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CATIONIC POLYMERIZATION OF VINYL ETHERS WITH A BENZOATE OR PHENYLACETATE PENDANT: SYNTHESIS OF NEW POLY(CARBOXYLIC ACID)S WITH POLY(VINYL ETHER) BACKBONE

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NOTE

CATIONIC POLYMERIZATION OF VINYL ETHERS WITH A BENZOATE OR PHENYLACETATE PENDANT: SYNTHESIS OF NEW POLY(CARBOXYLIC ACID)S WITH POLY(VINYL ETHER) BACKBONE

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Key Words: Poly(carboxylic Acid), Cationic Polymerization, Vinyl Ether, Benzoic Acid, Phenylacetic Acid, Solubility Characteristics

INTRODUCTION

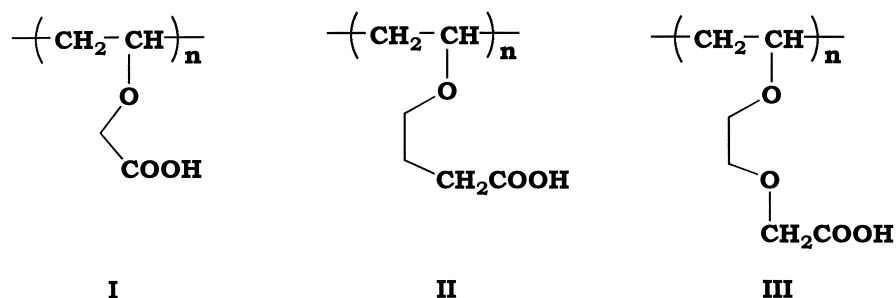
A variety of poly(carboxylic acid)s and their crosslinking forms are known and many of them are produced commercially. Poly(carboxylic acid)s has been prepared mainly by radical polymerization of vinyl monomers with a carboxyl group [1]. Recently, it was reported that anionic polymerization of vinyl monomers with a protected carboxyl group and the subsequent deprotection reaction of the resultant polymer led to well-defined poly(carboxylic acid)s [2].

This study concerns the synthesis of new poly(carboxylic acid)s by cationic polymerization. Vinyl ether is a monomer that can form high-molecular-weight polymer only by cationic mechanism. The reported examples of

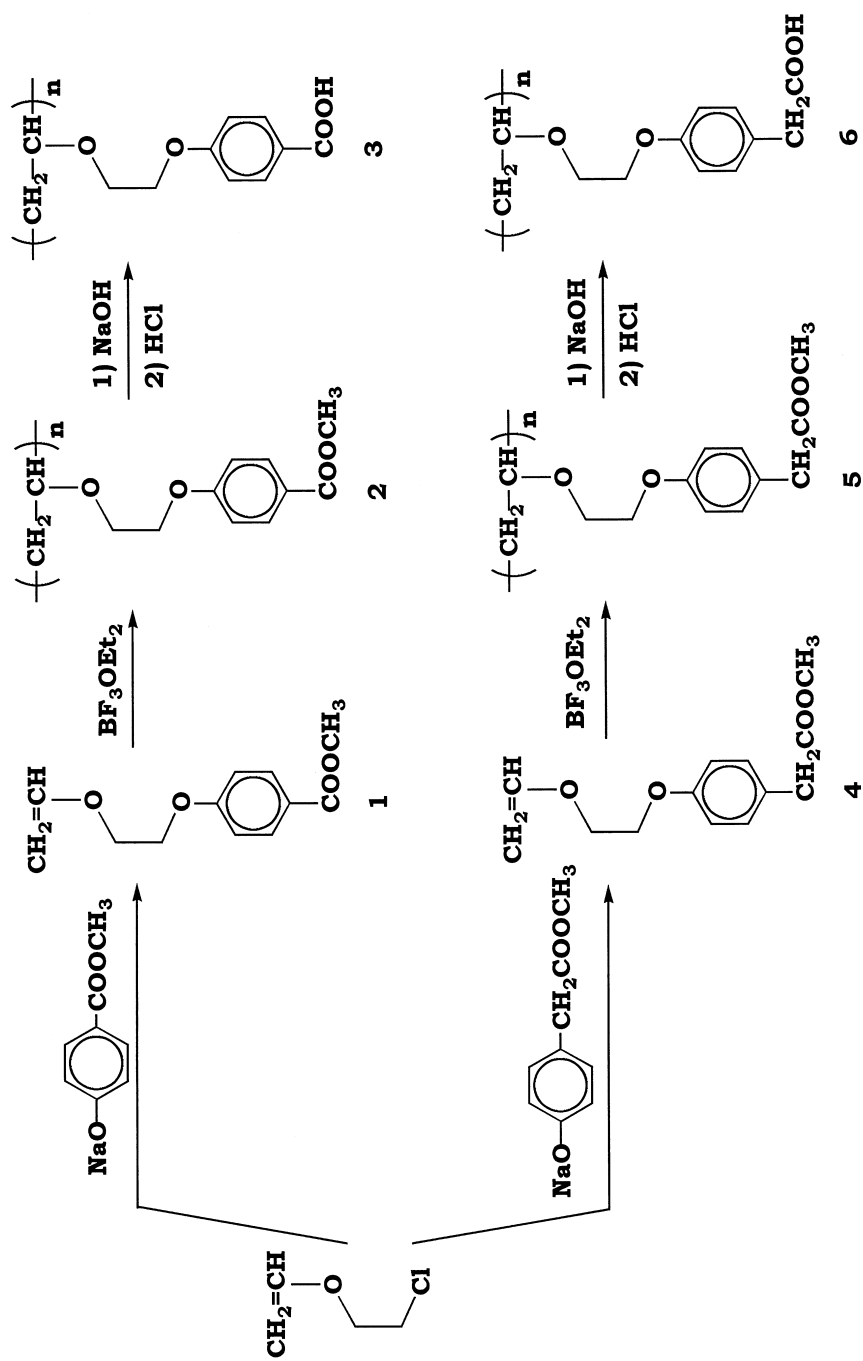
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poly(carboxylic acid)s with poly(vinyl ether) backbone include polymers I-III (Scheme 1). Polymer I [3] and III [4] were prepared by the cationic polymerization of vinyl ethers with the corresponding carboxylic ester pendant followed by the hydrolysis of the ester pendants of the obtained polymers. Synthesis of the two monomers, however, require either multi-stepped reaction procedures [3, 4] or the use of toxic mercuric salt as a catalyst [5, 6]. Polymer II [7] was obtained from a vinyl ether with a malonate pendant, which is produced by a relatively simple reaction based on the classical malonic ester synthesis, but in turn, the conversion of the malonate function in the polymer pendants into the monocarboxylic acid form need not only the hydrolysis reaction but also the decarboxylation process. Thus, the sort of the poly(carboxylic acid)s with poly(vinyl ether) backbone has been limited so far, and their synthetic routes are rather cumbersome.

In this study, we designed new vinyl ethers (**1** and **4**) that would be easily prepared and afford poly(carboxylic acid)s (**3** and **6**) via a simple hydrolysis reaction of the corresponding ester polymers (**2** and **5**) (Scheme 2). Polymers **3** and **6** differ from the reported acid polymers I-III in that both **3** and **6** have benzene ring spacers between the polymer main chains and the carboxylate moieties. Introduction of a benzene ring into the polymer pendant chain usually elevate a glass transition temperature of vinyl polymers; for example, T_g [8]: poly(methyl acrylate) 10°C vs. poly(4-methoxycarbonylstyrene) 113°C; poly(methyl vinyl ether) -31°C vs. poly(4-methoxystyrene) 113°C. Thus, poly(vinyl ether)s **3** and **6** may possess suitable physical properties for practical use especially at high temperature rather than the reported acid poly(vinyl ether)s **I-III**. As a result, cationic polymerization of **1** and **4** with BF₃OEt₂ initiator gave high-molecular-weight polymers **2** and **5** in high yield and the alkaline treatment cleanly converted **2** and **5** into poly(carboxylic acid)s **3** and **6**.



Scheme 1.



Scheme 2.

EXPERIMENTAL

Synthesis of 1

This monomer was synthesized by the nucleophilic substitution reaction of 2-chloroethyl vinyl ether with sodium *p*-methoxycarbonylphenoxide. The sodium salt was prepared as follows: commercial sodium hydride (as 60-72 wt% dispersion in mineral oil; 4.0 g, ca. 0.10 mol) was first washed by distilled tetrahydrofuran (THF) several times to remove the oil. In a 500 ml round-bottom flask fitted with a stirrer was charged with methyl *p*-hydroxybenzoate (15.2 g, 0.10 mol) and distilled THF (300 mL). The purified NaH was added slowly to the mixture with stirring during which hydrogen gas evolved. The precipitated salt was collected by filtration and purified by washing with THF (isolated yield, ca. 90%).

Then, the obtained salt was subjected to the reaction with 2-chloroethyl vinyl ether. In a 300-ml round-bottom flask fitted with a stirrer, a reflux condenser and a dropping funnel were charged with sodium *p*-methoxycarbonylphenoxide (16 g, 0.092 mol), tetra-*n*-butylammonium bromide (1.0 g), and *N,N*-dimethyl formamide (DMF) (50 mL). 2-chloroethyl vinyl ether (19.5 mL; 0.18 mol) was added dropwise to the mixture through the dropping funnel with stirring. After the addition was completed, the mixture was warmed to 100°C, stirred at this temperature for 6 hours, cooled down to room temperature, and poured into 1 L of water. The product monomer precipitated as white solid and was collected by filtration. The crude monomer was purified by recrystallization from *n*-hexane (isolated yield, ca. 50%); ¹H NMR: see Figure 1(A); ¹³C NMR (in CDCl₃): δ 51.9 (C-CH₃), 66.2, 66.5 (O-C-CH₂-C-CH₂-O), 87.2 (C-CH₂=), 114.2, 123.1, 131.6, 162.3 (C₆H₅), 151.5 (=C-H-O), 166.8 (C=O).

Synthesis of 4

This monomer was synthesized by the nucleophilic substitution reaction of 2-chloroethyl vinyl ether with sodium *p*-methoxycarbonylmethylphenoxide. The sodium salt was prepared by the reaction of methyl *p*-hydroxyphenylacetic acid (26.6 g, 0.16 mol) with NaH (ca. 0.16 mol) in DMF (150 mL) in a similar way for the synthesis of sodium *p*-methoxycarbonylphenoxide described above. The obtained solution of the salt in DMF was directly used for the subsequent reaction.

In a 300 ml round-bottom flask fitted with a stirrer, a reflux condenser and a dropping funnel were charged with the solution of sodium *p*-methoxycarbonylmethylphenoxide (ca. 0.16 mol) and tetra-*n*-butylammonium bromide (1.0 g). 2-Chloroethyl vinyl ether (30 mL; 0.29 mol) was added dropwise to the mixture through the dropping funnel with stirring. After the addition was completed, the mixture was warmed to 100°C, stirred at this temperature for 6 hours, cooled down to room temperature, and poured into 1 L of water. The oil phase was collected, washed by water, and fractionally distilled twice under reduced pressure in the presence of hydroquinone to give monomer **4** (isolated yield, ca. 22%): bp 140°C/0.12 mmHg; density, 1.12 g/cm³; ¹H NMR: see Figure 2(A); ¹³C NMR (in CDCl₃): δ 40.3 (CH₂-CO), 52.0 (CH₃), 66.4, 66.5 (O-CH₂-CH₂-O), 87.1 (CH₂=), 114.8, 126.6, 130.3, 157.8 (C₆H₅), 151.6 (=CH-O), 172.3 (COO).

Other Materials

Tetrahydronaphthalene (internal standard for gas chromatography) and methylene dichloride (polymerization solvent) was purified before use as described elsewhere [9, 10]. BF₃OEt₂ (Aldrich, distilled) was used as received.

Polymerization of **1** and **4**: Synthesis of **2** and **5**

Polymerization of **1** and **4** was performed under dry nitrogen in a glass tube equipped with a three-way stopcock [9, 10]. The reaction was initiated by adding a prechilled solution of BF₃OEt₂ to the monomer solution containing tetrahydronaphthalene. The polymerization was terminated with ammoniacal methanol. Monomer conversion was determined from the residual monomer concentration measured by gas chromatography with tetrahydronaphthalene as an internal standard.

The reaction mixture was diluted with methylene chloride, washed with de-ionized water, and evaporated to dryness under reduced pressure to give the product polymers. To obtain the samples for NMR structural analysis, these polymers were further purified by reprecipitation in methanol from methylene chloride; polymer **2**: ¹H NMR: see Figure 1(B); ¹³C NMR (in CDCl₃): δ 38-42

(CH-CH₂-CH), 51.8 (CH₃), 67.1, 67.7 (O-CH₂-CH₂-O), 74.2 (CH₂-CH-O), 114.1, 122.8, 131.5, 162.5 (C₆H₅), 166.6 (COO); polymer **5**: ¹H NMR: see Figure 2(B);

¹³C NMR (in CDCl₃): δ 38-42 (CH-CH₂-CH), 40.1 (CH₂-CO), 51.9 (CH₃), 67.2, 67.6

(O- $\underline{\text{C}}\text{H}_2\text{-}\underline{\text{C}}\text{H}_2\text{-O}$), 74.3 ($\text{C}\text{H}_2\text{-}\underline{\text{C}}\text{H-O}$), 114.6, 126.1, 130.3, 158.0 ($\underline{\text{C}}_6\text{H}_5$), 172.2 ($\underline{\text{C}}\text{OO}$).

Hydrolysis of Polymer 2: Synthesis of Polymer 3

To a solution of precursor polymer **2** (0.35 g) in DMF (30 ml) was added sodium hydroxide (0.32 g, 5 equiv. to the COOEt units in the sample) with 0.5 ml of water, and the mixture was stirred overnight. The filtrate was evaporated to dryness, the residue containing the resulting sodium salt was dissolved in water (40 mL), and the resultant solution was filtrated to remove any suspended solid present. Then, the solution was neutralized with 0.2 mol/L-hydrochloric acid, from which the acid polymer precipitated. The precipitated polymer was collected by filtration and dried under reduced pressure. The polymer was further purified by reprecipitation in methanol from DMSO (isolated yield, ca. 70%): ^1H NMR: see Figure 1(C); ^{13}C NMR (in DMSO- d_6): δ 38-42 ($\text{C}\text{H-}\underline{\text{C}}\text{H}_2\text{-}\underline{\text{C}}\text{H}$, overlapping with the solvent peaks), 66.2, 67.5 (O- $\underline{\text{C}}\text{H}_2\text{-}\underline{\text{C}}\text{H}_2\text{-O}$), 73.4 ($\text{C}\text{H}_2\text{-}\underline{\text{C}}\text{H-O}$), 113.9, 123.1, 131.2, 161.9 ($\underline{\text{C}}_6\text{H}_5$), 167.0 ($\underline{\text{C}}\text{OO}$).

Hydrolysis of Polymer 5: Synthesis of Polymer 6

To a solution of precursor polymer **5** (0.50 g) in DMF (30 mL) was added sodium hydroxide (0.42 g, 5 equiv. to the COOEt units in the sample) with 0.5 ml of water, and the mixture was stirred overnight. The subsequent procedures were carried out in a similar way to that for the hydrolysis of **2** described above. Polymer **6** was obtained as a white solid powder and purified by washing with water (isolated yield, ca. 70%): ^1H NMR: see Figure 2(C); ^{13}C NMR (in DMSO- d_6): δ 38-42 ($\text{C}\text{H-}\underline{\text{C}}\text{H}_2\text{-}\text{C}\text{H}$, overlapping with the solvent peaks), ~ 40 ($\underline{\text{C}}\text{H}_2\text{-CO}$, overlapping with the solvent peaks), 66.4, 67.2 (O- $\underline{\text{C}}\text{H}_2\text{-}\underline{\text{C}}\text{H}_2\text{-O}$), 73.6 ($\text{C}\text{H}_2\text{-}\underline{\text{C}}\text{H-O}$), 114.1, 126.8, 130.2, 157.2 ($\underline{\text{C}}_6\text{H}_5$), 172.8 ($\underline{\text{C}}\text{OO}$).

Measurements

The molecular weight distribution (MWD) of the polymers were measured by means of gel-permeation chromatography (GPC) in tetrahydrofuran at 38°C on a Shimadzu LC-10AD chromatograph equipped with polystyrene gel column and a refractive index detector [9, 10]. The number-average molecular weight (\overline{M}_n) and polydispersity ratio ($\overline{M}_w / \overline{M}_n$) were calculated from chromatograms based on a polystyrene calibration. $^1\text{H-NMR}$ (500 MHz) and $^{13}\text{C-NMR}$ (125 MHz) spectra were recorded on Jeol LA-500 instrument in CDCl_3 at room temperature with tetramethylsilane as an internal standard.

RESULTS AND DISCUSSION

Table 1 shows the results of cationic polymerizations of monomer **1** and **4** with BF_3OEt_2 as a Lewis acid initiator in methylene chloride solvent at low temperatures (-40 – -78°C). Both the polymerizations proceeded up to high yield (100-82%) and gave polymers of relatively high molecular weights ($> 4 \times 10^4$). The broad molecular weight distributions of the obtained polymers may be due to the occurrence of chain transfer reaction.

Figure 1A and B shows the ^1H NMR spectra of monomer **1** and its polymer thus obtained, respectively. In Figure 1B, the vinyl proton resonances of **1** (peaks **a** and **b** in Figure 1A) disappeared (shown by the thick arrows), and a new broad absorption **a** is seen around δ 1.6 which is assigned to the main-chain methylene groups. The signal due to the pendant benzoate methyl group (**g**) and aromatic protons (**e** and **f**) remain intact. No signals due to by-products and/or side reactions of the pendant functional groups were observed. Thus, the polymer possesses the structure **2**.

Figure 1C illustrates the ^1H NMR spectrum of the polymer produced by the treatment of polymer **2** with aqueous NaOH (see Experimental). Comparison between the spectra of the precursor polymer (B) and of the product (C) shows the conversion of the pendant benzoate groups into the corresponding acid groups. In spectrum C, the ester absorption (peak **g** in Figure 1B) is absent (shown by the thick arrow), whereas no changes occurred in the other absorptions (peaks **a** - **f**). The structure **3** was also established by ^{13}C NMR analysis; the signal of the ester methyl carbon (δ 51.8 ppm for polymer **2**) completely disappeared and the other carbons resonated at similar positions as those of polymer **2** (see Experimental).

TABLE 1. Cationic Polymerization of Monomers **1** and **4** in CH_2Cl_2 with BF_3OEt_2 ^a

| Monomer | Temperature, $^\circ\text{C}$ | Conversion, % | \bar{M}_n ^b | \bar{M}_w/\bar{M}_n ^b |
|----------|-------------------------------|---------------|--------------------------|------------------------------------|
| 1 | -40 | 100 | 46500 | 4.67 |
| 4 | -78 | 82 | 45300 | 2.40 |

a) $[\mathbf{1}]_0 = [\mathbf{4}]_0 = 0.30\text{M}$; $[\text{BF}_3\text{OEt}_2]_0 = 5.0 \text{ mM}$; polymerization time, 1h.

b) Measured by GPC (polystyrene calibration).

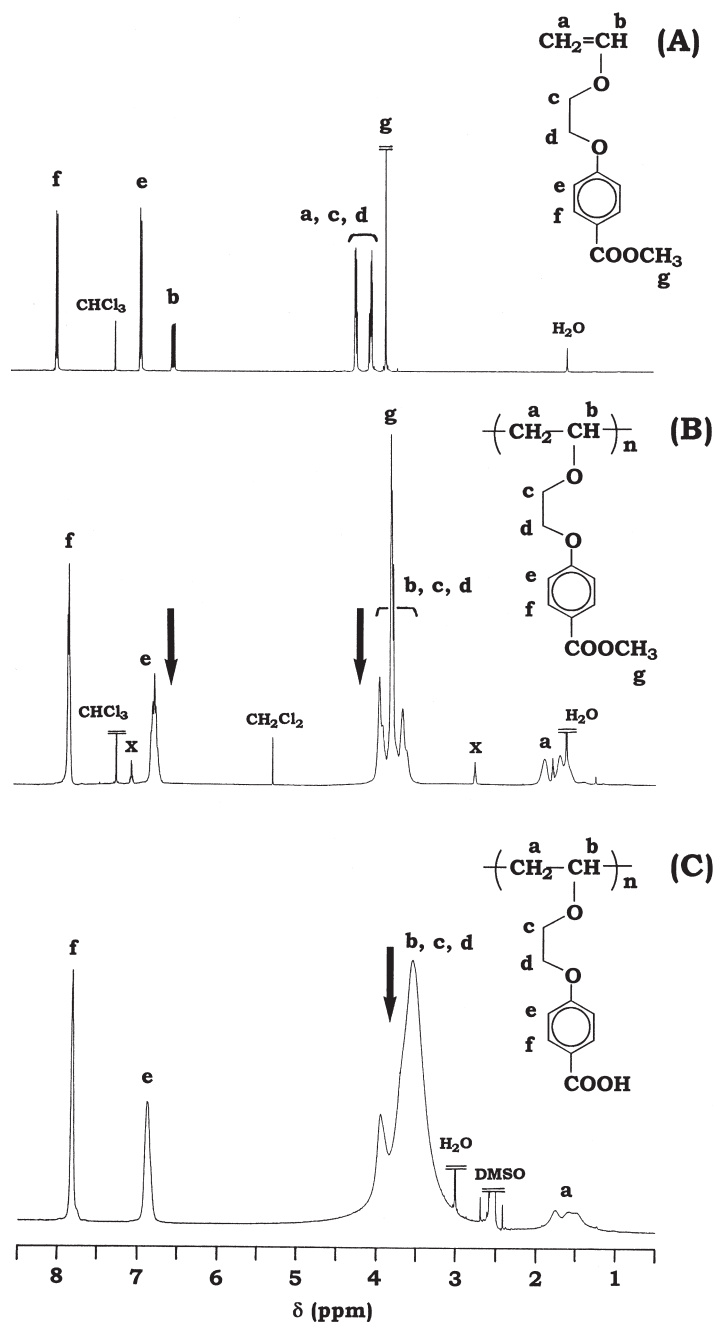


Figure 1. ^1H NMR spectra in CDCl_3 (A and B) and in $\text{DMSO}-d_6$ (C): (A) monomer **1**; (B) polymer **2** ($\bar{M}_n = 46500$, $\bar{M}_w / \bar{M}_n = 4.67$); (C) polymer **3** obtained from sample B. The signals marked X are due to the unremoved tetrahydronaphthalene (internal standard for gas chromatography).

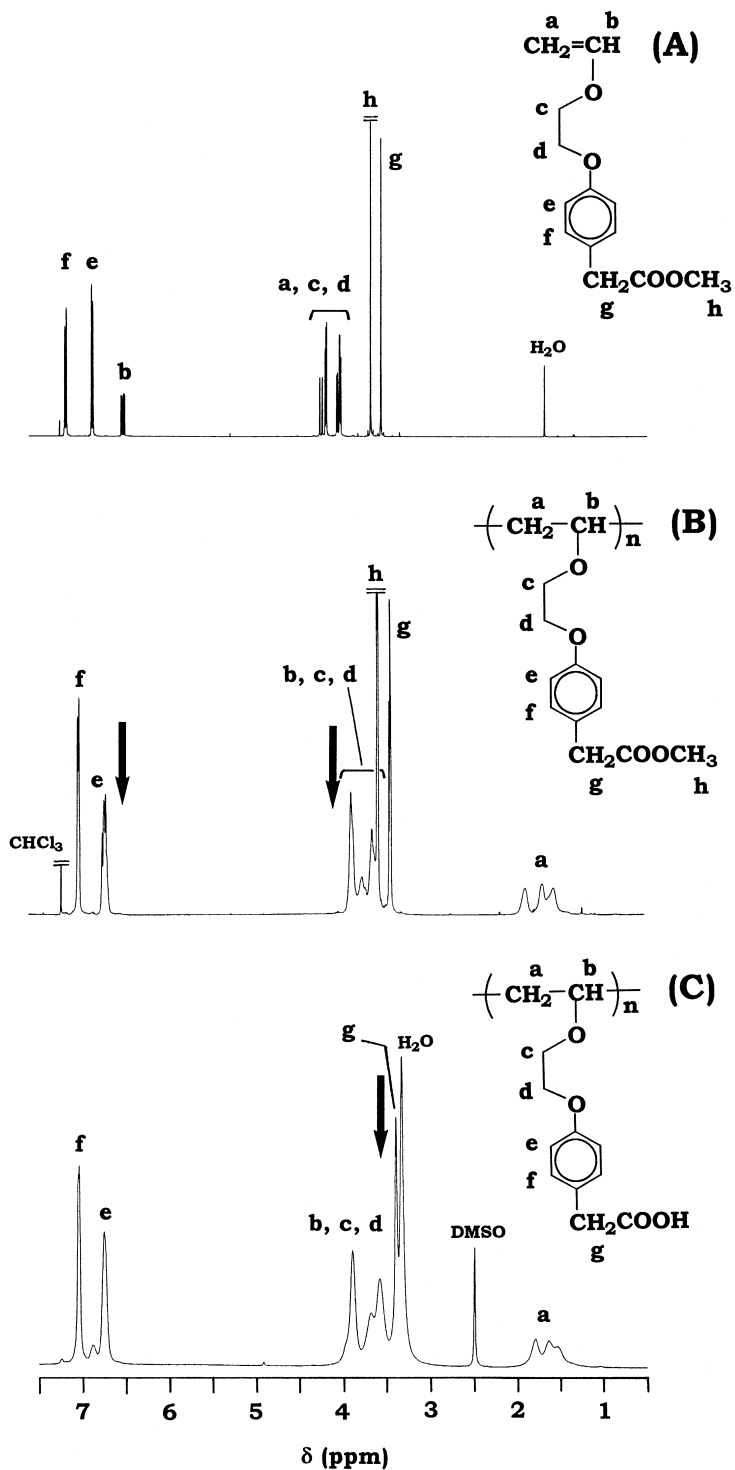


Figure 2. ^1H NMR spectra in CDCl_3 (A and B) and in $\text{DMSO}-d_6$ (C): (A) monomer **4**; (B) polymer **5** ($M_n = 45300$, $M_w / M_n = 2.40$); (C) polymer **6** obtained sample B.

TABLE 2. Solubility of Polymers^a

| Solvent | ϵ^b | Polymer | | | |
|---------------------------------|--------------|-----------------------|-----------------------|-----------------------|-----------------------|
| | | 2 ^c | 3 ^d | 5 ^e | 6 ^f |
| <i>n</i> -Hexane | 1.8799 | X | X | X | X |
| Toluene | 2.379 | O | X | O | X |
| Chloroform | 4.806 | O | X | O | X |
| THF ^g | 7.58 | O | X | O | O |
| CH ₂ CH ₂ | 8.93 | O | X | O | X |
| Ethanol | 24.55 | X | X | X | O |
| Methanol | 32.70 | X | X | X | O |
| DMF ^h | 36.71 | O | O | O | O |
| DMAc ⁱ | 37.78 | O | X | O | O |
| DMSO ^j | 46.68 | O | O | O | O |
| Water | 78.304 | X | X | X | X |
| Aqueous NaOH | - | X | O | X | O |

a) 1 wt/vol%; at room temperature; O: soluble; X: insoluble.

b) Dielectric constants at 20 - 25°C; ref. [11].

c) $\overline{M}_n = 46500$; $\overline{M}_w/\overline{M}_n = 4.67$.

d) Obtained from polymer **2** (see ^e).

e) $\overline{M}_n = 45300$; $\overline{M}_w/\overline{M}_n = 2.40$.

f) Obtained from polymer **5** (see ^e).

g) Tetrahydrofuran.

h) *N,N*-Dimethylformamide.

i) *N,N*-Dimethylacetamide.

j) Dimethyl sulfoxide.

Figure 2A and B compares the ¹H NMR spectra of monomer **4** and its polymer. Spectrum B is consistent with the poly(vinyl ether) backbone and the phenylacetate pendants. For instance, the vinyl proton resonances of **4** (peak a and b in Figure 1A) are absent (shown by the thick arrows) and the main-chain methylene appear as signal **a**. The absorption due to the acetate moiety (peaks **g** and **h**) are clearly seen in the same position as those for monomer **4** (peak **g** and

h in Figure 2A). No signals indicative of side reactions during the polymerization are present.

Figure 2C illustrates ^1H NMR spectrum of the polymers obtained by hydrolysis reaction of polymer **5** (see Experimental). After hydrolysis, the peak of the ester methyl group (**h** in Figure 2B) disappeared (shown by the thick arrow), whereas the peak of the methylene group adjacent to the carbonyl carbon (**g**) is still observable. All other absorptions (**a** - **f**) were virtually unchanged during the reaction. The ^{13}C NMR spectrum of the same hydrolyzed polymer provided further evidence for the quantitative conversion of the acetate group of polymer **5** into the corresponding acid form; the signal of the ester methyl carbon (δ 51.9 ppm for polymer **5**) completely disappeared and the other carbon signals were consistent with the structure **6** (see Experimental).

Table 2 shows the solubilities of the precursor ester polymers, **2** and **5**, and the acid polymers, **3** and **6**. The ester polymers **2** and **5** exhibited the same solubility against the solvents employed; they were soluble in common organic solvents but insoluble in alcohols and water. In contrast, the solubility characteristics of the acid polymers **3** and **6** were considerably different. Polymer **3** was soluble only in polar organic solvents such as DMF and DMSO and in aqueous NaOH solution. Polymer **6** was soluble not only in DMF and DMSO but also in methanol, ethanol, and even THF. Thus, although there is only a subtle difference in structure between polymers **3** and **6**, polymer **6** exhibited solubility in the wider range of solvent polarity than polymer **3**.

CONCLUSION

Despite the existence of multiple polar functional groups (ester, oxyethylene, and aromatic ring) in their pendant, vinyl ethers **1** and **4** formed high-molecular-weight polymers having the expected structures **2** and **5** by cationic polymerization with BF_3OEt_2 initiator. The simple alkaline hydrolysis of the ester pendants of the obtained polymers afforded the new poly(vinyl ether)s with benzoic acid or phenylacetic acid pendant chains (**3** or **6**).

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