_0/[\underline{4}]_0 = 5, 50, \text{ and } 100$;

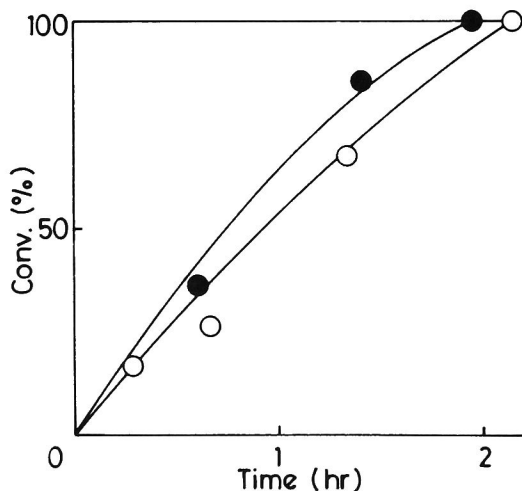


Figure 2. Time-conversion curves for the polymerization of ethyl vinyl ether in toluene at -40°C and $[\text{M}]_0 = 0.50 \text{ M}$. Initiator (mM): (●) HI/I₂, 10/5; (○) $\underline{4}/\text{I}_2$, 10/5.

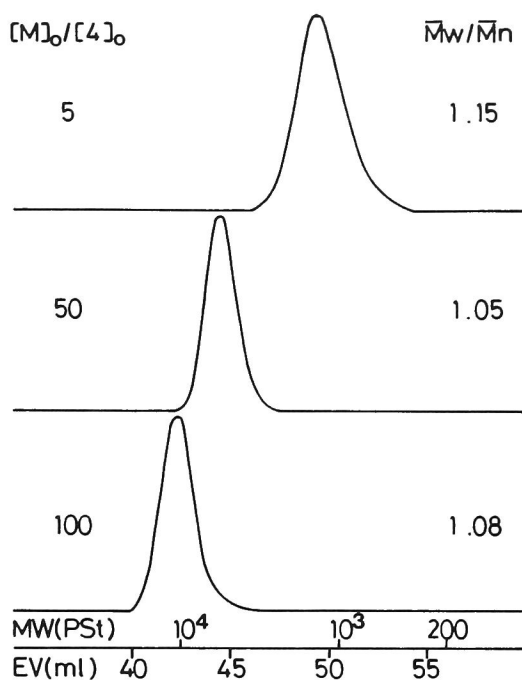


Figure 3. Effect of $[M]_0/[4]_0$ feed ratio on the MWD of macro-monomer 1. See Table I for reaction conditions.

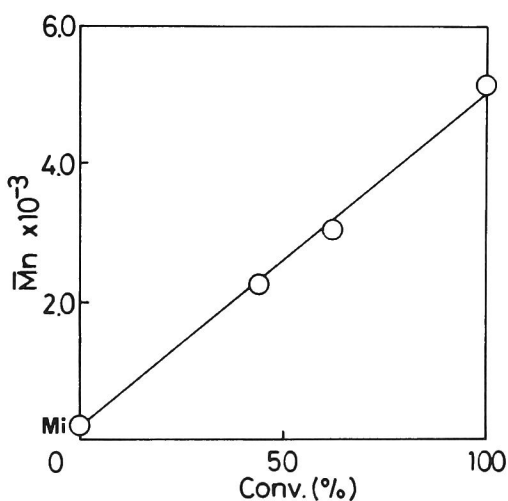


Figure 4. Relationship between conversion and $\bar{M}_n$ in the polymerization of ethyl vinyl ether by 4/ I_2 in toluene at -40°C : $[M]_0 = 0.05 \text{ M}$; $[4]_0/[I_2]_0 = 10/5 \text{ (mM)}$. Mi indicates the molecular weight of initiator 4.

conversion ~100 %). Every polymer has a very narrow MWD, the peak molecular weight of which is increasing progressively with increasing $[M]_0/[4]_0$ ratio. Furthermore, an increase of their molecular weight proportional to vinyl ether conversion (Figure 4) shows that 4, in conjunction with iodine, initiates the living polymerization of ethyl vinyl ether.

SEC analysis using refractometric and UV ($\lambda = 255$ nm) dual detectors established that the samples contain methacrylate end groups over the whole range of their MWD.

Characterization of Macromonomer.

The structure and olefinic end functionality (F_n) of the macromonomers have been determined by 1H and ^{13}C NMR spectroscopy. Figure 5 shows the 1H NMR spectra of the macromonomers having 5 (Figure 5A) and 100 (Figure 5B) ethyl vinyl ether units in the pendant. The signals of the head methacrylate group [2.0 ($=C(CH_3)CO-$), 4.2 ($-COO-CH_2-$), and 5.6 and 6.1 ppm ($CH_2=$)] and the end acetal group [3.3 ($-OCH_3$) and 4.6 ppm ($-O-CH-O-$)] are clearly seen, together with the large three signals due to the poly(ethyl vinyl ether) chain [1.2 ($-OCH_2CH_3$), ~ 1.6 ($-(CH_2-CH)-_n$), and ~ 3.5 ppm ($-CH-O-CH_2-$)]. The numbers in Figure 5A indicate the relative signal intensities in percent determined from integrated peak areas; those in parentheses show the corresponding calculated values based on the assigned structure 6. The agreement between the calculated and observed values is satisfactory, and no peaks assignable to other structures were detected. The ^{13}C NMR spectra of the macromonomers (e.g., Figure 6) also confirmed their expected structure 1.

The number of the terminal methacrylate per polymer molecule (F_n) for macromonomer 1 was determined from the ratio of the integrated 1H NMR peak areas in Figure 5: $a/2k = (\text{methacrylate olefin})/(\text{acetal end})$. The $a/2k$ value directly gives the end functionality F_n . In addition, the a/c ratio [$= (\text{methacrylate$

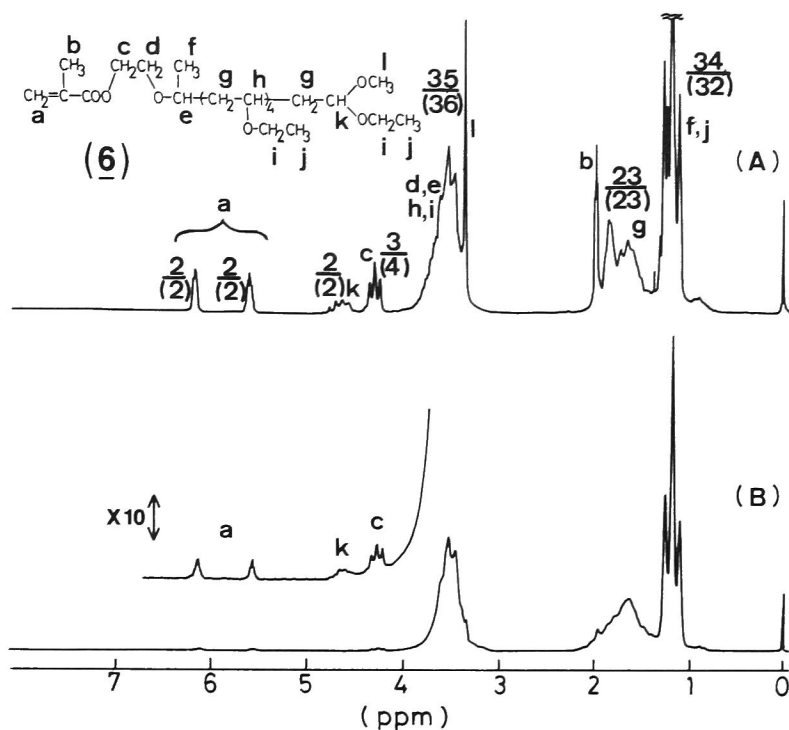


Figure 5. ^1H NMR spectra of macromonomers **1** having 5 (A) and 100 (B) ethyl vinyl ether units (samples 1 and 3, Table I, respectively).

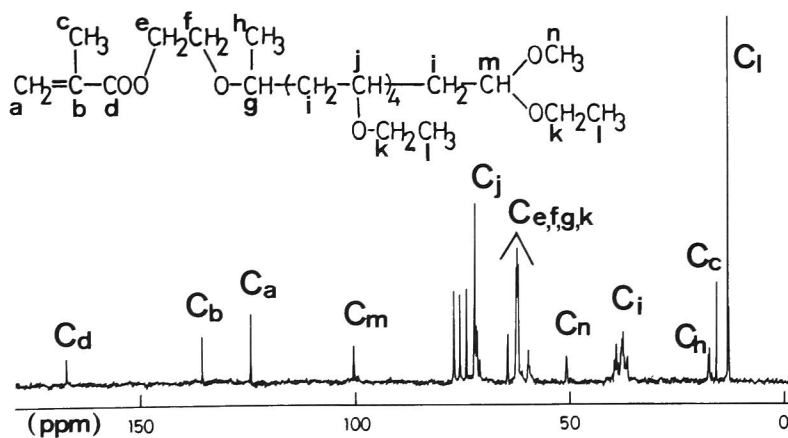


Figure 6. ^{13}C NMR spectrum of macromonomer **1** having 5 ethyl vinyl ether units (sample 1, Table I).

olefin)/(VEM residue)] indicates the number of methacrylate olefins per VEM head group and should be unity when methacrylate-consuming side reactions are absent in the macromonomer synthesis. Table I shows these ratios for a series of macromonomer 1 with three molecular weights. The $a/2k$ (F_n) and a/c values for all macromonomers are very close to unity within the experimental error, indicating that they carry one methacrylate function per one molecule.

The macromonomer synthesis route illustrated in eqs 2 and 3 is applicable to vinyl ethers other than ethyl vinyl ether, including those with a functional group, which undergo living polymerization in the presence of HI/I_2 .

Radical homopolymerization of macromonomer 1 and its copolymerization with methyl methacrylate were carried out in benzene solution with azobisisobutyronitrile (AIBN) as an initiator, to yield high molecular weight polymers, as shown in Tables II and III.

TABLE I

Synthesis of Macromonomer (Mac.) 1 in Toluene at $-40^\circ\text{C}^{\text{a)}$

No.	[Mac.] ₀ (M)	[<u>4</u>] ₀ (M)	[Mac.] ₀ [<u>4</u>] ₀	Time (h)	$\bar{M}_n^{\text{b)}$ $\times 10^{-3}$	$\frac{\bar{M}_w^{\text{b)}}}{\bar{M}_n}$	$\frac{a^{\text{c)}}}{2k} (F_n)^{\text{d)}$	$\frac{a^{\text{c)}}}{c}$
1	0.1	0.02	5	0.5	1.2	1.15	0.99	0.97
2	0.5	0.01	50	2	5.4	1.05	1.05	0.97
3	1.0	0.01	100	3	9.7	1.08	0.99	1.06

a) $[I_2]_0 = 0.005 \text{ M}$; conversion $\sim 100 \%$.

b) Measured by SEC.

c) ^1H NMR peak intensity ratio; see Figure 5 and text.

d) Number-average end functionality of Macromonomer 1.

TABLE II

Homopolymerization of Macromonomer (Mac.) 1 by AIBN^{a)}

Macromonomer (n)	[Mac.] ₀ (mM)	[AIBN] ₀ (mM)	$\frac{[\text{Mac.}]_0}{[\text{AIBN}]_0}$	Conv. ^{b)} (%)	$\bar{M}_w^c)$ x10 ⁻³	$\bar{M}_n^c)$ x10 ⁻³	DP ^{d)}
10	135	4.4	30	20	69	43	33
10	135	9.2	15	46	63	31	24
10	200	35	5.7	83	64	18	14
50	77	330	0.23	44	41	20	4

a) In benzene at 60°C for 18 h.

b) Measured by SEC.

c) Calculated from PSt calibration.

d) $M_n(\text{Product})/M_n(\text{Macromonomer})$.

TABLE III

Copolymerization of Macromonomer (Mac.) 1 with MMA^{a)}

Macromonomer (n)	[Mac.] ₀ (mM)	[MMA] ₀ (M)	$\frac{[\text{MMA}]}{[\text{Mac.}]}$	Conv.(%) ^{b)} (Mac.)	$\bar{M}_w^c)$ x10 ⁻³	$\bar{M}_n^c)$ x10 ⁻³
10	21	0.83	40	87	15	6.8
10	21	1.67	80	91	29	9.4
10	11	1.57	150	100	26	2.6
50	17	0.84	50	43	63	11

a) In benzene at 60°C for 18 h. $[\text{AIBN}]_0 = 6 \text{ mol\%}$; MMA Conv. 100 %.

b) Measured by SEC.

c) Calculated from PSt calibration.

REFERENCES AND NOTES

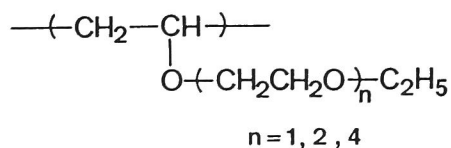
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CHAPTER 7

SYNTHESIS OF COMB-LIKE POLYMERS HAVING POLYOXYETHYLENE PENDANT WITH NARROW MOLECULAR WEIGHT DISTRIBUTION

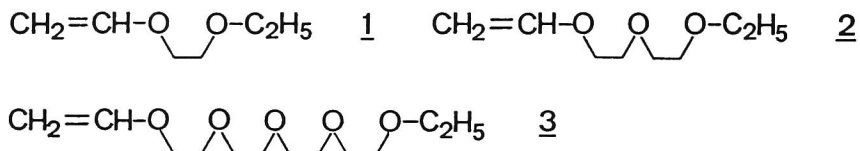
ABSTRACT

Vinyl ethers having oxyethylene units $[\text{CH}_2=\text{CHO}-\text{-(CH}_2\text{CH}_2\text{O)}_n\text{-C}_2\text{H}_5, n = 1 - 4]$ were cleanly polymerized by the HI/I_2 initiator in a nonpolar solvent (toluene) at low temperatures (-15° and -40°C) to yield living-like polymers with a very narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n \leq 1.2$); the oxyethylene units in the monomers hardly disturbed the polymerization. The number-average molecular weight of the polymers increased proportionally to monomer conversion and the monomer-to-HI feed ratio. The polymerization rates of the polyether-containing vinyl ethers were much greater than those of alkyl vinyl ethers under similar conditions, and it is presumed that the pendant ether oxygens intramolecularly activate the growing end. The polymers were soluble in methanol (with $n \geq 1$) and in water (with $n \geq 2$), depending on the number of oxyethylene units in the pendant, and formed complexes with alkali metal ions.



INTRODUCTION

In the cationic polymerization of styrene by Lewis acids, ethers¹⁾ and esters^{2,3)} often act as strong chain-transfer agents that severely reduce polymer molecular weight via nucleophilic reactions of their oxygen atoms with the propagating carbocation. In spite of this fact, the author et al. have recently found⁴⁻⁶⁾ that vinyl ethers with an ester pendant group cleanly form "living" polymers in the presence of the HI/I₂ initiator.^{7,8)} The pendant ester groups of the resultant polymers were subsequently hydrolyzed into hydroxyl groups to give water-soluble polyalcohols having a narrow molecular weight distribution (MWD).⁶⁾



In this study, the author now turns his attention to vinyl ethers 1 - 3 containing oxyethylene units in the pendant, as another class of vinyl ethers whose substituents may result in frequent chain-transfer reactions. The first objective was to examine the possibility of living cationic polymerization of 1 - 3, focusing on the effects of their potentially deleterious polyether pendants.

The second objective involves the one-step synthesis of water-soluble polymers with a narrow MWD directly from 1 - 3. The targets are comb-like polymers consisting of hydrophilic poly(ethylene oxide) chains attached to a poly(vinyl ether) backbone, which will be useful in metal-cation binding and phase-transfer catalysis. In addition, the living polymerization of 1 - 3, if achieved, will enable one to prepare comb-like polymers having a

controlled "number" and "chain length" of the poly(ethylene oxide) pendants, the former being regulated by the molecular-weight control of the backbone poly(vinyl ether).

Although not a few polyether-containing vinyl ethers, including 1 - 3, have been prepared and studied briefly,^{9,10}) none of them have led to living polymers yet.¹¹) The author now reports the successful living polymerization of vinyl ethers 1 - 3 initiated by a mixture of hydrogen iodide and iodine (HI/I₂) to give well-controlled comb-like polymers of unique solubility characteristics.

EXPERIMENTAL SECTION

Materials. The monomers 1 - 3 were synthesized by substitution reactions of 2-chloroethyl vinyl ether, in the presence of $n\text{Bu}_4\text{NI}$, with the sodium alkoxides obtained from the corresponding alcohols (ethanol for 1, ethylene glycol monoethyl ether for 2, and triethylene glycol monoethyl ether for 3) and metal sodium.

Procedures. The purification of the monomers and initiators and polymerizations were carried out as reported.^{4,7}) The MWD of the product polymers were measured by size exclusion chromatography in chloroform on a JASCO Trirotar chromatograph equipped with three polystyrene gel columns [Shodex A-802 and A-804 (x2)]. The $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ ratio were determined on the basis of a polystyrene calibration. ¹³C NMR spectra were measured on a JEOL FX90Q spectrometer (22.5 MHz) in CDCl₃, at room temperature.

The metal ion transport by poly 2 and poly 3 (1.0 mM) through a liquid (CH₂Cl₂) membrane was measured using a U-shaped tube.¹²) Metal nitrate (1.0 M) was dissolved in aqueous phase I, and the ion transport was monitored by the absorption of metal ion in aqueous phase II using atomic absorption spectrometer (Jarrel ash AA 780).

RESULTS AND DISCUSSION

Polymerization.

Vinyl ethers 1 - 3 were polymerized in toluene at -15° or -40°C with HI/I_2 and BF_3OEt_2 as initiators. Under these conditions, the polymerizations by both initiators were quantitative and completed in 1 h. Figure 1 shows the MWD of the poly 1 - poly 3 thus prepared (conversion $\sim 100\%$). BF_3OEt_2 gave high molecular weight polymers with a broad MWD ($\bar{M}_w/\bar{M}_n \sim 3$). On the other hand, the HI/I_2 initiator led to polymers with a very narrow MWD ($\bar{M}_w/\bar{M}_n \sim 1.1$) irrespective of the number of the oxyethylene units in the pendant.

Figure 2 shows the relationship between monomer conversion and the $\bar{M}_n$ or $\bar{M}_w/\bar{M}_n$ ratio of poly 1 and poly 2. For each polymer, the $\bar{M}_n$ increased in proportion to conversion and the $\bar{M}_w/\bar{M}_n$ ratio was less than 1.2 irrespective of conversion. The $\bar{M}_n$ of the polymers could also be controlled by regulating the monomer-to-initiator feed ratio ($[\text{M}]_0/[\text{HI}]_0$) (Figure 3). Similar results were obtained for 3.

These facts show the formation of "living-like" polymers with a sufficiently long lifetime from vinyl ethers 1 - 3. These

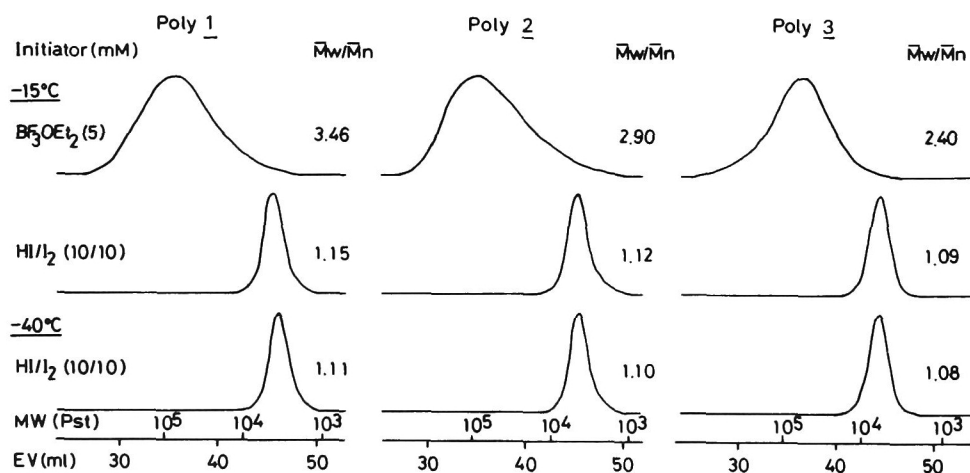


Figure 1. MWDs of poly 1 - poly 3 obtained with BF_3OEt_2 and HI/I_2 : $[\text{M}]_0 = 5 \text{ vol\%}$; conversion $\sim 100\%$.

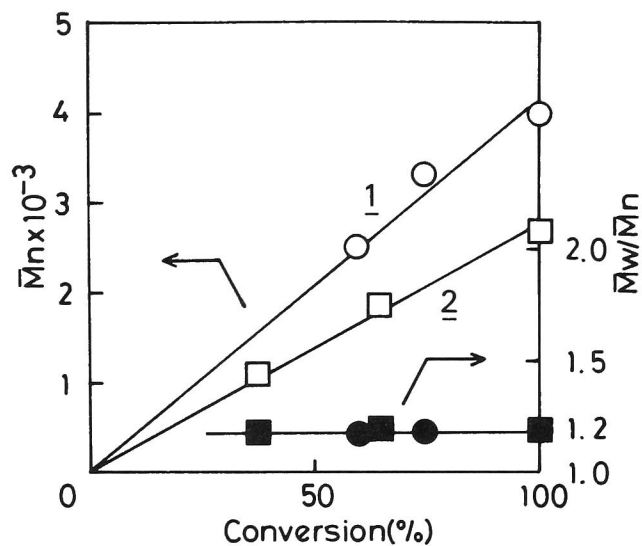


Figure 2. Relationship between conversion and $\bar{M}_n$ or $\bar{M}_w/\bar{M}_n$ ratio in the polymerization of 1 and 2 by HI/I₂ in toluene at -40°C: $[M]_0 = 5$ vol%; $[HI]_0 = 10$ mM; $[I_2]_0 = 2$ mM.

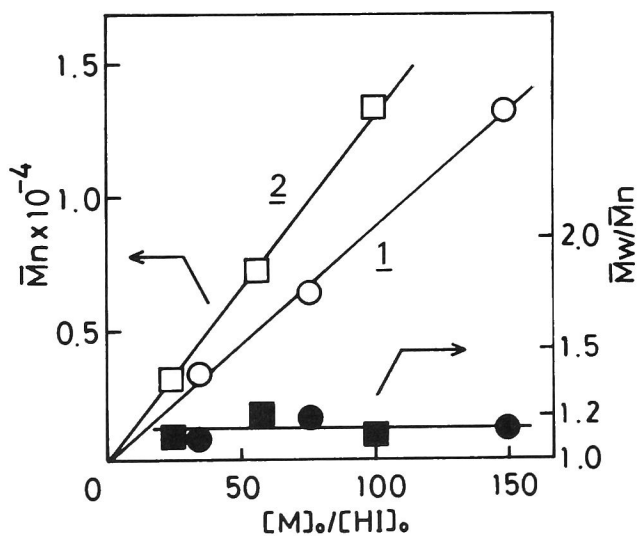


Figure 3. $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ ratio as a function of the monomer-to-initiator feed ratio ($[M]_0/[HI]_0$) in the polymerizations of 1 and 2 by HI/I₂ in toluene at -40°C; conversion ~100%.

polymers, however, cannot be referred to as "living" in a strict sense. For example, the addition of a fresh feed of the monomers to a completely polymerized solution indeed led to an increase in polymer molecular weight, but its extent was less than that expected from the linear $\bar{M}_n$ -conversion plot for the first-stage polymerization (cf. Figure 2). Furthermore, the MWD of poly 1 - poly 3 ($\bar{M}_w/\bar{M}_n \leq 1.2$; Figures 1 and 2) is somewhat broader than those of living poly(alkyl vinyl ethers) ($\bar{M}_w/\bar{M}_n \leq 1.1$), and it becomes even broader after the monomer addition.

Polymer Structure, Solubility, and Interaction with Metal Cations.

The structure of poly 1 - poly 3 was studied by ^1H and ^{13}C NMR spectroscopy. As a typical example, Figure 4 illustrates the ^{13}C NMR spectra of 2 and its polymer obtained with HI/I_2 . In the

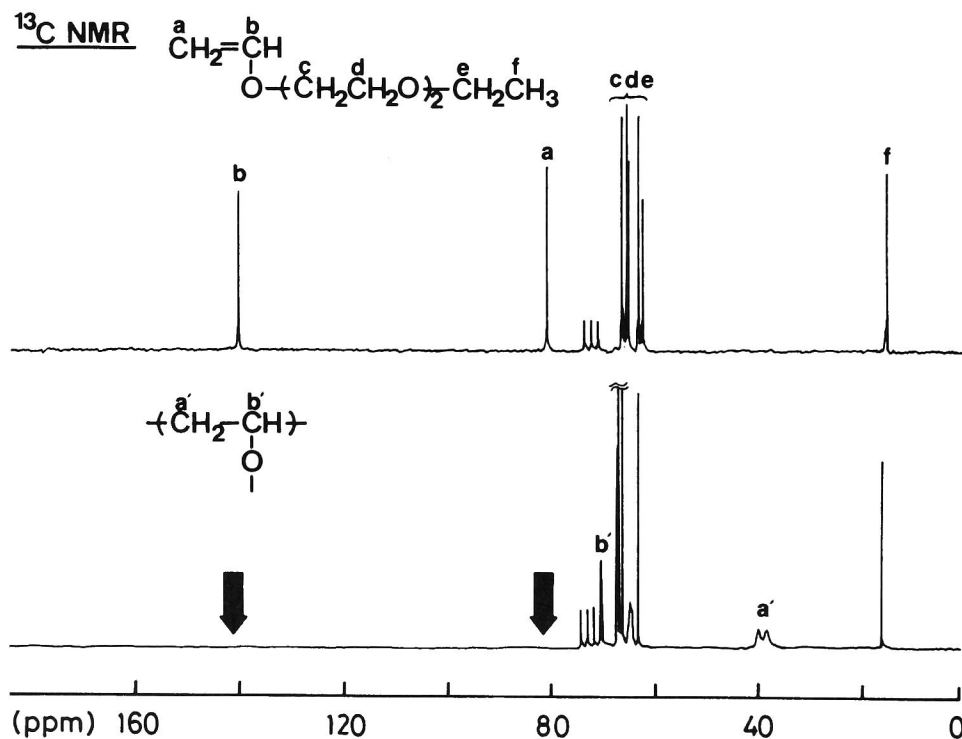


Figure 4. ^{13}C NMR spectra of 2 and poly 2 obtained with HI/I_2 in toluene at -40°C (cf. Figure 1).

spectrum of poly 2, the absorptions of the vinyloxy group of 2 are absent [86.0 (CH₂=) and 151.3 ppm (CH=)], the backbone saturated carbons are clearly observable [39.3, 41.0 (-CH₂) and 74.0 ppm (-CH-)], while the pendant poly(oxyethylene) signals are the same as those of the monomer 2. Thus the possibility of side reactions involving the poly(oxyethylene) group is excluded, and the polymerizations of 1 - 3 with the HI/I₂ initiator were proved to give polymer 4 (Table I).

Table I compares the solubility characteristics of poly 1 - poly 3 and poly(ethyl vinyl ether) at room temperature. All these polymers are soluble in common organic solvents such as toluene, dichloromethane, and acetone. Poly 1, having one oxyethylene unit per pendant, is soluble in methanol, which is a non-solvent for poly(ethyl vinyl ether); poly 2 and poly 3, each having two or more oxyethylene units per pendant, are soluble not only in methanol but also in water irrespective of their molecular weight.

TABLE I

Solubility^{a)} of Poly(vinyl ethers):

Dependence on the Number of Ether Oxygens in the Pendant

$\begin{array}{c} \text{---}(\text{CH}_2\text{---CH})\text{---} \\ \\ \text{O---}(\text{CH}_2\text{CH}_2\text{O})_n\text{---C}_2\text{H}_5 \end{array}$				<u>4</u>
Solvent	n = 0	n = 1	n ≥ 2	
Toluene, CH ₂ Cl ₂	○	○	○	
Acetone, Ether	○	○	○	
CH ₃ OH	X	○	○	
H ₂ O	X	X	○	

a) At room temperature; (○) soluble, (X) insoluble.

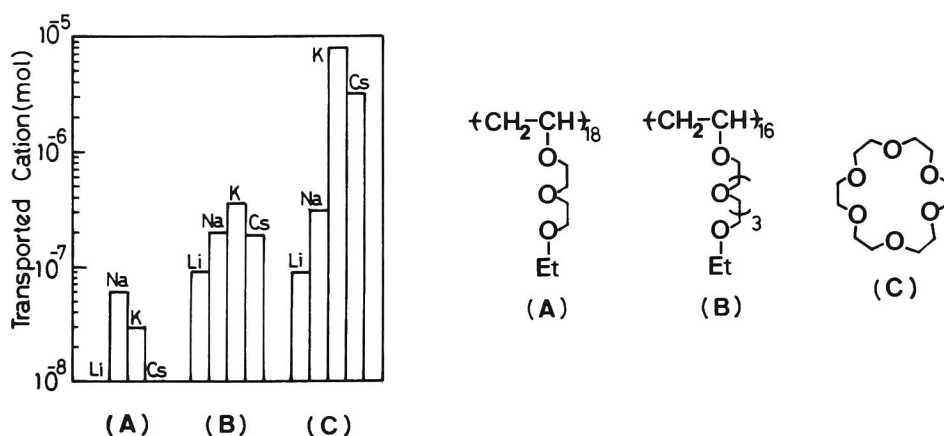


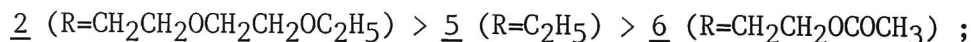
Figure 5. Amount of transported metal ion through dichloromethane membrane after 5 h. [metal nitrate]₀ = 1.0 M; [A]₀ = [B]₀ = [C]₀ = 1.0 × 10⁻³ M.

Thus the solubility of poly 1 - poly 3 clearly depends on the number of oxyethylene units in the pendant.

The comb-like polyoxyethylenes were furthermore examined with the ion transport. As shown in Figure 5, poly 2 and poly 3 were found to form complexes with alkali metal ions, and to transport through liquid dichloromethane membrane. Poly 3 was more efficient than poly 2 and transported even such a large Cs⁺ ion, because of its long polyoxyethylene pendant.

Reactivity of Vinyl Ethers 1 - 3.

The rate of the HI/I₂-initiated polymerization of 2 was compared with those of ethyl vinyl ether (CH₂=CHO-C₂H₅, 5) and 2-acetoxyethyl vinyl ether (CH₂=CHO-CH₂CH₂OCOCH₃, 6). As shown in Figure 6, the polymerization rates of the three vinyl ethers (CH₂=CHO-R) clearly depended on the substituents R and decreased in the order:



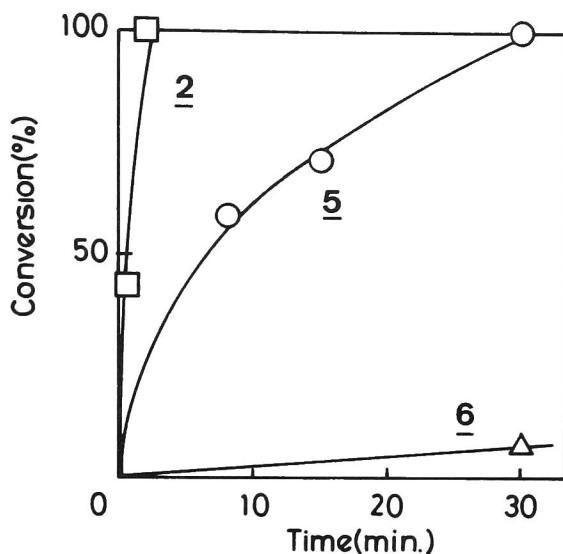


Figure 6. Effect of the substituent (R) on the polymerization rates of vinyl ethers ($\text{CH}_2=\text{CHO}-\text{R}$) by HI/I_2 in toluene at -40°C .

R: A, $\text{-(CH}_2\text{CH}_2\text{O)}_n\text{-C}_2\text{H}_5$ (2)

B, $-\text{C}_2\text{H}_5$ (5)

C, $-\text{CH}_2\text{CH}_2\text{OCOCH}_3$ (6)

the rate difference between 2 and 5 or 5 and 6 was greater than an order of magnitude.

In general, the rate of homopolymerization is a function of the reactivities of the monomer and the growing intermediate derived from it. On the basis of the following experimental results, the author proposes that the markedly high polymerization rates of monomer 1 - 3 are due to not their own reactivities but the activation of the growing species.

First, no differences were found among the ^{13}C NMR chemical shifts of the vinyl carbons of monomers 2, 5, and 6 (in CDCl_3): 2, 86.0 ($\text{CH}_2=$) and 151.3 ppm ($\text{CH}=$); 5, 86.0 and 151.6 ppm; 6, 86.5 and 151.1 ppm. Thus, the electron density (or static nucleophilicities) of these olefinic groups are nearly the same, because their polar substituents, though ranging from the electron-donating polyether for 2 to the electron-withdrawing ester for 6, are

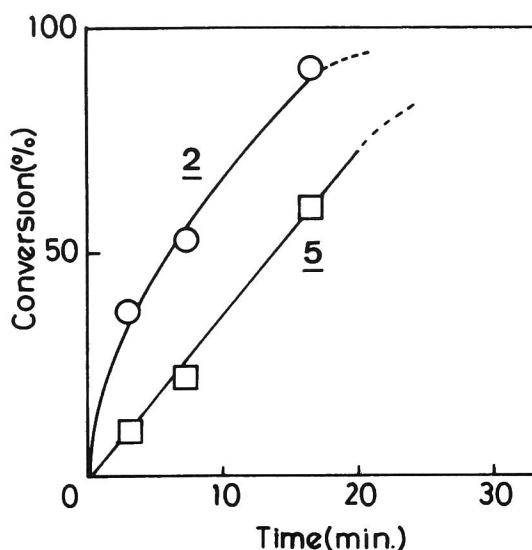


Figure 7. Time vs. conversion curves for the copolymerization between 2 and 5 by HI/I₂ in toluene at -40°C: [2]₀ = [5]₀ = 0.25 M each; [HI]₀ = 10 mM; [I₂]₀ = 4 mM.

separated from them by a saturated oxyethylene unit.

Second, the oxyethylene-containing monomer 2 was only slightly more reactive than alkyl vinyl ether 5 in the copolymerization by HI/I₂ (Figure 7), again indicating the similarity of 2 and 5 in polymerization reactivity.

Steric Structure of the Polymers.

To find evidence for the activation of the propagating species derived from monomers 1 - 3, the author then compared, by ¹³C NMR spectroscopy, the steric structure of poly 2 and poly 5, both obtained by HI/I₂ initiator at -40°C. Figure 8 shows the main-chain methylene signals, which consist of two peaks assignable to the meso and racemic diads from the higher field.¹³⁾

The spectrum of poly 2 (Figure 8C) obtained in nonpolar toluene solvent is similar to that of poly 5 (Figure 8B) prepared in a more polar medium, nitroethane; both polymers consist of comparable amounts of the meso and racemic diads. The poly 2,

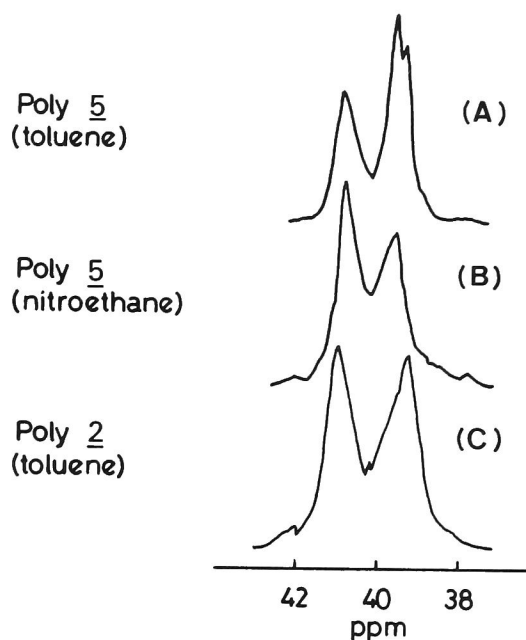


Figure 8. Partial ^{13}C NMR spectra (main-chain methylene region) of poly 5 and poly 2 obtained with HI/I_2 at -40°C . Polymer and polymerization solvent: (A) poly 5, toluene, (B) poly 5, nitroethane; (C) poly 2, toluene. The $\bar{M}_n$ s of these polymers are $(5 - 10) \times 10^3$ (by size exclusion chromatography).

however, clearly differs in steric structure from poly 5 (Figure 8A) obtained in the same solvent (toluene), the latter having a higher meso content. The similarity between Figure 8B and C, shows that the propagating species of 2 in toluene is similar in nature to that of 5 in the polar solvent, where the active end should be highly dissociated. The author proposes, therefore, that the growing end of 2 is considerably dissociated even in nonpolar toluene solvent via the intramolecular solvation of the neighboring oxyethylene units in the pendant, and thereby it is more active than the growing ends of 5 and 6 under the same conditions.

In conclusion, vinyl ethers 1 - 3 with oxyethylene units in the pendant can be polymerized into living-like polymers by HI/I_2 initiator in nonpolar solvent at low temperature. It was also

found, however, that the MWD of poly 1 - 3 is somewhat broader than those of living poly(vinyl ethers) with alkyl or ester pendants, probably because chain transfer tends to occur to some extent in the polymerization of 1 - 3, where the propagating species is internally activated (more dissociated) by the oxyethylene pendant.

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PART III

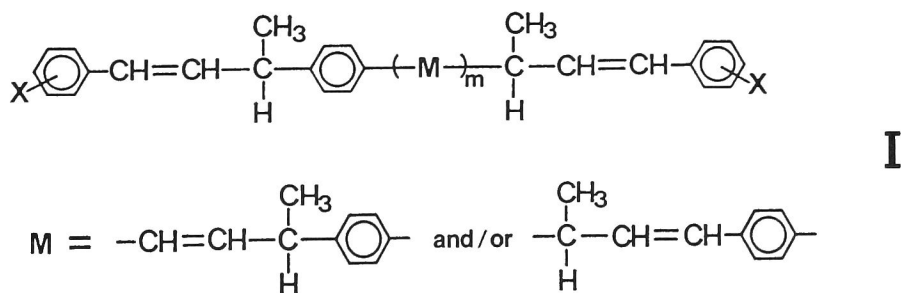
SYNTHESIS OF FUNCTIONALIZED LINEAR POLY(DIVINYLBENZENE)

CHAPTER 8

SYNTHESIS OF α,ω -BIFUNCTIONAL LINEAR POLY(DIVINYLBENZENE)

ABSTRACT

Linear poly(divinylbenzene) (I) having a variety of functional groups (X = acetoxyl, hydroxyl, and chloromethyl) at both chain ends was prepared by copolymerization of divinylbenzene (DVB) and a substituted styrene (Sts) initiated by acetyl perchlorate in benzene solvent at 70°C. The molecular weight of polymer I ($\bar{M}_n = 3 \times 10^2 - 2 \times 10^3$) could be controlled by regulating the feed ratio of DVB and Sts. Polymer I of higher molecular weight ($> 3 \times 10^3$) was also synthesized by the reaction of Sts with a linear poly(DVB) having vinyl termini. Polymer end-group analysis by ^1H NMR spectroscopy showed that the functionality of polymer I, obtained after quantitative reaction of DVB, is close to two for the three functional groups. The relative reactivities of DVB and Sts were also discussed on the basis of the end-group analysis.



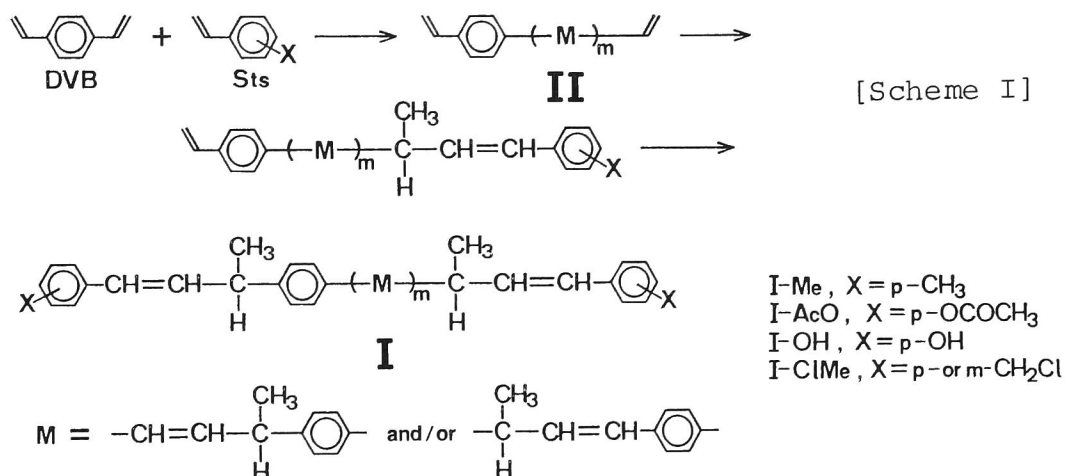
INTRODUCTION

α,ω -Bifunctional (telechelic) oligomers and polymers have elicited active interest among polymer chemists because of their versatility in elastomer synthesis, chain extension, network formation, and the like.¹⁾ Conventional syntheses of telechelic polymers via cationic polymerization proceed through many steps, involving preparation of prepolymers and subsequent functionalization of their chain ends.²⁾ Careful and often cumbersome purification of the prepolymers is mandatory for the high functionality and yield of telechelic polymers. Another approach to the functionalized polymer synthesis is the "inifer" method,^{2a)} which, although simple and effective, is thus far confined to α,ω -tert.-chlorinated polyisobutylene; introduction of other functional groups requires polymer reactions of the isolated polyisobutylene dichloride.^{2a)}

This chapter presents a new, single-step synthesis of a series of α,ω -bifunctional linear poly(divinylbenzene) (I) by the cationic polymerization of divinylbenzene (DVB) in the presence of a substituted styrene (Scheme I). The synthesis is based on the recent finding by Hasegawa and Higashimura³⁾ that DVB, in conjunction with acetyl perchlorate (AcClO_4) initiator, polymerizes without cross-linking to give linear polymer II (Scheme I). The key process of the linear DVB polymerization is the counteranion-assisted⁴⁾ facile β -proton elimination from the propagating cation. Because of this frequent chain transfer, each vinyl group of DVB monomer can undergo only "dimerization" to give a linear unsaturated polymer backbone (II) capped with vinyl groups at both ends.

It occurred to the author that when such DVB polymerization was carried out in the presence of a substituted styrene, the resulting poly(DVB) would possess styrene units, instead of vinyl

groups, at both termini (Scheme I). Once the propagating DVB cation reacts with the styrene (a monofunctional monomer) to form the styryl-type cation, it would quickly release its β -proton,⁴⁾ yielding polymer I that lacks polymerizable vinyl groups. The ring substituent of the terminal styrene unit thus serves as an end-functional group. In view of the wide variety of substituted styrenes, the method outlined in Scheme I will enable the synthesis of telechelic poly(DVB)'s with various functional groups.



In this work the author has prepared telechelic poly(DVB)'s having acetoxyl (I-AcO) and chloromethyl (I-ClMe) termini by the AcClO_4 -initiated polymerization of DVB in the presence of the corresponding substituted styrenes. Quantitative hydrolysis of I-AcO gave the α,ω -dihydroxy derivative, I-OH. The relative reactivities of DVB and several styrenes in the cationic linear oligomerization were also evaluated on the basis of end-group analysis of these polymers.

EXPERIMENTAL SECTION

Materials. An isomeric mixture of DVB ($[\underline{m}\text{DVB}]/[\underline{p}\text{DVB}] = 70/30$) with ethylvinylbenzene and diethylbenzene (0.7 % in total, by gas

chromatography) was obtained by size exclusion chromatographic fractionation of commercial DVB as reported.³⁾ pDVB (purity > 99%) was isolated from this mixture by the method of Storey et al.⁵⁾ The residual fraction was further separated by preparative size exclusion chromatography to give mDVB ($[\underline{m}DVB]/[\underline{p}DVB] = 92/8$).

p-Methylstyrene (pMeSt) was synthesized from p-methylacetophenone as reported.⁶⁾ p-Acetoxystyrene (pAcOSt; Maruzen Oil Co.) and chloromethylstyrene (ClMeSt; $[\underline{m}ClMeSt]/[\underline{p}ClMeSt] = 2/1$; Tokyo Kasei Co.) were obtained commercially. The three monomers were purified by distillation over CaH₂ under reduced pressure before use (gas chromatographic purity: pMeSt, > 99%; pAcOSt, 97%; ClMeSt, 98%).

AcClO₄ was synthesized as described elsewhere.⁷⁾ Benzene as solvent was purified by distillation over CaH₂ at least twice before use.

Procedures. Polymerizations were carried out in a baked Erlenmeyer flask equipped with a three-way cock under a dry nitrogen atmosphere. The reaction was initiated by addition of the initiator solution with a syringe into the monomer solution (a mixture of DVB and a substituted styrene). After the desired time, the polymerization was stopped by addition of methanol containing a small amount of aqueous ammonia. Conversions of DVB and Sts were determined from the residual monomer concentrations by gas chromatography, with bromobenzene as internal standard. The reaction solution after quenching was washed with water to remove the initiator residue, and the products were recovered from the organic layer by evaporation of the unreacted monomers and solvent under reduced pressure.

The apparent molecular weight distribution of the product was determined by size exclusion chromatography (SEC; JASCO Trirotar chromatograph, JSP-101 polystyrene gel column, 20 mm i.d. x 500 mm, CHCl₃ eluent, refractive index detector). When necessary, the fractions in the molecular weight range $2 \times 10^2 - 1 \times 10^3$ were

separated from the product by preparative SEC with recycling. The structure of the products was determined by ^1H NMR spectroscopy (60 and 90 MHz) in CCl_4 or CDCl_3 solution and by infrared (IR) spectroscopy (Shimadzu IR-27G). The number-average molecular weight ($\bar{M}_n$) was measured by vapor pressure osmometry (VPO; Hitachi 117 molecular weight apparatus) in benzene solution at 30°C.

The base-catalyzed hydrolysis of polymer I-AcO to I-OH was performed as follows.^{8,9)} A sample of I-AcO (0.3 g, ca. 2 equiv. of $-\text{OCOCH}_3$, $\bar{M}_n \sim 600$) was dissolved in purified 1,4-dioxane (9.0 ml), and hydrazine hydrate (1.0 ml, 0.02 mol) was added. the mixture was stirred for 4 h at room temperature, neutralized with diluted hydrochloric acid, and washed with distilled water. The organic phase was evaporated to dryness and the the residue was vacuum-dried overnight to give white polymer I-OH in quantitative yield; see Results and Discussion for the spectroscopic characterization of this product.

RESULTS AND DISCUSSION

Copolymerization of pDVB with pMeSt: Orienting Experiments.

To find out optimum conditions for the preparation of polymer I according to Scheme I, preliminary model experiments were performed on the copolymerization of pDVB with pMeSt that seems similar in reactivity to pDVB. The copolymerization was carried out with AcClO_4 initiator in benzene at 70°C (a low monomer concentration). In the absence of pMeSt, pDVB polymerizes quantitatively to linear unsaturated polymers (II) under these conditions.³⁾

Figure 1 shows the molecular weight distribution of the products obtained at various monomer feed ratios ($[\text{pDVB}]_0/[\text{pMeSt}]_0$) and conversions. At the same monomer feed ratio, the average molecular weight of the products increased gradually with

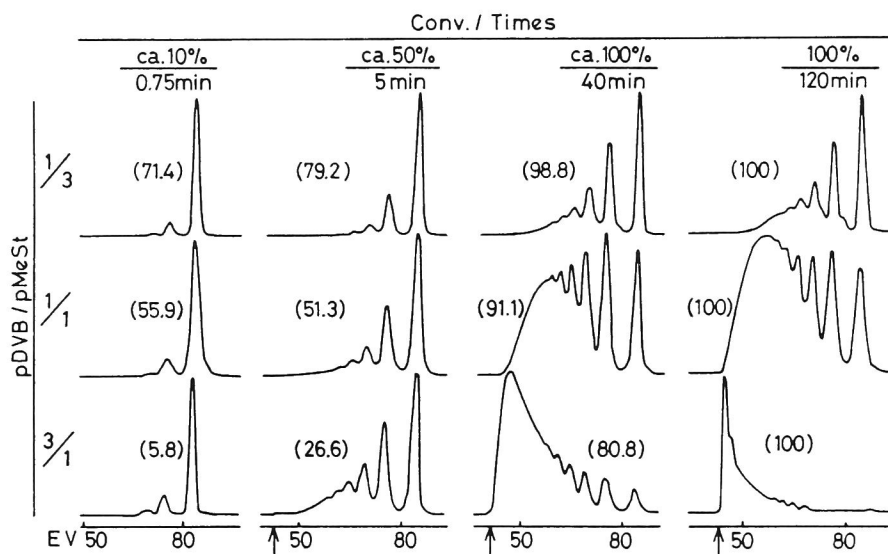


Figure 1. Effect of feed composition and conversion on the product distribution in the copolymerization of pDVB and pMeSt by AcClO_4 in benzene. The arrows indicate the exclusion limit of the SEC column. The values in parentheses indicate the percent of ring-substituted methyl groups in all end groups. $[\text{pDVB}]_0 + [\text{pMeSt}]_0 = 0.10 \text{ M}$, $[\text{AcClO}_4]_0 = 0.20 \text{ mM}$; 70°C .

increasing conversions of both monomers. Interestingly, higher oligomers and polymers further increased with reaction time even after pDVB was completely consumed. This tendency was more pronounced when pDVB was richer in the monomer feed. The average molecular weight at similar conversions increased with increasing pDVB feed ratio. These increases in polymer molecular weight are due to chain extension via the vinyl groups of terminal DVB units.³⁾

Figure 2 shows the ^1H NMR spectra of the copolymerization products together with the spectrum of a sample of linear homopoly(DVB) ($\bar{M}_n \sim 1000$).³⁾ The spectrum (Figure 2B) of the copolymerization product obtained at ca. 50 % conversions of both monomers is quite similar to that of linear poly(DVB) (Figure 2A),

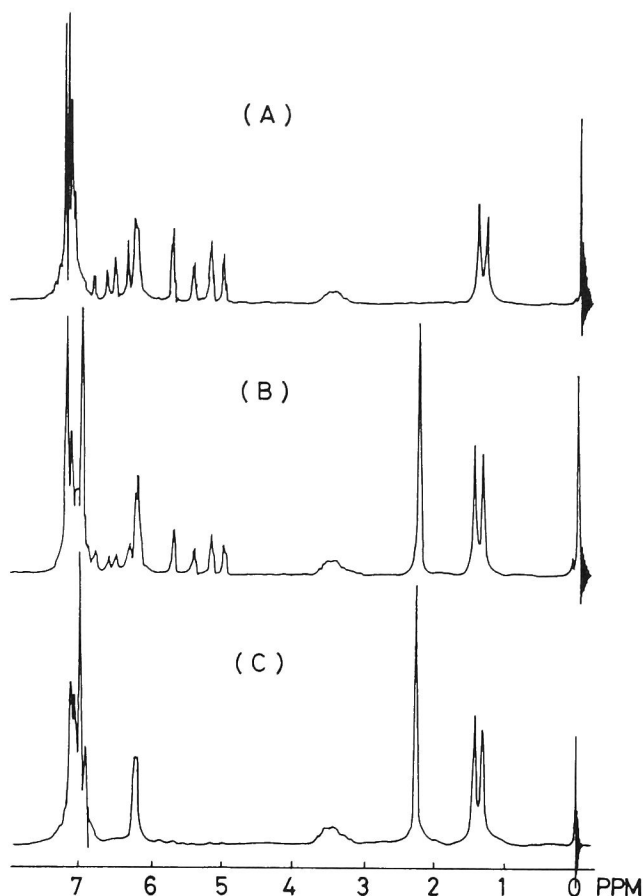


Figure 2. ^1H NMR spectra of linear poly(DVB) (A) and $\underline{\text{pDVB}}\text{-}\underline{\text{pMeSt}}$ copolymerization products (B and C) obtained by AcClO_4 initiator in benzene at 70°C . Reaction time: (A) 10 min; (B) 5 min; (C) 40 min. Conversion: (A) ca. 70 %; (B) ca. 50 % (both $\underline{\text{pDVB}}$ and $\underline{\text{pMeSt}}$); (C) ca. 100 %. $[\underline{\text{pDVB}}]_0 = [\underline{\text{pMeSt}}]_0 = 0.050 \text{ M}$, $[\text{AcClO}_4]_0 = 0.20 \text{ mM}$.

which is characterized by the absorptions of vinyl (4.7 - 6.8 ppm), trans-olefin (6.2 ppm), methine (3.5 ppm), and aliphatic methyl (1.4 ppm) groups. In addition, Figure 2B exhibits a sharp singlet (2.3 ppm) due to the ring-methyl group. These results show that the copolymerization product has the expected linear unsaturated structure I-CH_3 (Scheme I) and that the polymer is capped with either the $\underline{\text{pDVB}}$ or $\underline{\text{pMeSt}}$ unit. On the other hand, the absorption

of the vinyl group completely disappeared in the spectrum (Figure 2C) for the product at the end of the reaction. This final product possesses, therefore, pMeSt terminal units only. The absence of signals due to the $-\text{CH}_2\text{CH}<$ group in both spectra 2B and 2C demonstrates that under the present conditions neither pDVB nor pMeSt undergoes conventional vinyl polymerization. Thus, it was confirmed that polymer I could be obtained by the reaction shown in Scheme I, which proceeds via repetition of the "dimerization" of the vinyl groups of DVB (and/or its oligomers) and terminates when pMeSt is incorporated in the polymer chain.

The ^1H NMR spectra of the lowest six oligomer fractions (molecular weight $2 \times 10^2 - 1 \times 10^3$; cf. Figure 1) isolated by SEC were all consistent with the structure of I- CH_3 (Scheme I). The number of terminal vinyl and/or methyl groups per oligomer was

TABLE I
End-Group Ratios ($-\text{C}=\text{C}/-\text{C}_6\text{H}_4\text{CH}_3$) for Polymer I-Me^{a)}

Time (min)	Conv. (%)	$\frac{[\text{pDVB}]_0}{[\text{pMeSt}]_0}$	$(-\text{C}=\text{C}/-\text{C}_6\text{H}_4\text{CH}_3)$				
			$n^b)= 2$	$n= 3$	$n= 4$	$n= 5$	overall
5	ca. 50	1/1	1.06	0.88	0.90	0.97	0.95
		3/1	3.07	2.47	2.55	2.92	2.76
40	ca. 100	1/1	0.08	0.10	0.08	0.07	0.10
		3/1	0.12	0.22	0.23	0.24	0.24
120	100	1/1	0.00	0.00	0.00	0.00	0.00
		3/1	0.00	0.00	0.00	0.00	0.00

a) $[\text{pDVB}]_0 + [\text{pMeSt}]_0 = 0.1 \text{ M}$, initiator AcClO_4 , $[\text{AcClO}_4]_0 = 0.2 \text{ mM}$, solvent benzene, 70°C .

b) The number of monomer units (pDVB and/or pMeSt); e.g., the fraction with $n = 3$ contains DVB-DVB-DVB, DVB-DVB-Sts, and Sts-DVB-Sts.

determined from the integrated peak area ratio of vinyl and ring-methyl protons to phenyl protons. This number was approximately 2 for all fractions.

Table I shows the relative numbers of the terminal vinyl to ring-methyl groups in each oligomer fraction. This ratio was dependent on the monomer feed composition and conversion but independent of the molecular weight of the oligomers provided they were formed under the same reaction conditions. The number of vinyl end groups decreases with decreasing DVB feed or at high conversion and completely disappears at 100 % conversion.

α,ω -Diacetoxypoly(divinylbenzene) (I-AcO).

To introduce acetoxy groups (AcO) into both ends of linear poly(DVB), pDVB and pAcOSt were copolymerized by AcClO_4 in benzene at 70°C ($[\text{pDVB}]_0 + [\text{pAcOSt}]_0 = 0.10 \text{ M}$, $[\text{pDVB}]_0/[\text{pAcOSt}]_0 = 1/1$). pDVB was quantitatively consumed within 1 h, but the polymerization solution was allowed to stand another hour for complete reaction of the terminal vinyl groups with pAcOSt.

Figures 3A and 4A show, respectively, the ^1H NMR spectrum and the molecular weight distribution of the product obtained at quantitative conversion of pDVB and pAcOSt. The spectrum exhibited the sharp singlet (2.2 ppm) characteristic of the acetoxy group and all signals due to the linear poly(DVB) backbone; absorptions of a terminal vinyl group were absent. The IR spectrum also showed the presence of the acetoxy group [$1760 (\nu_{\text{C=O}})$ and $1200 \text{ cm}^{-1} (\nu_{\text{C-O}})$]. Therefore, the copolymerization product is of structure I-AcO and its acetoxy functionality is close to 2.0. This conclusion was supported by ^1H NMR analysis of the oligomers separated from the same product.

α,ω -Dihydroxypoly(divinylbenzene) (I-OH).

Polymer I-OH was prepared by the base-catalyzed hydrolysis of polymer I-AcO (see Experimental Section). Figure 3B shows the ^1H

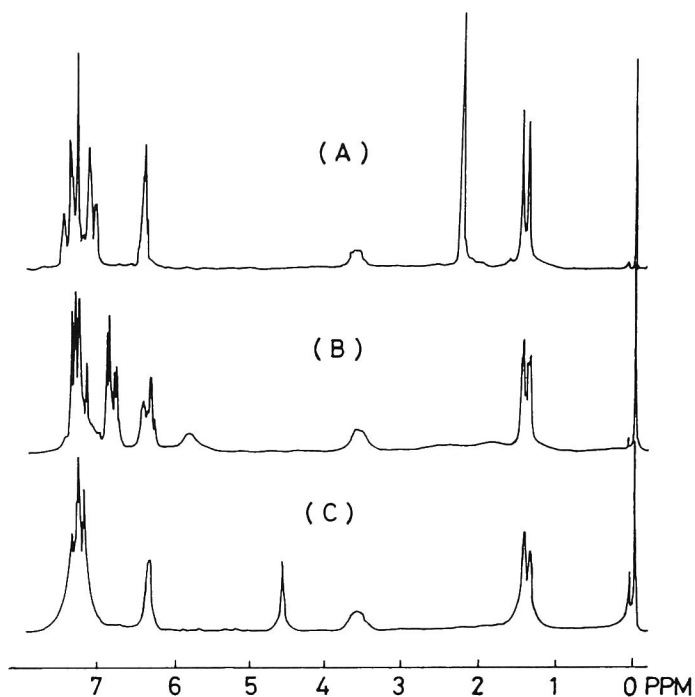


Figure 3. ^1H NMR spectra of polymer I-AcO (A), I-OH (B), and I-ClMe (C) obtained by AlCl_3 in benzene at 70°C : $[\text{pDVB}]_0 + [\text{Sts}]_0 = 0.10 \text{ M}$, $[\text{AlCl}_3]_0 = 0.20 \text{ mM}$. (A) $[\text{pDVB}]_0/[\text{pAcOSt}]_0 = 1/3$; (C) $[\text{pDVB}]_0/[\text{ClMeSt}]_0 = 1/1$.

NMR spectrum of the product after the hydrolysis. On hydrolysis the absorption of the acetyl group (2.2 ppm; see Figure 3A) disappeared completely, and the hydroxyl peak ($\sim 5.8 \text{ ppm}$) was observed; the multiplet of a terminal vinyl group was not detected. Similarly, in the IR spectrum the bands due to the acetoxy group were replaced by the hydroxyl absorption [3300 cm^{-1} ($\nu_{\text{O-H}}$)]. Therefore, the product was confirmed to have structure I-OH.

Attempts to prepare polymer I-OH directly by copolymerization of *p*-hydroxystyrene and DVB remained unsuccessful because of the very high cationic polymerizability of the former.

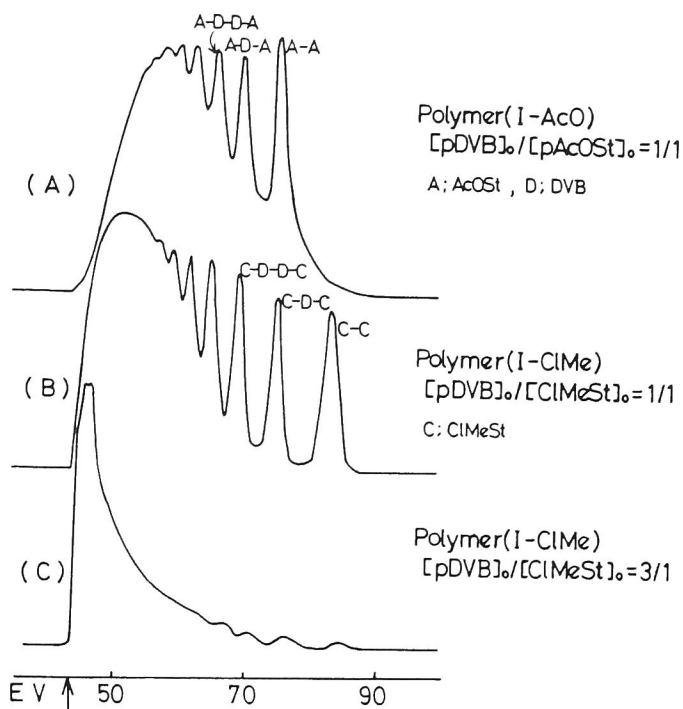


Figure 4. Molecular weight distributions of polymer I-AcO (A) and I-ClMe (B and C) obtained by AcClO_4 in benzene at 70°C $[\underline{\text{pDVB}}]_0 + [\text{Sts}]_0 = 0.10 \text{ M}$, $[\text{AcClO}_4]_0 = 0.20 \text{ mM}$. The arrow indicates the exclusion limit of the SEC column.

α,ω -Bis(chloromethyl)poly(divinylbenzene) (I-ClMe).

This polymer was synthesized by copolymerization of ClMeSt and DVB. The copolymerization was effected by AcClO_4 in benzene at 70°C for 2 h ($[\underline{\text{pDVB}}]_0 + [\text{ClMeSt}]_0 = 0.10 \text{ M}$, $[\underline{\text{pDVB}}]_0/[\text{ClMeSt}]_0 = 1/1$ and $3/1$; conversions of both monomers $\sim 100\%$).

The copolymerization products had the expected ^1H NMR spectra (e.g., Figure 3C) with the absorption of the chloromethyl group ($\sim 4.5 \text{ ppm}$) and resonances characteristic of the linear poly(DVB) backbone; no vinyl end groups were detected by NMR. The spectral pattern did not depend on the $[\text{DVB}]_0/[\text{ClMeSt}]_0$ ratio. Therefore the products were identified as polymer I-ClMe (Scheme I).

Traces B and C of Figure 4 compare the molecular weight

distributions of polymer I-ClMe obtained at two monomer feed ratios. Oligomer fractions were clearly reduced at the higher pDVB concentration. This indicates that the molecular weight of polymer I-ClMe can be controlled by regulating the starting monomer composition ($[pDVB]_0/[ClMeSt]_0$), with polymer structure being unchanged.

Comparison of traces A and B of Figure 4 suggests that the molecular weight of polymer I changes with the reactivity of Sts. That is, ClMeSt, which is less reactive than pAcOSt (see below), leads to polymer I of higher molecular weight.

The results described above thus show that linear poly(DVB)'s with a variety of end functional groups and molecular weights can be obtained easily by copolymerization of DVB with substituted styrenes.

Synthesis of α,ω -Bifunctional Poly(DVB) with Higher Molecular Weight.

As Figures 1 and 4 show, it was rather difficult to obtain polymer I with high molecular weight in the copolymerization of a substituted styrene and DVB, because the reactivities of both monomers are close (see Table III). For the preparation of such polymer I, linear poly(DVB) (II) with a high molecular weight was synthesized first, to which functional end groups were introduced in situ by the reaction of the terminal vinyl groups of II with a substituted styrene.

For instance, DVB (0.05 M) was polymerized by $AcClO_4$ initiator in benzene at 70°C up to 98 % conversion ($\bar{M}_n$ of the poly(DVB) ~ 2000), and pAcOSt (0.05 M) was added to the polymerization solution. The reaction was stopped when ca. 50 % of pAcOSt reacted. The main portion of the product consists of polymers, the molecular weights of which apparently exceed the exclusion limit (ca. 2×10^3) of the SEC column. The byproduct eluting at the largest elution volume is the linear pAcOSt dimer⁸) that can be

readily separated from the polymers by extraction with methanol. The polymers thus purified showed ^1H NMR spectra fully consistent with acetoxy-capped polymer I-AcO. Thus the successive reaction of DVB and pAcOSt can lead to a much higher molecular weight of polymer I-AcO than their simultaneous reaction (copolymerization) does.

Hasegawa and Higashimura previously reported that linear poly(DVB) with high molecular weight ($\bar{M}_n > 10^4$) can be prepared by sequential DVB addition.³⁾ Therefore, the reaction of such poly(DVB) with a substituted styrene will yield α,ω -bifunctional polymer I with a high molecular weight.

Relative Reactivity of DVB and Substituted Styrenes.

An interesting spin-off of this study, as described below, is that the author can evaluate the reactivity of DVB relative to styrenes on the basis of end-group analysis on polymer I.

In the linear DVB polymerization in the presence of a substituted styrene (Sts), produced polymers can be classified into the following three types: $\text{DVB}-(\text{DVB})_{n-2}\text{DVB}$ (DD), $\text{DVB}-(\text{DVB})_{n-2}\text{Sts}$ (DD), and $\text{Sts}-(\text{DVB})_{n-2}\text{Sts}$ (SS). DD and SS are capped at both ends with DVB and Sts units, respectively; DS has a DVB unit at one end and a Sts unit at the other. The probabilities of obtaining these three polymers with the degree of polymerization n are as follows: DD, r^{n-1} ; DS, $r^{n-2}(1-r)$; and SS, $r^{n-3}(1-r)^2$ (where r is the probability that poly(DVB) reacts with the vinyl groups of DVB monomer and oligomers). The probability r was assumed to be independent of n . This process involves addition of poly(DVB) cation or protonated DVB to a vinyl group and subsequent deprotonation from the resulting carbocation.

The probability r is given by

$$r = \frac{k_D[-\text{C}=\text{C}]^2}{k_D[-\text{C}=\text{C}]^2 + k_S[-\text{C}=\text{C}][\text{Sts}]} = \frac{1}{1 + k_S[\text{Sts}]/k_D[-\text{C}=\text{C}]} \quad (1)$$

where $[Sts]$ indicates the concentration of unreacted Sts monomer, and $[-C=C]$ is that of the vinyl groups in the unreacted DVB monomer and its oligomers. k_D and k_S represent the overall rate constants for the incorporation of DVB and Sts units, respectively, into the chain end of poly(DVB). k_D/k_S indicates the relative reactivity of DVB and Sts toward poly(DVB).

Experimentally, r and hence k_D/k_S can be determined from the relative numbers ($C=C/X$) of terminal DVB and Sts units in a product on the basis of the equation

$$\frac{C=C}{X} = \frac{2[DD] + [DS]}{2[SS] + [DS]} = \frac{r^2 + r}{r^2 - 3r + 2} \quad (2)$$

where the brackets mean the relative amount of the indicated polymer. Eq 2 requires that the end-group ratio $C=C/X$ be independent of n , which was actually the case (Table I).

Table II lists end-group ratios ($C=C/X$) for polymer I- CH_3 at various monomer feed ratios together with r and k_D/k_S values calculated by eq 2 and 1. These data are for the products obtained at ca. 50 % conversion of both $pDVB$ and $pMeSt$, so that on calculation of k_D/k_S ratios, the monomer concentrations in eq 1 were taken as the means of the corresponding initial and final concentrations.

In spite of the large changes in the end-group ratio (or r), the k_D/k_S values remained practically constant over a wide range of the monomer feed ratio. This constancy strongly supports the reasonableness of the treatment and the k_D/k_S values. Table II indicates that each vinyl group of $pDVB$ is 2 - 3 times less reactive than that of $pMeSt$.

Table III summarizes the reactivity ratios (k_D/k_S) for $pDVB$, $mDVB$, and various styrenes obtained by the method. The relative reactivities of the five monomers are in the order $pMeSt > pAcOSt > pDVB > mDVB > ClMeSt$ (m, p). $pDVB$ is about 1.7 times as reactive as

TABLE II

Effect of Monomer Composition on k_D/k_S in the
Copolymerization of $\underline{p}$ DVB and $\underline{p}$ MeSt
by AcClO_4 in Benzene^{a)}

$\frac{[\underline{p}\text{DVB}]_0}{[\underline{p}\text{MeSt}]_0}$	$\frac{-\text{C}=\text{C}}{-\text{C}_6\text{H}_4\text{CH}_3}$	r	k_D/k_S
1/3	0.26	0.26	1/2.0
1/1	0.95	0.49	1/2.2
3/2	1.11	0.50	1/3.2
3/1	2.76	0.68	1/3.2
7/1	7.62	0.83	1/3.1

a) $[\underline{p}\text{DVB}]_0 + [\underline{p}\text{MeSt}]_0 = 0.10 \text{ M}$, $[\text{AcClO}_4]_0 = 0.2 \text{ mM}$,
70°C.

TABLE III

Relative Reactivity (k_D/k_S) of DVB in the
Copolymerization with Substituted Styrenes (Sts)
by AcClO_4 in Benzene^{a)}

Monomer (1/1)	$\frac{-\text{C}=\text{C}}{-\text{C}_6\text{H}_4\text{X}}$	r	k_D/k_S
$[\underline{m}\text{DVB}]_0/[\underline{p}\text{MeSt}]_0$	0.52	0.38	1/3.7
$[\underline{p}\text{DVB}]_0/[\underline{p}\text{MeSt}]_0$	0.95	0.49	1/2.2
$[\underline{p}\text{DVB}]_0/[\underline{p}\text{AcOSt}]_0$	1.93	0.62	1/1.3
$[\underline{p}\text{DVB}]_0/[\text{ClMeSt}]_0$	7.44	0.83	1/0.4

a) $[\text{DVB}]_0 = [\text{Sts}]_0 = 0.05 \text{ M}$, $[\text{AcClO}_4]_0 = 0.2 \text{ mM}$, 70°C,
conversion ca. 50 %.

mDVB. The order found for pMeSt, pAcOSt, and ClMeSt agrees with that hitherto known in their conventional cationic polymerizations. For a given DVB/Sts pair, it may be possible to prepare polymer I of desired molecular weight by regulating the monomer feed ratio $[DVB]_0/[Sts]_0$ according to the k_p/k_s , because the molecular weight of polymer I is critically dependent upon the feed ratio and the DVB/Sts pair (k_p/k_s) (see Figure 4).

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CHAPTER 9

SYNTHESIS OF POLY(DIVINYLBENZENE) WITH HYDROXY PENDANTS AND/OR ENDGROUPS

ABSTRACT

Poly(divinylbenzene) [poly(DVB)] derivatives having hydroxyl terminals and/or pendants were synthesized by chemical modifications (hydration and hydroxylation) of unsaturated linear poly(DVB) (I), which was prepared by the polymerization of DVB initiated by acetyl perchlorate. Hydroboration of both terminal and in-chain carbon-carbon double bonds in I with $\text{BH}_3 \cdot \text{THF}$ complex yielded a fully hydrated poly(DVB) II, in which hydrophilic and hydrophobic groups are placed alternately. Selective hydroboration of the vinyl endgroups in I with 9-borabicyclo[3.3.1]nonane led to an α, ω -dihydroxypoly(DVB) (III). Reaction of I with m-chloroperbenzoic acid gave fully epoxidated poly(DVB) IV, which was subsequently hydrated to yield polymer V consisting of glycol repeat units and terminals. The physical properties and reactions (chain extension and crosslinking) of these polymers were also studied.

INTRODUCTION

Chemical modification of unsaturated hydrocarbon polymers by reactions of their carbon-carbon double bonds can give polymers with improved chemical and physical properties (polymer reforming) or with useful functional groups (polymer functionalization).¹⁻³⁾ For instance, polydienes (e.g., polybutadiene and polyisoprene) reformed by introduction of hydroxyl, thiol, or halogen groups are of superior performance to their virgin polymers.^{1,2)}

Another method to synthesize reformed or functionalized polymers is polymerization of a monomer with an appropriate substituent. Although often more cumbersome than this method, the chemical modification of polymers is advantageous because it allows a choice of functional groups to be introduced and an easier control of the structure and molecular weight of target polymers; a functional group in a monomer often acts as a retarding, chain-transfer, or terminating agent.

A literature survey indicates that the chemical modifications thus far reported mostly involve rubbery (soft) polymers such as polybutadiene and polyisoprene (see above). In spite of the potential usefulness of functionalized rigid (hard) polymers, few studies concern chemical modification of such materials [e.g., poly(phenylacetylene)⁴⁾].

This series of studies concerns the synthesis of functionalized rigid polymers based on linear unsaturated poly(divinylbenzene) I, which was obtained by the cationic polymerization of divinylbenzene (DVB) with acetyl perchlorate as initiator.⁵⁾ Poly(DVB) I has vinyl groups at both chain-ends and repeat units consisting of alternating phenyl and olefinic groups. These three unsaturated moieties, differing chemically and sterically, offer possibilities to introduce a variety of functional groups at selected sites of polymer I. In fact, in a previous chapter⁶⁾ the

EXPERIMENTAL SECTION

Materials. The syntheses of linear poly(DVB) I⁵⁾ ($\bar{M}_n = 1 \times 10^3 - 2 \times 10^3$) and the unsaturated styrene dimer (1,3-diphenyl-1-butene)⁷⁾ were described elsewhere. 9-Borabicyclo[3.3.1]nonane (9-BBN) and $\text{BH}_3 \cdot \text{THF}$ complex (1 M) were commercially obtained as THF solutions from Aldrich; the 9-BBN concentration was determined by the hydroboration of styrene with the solution. 4,4'-Diphenylmethane diisocyanate was distilled under reduced pressure. Commercial m-chloroperbenzoic acid, di-n-butyltin dilaurate, 4,4'-methylenedianiline (Wako Chemicals), and triphenylmethane triisocyanate (Daiichi Kogyo Seiyaku), all guaranteed reagents, were used without further purification.

Characterization. The apparent molecular weight distribution of polymers I - IV was determined by size exclusion chromatography (SEC; JASCO Trirotar chromatograph, JSP-101 polystyrene gel column 20 mm i.d. x 500 mm; CHCl_3 eluent; a refractive index detector). The structure of the products was determined by ^1H (90 MHz) and ^{13}C (22.5 MHz) NMR (JEOL FX90Q in CDCl_3 and CD_3OD), and infrared (IR) (Shimadzu IR-27G) and ultraviolet (UV) (Shimadzu UV 190) spectroscopy.

Polymer Reactions.

Polymer II by Hydroboration with $\text{BH}_3 \cdot \text{THF}$ Complex.^{4,8)} This polymer was obtained by the hydroboration of linear poly(DVB) I with $\text{BH}_3 \cdot \text{THF}$ complex. The reaction was carried out under a dry nitrogen atmosphere in a flask equipped with a stirrer. In this reactor a portion of I (0.6 g, 5.2 mmol of repeat units) was dissolved in a solution of BH_3 in THF (15.7 ml; 15.7 mmol). The mixture was stirred for 3 h at 50°C, cooled to room temperature, and diluted with 1,4-dioxane (40 ml). Then 6 N aqueous NaOH solution (2.6 ml) and 30 % aqueous H_2O_2 (10.0 ml) were added

dropwise in this order, and stirring was continued for 24 h to complete oxidation. The remaining peroxide was decomposed by the addition of 20 % aqueous NaHSO₃ solution. The resulting mixture was neutralized with 1N hydrochloric acid and extracted with ether. The ether layer was washed with water, dried overnight with anhydrous MgSO₄, evaporated to dryness under reduced pressure, and dried in vacuo to give polymer II in nearly quantitative yield. The product was free of vinyl and olefinic double bonds according to ¹H (Figure 4) and ¹³C NMR. The ¹³C NMR peak assignments for starting polymer I and the hydration product are as follows: polymer I, δ (ppm); 113.1 (C_a), 136.6 (C_b) (terminal C_aH₂=C_bH-)-, 42.2 (C_c), 21.2 (C_d), 128 (C_e), 134.8 (C_f) (main chain -C_cH(C_dH₃)-C_eH=C_fH--); hydration product, δ (ppm); 62.9 (C_g), 38.3 (C_h) (terminal HO-C_gH₂-C_hH₂--), 35.7 (C_i), 21.9, 22.5 (C_j), 46.9 (C_k), 71.8 (C_l) (VI type main chain -C_iH(C_jH₃)-C_kH₂-C_lH(OH)--), 44.8 (C_m), 16.2, 17.3 (C_n), 76.4 (C_o), 40.0, 40.9 (C_p) (VII type main chain -C_mH(C_nH₃)-C_oH(OH)-C_pH₂--).

Hydroboration of styrene and its dimer⁷⁾ (1,3-diphenyl-1-butene), as model reactions for that of polymer I, was carried out in a manner similar to that above.

Polymer III by Hydroboration with 9-BBN.⁹⁾ Poly(DVB) I (0.1 g, 0.48 mmol of terminal groups) was dissolved in a solution of 9-BBN in THF (1.1 ml, 0.51 mmol; 1.0 - 1.1 equiv. to the terminal vinyl groups of I) and the mixture was stirred at room temperature for 3 h. The subsequent oxidation with alkaline H₂O₂ (see above) was carried out at 50°C for 3 h and the reaction mixture was worked up in the same manner as described above to yield polymer III nearly quantitatively (~90%).

Polymer IV by Epoxidation.^{10,11)} A three-neck flask, equipped with a stirrer, reflux condenser, and dropping funnel and screened from light, was charged with linear poly(DVB) I (0.3 g), distilled

dichloromethane (CH_2Cl_2) (15 ml), and NaHCO_3 (0.45 g) as buffer reagent. A 7 % solution of m-chloroperbenzoic acid in CH_2Cl_2 (7.4 ml; equivalent to all the double bonds in I) was added dropwise over a period of 30 min at room temperature and the mixture was stirred for 24 h. The remaining peracid was decomposed by the addition of 20 % aqueous NaHSO_3 solution. The reaction mixture was diluted with CH_2Cl_2 and washed successively with 5 % aqueous NaHCO_3 and distilled water. The organic layer was separated and dried over anhydrous MgSO_4 . Evaporation of the solvent gave polymer IV in nearly quantitative yield.

Styrene and its linear dimer were epoxidized in a similar manner.

Polymer V by Hydration of IV.¹²⁾ Polymer V was obtained by adding dropwise concentrated sulfuric acid (0.2 ml) to a solution of epoxidized polymer IV (0.4 g) in a 1,4-dioxane - water mixture (1:1, v/v) (100 ml) and stirring vigorously at room temperature for 8 h.

Reactions of Hydroxylated and Epoxidated Poly(DVB).

Chain Extension of Polymer III with Diisocyanate. Poly(DVB) III was mixed with 4,4'-diphenylmethane diisocyanate and di-n-butyltin dilaurate as a catalyst in dimethylformamide (DMF) at a molar ratio of 1 : 1 : 8×10^{-4} : 32. The mixture was stirred at room temperature for the desired time and poured into a large amount of methanol. The precipitated products were recovered by filtration and purified by reprecipitating three times into methanol.

Network Formation of Polymer III with Triisocyanate. A 20 % solution of triphenylmethane triisocyanate in CH_2Cl_2 (two-thirds equiv. to polymer III) was added to polymer III in DMF and the solution was stirred at room temperature. Complete gelation took

place within 20 - 30 min, and the gel was vacuum-dried to remove the incorporated solvent.

Crosslinking of Polymer IV with Diamine. Ethyl acetate solutions of epoxidated polymer IV and methylenedianiline (epoxy/-NH₂ = 2/1) were thoroughly mixed and the solvent was evaporated at room temperature. The residue was maintained at 100°C for 2 h to yield a hard, resin-like material.

RESULTS AND DISCUSSION

Hydroboration with BH₃·THF Complex.

Both terminal and in-chain carbon-carbon double bonds of poly(DVB) I were fully hydrated by hydroboration with BH₃·THF complex (Scheme I). Figure 1 shows the ¹H NMR spectra of starting polymer I (Figure 1A) and the product obtained after the hydration (Figure 1B). An H - D exchange experiment using CD₃OD (the broken

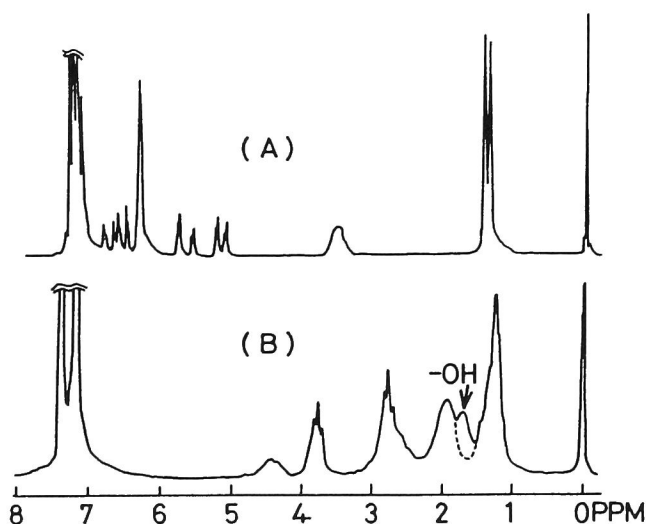


Figure 1. ¹H NMR spectra of (A) linear poly(DVB) I ($\bar{M}_n \sim 10^3$) and (B) a hydration product obtained with BH₃·THF complex.

line in Figure 1B) led to the disappearance of the peak at 1.6 ppm. Upon hydration the absorptions of the main chain double bonds (δ 6.2 ppm) and the terminal vinyl groups (δ 5 - 6, 6.5 - 7 ppm) of I (see Figure 1A) disappeared completely, and a broad signal of hydroxyl groups ($\delta \sim 1.6$ ppm) in turn appeared along with the peaks assignable to methyl (δ 1.0 - 1.5 ppm), methylene (1.8 - 2.2 ppm), and methine (2.5 - 4.8 ppm) protons in the main chain. The two triplets at δ 2.8 and 3.8 ppm were assigned to the terminal ethylene group ($-\text{C}_6\text{H}_5-\text{CH}_2\text{CH}_2\text{OH}$) (see below).

Figure 2 shows ^1H NMR spectra of the hydration products of styrene and its linear dimer (1,3-diphenyl-1-butene) as models for the terminal group and the repeat unit of polymer II, respectively. Peak assignments, based on chemical shifts and decoupling measurements, are also shown. The complicated coupling patterns of peaks (c, d, f, and g) indicate two isomers VI and VII in the hydration product, as shown in Figure 2A. The formation of the two isomers was also supported by the well-resolved signals b and e for two kinds of methine protons α to a hydroxyl group. Integration of these peaks showed that VI is formed more favorably than VII (VI : VII = 7 : 3), probably due to differences in the steric

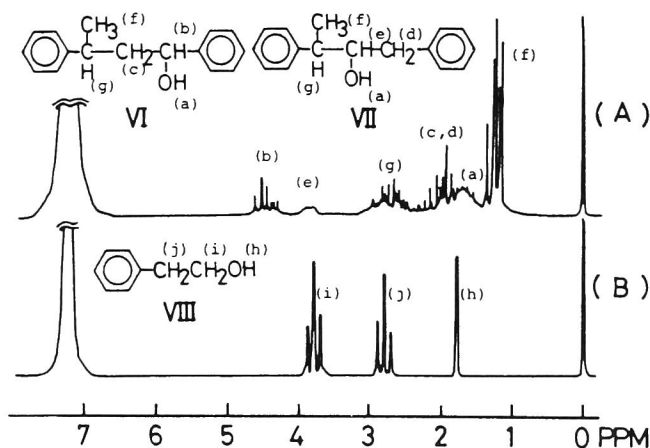


Figure 2. ^1H NMR spectra of (A) hydrated styrene dimer (two isomers) and (B) hydrated styrene (2-phenylethanol).

hinderance on hydroboration. The ^1H NMR spectrum in Figure 1B consists of all the resonances found in those of the terminal and main-chain models (Figure 2). The ^{13}C NMR spectra of starting polymer I and the hydration product were identical with those of the corresponding models (see Experimental Section). According to these NMR results, the hydration product is of structure II.

Figure 3 shows the IR spectra of the hydration product and a sample of poly(DVB) I. On hydration the absorptions of vinyl group at 900 and 990 cm^{-1} ($\delta\text{s-CH=CH}_2$) and trans-olefin at 970 cm^{-1} disappeared completely, and in turn hydroxyl absorptions [3300cm^{-1} ($\nu_{\text{O-H}}$) and 1100 cm^{-1} ($\nu_{\text{C-O}}$)] were observed; the pattern in the 2800 to 3000 cm^{-1} region (aliphatic C-H stretching) also changed.

The hydration product exhibited no UV absorption at 295 nm assigned to $-\text{CH=CH}-\text{C}_6\text{H}_4-$. According to SEC measurements, the molecular weight distribution of the hydration product was practically the same as that of the starting poly(DVB), indicating that backbone degradation did not occur during either the hydroboration or subsequent oxidation of polymer I.

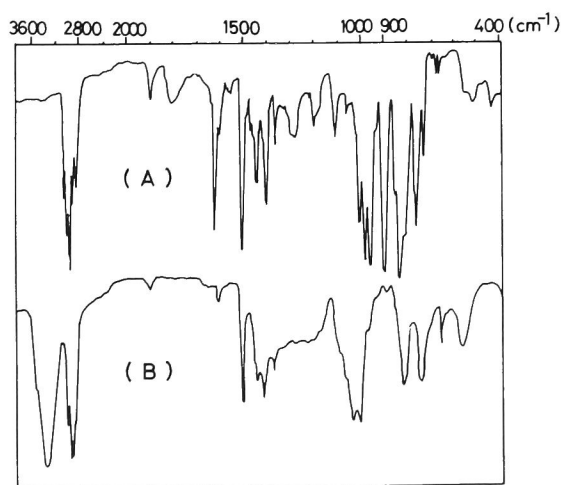


Figure 3. IR spectra of (A) linear poly(DVB) I ($\bar{M}_n \sim 10^3$) and (B) a hydration product obtained with $\text{BH}_3 \cdot \text{THF}$ complex.

All these spectroscopic data confirm quantitative hydration of the in-chain and terminal double bonds in polymer I. Consequently, the author can obtain a novel rigid polymer II consisting of alternating hydrophobic and hydrophilic groups.

The solubilities of linear poly(DVB) (I) and hydrated poly(DVB) (II) are listed in Table I. The linear poly(DVB), as with polystyrene, was soluble in nonpolar solvents such as aromatic (benzene) and halogenated (CCl_4) hydrocarbons and polar solvents such as ketones (acetone) and heterocycle amines (pyridine), but was insoluble in water and alcohols. Interestingly, the hydroxy derivative II dissolved not only in good solvents for I but also in alcohols.

TABLE I
Solubility of Poly(DVB) I and Hydrated Polymer II^{a)}

Solvent	Poly(DVB)(I)	Hydrated polymer II
H_2O	X	X
CH_3OH	X	○
$\text{C}_2\text{H}_5\text{OH}$	X	○
C_6H_6 , CCl_4	○	○
 ,  , $(\text{CH}_3)_2\text{CO}$	○	○
$\text{HCON}(\text{CH}_3)_2$, 	○	○

a) (○) soluble; (X) insoluble.

Hydroboration with 9-BBN.

9-Borabicyclo[3.3.1]nonane (9-BBN), a sterically hindered borane, is a highly selective hydroborating agent that reacts with a vinyl group 100 times faster than with an aliphatic internal, disubstituted double bond (e.g., 1-hexene vs. 2-pentene).⁹⁾ This suggests that the terminal vinyl groups in polymer I may be hydroborated selectively by 9-BBN, with the sterically crowded in-chain double bonds kept intact. To synthesize an α,ω -bifunctional polymer from I, we thus studied the hydroboration of poly(DVB) I with 9-BBN.

Figure 4A shows the ^1H NMR spectrum of the hydration product thus obtained from I with 9-BBN. The spectrum differed considerably from that of polymer II (see Figure 1B) obtained by the hydroboration with $\text{BH}_3\cdot\text{THF}$ complex. In particular, the product exhibited a sharp absorption δ 6.4 ppm due to the olefinic protons in the main chain $[-\text{C}_6\text{H}_4-\text{CH}(\text{CH}_3)-\text{CH}=\text{CH}-]$, whereas vinyl protons (δ 5 - 6 and 6.5 - 7 ppm) were absent. No absorptions of a saturated hydrocarbon skeleton [methyl (1 - 1.2 ppm) and methine (ca. 4.5 ppm)] were detected by the ^1H NMR apparatus. The existence of (terminal) hydroxyl groups was indicated by the two ethylene signals at 2.8 and 3.8 ppm $(-\text{C}_6\text{H}_4-\text{CH}_2\text{CH}_2\text{OH})$ together with the broad

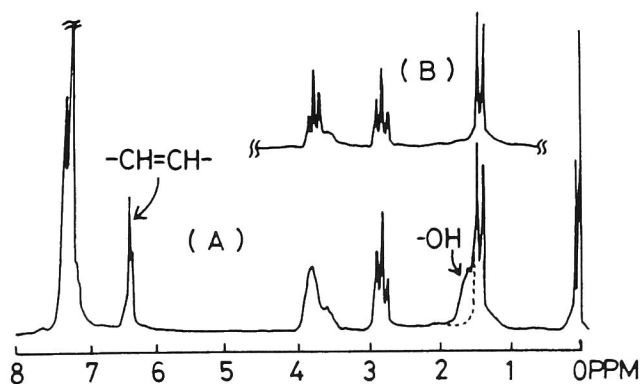


Figure 4. ^1H NMR spectra of a hydration product obtained with 9-BBN, measured in (A) CDCl_3 and (B) $\text{CDCl}_3 + \text{CD}_3\text{OD}$.

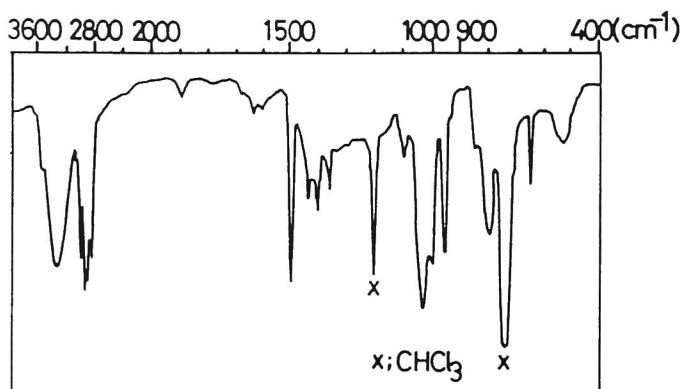


Figure 5. IR spectrum of a hydration product obtained with 9-BBN.

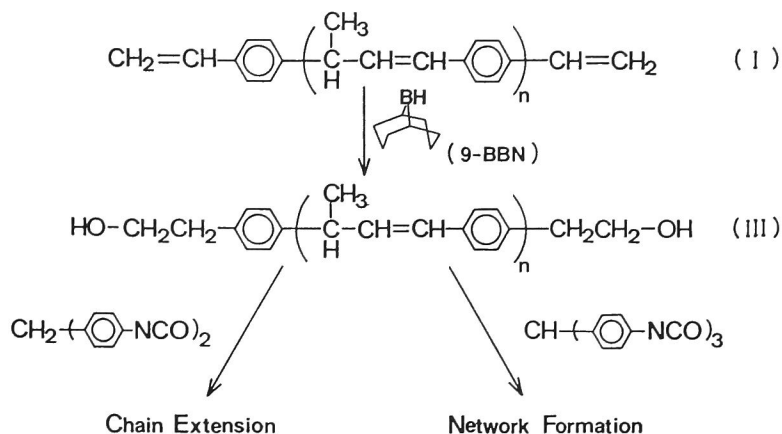
absorption of the alcoholic proton (δ 1.7 ppm). An H - D exchange experiment using CD_3OD (Figure 4B) led to the complete disappearance of the latter peak; the 3.8 ppm absorption now showed a fine structure. The author thus concluded that polymer diol III was obtained by the selective terminal hydration of poly(DVB) I with 9-BBN.

Figure 5 shows the IR spectrum of the product with 9-BBN. The spectrum showed the presence of OH groups [$3400 (\nu_{\text{O-H}})$ and $1100 \text{ cm}^{-1} (\nu_{\text{C-O}})$] and the absence of vinyl terminals [990 and $900 \text{ cm}^{-1} (\delta_{\text{s-CH=CH}_2})$] in the product, coupled with the retention of the unsaturated backbone of polymer I [$2800 - 3000 (\nu_{\text{C-H, aliphatic}})$ and $970 \text{ cm}^{-1} (\text{trans-olefin})$].

The results described above thus show the α,ω -bifunctional polymer (III) having a primary alcoholic OH group at both ends can be easily obtained by the hydroboration of poly(DVB) with 9-BBN.

Reactions of Polymer III with Isocyanates.

Since polymer III is a telechelic polymer,¹³⁾ the possibilities of chain extension and network formation with isocyanates were studied.



[Scheme II]

Chain Extension with Diisocyanate. Polymer III ($\bar{M}_n \sim 2 \times 10^3$) was treated with 4,4'-diphenylmethane diisocyanate at room temperature in DMF (see Experimental Section). A white powdery polymer of a high molecular weight ($\bar{M}_n \sim 10^4$) with a broad molecular weight distribution was obtained. This molecular weight corresponded to DP (or number of chain extensions) ~ 5 with respect to prepolymer III. Consequently, effective chain extension is possible for III by the reaction with a diisocyanate.

Network Formation with Triisocyanate. Triphenylmethane triisocyanate as trifunctional coupling reagent was allowed to react with polymer III in a DMF/CH₂Cl₂ mixed solvent at room temperature. The reaction mixture became increasingly viscous in 10 min and finally underwent gelation in 20 - 30 min. After an additional hour, the product was taken out, and solvent was removed under reduced pressure to yield a hard rubber-like polymer. This polymer showed an IR absorption of in-chain double bonds at 970 cm⁻¹. The successful network formation of polymer III should be of interest in that the product is an "unsaturated" network in which crosslinks consist of unsaturated repeat units.

Epoxidation of Polymer I.

Linear poly(DVB) I was epoxidated by m-chloroperbenzoic acid. Figure 6 shows the ^1H NMR spectra of the epoxidated product and the starting polymer I. On epoxidation the signals of the olefinic protons in the main chain (δ 6.2 ppm) and the vinyl endgroups (δ 5 - 6, 6.5 - 7 ppm) of I completely disappeared and methyl (δ 1.2 ppm), methine, and terminal methylene peaks (δ 2.5 - 3.8 ppm) were newly observed.

Figure 7 shows the ^1H NMR spectra of epoxidized styrene and its linear dimer as model compounds for the end group and repeat unit of polymer IV (Scheme I), respectively; peak assignments are also shown in Figure 7. Comparison of the spectra in Figure 6 and 7 indicates that the spectrum of the epoxidation product (Figure 6B) contains signals due to both in-chain (Figure 7A) and terminal (Figure 7B) epoxy units; and no signals assignable to other structures could be detected. In the IR spectrum the bands due to the olefinic groups of polymer I were replaced by the epoxy absorptions at 1250 cm^{-1} ($\nu_{\text{S}} - \text{C}_{\text{O}}\text{C}-$) and 880 cm^{-1} ($\nu_{\text{AS}} - \text{C}_{\text{O}}\text{C}-$). These

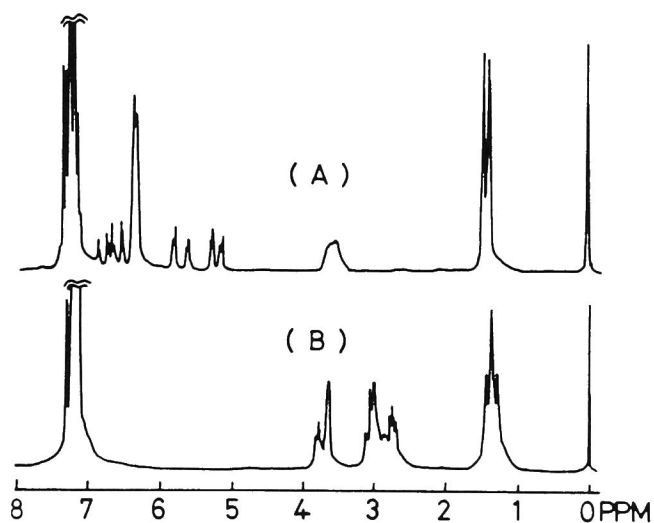


Figure 6. ^1H NMR spectra of (A) linear poly(DVB) I ($\bar{M}_n \sim 10^3$) and (B) an epoxidated product.

Hydration of the oxirane units of polymer IV by an acid such as sulfuric acid¹²) yielded a polymer having glycol (1,2-diol) repeat units (V in Scheme I). As the hydration proceeded, the IR absorption of hydroxyl groups at 3400 cm^{-1} ($\nu_{\text{O-H}}$) appeared in place of decreasing epoxy band at 1250 cm^{-1} ($\nu_{\text{S-C-O-C}}$). Unfortunately, the product was insoluble in all solvents tried, including water and alcohols, probably because strong intra- and/or intermolecular hydrogen bonding in polymer V prevents solvation.

Epoxidated poly(DVB) (IV) readily reacted with a diamine (4,4'-methylenedianiline) to give a crosslinked material (see Experimental Section). The product was an extremely hard resin that was insoluble in all organic solvents.

The results described above show that IV is a potentially useful new reactive polymer. It may also be possible to vary the extent of epoxidation of polymer I to give a partly epoxidated, linear unsaturated poly(DVB), the C=C double bonds of which allows one to introduce desired functional groups into the rigid, epoxidated poly(DVB) backbone. Thus, the hydration, epoxydation, and hydroxylation described in this work represent only a part of the possible chemical modifications of unsaturated poly(DVB) I.

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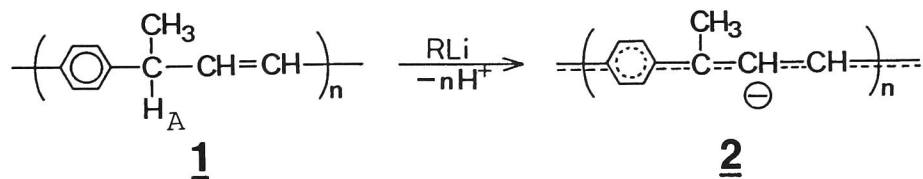
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CHAPTER 10

SYNTHESIS OF POLYMERIC DELOCALIZED CARBANION OF POLY(DIVINYLBENZENE) AND ITS REACTIONS

ABSTRACT

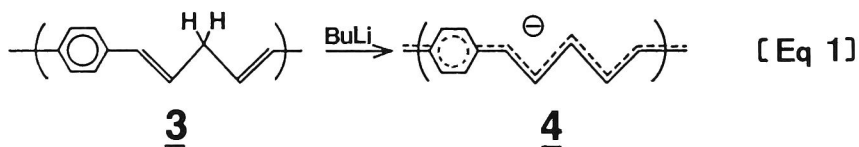
A polymeric delocalized carbanion of poly(divinylbenzene) [poly(DVB)] (2) was obtained by the proton abstraction with alkyllithium from the acidic methine moieties (H_A) of linear poly(DVB) (1), which was prepared by the polymerization of DVB initiated by acetyl perchlorate. The formation of polyanion 2 was confirmed by UV-visible spectroscopy ($\lambda_{\max} = 630 \text{ nm}$) and the reaction with methyl iodide to give methylated poly(DVB). Delocalized polyanion 2 reacted with various electrophilic reagents in THF at 60°C , to yield poly(DVB) derivatives having pendant trimethylsilyl, vinyl, vinyloxy, hydroxyl, and carboxyl groups. Proton abstraction with base and subsequent reactions with electrophiles were also studied with the linear unsaturated dimer of styrene (1,3-diphenyl-1-butene), as a model for poly(DVB) 1.



INTRODUCTION

Allylic proton abstraction with base from polydienes (polybutadiene, polyisoprene, etc.) gives carbanions along the polymer chain, which can be utilized to introduce pendant functional groups¹⁾ or to initiate graft polymerization.²⁾ For chemical modification of polydienes, however, this method has not widely been employed, because the allylic protons are so weakly acidic that their abstraction is usually inefficient even in the presence of an activated base (e.g., $n\text{BuLi}/t\text{BuOK}$).

Recently, Gordon III et al. have reported an efficient proton abstraction from the relatively acidic doubly allylic methylene moieties of poly(*p*-phenylene pentadienylene) (3) and related polymers to form delocalized polyanions like 4 (eq 1).^{3,4)} Although



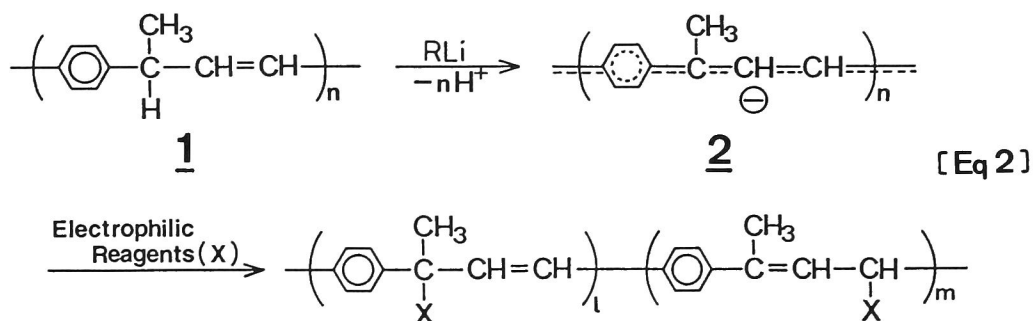
their investigations were primarily directed toward the syntheses of electrically conducting polymers, it occurred to the author that the proton abstraction which led to delocalized polyanions would also be useful for chemical modification of unsaturated polymers. Specifically, treatment of such polyanions with appropriate electrophiles would allow the author to attach a variety of pendant functional groups to the precursor polymers.

One drawback of this otherwise attractive chemical modification method is the limited range and rather cumbersome syntheses of precursor polymers that should have relatively acidic protons along their backbone. For example, the synthesis of 3 involves a consecutive Wittig condensation in THF at -78°C .⁴⁾

In 1980 Hasegawa and Higashimura reported that the cationic

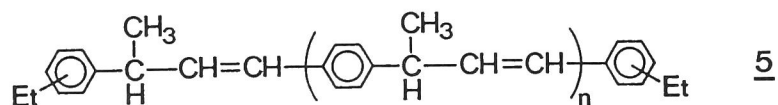
polymerization of divinylbenzene (DVB) initiated by acetyl perchlorate provides a linear poly(DVB) 1 (eq 2)⁵⁾ which is analogous in structure to 3. The repeat unit of 1 contains a methine moiety flanked with a phenyl group and an olefinic double bond; therefore, its tertiary proton is both allylic and benzylic, and would be as acidic as the doubly allylic protons of 3.

These structural features of 1, coupled with its easy synthesis, prompted the author to investigate, in this work, (1) the formation of delocalized polyanion 2 from 1 by proton abstraction with base (eq 2) and (2) introduction of pendant functional groups to 1 via reactions of polyanion 2 with electrophiles (X) such as trimethylchlorosilane, allyl bromide, 2-chloroethyl vinyl ether, ethylene oxide, and carbon dioxide.



EXPERIMENTAL SECTION

Materials. The synthesis of linear poly(DVB) 1 has been described.^{5,6)} Most of the samples used in this study were of low molecular weight ($\bar{M}_w = 1000 - 4300$) and capped with m- or p-ethylstyrene, as shown below:⁶⁾



For some experiments, the DVB trimer (5, $n = 1$) and tetramer (5, $n = 2$) were separated from a higher molecular weight sample of 5 by preparative SEC. The unsaturated dimer of styrene (1,3-diphenyl-1-butene), as a model for the repeat unit of 1 and 5, was obtained as previously reported by Higashimura et al.⁷⁾

Commercial n-butyllithium (nBuLi) solution in n-hexane (Wako Chemicals, 1.0 M) and phenyllithium (PhLi) solution in cyclohexane/diethyl ether (Aldrich, 1.7~2.0 M), both guaranteed reagents, were used without further purification. Methyl iodide, trimethylchlorosilane, allyl bromide, and 2-chloroethyl vinyl ether were all distilled over CaH₂. Ethylene oxide and carbon dioxide were dried before use by passing the gases through columns packed with desiccating agents (CaCl₂ and CaH₂ for ethylene oxide; CaCl₂ and P₂O₅ for carbon dioxide).

Analytical Methods. The molecular weight and molecular weight distribution of polymers were measured by SEC using polystyrene gel columns; the $\bar{M}_w$ and $\bar{M}_n$ were calculated on the basis of a polystyrene calibration. The structure of the products was determined by ¹H (90 MHz) and ¹³C (22.5 MHz) NMR (JEOL FX90Q, in CDCl₃) and ultraviolet (UV) (Shimadzu UV 190) spectroscopy.

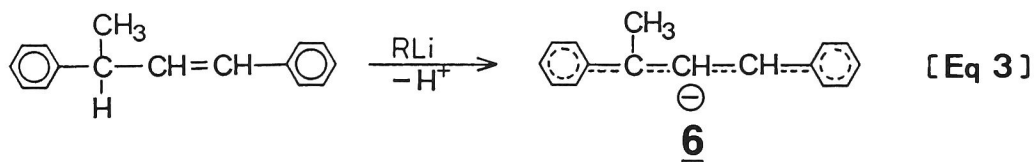
Proton Abstraction with Base from Linear Poly(DVB) 5. Proton abstraction with base was carried out under a nitrogen atmosphere in a baked Erlenmeyer flask equipped with a magnetic stirrer bar and a three-way stopcock. A solution of nBuLi or PhLi (5 ml; 10 mmol) was added dropwise with a syringe to a THF solution of 5 (10 ml; 1.5 mmol of repeat units) with stirring at 60°C. The mixture immediately became intensely blue-black and partly heterogeneous. Proton abstraction from the styrene dimer was carried out in a similar manner ($[RLi]_0/[styrene\ dimer]_0 = 1\sim 2$).

Reactions of Delocalized Polyanion 2 with Electrophilic Reagents. Polyanion 2 in THF, obtained from 5 as described above, was then treated in situ with excess electrophilic reagents at 60°C. As electrophiles, trimethylchlorosilane, allyl bromide, and 2-chloroethyl vinyl ether were added dropwise via a dry syringe; dried ethylene oxide and carbon dioxide were bubbled into the solution and the products were hydrolyzed with a few drops of conc. hydrochloric acid. The reactions were completed within one min, as indicated by the complete disappearance of the blue-black color. The reaction mixtures were then washed with water, and the products were recovered by evaporation of volatiles under reduced pressure.

RESULTS AND DISCUSSION

Proton Abstraction from Linear Poly(DVB) 5.

Preparation of Delocalized Polyanion 2. The methine protons of poly(DVB) 5 and its model compounds (the unsaturated styrene dimer and the DVB trimer and tetramer) were abstracted by treatment with nBuLi and PhLi to yield delocalized anions (e.g., 2). Figure 1A shows the UV-visible spectrum of a mixture of the styrene dimer with nBuLi. When the base was added to a colorless transparent solution of the dimer in THF, it immediately turned purple and a strong absorption appeared at 564 nm. The observed absorption maximum ($\lambda_{\max}$) is close to the estimate value (561 nm) for anion 6 (eq 3) based on the absorptions of analogous conjugated anions [$\lambda_{\max}$ (nm): $\text{C}_6\text{H}_5\text{-CH}_2\text{Li}$; 330, $\text{C}_6\text{H}_5\text{-CHLi-CH=CH}_2$; 395, $\text{C}_6\text{H}_5\text{-CHLi(CH}_3\text{)-C}_6\text{H}_5$; 496].⁸⁾ This result indicates that 1,3-diphenylbutenyl anion (6) can be easily obtained from the styrene dimer by proton



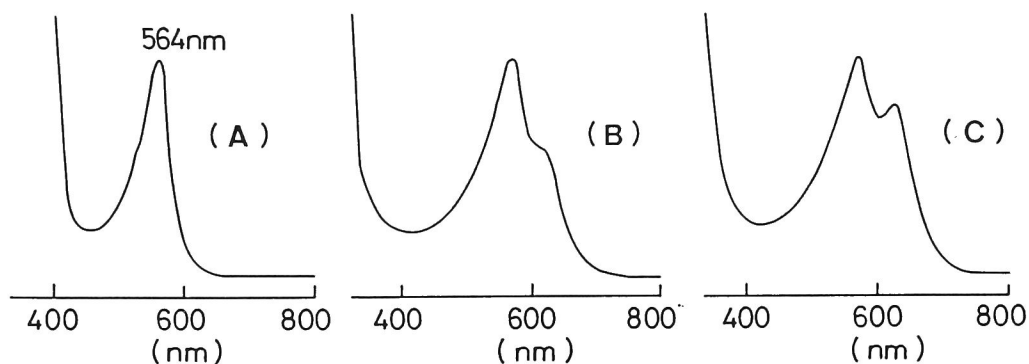


Figure 1. UV-visible spectra of mixtures of the unsaturated styrene dimer (A), DVB trimer (B), and DVB tetramer (C) with $n\text{BuLi}$ in THF at 25°C : $[\text{styrene dimer}]_0 = [\text{DVB unit}]_0 = 10 \text{ mM}$, $[n\text{BuLi}]_0 = 0.50 \text{ mM}$.

abstraction with base (eq 3).

The DVB trimer and tetramer (5, $n = 1$ and 2 , respectively) also gave the corresponding polyanions (2) when treated with $n\text{BuLi}$ (Figure 1B and C). The spectra exhibited not only the 564 nm band for 6 but an additional red-shifted absorption at 620 nm, the latter indicating the formation of a longer conjugated system than 6.

Linear poly(DVB) 5 ($\bar{M}_w = 4300$) was treated with $n\text{BuLi}$ in the same procedures (Figure 2). The pale yellow solution of 5 (Figure 2A) immediately turned intensely blue-black, and a broad absorption appeared in the region from 500 to 780 nm [$\lambda_{\text{max}} = 632$ and 660 (shoulder) nm] (Figure 2B). The expanded range of the absorption and its bathochromic shift from 564 and 620 nm (Figure 1) show the formation of a highly conjugated polyanion 2. Neutralization of the blue-black solution of 2 with alcohols immediately regenerated a pale yellow solution (Figure 2C) similar to that of the untreated polymer 5.

The reaction of 5 with PhLi also led to polyanion 2 that exhibited nearly the same absorption pattern as that obtained with $n\text{BuLi}$.

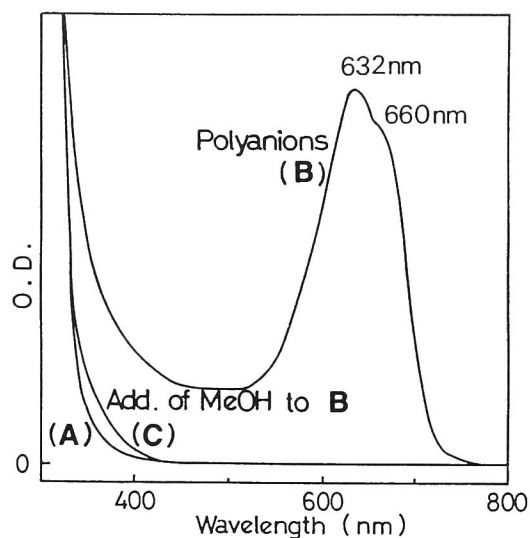
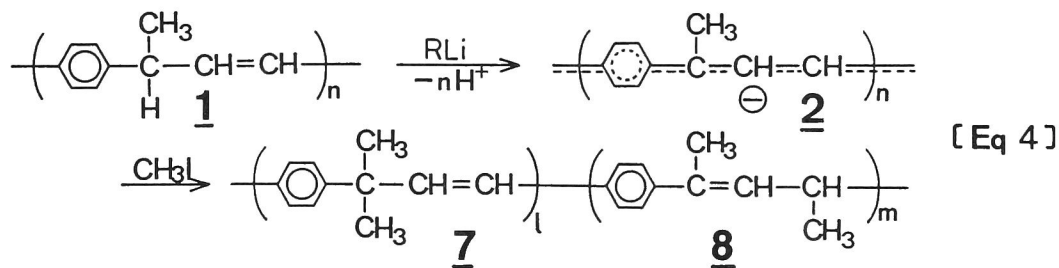


Figure 2. UV-visible spectra in THF at 25°C: (A) poly(DVB) 5 ($\bar{M}_w = 4300$), $[\text{DVB unit}]_0 = 10 \text{ mM}$; (B) after addition of $n\text{BuLi}$ to solution A, $[n\text{BuLi}]_0/[\text{DVB unit}]_0 = 0.1$; (C) after neutralization of solution B with methanol.

Reactions of Delocalized Polyanion 2 with Methyl Iodide. Carbanions like 2 are known to react with alkyl halides (e.g., methyl iodide) to yield alkylated products, whereas neither the methine moiety nor the olefinic double bond of poly(DVB) 5 is reactive to them. To determine the degree of deprotonation of poly(DVB) 5 by alkyllithium, therefore, polyanion 2 was treated in situ with methyl iodide, and the resulting methylated product was characterized by ^1H and ^{13}C NMR. Because each carbanionic site in 2 is allylic and ambivalent, its methylation with methyl iodide gives two isomeric structures 7 and 8 (eq 4).



Model experiments were first performed on the styrene dimer anion 6. Thus, the styrene dimer was deprotonated with $\underline{n}\text{BuLi}$ or PhLi in THF at 60°C and then treated with methyl iodide. Figure 3 shows the ^1H NMR spectra of the methylated products (B with $\underline{n}\text{BuLi}$ and C with PhLi) and the starting styrene dimer (A) along with peak

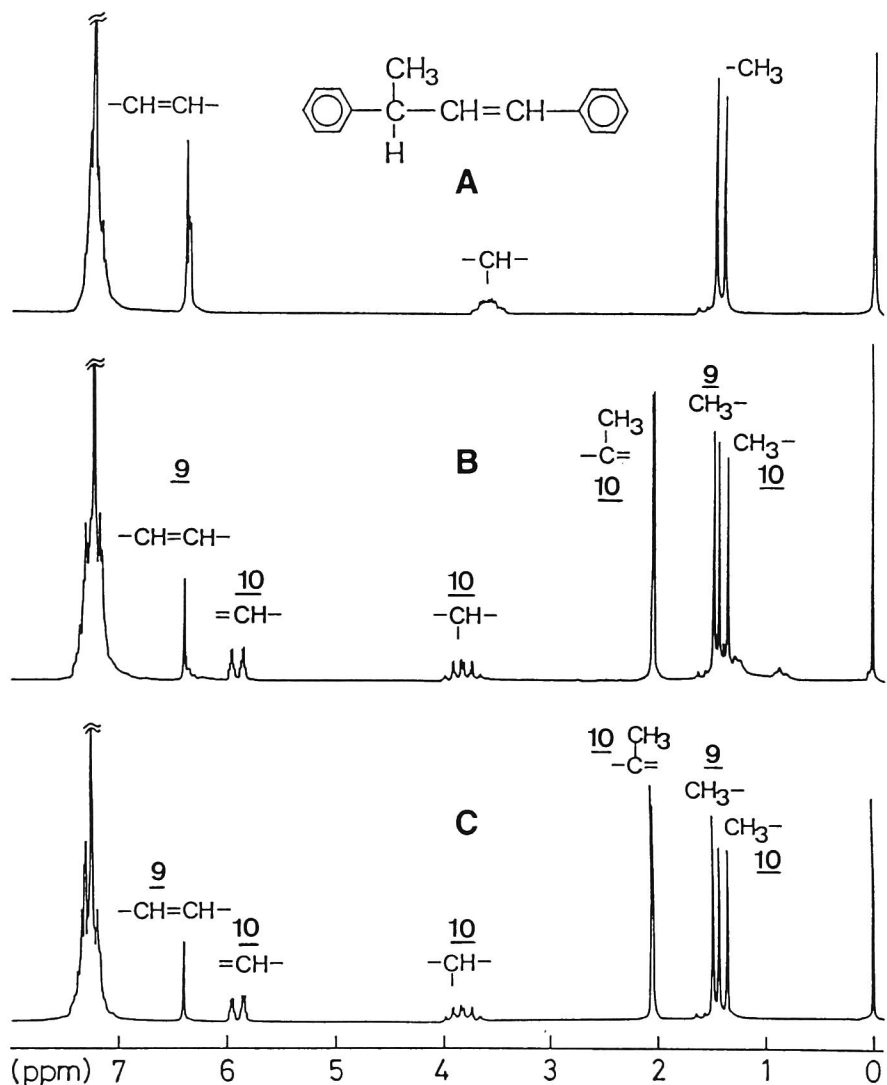
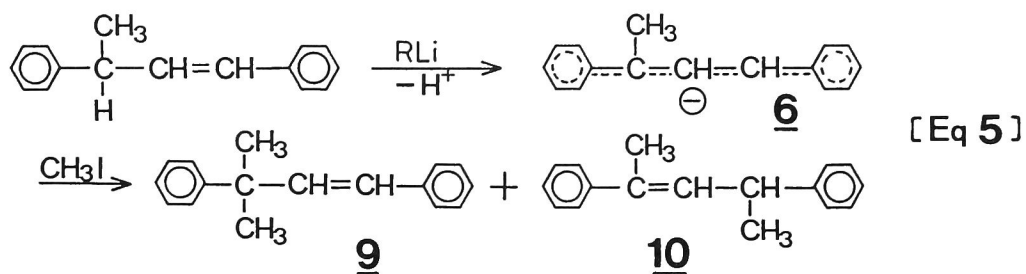


Figure 3. ^1H NMR spectra of the unsaturated styrene dimer (A) and its methylated products obtained by proton abstract with $\underline{n}\text{BuLi}$ (B) or PhLi (C) in THF at 60°C : $[\text{styrene dimer}]_0 = 0.1 \text{ M}$, $[\text{alkyl-lithium}]_0/[\text{styrene dimer}]_0 = 1\sim 2$.

assignments. In both spectra 3B and 3C, the absorptions of the alkyl and olefinic protons of the styrene dimer are completely absent and peaks assignable to the methyl adducts were newly observed. Their spectral patterns further showed that the methyl adducts are composed of two isomers (9 and 10) derived from the charge delocalization of the 1,3-diphenylbutenyl anion (eq 5).



According to ^1H NMR analysis, 10 is formed more favorably than 9 (9 : 10 = 37 : 63). The formation of 9 and 10 was also confirmed by ^{13}C NMR (see Figure 5A). All these NMR analyses thus established the quantitative ionization of the styrene dimer into 6.

In Figure 3B, however, small additional absorptions were detected in the alkyl region, which were assigned to the *n*-butyl moiety of *n*BuLi added to the olefinic double bond of the styrene dimer [CH_3 -; 0.9 ppm, $-(\text{CH}_2)_3$; 1.3 ppm]. This side reaction is most likely due to the high nucleophilicity of *n*BuLi.

After establishing the formation of 9 and 10 from model anion 6, deprotonated poly(DVB) ($\bar{M}_w = 1000$) were treated with methyl iodide. Figure 4 compares the ^1H NMR spectra of the starting poly(DVB) 5 (A) and the methylated product (B). In Figure 4B, the absorption of the methine protons of 5 was almost completely absent, and the peaks of structures 7 [δ (ppm); 1.5 ($-\text{CH}_3$) and 6.4 ($-\text{CH}=\text{CH}-$)] and 8 [δ (ppm); 1.4 ($-\text{CH}_3$), 2.1 ($-\text{C}(\text{CH}_3)=$), 3.8 ($-\text{CH}-$), and 5.9 ($-\text{C}=\text{CH}-$)] appeared. No signals assignable to other structures than 7 and 8 could be detected. ^{13}C NMR analysis also

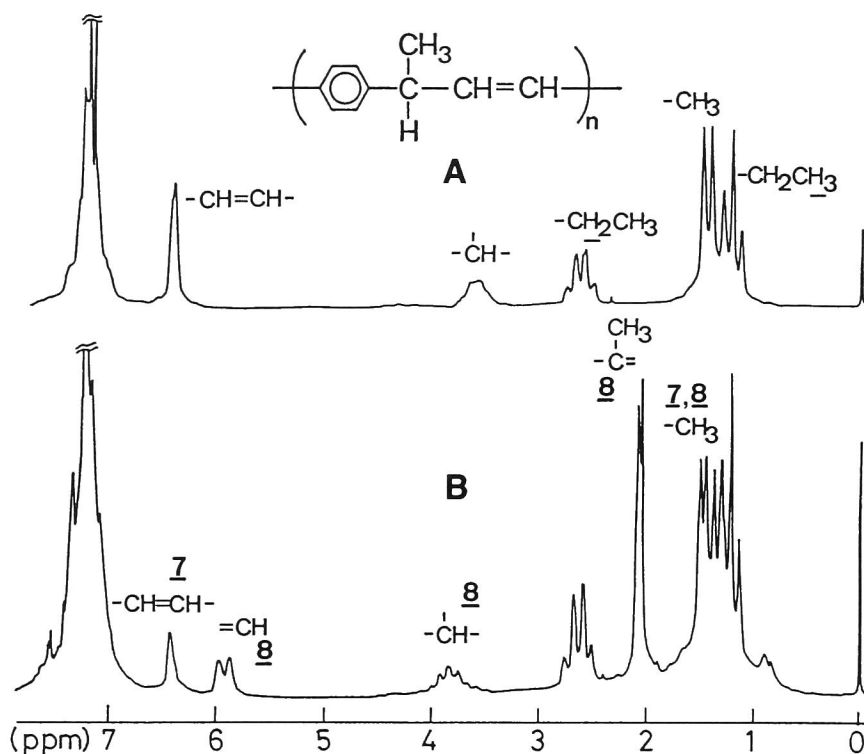


Figure 4. ^1H NMR spectra of linear poly(DVB) 5 (A) and a methylated product (B): $[\text{DVB unit}]_0 = 0.15 \text{ M}$, $[\text{PhLi}]_0/[\text{DVB unit}]_0 = 5 \sim 10$.

supported the expected structures. These NMR results show a high degree ($> 95\%$) of deprotonation from 5, which in turn confirms the formation of polyanion 2 with an almost fully conjugated backbone that is free of non-conjugating methine residues.

Reactions of Polyanion 2 with Electrophilic Compounds: Preparation of Pendant-Functionalized Poly(DVB) Derivatives.

Carbanions of the type R^-Li^+ are known to readily react with electrophiles X (alkyl halides, carbonyl compounds and so on) to yield addition products R-X. Delocalized polyanion 2 is, therefore, expected to undergo similar reactions. With the use of electrophiles that carry a functional group or its precursor, these reactions will give poly(DVB) with functional pendant groups. To

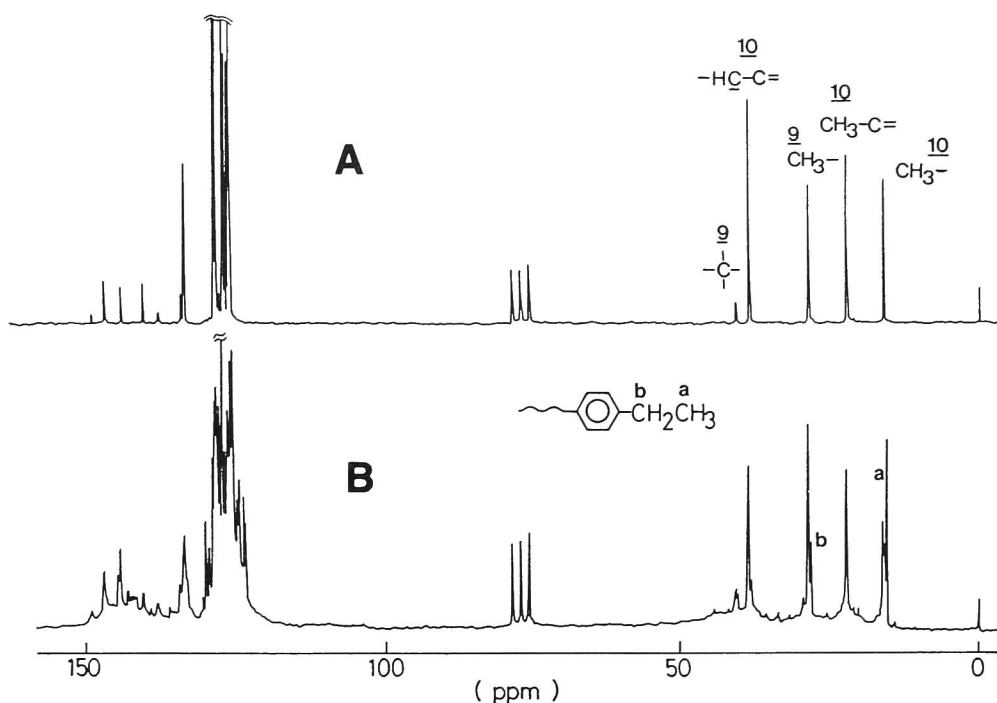
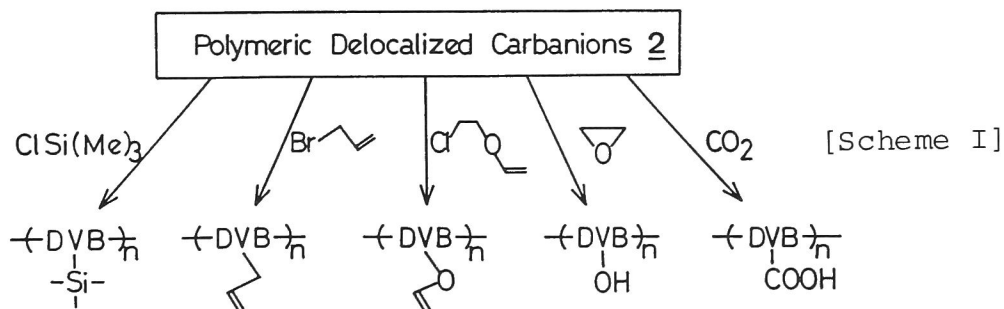


Figure 5. ^{13}C NMR spectra of (A) methylated styrene dimer (sample C, Figure 2) and (B) methylated poly(DVB) (sample B, Figure 3).

test such possibilities, a number of electrophilic compounds were allowed to react with polyanion 2 derived from poly(DVB) 5 (Scheme I). The three halogen-containing compounds, trimethylchlorosilane, allyl bromide, and 2-chloroethyl vinyl ether, led to silyl, vinyl, and vinyloxy pendants, respectively; hydroxylated and carbonated poly(DVB) were obtained by the reactions with ethylene oxide and carbon dioxide, respectively.



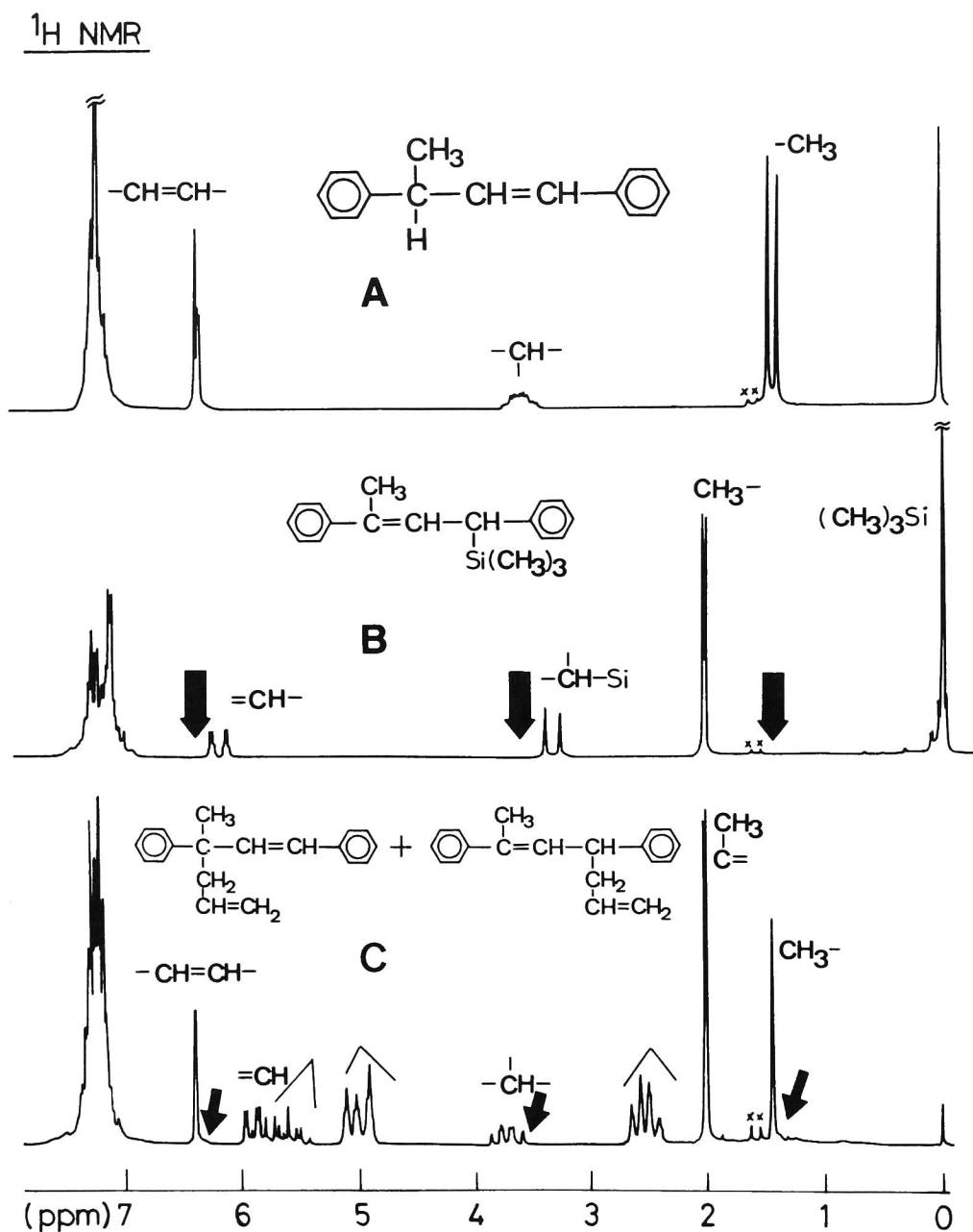


Figure 6. ^1H NMR spectra of the unsaturated styrene dimer (A) and the adducts with Me_3SiCl (B) and with $\text{CH}_2=\text{CH}-\text{CH}_2\text{Br}$ (C) to styrene dimer anion 6: $[\text{styrene dimer}]_0 = 0.1 \text{ M}$, $[\text{PhLi}]_0/[\text{styrene dimer}]_0 = 1 \sim 2$.

Figure 6 shows the ^1H NMR spectra of the adducts of trimethylchlorosilane and allyl bromide to the styrene dimer anion 6 as a model for polyanion 5. Upon treatment of 6 with these electrophiles, the absorptions of the methyl (δ 1.4 ppm), methine (δ 3.6 ppm), and olefinic protons (δ 6.3 ppm) of the starting styrene dimer disappeared completely. The products in turn showed the main chain peaks of similar to those of 9 and 10 (cf. Figure 3) [9 type; 1.5 ppm ($-\text{CH}_3$) and 6.4 ppm ($-\text{CH}=\text{CH}-$), 10 type; 1.4 ppm ($-\text{CH}_3$), 2.1 ppm ($-\text{C}(\text{CH}_3)=$), 3.8 ppm ($-\text{CH}-$), and 5.9 ppm ($=\text{CH}-$)], together with the characteristic signals due to trimethylsilyl (Figure 6B) or allyl (Figure 6C) group. Similarly, the other electrophiles also reacted with 6 to form in quantitative yield styrene dimers with a pendant vinyloxy, hydroxyl, or carboxyl group (see Table I).

TABLE I
Reactions of Delocalized Polyanion 2
with Electrophilic Reagents in THF at 60°C.

Electrophilic Reagent	Conv. (%) ^{a)}		$\begin{array}{c} \text{C} \\ \\ -\text{C}-\text{C}=\text{C}- \\ \\ \text{X} \end{array} \bigg/ \begin{array}{c} \text{C} \\ \\ -\text{C}=\text{C}-\text{C}- \\ \\ \text{X} \end{array}$			a)
	St dimer	Poly(DVB) ^{b)}				
CH_3I	100	95	37	/	63	
$(\text{CH}_3)_3\text{SiCl}$	100	90	0	/	100	
$\text{CH}_2=\text{CHCH}_2\text{Br}$	100	95	38	/	62	
$\text{CH}_2=\text{CHOC}_2\text{H}_4\text{Cl}$	100	95	28	/	72	
	100	80	30	/	70	
CO_2	100	90	19	/	81	

a) Determined by ^1H NMR.

b) 5, $\bar{M}_w = 1000$.

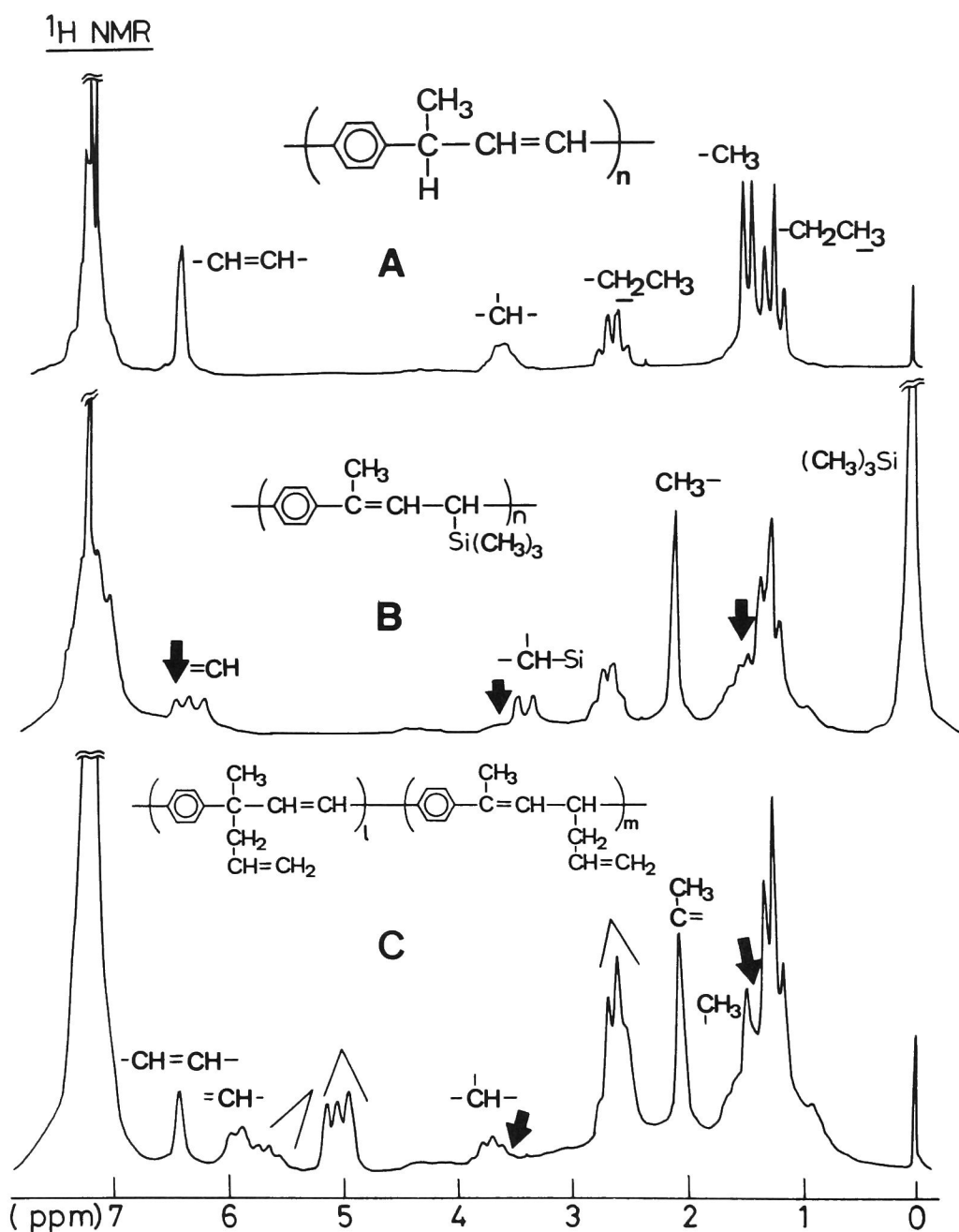


Figure 7. ^1H NMR spectra of poly(DVB) 5 ($\bar{M}_w = 1000$) (A) and adducts with Me_3SiCl (B) and with $\text{CH}_2=\text{CH}-\text{CH}_2\text{Br}$ (C) to poly(DVB) anion 2: $[\text{DVB unit}]_0 = 0.15 \text{ M}$, $[\text{PhLi}]_0/[\text{DVB unit}]_0 = 5 \sim 10$.

Because of the allylic charge delocalization in anion 6, the obtained adducts consisted of two isomers corresponding to the methylated versions 9 and 10 (eq 5). Table I lists the ratios of such two isomers. The preference for the secondary carbon (e.g., 9) over the tertiary carbon (e.g., 10) is in accordance with the chemistry of the S_N2-type reactions; in particular trimethylchlorosilane, a sterically hindered halide, selectively attacked the secondary carbon rather than the tertiary position.

To introduce various functional pendant groups to poly(DVB), delocalized polyanion 2 was allowed to react with the five electrophilic reagents. Figure 7 shows the ¹H NMR spectra of the starting poly(DVB) (A) and the products obtained by the reactions with trimethylchlorosilane (B) and allyl bromide (C). Comparison of these spectra indicates an almost complete quenching of polyanion 2 with the electrophiles. Thus, the methyl (δ 1.4 ppm) and methine peaks (δ 3.6 ppm) of the starting poly(DVB) almost disappeared, in the spectra of the products, which exhibit signals due to the main-chain skeleton of the two isomers (7 and 8) and to the substituents derived from the electrophiles.

The functional yield could be determined from a decrease in the methine protons (δ 3.6 ppm) in the ¹H NMR spectra. As shown in Table I, more than 90 % of the anionic sites of 2 reacted with the added electrophiles except for ethylene oxide.

In conclusion, deprotonation of poly(DVB) 5, followed by treatment of the resulting polyanion 2 with electrophiles, provides an efficient method for the synthesis of functionalized linear poly(DVB).

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LIST OF PUBLICATIONS

CHAPTER 1	Macromolecules, <u>18</u> , 2097 (1985)
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CHAPTER 5	Polym. J., <u>16</u> , 249 (1984)
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