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Living Cationic Polymerization of Vinyl Ethers with a Functional Group

5. Vinyl Ethers with Oxyethylene Units in the Pendant

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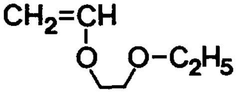
SUMMARY

Vinyl ethers having oxyethylene units [$CH_2{=}CHO{-}(CH_2CH_2O)_n{-}C_2H_5$, n =1-4] were cleanly polymerized by the HI/I2 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 (poly)ether-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.

INTRODUCTION

In the cationic polymerization of styrene by Lewis acids, ethers (1) 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, we have recently found (4,5) that vinyl ethers with an ester pendant group cleanly form "living" polymers in the presence of the HI/I_2 initiator (6-8). 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).



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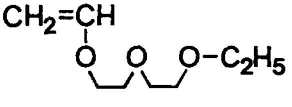

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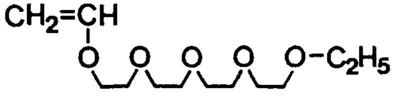

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In this study, we now turn our attention to vinyl ethers 1 - 3 containing oxyethylene units in the pendant, as another class of vinyl ethers whose substituents may result in frequent chain-transfer reactions. Our first objective was to examine the possibility of living cationic polymerization of 1 - 3 , focusing on the effects of their potentially deleterious (poly)ether pendants.

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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). We now report, in this paper, the successful living polymerization of vinyl ethers **1** - **3** initiated by a mixture of hydrogen iodide and iodine (HI/I_2) to give well-controlled comb-like polymers of unique solubility characteristics.

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 hour. Figure 1 shows the MWD of the poly **1**—poly **3** thus prepared (conversion~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 ($[M]_0/[HI]_0$) (Figure 3). Similar results were obtained for **3**.

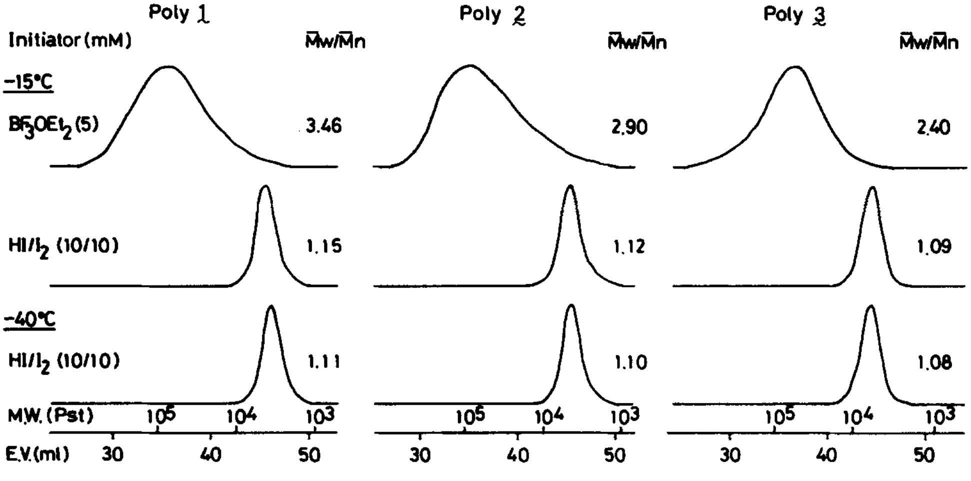


Figure 1. MWDs of poly **1**—poly **3** obtained with BF_3OEt_2 and HI/I_2: $[M]_0$ = 5vol%; conversion~100%.

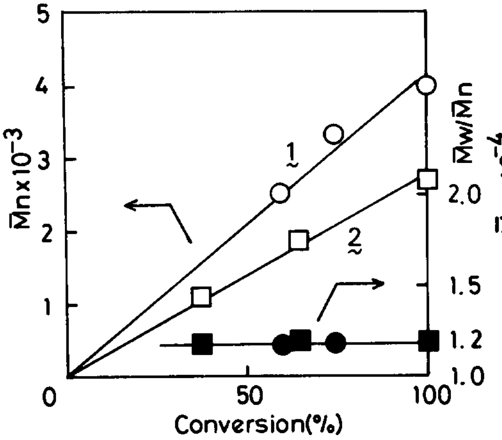


Figure 2. Relationship between conversion and $\overline{Mn}$ or $\overline{Mw}/\overline{Mn}$ ratio in the polymerization of 1 and 2 by HI/I_2 in toluene at -40°C: $[M]_0$ =5vol%; $[HI]_0$ =10mM; $[I_2]_0$ =2mM.

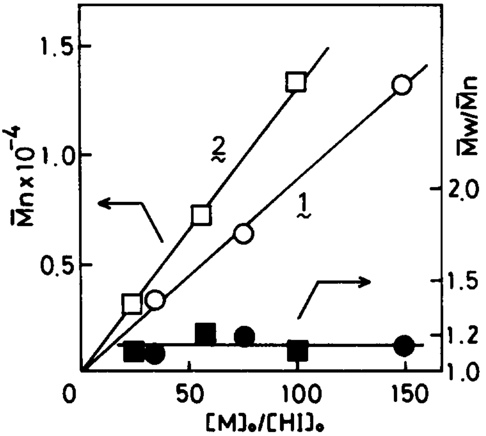


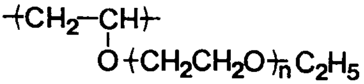
Figure 3. $\overline{Mn}$ and $\overline{Mw}/\overline{Mn}$ ratio as a function of the monomer-to-initiator feed ratio ($[M]_0/[HI]_0$) in the polymerizations of 1 and 2 by HI/I_2 in toluene at -40°C; conversion∼100%.

These facts show the formation of "living-like" polymers with a sufficiently long lifetime from vinyl ethers 1 - 3. These 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 $\overline{Mn}$-conversion plot for the first-stage polymerization (cf. Figure 2). Furthermore, the MWD of poly 1 – poly 3 ($\overline{Mw}/\overline{Mn}$ ≤ 1.2; Figures 1 and 2) is somewhat broader than those of living poly(alkyl vinyl ethers) ($\overline{Mw}/\overline{Mn}$ ≤ 1.1), and it becomes even broader after the monomer addition.

Polymer Structure and Solubility

The structure of poly 1 – poly 3 was studied by ^{1}H 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 spectrum of poly 2, the absorptions of the vinyloxyl group of 2 are absent [86.0 (CH_2=) and 151.3 ppm (CH=)], the backbone saturated carbons are clearly observable [39.3, 41.0 ($-CH_2-$) 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 HI/I_2 initiator were proved to give polymer 4.

Table 1 compares the solubility characteristics of poly 1 – poly 3 and poly(ethyl vinyl ether) at room temperature. All these polymers are soluble


$$-\!\!\left(CH_2-\underset{O(CH_2CH_2O)_nC_2H_5}{\underset{|}{CH}} \right)\!\!-$$

n = 1,2,4 4

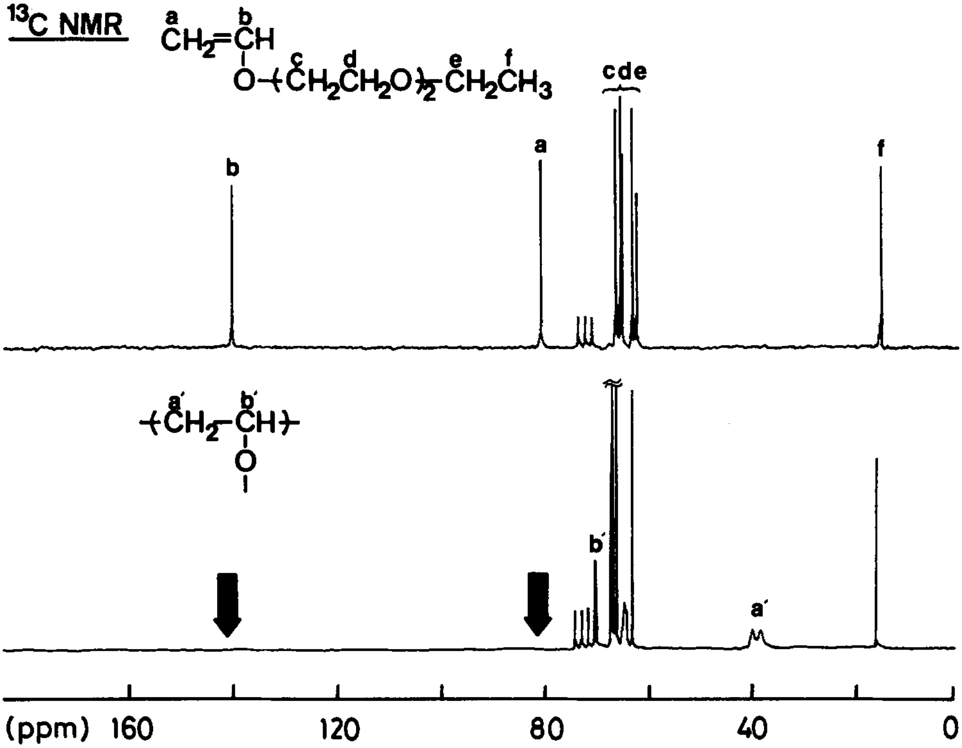
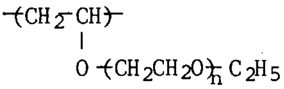


Figure 4. ^{13}C NMR spectra of 2 and poly 2 obtained with HI/I_2 in toluene at -40°C (cf. Figure 1).

TABLE I

Solubility[a] of Poly(Vinyl Ethers): Dependence on the Number of Ether Oxygens in the Pendant.



$-(CH_2-CH)-$ with $O-(CH_2CH_2O)_n-C_2H_5$ on CH

Solvent	n =0	n =1	n ≥2
toluene, CH_2Cl_2	sol	sol	sol
acetone, ether	sol	sol	sol
CH_3OH	insol	sol	sol
H_2O	insol	insol	sol

a) room temperature

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 more than two oxyethylene units per pendant, are soluble not only in methanol but also in water irrespective of their molecular weight. Thus the solubility of poly 1 – poly 3 clearly depends on the number of oxyethylene units in the pendant.

Reactivity of Vinyl Ethers 1 - 3

The rate of the HI/I_2-initiated polymerization of 2 was compared with those of ethyl vinyl ether (CH_2=CHO-C_2H_5, 5) and 2-acetoxyethyl vinyl ether (CH_2=CHO-$CH_2CH_2OCOCH_3$, 6). As shown in Figure 5, the polymerization rates of the three vinyl ethers (CH_2=CH-OR) clearly depended on the substituents R and decreased in the order: 2 (R=$CH_2CH_2OCH_2CH_2OC_2H_5$) > 5 (R=C_2H_5) > 6 (R=$CH_2CH_2OCOCH_3$); 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, we propose 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 : 2, 86.0 (CH_2=) and 151.3 ppm (CH=); 5, 86.0 and 151.6 ppm; 6, 86.5 and 151.1 ppm (in $CDCl_3$). Thus, the electron densities (or 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 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/I_2 (Figure 6), again indicating the similarity of 2 and 5 in polymerization reactivity.

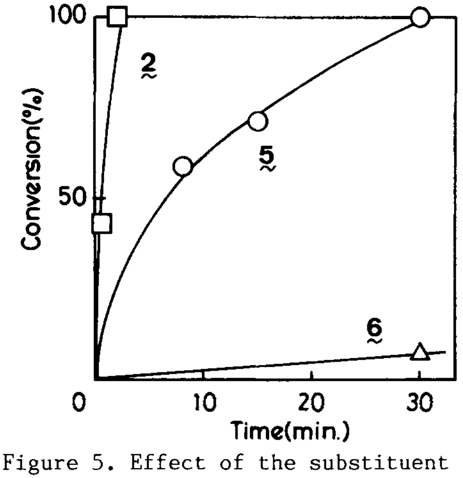


Figure 5. Effect of the substituent (R) on the polymerization rates of vinyl ethers(CH_2=CH-OR) by HI/I_2 in toluene at -40°C.
R: A, $-(CH_2CH_2O)_n C_2H_5$ (2)
B, $-C_2H_5$ (5)
C, $-CH_2CH_2OCOCH_3$ (6)

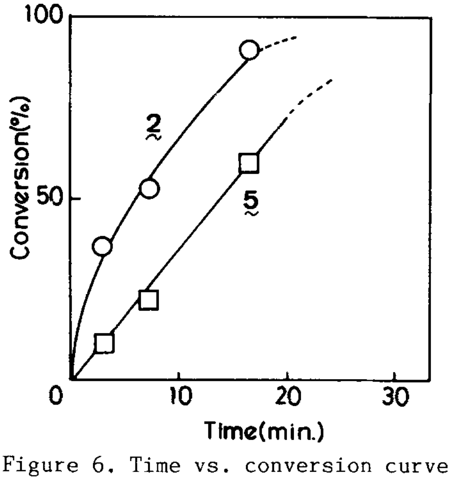


Figure 6. Time vs. conversion curves for the copolymerization between 2 and 5 by HI/I_2 in toluene at -40°C: $[2]_0$ = $[5]_0$ =0.25M each; $[HI]_0$ =10mM; $[I_2]_0$ =4mM.

Steric Structure of the Polymers

To find evidence for the activation of the propagating species derived from monomers 1 - 3, we then compared, by ^{13}C NMR spectroscopy, the steric structure of poly 2 and poly 5, both obtained by HI/I_2 initiator at -40°C. Figure 7 shows the main-chain methylene signals, which consist of two peaks assignable to the meso and racemic diads from the higher field (12).

The spectrum of poly 2 (Figure 7C) obtained in nonpolar toluene solvent is similar to that of poly 5 (Figure 7B) prepared in a more polar medium, nitroethane; both polymers consist of comparable amounts of the meso and racemic diads. The poly 2, however, clearly differs in steric structure from poly 5 (Figure 7A) obtained in the same solvent (toluene), the latter having a higher meso content. The similarity between Figure 7, B 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. We propose, 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.

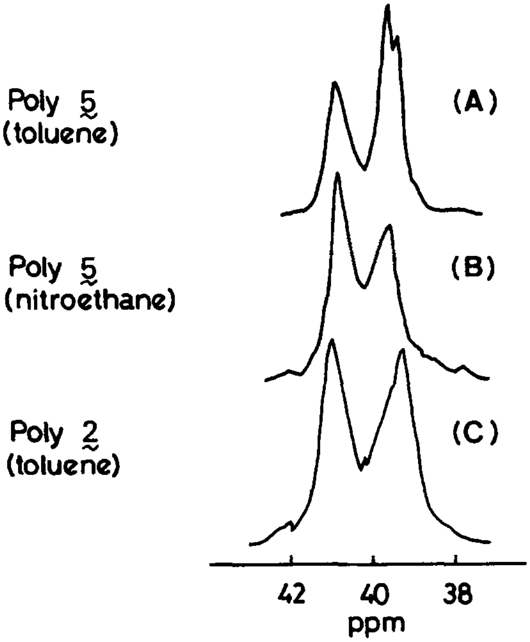


Figure 7. Partial ^{13}C NMR spectra (main-chain methylene region) of poly 5 and poly 2 obtained with HI/I_2 at -40°C. Polymer and polymerization solvent: (A) poly 5, toluene; (B) poly 5, nitroethane; (C) poly 2, toluene. The $\bar{M}$ns of these polymers are $(5-10)\times10^3$ (by size exclusion chromatography).

EXPERIMENTAL

Materials

The monomers **1** - **3** were synthesized by substitution reactions of 2-chloroethyl vinyl ether, in the presence of nBu_4NI, 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 (4,6). The MWD of the product polymers were measured by size-exclusion chromatography in chloroform on a Jasco Trirotar-II chromatograph equipped with three polystyrene gel columns (Shodex A-802, A-804, and A-804). The $\overline{M}n$ and $\overline{M}w/\overline{M}n$ ratio were determined on the basis of a polystyrene calibration. ^{13}C NMR spectra were measured on a JEOL FX90Q spectometer (22.5 MHz) in $CDCl_3$, at room temperature.

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