Articles

Living Cationic Polymerization of Vinyl Ethers with a Functional Group. 1. Polymerization of 2-Acetoxyethyl Vinyl Ether and Synthesis of Polyalcohols with a Narrow Molecular Weight Distribution

Sadahito Aoshima, Takayuki Nakamura, Norimasa Uesugi, Mitsuo Sawamoto, and Toshinobu Higashimura*

Department of Polymer Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan. *Received February 20, 1985*

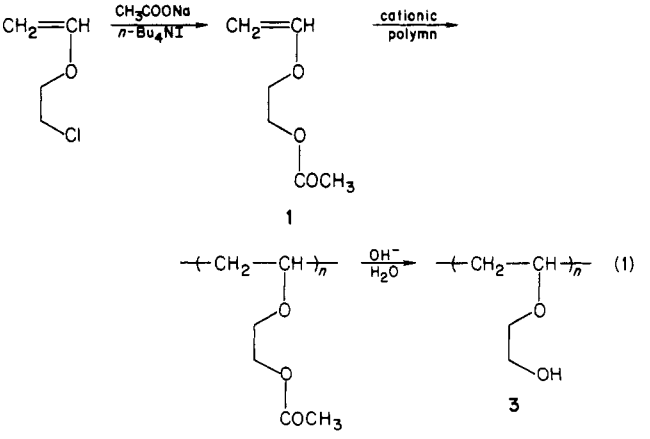
ABSTRACT: "Living" cationic polymerization of 2-acetoxyethyl vinyl ether (AcOVE, CH_2=$CHOCH_2CH_2OCOCH_3$) was achieved by the hydrogen iodide/iodine (HI/I_2) initiating system in toluene at −15 and −40 °C to give polymers with a narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n \leq 1.2$). 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 BF_3OEt_2-catalyzed 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 we started a systematic search of living cationic polymerization of vinyl ethers and related monomers[1] and found that hydrogen iodide combined with iodine (HI/I_2 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 our living systems to vinyl ethers (CH_2=$CHOCH_2CH_2R$) with a polar functional pendant (R) that may adversely affect their polymerization. Substituent R may include ester, alkoxycarbonyl, polyether, substituted phenoxyl, 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-(vinyloxy)ethyl 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 paper of our series 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) [poly(HOVE); 3][6] (eq 1).



We focus on (i) whether the polar ester function of AcOVE affects its cationic polymerization, (ii) the possibility of living polymerization of AcOVE to yield monodisperse poly(AcOVE), and (iii) the synthesis of polyalcohol 3 with controlled molecular weight (distribution) via base-cata-

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lyzed deacetylation (hydrolysis) of poly(AcOVE).

Experimental Section

Materials. 2-Chloroethyl vinyl ether (CEVE) was prepared by partial dehydrochlorination of bis(2-chloroethyl) ether with sodium hydroxide.[7] Boron trifluoride etherate (BF_3OEt_2) was purified by distillation of a commercial product under reduced pressure. Trifluoromethanesulfonic acid (CF_3SO_3H) (Sumitomo 3M, purity >98%) was used as received. Hydrogen iodide was obtained as an *n*-hexane solution (ca. 0.6 M) as reported.[2] Iodine was sublimed at 100 °C in the presence of potassium iodide. Both initiators were stored under dry nitrogen in ampules in the dark. Polymerization solvents and bromobenzene (internal standard for gas chromatography) were purified by the usual methods and distilled over calcium hydride at least twice before use.

Synthesis of AcOVE. This was prepared by the phase-transfer-catalyzed substitution reaction of CEVE with sodium acetate (eq 1).[5] In a 500-mL, three-necked, round-bottomed flask equipped with a reflux condenser, paddle stirrer, drying tube (calcium chloride), 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, 1 H, CH=), ~4 (m, 2 H, CH_2=), 4.2–4.1 and 3.9–3.7 (m, 4 H, OCH_2CH_2O), 2.1 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 170.0 (C=O), 151.1 (CH=), 86.5 (CH_2=), 65.5 and 62.1 (OCH_2CH_2O), 20.2 (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 extracted 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(×2) for the polymers (8.0 mm i.d. × 500 mm each) and JSP-101 for the oligomers (20 mm i.d. × 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 FX-90Q spectrometer. IR spectra (KBr) were recorded on a Shimadzu IR-435 spectrometer.

Table I
Polymerization of AcOVE by Acid Initiators in Toluene at −15 °C[a]

initiator	concn, mM	time, h	conv, %	$\bar{M}_w \times 10^{-3}$ [b]	$\bar{M}_n \times 10^{-3}$ [b]
CF_3SO_3H	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] $[M]_0$ = 10 vol % (0.76 M). [b] By SEC; polystyrene calibration.

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 CF_3SO_3H 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 CF_3SO_3H and BF_3OEt_2 were almost completed within 10 min. The products obtained with CF_3SO_3H 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).

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 × 10^4, $\bar{M}_n$ = 5.0 × 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.

Living Polymerization by HI/I_2 Initiator. The vinyl ethers thus far found to form living polymers with HI/I_2 initiator are all alkyl[2,3] and chloroalkyl[8] 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, we studied the possibility of living polymerization of AcOVE with HI/I_2 and related initiators.

Thus the acetoxy monomer was polymerized in toluene at −15 or −40 °C by HI/I_2 initiator; for comparison, iodine or hydrogen iodide alone and BF_3OEt_2 were also used as initiators. As shown in Figure 1, the polymerizations by HI/I_2 and iodine proceeded without an 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

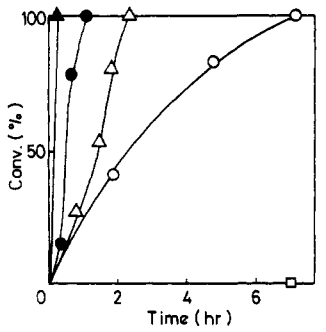


Figure 1. Time–conversion curves for the polymerization of AcOVE in toluene at −15 °C and $[M]_0$ = 5 vol % (0.38 M). Initiator and $[C]_0$ (mM): (▲) BF_3OEt_2, 4.0; (●) HI/I_2, 10/10; (○) HI/I_2, 10/10 (−40 °C); (△) I_2, 20; (□) HI, 10.

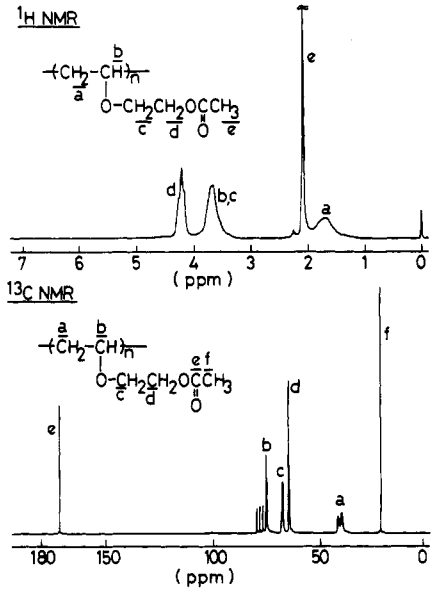


Figure 2. ^1H and ^{13}C NMR spectra of poly(AcOVE) ($\bar{M}_n$ = 12300) obtained with HI/I_2 in toluene at −40 °C: $[M]_0$ = 5 vol % (0.38 M); $[HI]_0$ = 4.1 mM; $[I_2]_0$ = 2.5 mM. Conversion was 100%.

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 ($\bar{M}_w/\bar{M}_n \leq 1.2$) 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/I_2. In contrast, the polymer obtained by BF_3OEt_2 exhibited a much broader MWD extending to molecular weight ca. 10^5. Thus, HI/I_2 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/I_2 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

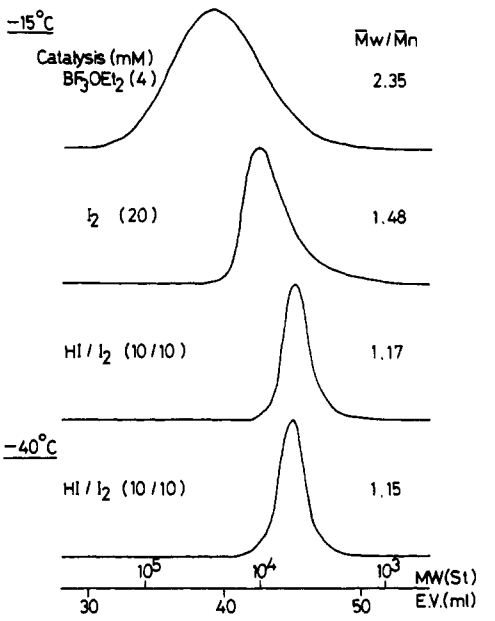


Figure 3. MWD of poly(AcOVE) obtained in toluene at −15 or −40 °C: $[M]_0$ = 5 vol % (0.38 M). Initiators and $\bar{M}_w/\bar{M}_n$ as indicated.

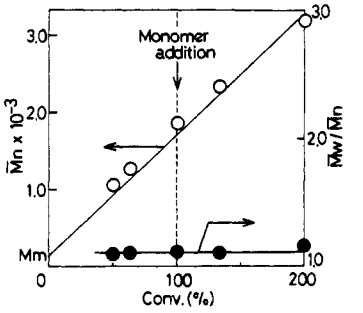


Figure 4. Relationship between conversion and $\bar{M}_n$ or $\bar{M}_w/\bar{M}_n$ ratio before and after the monomer addition in the AcOVE polymerization by HI/I_2 in toluene at −40 °C: $[M]_0 = [M]_{add}$ = 0.20 M; $[HI]_0$ = 24 mM; $[I_2]_0$ = 20 mM. M_m indicates the molecular weight of AcOVE monomer.

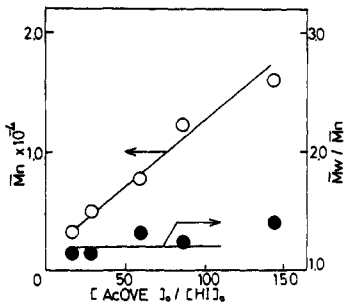


Figure 5. $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ ratio as functions of the monomer-to-initiator feed ratio $[M]_0/[HI]_0$ in the AcOVE polymerization by HI/I_2 in toluene at −40 °C, conversion ~ 100%.

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

Table II
Solubility of Poly(2-hydroxyethyl vinyl ether) 3 and Related Polymers $-(CH_2CHX)_n-$

	X = OH[a] 5[b]	X = $O(CH_2)_2OH$ 3	X = $CH(OH)CH_3$[a] 6[c]	X = $O(CH_2)_2OCOCH_3$ 2
		Repeat Unit		
formula	C_2H_4O	$C_4H_8O_2$	C_4H_8O	$C_6H_{10}O_3$
C/O	2/1	2/1	4/1	2/1
C/OH	2/1	4/1	4/1	6/0
		Polymer Solubility[d]		
H_2O	○	○	×	×
CH_3OH	×	△	○	×
dioxane	×	×	○	○
THF	×	×	○	○
acetone	×	×		○
CH_2Cl_2	×	×		○

[a] Reference 12. [b] Poly(vinyl alcohol). [c] Poly(2-hydroxy-3-butene). [d] (○) soluble, (△) swelling, (×) insoluble. The solubilities of 2 and 3 were measured on 1% (w/v) solutions at room temperature.

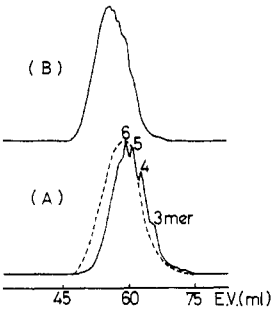


Figure 6. MWD of AcOVE oligomers obtained by HI/I_2 in toluene at −40 °C: (A) $[M]_0$ = 0.10 M, $[HI]_0$ = 20 mM, $[I_2]_0$ = 20 mM, $\bar{M}_w/\bar{M}_n$ = 1.17; (B) $[M]_0$ = 0.20 M, $[HI]_0$ = 22 mM, $[I_2]_0$ = 20 mM, $\bar{M}_w/\bar{M}_n$ = 1.12. (---) Poisson distribution with the same peak molecular weight as that of oligomer A.

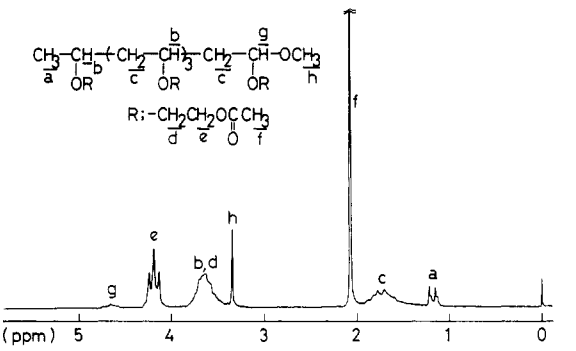


Figure 7. ^1H NMR spectrum of oligomer A shown in Figure 6A.

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.

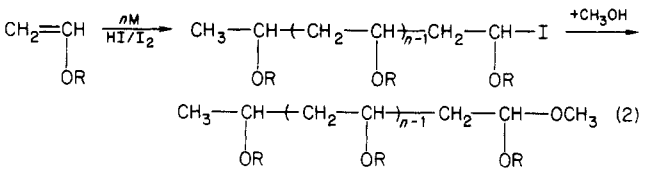
These results demonstrate the formation of "living"[9,10] polymers from AcOVE by HI/I_2 initiator. It should be emphasized that living cationic polymerization is possible with HI/I_2 initiator even for a vinyl monomer with a polar ester group.

Living Oligomers and End-Group Analysis. In the course of our study, we found that HI/I_2-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 (5.0 and 9.1). 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 6A exemplifies this agreement, where the broken-line curve indicates the calculated Poisson distribution.

Figure 7 presents the ^1H NMR spectrum of oligomer A 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 ($CH_3CH(OR)$; R=$CH_2CH_2OCOCH_3$); the triplet (g) at 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 ($CH_2CH(OR)OCH_3$).

According to our recent mechanistic study on the HI/I_2-initiated polymerization,[11] the propagating living end consists of a $-CH(OR')-I$ 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 C=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 $[-CH_2CH(OR)-]$ to the head methyl or tail methoxyl protons gave the number-average degree of polymerization ($\bar{P}_n$) of oligomer B (=8.5), which was in good agreement with the $[M]_0/[HI]_0$ 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 × 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

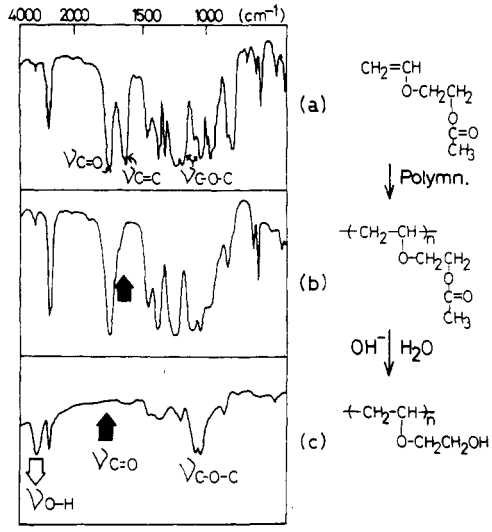


Figure 8. Hydrolysis of poly(AcOVE) monitored by IR spectroscopy: (a) AcOVE monomer; (b) poly(AcOVE) ($\bar{M}_w$ = 11.0 × 10^4) prepared with BF_3OEt_2; (c) hydrolysis product [poly(HOVE)] from sample b.

spectra expected for poly(HOVE): ^{1}H NMR (D_2O) δ 3.9 (m, 5 H, $CHOCH_2CH_2O$), 2.0 (m, 2 H, CCH_2C); ^{13}C NMR (D_2O) δ 74.8 (CH), 70.2 (CH_2OH), 61.6 (OCH_2), 40.7 and 39.1 (CCH_2C). 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).

Registry No. **1**, 6026-79-5; **2**, 31742-55-9; CEVE, 110-75-8; sodium acetate, 127-09-3; hydrogen iodide, 10034-85-2; iodine, 7553-56-2.

References and Notes

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(9) In the following part of this paper, 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 our 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 10 000.[10]
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Polymerization of Monomers Containing Functional Silyl Groups. 1. Anionic Living Polymerization of (4-Vinylphenyl)dimethyl-2-propoxysilane

Akira Hirao, Takahiro Nagawa, Toshio Hatayama, Kazuo Yamaguchi, and Seiichi Nakahama*

Department of Polymer Chemistry, Faculty of Engineering, 2-12-1, Ohokayama, Meguro-ku, Tokyo 152, Japan. *Received January 24, 1985*

ABSTRACT: Anionic polymerization of (4-vinylphenyl)dimethyl-2-propoxysilane (**4**) was investigated under various conditions: at −78, 0, and +30 °C in THF with lithium and potassium as the countercation. **4** has been readily polymerized by either oligo(α-methylstyryl)lithium or -potassium to form polymers of any desired molecular weight with narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n$ = 1.04–1.1). The propagating active end of the polymer with potassium cation is found to be stable at −78 °C for 24 h. The glass transition temperature and solubility of the resulting polymer were measured. Cross-linking of the polymer through hydrolysis of pendant alkoxysilyl groups was examined.

Introduction

A variety of applications of organic–inorganic composite materials have been developed in recent years. Polymers having alkoxysilyl functions have attracted special interest in this regard because they may be used for the purpose of grafting polymers onto inorganic solid surfaces like silica and metal oxides as well as for cross-linking between polymer chains through hydrolysis of alkoxysilyl groups

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