

Synthesis and Characterization of Poly(hydroxyether). I. Poly(hydroxyether) Based on 2,2-Bis(4-hydroxyphenyl)hexafluoropropane and 2,2-Bis(4-hydroxyphenyl)propane

TETSUYA FUKUOKA, HIDEKI TATEHATA, AKIRA MOCHIZUKI

Research and Development Center, Terumo Corporation, Inokuchi 1500, Nakaimachi, Ashigarakami-gun, Kanagawa, 259-0151, Japan

Received 14 March 2000; accepted 12 August 2000

ABSTRACT: Linear poly(hydroxyethers) (PHEs) were prepared by the base-induced condensation of bisphenols with epichlorohydrin in a polar mixed solvent. The bisphenols used were 2,2-bis(4-hydroxyphenyl)propane (bisphenol A) and 2,2-bis(4-hydroxyphenyl)-hexafluoropropane (bisphenol AF). Bisphenol A-based homo-PHE (HPHE-A), bisphenol AF-based homo-PHE (HPHE-AF), and copoly(hydroxyethers) (CPHEs) based on both the bisphenols with various compositions were characterized in terms of chemical structure, thermal property, solubility, and contact angle. The incorporation of bisphenol AF unit into HPHE-A brought about the increases in the glass-transition temperature, the solubility in organic solvents, and the hydrophobicity. The sequence of the repeating unit in the copolymer was analyzed by $^1\text{H-NMR}$ and the result agreed well with the one calculated as a random copolymer. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1687–1696, 2001

Key words: poly(hydroxyether); preparation; characterization; NMR; DSC; solubility; contact angle

INTRODUCTION

Epoxy resin has been widely used in specific fields such as the semiconductor industry, industrial adhesives, paint materials, and so on, because of its excellent properties in wettability, adhesive strength, thermal stability, and mechanical strength. The resin in these applications is usually used as crosslinked material and thus most of the research on the resin has been concerned with those of low molecular weight.^{1,2} The high molecular weight epoxy resin with a linear structure is known as poly(hydroxyether) (PHE), and has

thermoplastic property. PHE can be prepared by polycondensation of highly purified bisphenol with epichlorohydrin in a 1 : 1 molar ratio or by the reaction of diglycidyl ether of bisphenol with bisphenol in a 1 : 1 molar ratio. PHE based on bisphenol A is commercialized in the field of hot-melt adhesive. These above-mentioned typical properties observed in epoxy resin and PHE are attributed to the ether linkage and hydroxy group in the repeating unit of the polymers. The hydroxy group, however, causes a higher degree of water absorption than that of common commercialized polymers based on bisphenol A (e.g., polycarbonate and polysulfone) and this property will limit the practical usage of the polymers to specific fields. The low molecular weight epoxy resin and the intermediate composed of the different bisphenols have been investigated in terms of the

Correspondence to: A. Mochizuki (E-mail: Akira_Mochizuki@terumo.co.jp)

Journal of Applied Polymer Science, Vol. 80, 1687–1696 (2001)
© 2001 John Wiley & Sons, Inc.

reaction kinetics, the improvements of the thermal stability and hydrophobicity, and the molecular weight distribution.^{3–5} Reports about PHE are concerned mainly with the evaluations of physical properties or the compatibility with engineering plastics. Silvis et al.⁶ and Shin et al.⁷ investigated the thermal property and mechanical strength of many kinds of the copoly(hydroxyethers) (CPHEs) based on bisphenol A and other bisphenols. However, they did not characterize the chemical structures of the polymers.

In this study we report on the preparation and characterization of the PHEs based on 2,2-bis(4-hydroxyphenyl)propane (bisphenol A) and 2,2-bis(4-hydroxyphenyl)hexafluoropropane (bisphenol AF) in terms of the chemical structure, monomer sequence, thermal property, contact angle, and solubility in organic solvents.

EXPERIMENTAL

Materials

Bisphenol AF [2,2-bis(4-hydroxyphenyl)hexafluoropropane], bisphenol A (2,2-bis(4-hydroxyphenyl)propane), and epichlorohydrin were purchased from Riedel-de-haën Aktiengesellschaft (Germany), Tokyo Chemical Industry (Japan), and Nacalai Tesque (Japan), respectively. Dimethylsulfoxide (DMSO) and *N,N*-dimethylacetamide (DMAc) were purchased from Toray Fine Chemicals (Japan) and Kokusan Chemical Works (Japan), respectively. Sodium hydroxide (NaOH) was purchased from Nacalai Tesque. These reagents were used without further purification.

Polymerization

The typical synthetic procedure of homo-PHE based on bisphenol-AF (HPHE-AF) is described below as a representative. In a 100-mL three-necked round-bottom flask equipped with a mechanical Teflon stirring wing and a three-way stopcock, 16.81 g of bisphenol AF (50 mmol), 4.63 g of epichlorohydrin (50 mmol), 17.35 g of DMSO, and 17.35 g of DMAc were placed and dissolved at room temperature. After nitrogen gas bubbled into the solution for 30 min, 4.31 g of 50 wt % aqueous NaOH solution (53 mmol) was added to the solution and the mixture was stirred vigorously. The solution color changed at once from light yellow to pink. The flask was placed in an oil bath at 70°C. After the reaction solution was stirred for 20 h, a highly viscous and

slightly yellow opaque solution was obtained. To neutralize the excess amount of NaOH in the reaction solution, 1N HCl solution was added and the reaction solution was stirred for 1 h. While the solution was cooled to room temperature, the reaction solution separated to two phases, a low viscous solution (an upper layer) and a high viscous solution (a lower layer). The upper layer was removed by decantation. Then, DMSO and DMAc were added to the residual solution to reduce the viscosity of the solution, and the solution was stirred at 70°C. The solution was filtrated through a glass filter (Advantec GB 100R; Toyo Roshi, Japan) to remove the by-product NaCl. The filtrate was poured into 1 L of water and thus the polymer was obtained as white fibril. The fibril was washed three times with hot water (~ 70°C), and was dried at 80°C *in vacuo* for one night. Homo-PHE based on bisphenol A (HPHE-A) and various copolymers of PHE (CPHE) based on bisphenol AF and bisphenol A were synthesized by varying the composition ratio of both bisphenols under similar conditions.

Characterization

Reduced viscosities for the PHEs were determined by using a Ubbelohde viscometer (polymer concentration 0.5 g/dL in DMAc at 25.0 ± 0.1°C). The viscosity for each sample was measured twice and the values were averaged.

¹H-NMR spectra were obtained in DMSO-*d*₆ at room temperature on a Varian NMR spectrometer Model Unity 400 (Varian Associates, Palo Alto, CA) at 400 MHz. The chemical shifts were referenced internally to DMSO-*d*₆ (2.50 ppm).

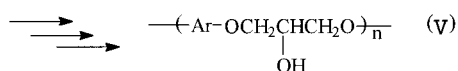
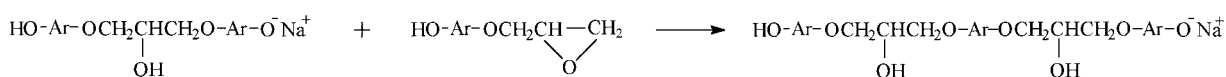
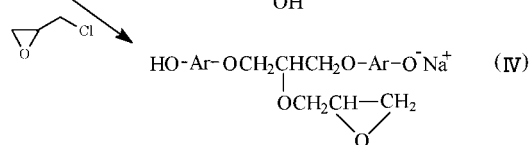
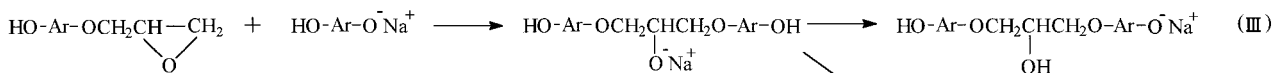
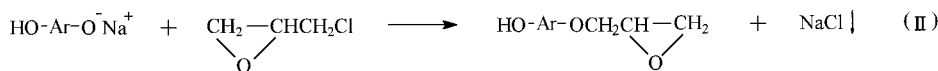
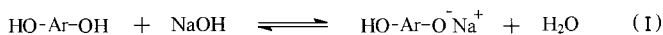
Differential scanning calorimetric (DSC) analysis of the polymers was carried out on a DSC-50 (Shimadzu, Japan) at the heating rate of 10°C/min under nitrogen atmosphere.

Static contact angles of water on the PHE films were measured using a Contact Angle Meter (Erma, Japan) at room temperature (~ 25°C). The films used were prepared as follows: the polymer was dissolved in hexafluoroisopropanol with 5 wt %. The solution was cast onto a petri dish and then the solvent was evaporated slowly at room temperature. The film thus obtained was dried *in vacuo* at 80°C for one night.

RESULTS AND DISCUSSION

Polymerization

The polymerization scheme of PHE is shown in **Scheme 1**. At first, bisphenol reacts with NaOH,



Scheme 1

resulting in phenolate anion (I) and the anion attacks epichlorohydrin (II) to yield a glycidylether. The other phenolate anion attacks the epoxide of the glycidylether and thus the hydroxyether (III) is produced. The end group of the ether (III) reacts with the glycidylether group of the other hydroxyether. In this manner the main chain extends and linear poly(hydroxyether) (V) is formed. At the same time, there is a possibility of forming a branch structure (IV). From the scheme it is predicted that the strength of nucleophilicity of the phenolate anion plays an important role in the copolymerization using plural bisphenols. That is, the sequence distribution of the repeating unit may be influenced by the difference of the nucleophilicity in the anion species. In general it is said that the strength of the nucleophilicity of the anion (base) is parallel to the

strength of the basicity of the base in a protic solvent. In that bisphenol AF has two strong electron-withdrawing trifluoromethyl groups, it will be more acidic than bisphenol A, which is proved by the following facts. The acid dissociation constants (pKa) of bisphenol A and bisphenol AF are 9.46 and 8.31, respectively,⁸ and the chemical

Table II Characteristic of Copoly(hydroxyether)

Feed Ratio ^a (Bisphenol AF/A)	Reduced Viscosity ^b	Observed Ratio ^c (Bisphenol AF/A Units)
0 : 100	1.06	0 : 100
20 : 80	0.85	21 : 79
40 : 60	0.83	42 : 58
50 : 50	0.89	50 : 50
60 : 40	0.81	61 : 39
80 : 20	0.72	80 : 20
100 : 0	0.85	100 : 0

The polymerization was carried out under the condition that the feed ratio of NaOH to epichlorohydrin was 1.02, except the case of the bisphenol AF-based homopolymer (ratio = 1.04).

^a The ratio of bisphenol AF to bisphenol A in the polymerization (mol/mol).

^b In DMAc at 25.0 ± 0.1°C.

^c The ratio of bisphenol AF unit to bisphenol A unit in the copolymer (mol/mol) determined by ¹H-NMR in DMSO-*d*₆ at room temperature.

Table I Characteristic of Bisphenol

Bisphenol	pKa ^a	Chemical Shift of Phenolic Proton ^b (ppm)
Bisphenol A	9.46	9.13
Bisphenol AF	8.31	9.86

^a Acid dissociation constant (see Ref. 8).

^b Measured by ¹H-NMR in DMSO-*d*₆ at room temperature.

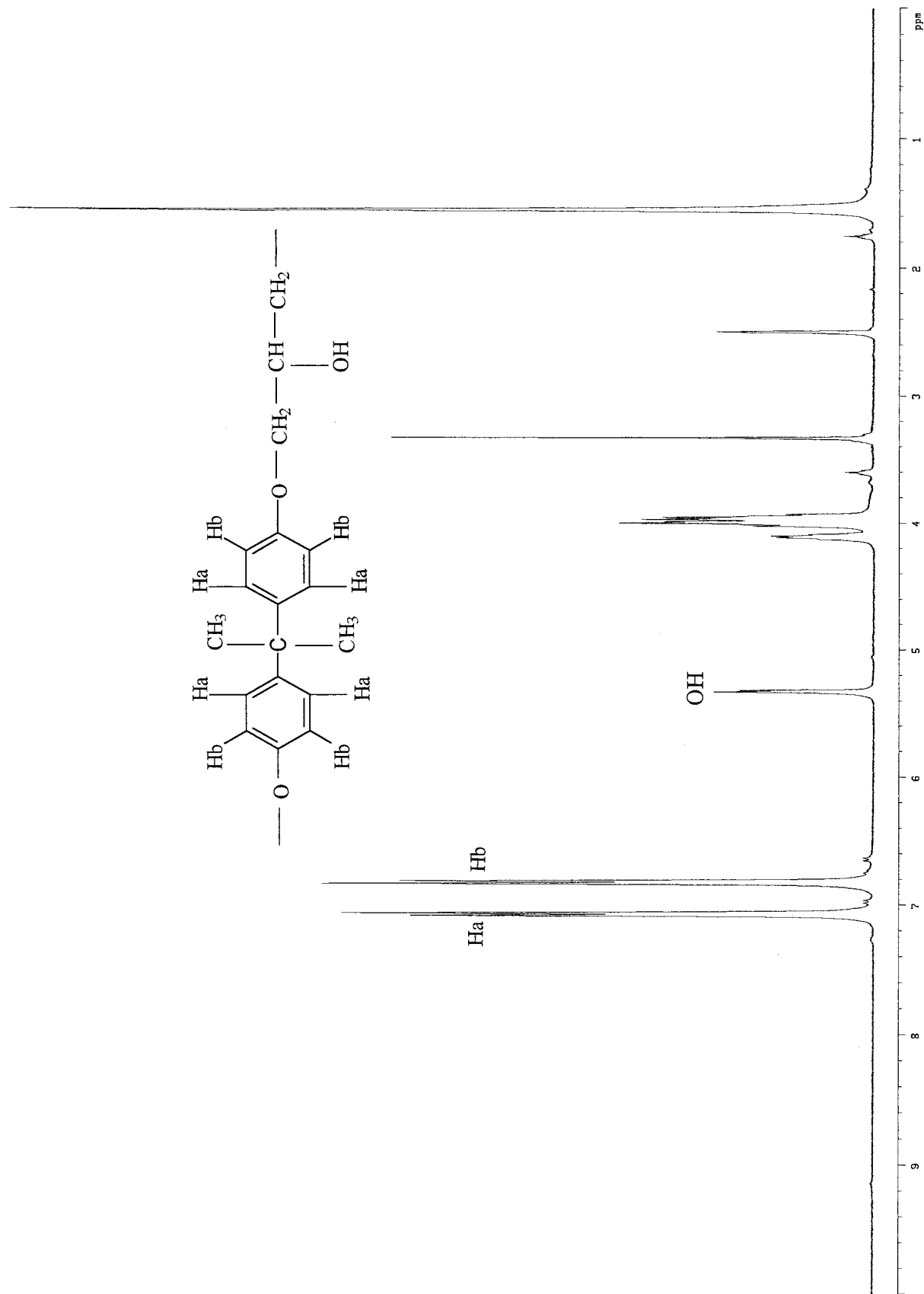


Figure 1 (a) ¹H-NMR spectra of poly(hydroxyethers). (a) Bisphenol A-based poly(hydroxyether) (HPHE-A); (b) Bisphenol AF-based poly(hydroxyether) (HPHE-AF); (c) Bisphenol AF and bisphenol A-based copoly(hydroxyether) (CPHE: AF : A = 50 : 50 mol/mol).

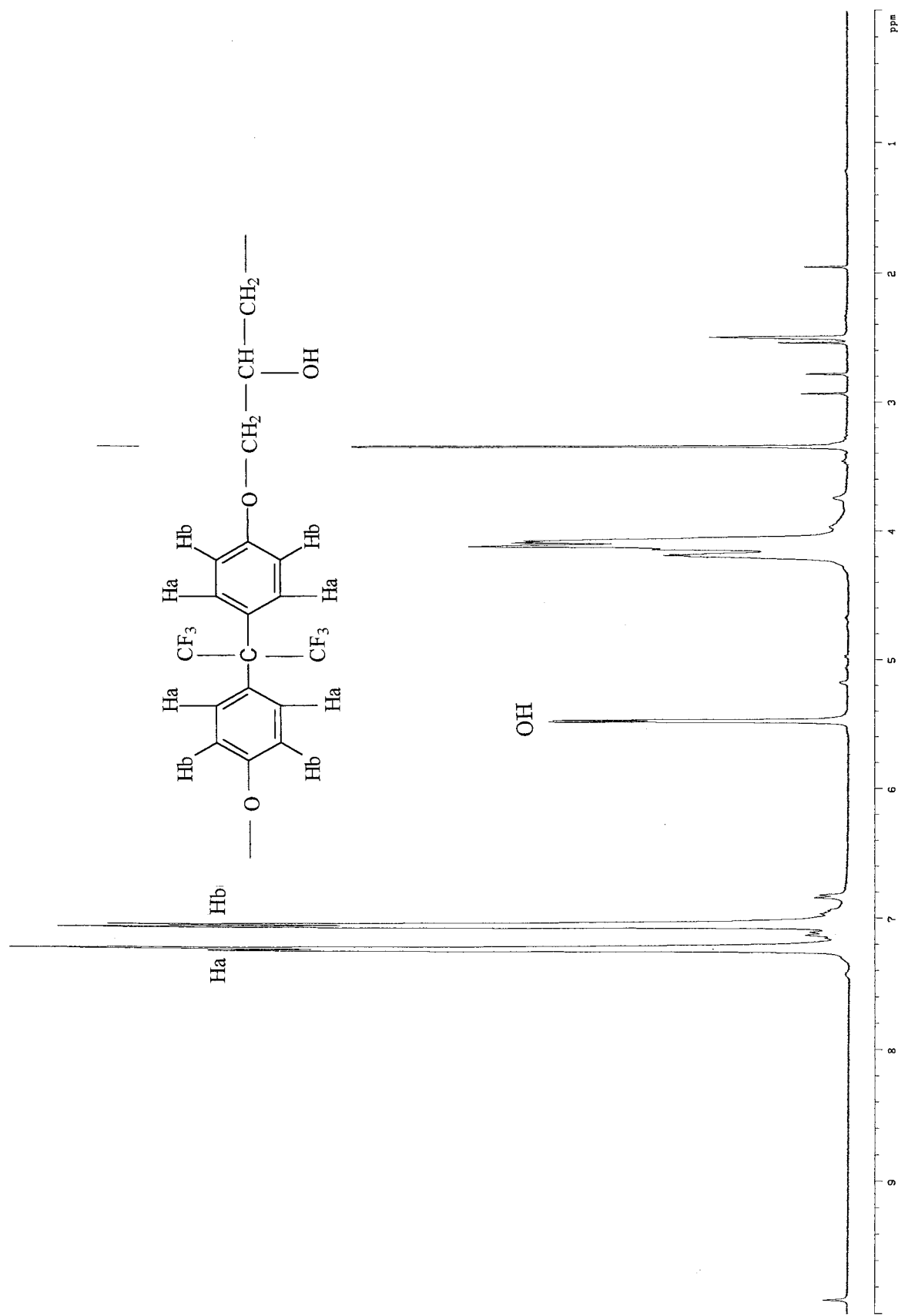


Figure 1(b) (Continued from the previous page)

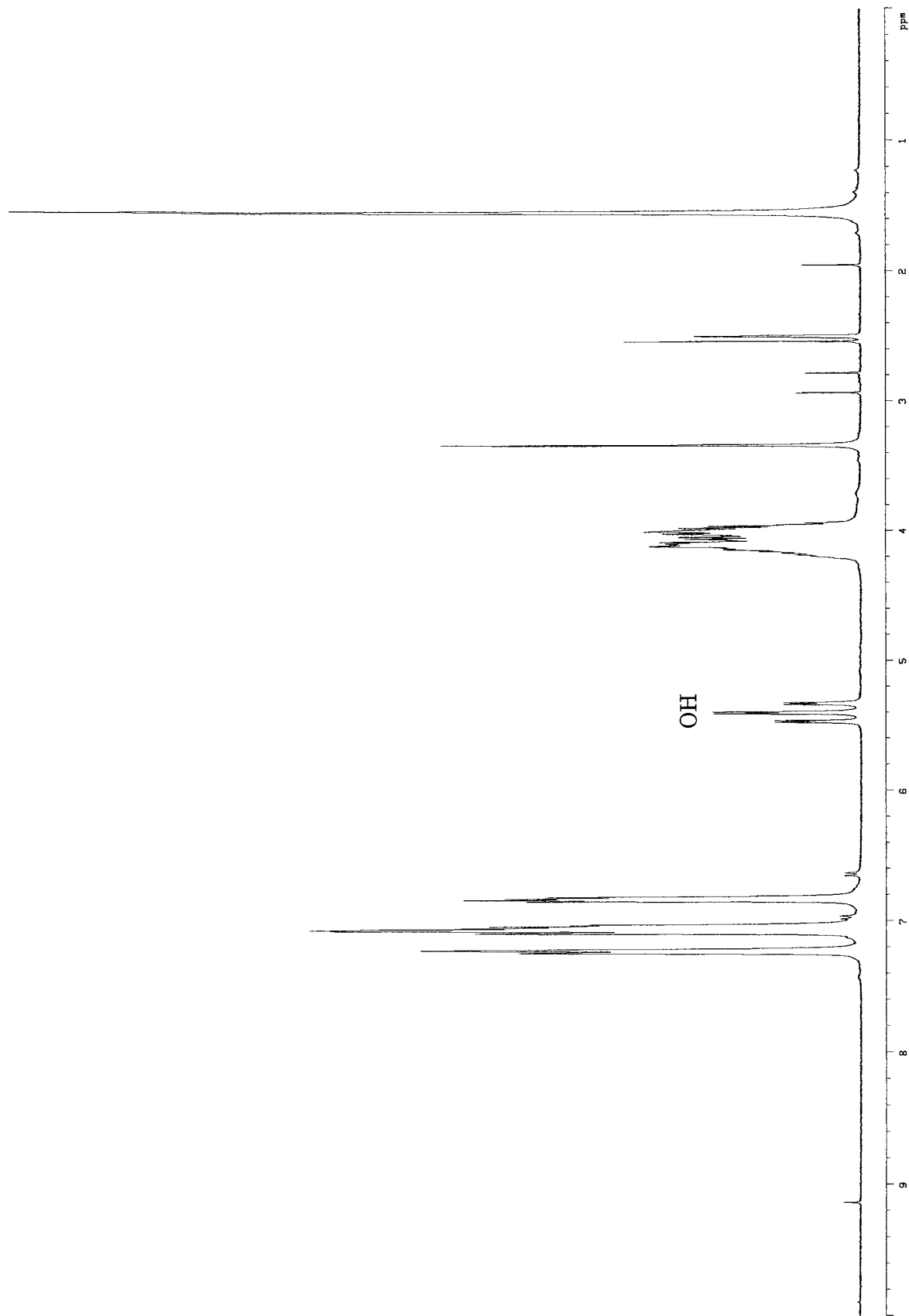


Figure 1(c) (Continued from the previous page)

shifts of phenolic protons of bisphenol A and bisphenol AF in NMR spectra are 9.13 and 9.86 ppm, respectively (Table I). Therefore, the nucleophilicity of the phenolate anion derived from bisphenol AF was anticipated to be lower than that of bisphenol A phenolate anion. That is, the condensation of bisphenol A with epichlorohydrin would occur faster than that of bisphenol AF in their copolymerization. Consequently, the sequence of the constitutional repeating unit in the copolymer would deviate from the random one.

The copolymerization of bisphenol A and bisphenol AF was carried out under the condition that the feed ratios of bisphenol AF to bisphenol A (AF : A) were 100 : 0, 80 : 20, 60 : 40, 50 : 50, 40 : 60, 20 : 80, 0 : 100 (mol/mol). The copolymerization results are listed in Table II. The reduced viscosities of the polymers are in the range of 0.72–1.06, producing tough films.

NMR Analysis

At first, the NMR analysis of the homopolymers HPHE-A and HPHE-AF is discussed. Their NMR spectra are shown in Figures 1(a) and (b), where the assignments of the main resonance peaks are also shown. In both the spectra, one can observe that two types of aromatic protons (Hb and Ha) on the bisphenol unit appear separately as two doublet peaks. The protons appearing at the higher field are assigned to Hb protons (3,3',5 and 5' positions) and those appearing at the lower field are assigned to Ha protons (2,2',6 and 6' positions). The protons Hb and Ha on the bisphenol A unit appear at 6.82 and 7.07 ppm, respectively, and the protons Hb and Ha on the bisphenol AF unit appear at 7.05 and 7.23 ppm, respectively. The obvious downfield shifts of the proton peaks on the bisphenol AF unit compared with those on the bisphenol A unit are the result of the electron-drawing trifluoromethyl group. The methylene and methine protons of oxy-(2-hydroxytrimethylene)oxy unit in HPHE-A and in HPHE-AF appear as multiplet peaks at 3.9–4.0, 4.10, 4.0–4.1, and 4.19 ppm, respectively. The methylene and methine protons of oxy-(2-hydroxytrimethylene)oxy group in HPHE-AF appear as multiplet peaks at 4.05–4.15 and 4.19 ppm, respectively. The doublet peak of hydroxyl proton of oxy-(2-hydroxytrimethylene)oxy group also shifts from 5.34 to 5.47 ppm. These results show that the downfield shifts of the proton peaks also occur on the oxy-(2-hydroxymethylene)oxy group because of the bisphenol AF unit.

Next, the NMR analysis for the copolymers is discussed. The representative NMR spectrum of the copolymer is shown in Figure 1(c), where the sample is CPHE (AF : A = 50 : 50). Quite similar spectra were obtained for other CPHEs, except the difference of the peak intensities. What appear to be three aromatic proton resonance peaks come to view in the range of 6.8–7.2 ppm. The peak at 6.83 ppm is assigned to the proton Hb on the bisphenol A unit and the doublet peak at 7.23 ppm to Ha on the bisphenol AF unit. The peak at 7.03–7.09 ppm, which looks like a multiplet, is interpreted by overlapping the proton peak (Ha) on the bisphenol AF unit with the proton peak (Hb) on the bisphenol AF unit. The composition ratio of both bisphenol units in the copolymer can be determined from the intensity ratio of the aromatic proton peaks at 6.83 and 7.23 ppm. The results are shown in Table II. The observed contents of the bisphenol AF unit are 21, 42, 50, 61, and 80 mol %. These values are in good agreement with the feed ratios. The methylene and methine protons of the oxy-(2-hydroxytrimethylene)oxy group in the copolymer are observed in the range of 3.3–4.2 ppm. The methyl protons of the bisphenol A unit appear at 1.55 ppm. On the basis of the NMR analysis of hydroxyl proton peaks in HPHE-A and HPHE-AF spectra, the doublet peaks in the range from 5.3 to 5.5 ppm should be assigned to the hydroxyl proton on the oxy-(2-hydroxytrimethylene)oxy group.

In the spectrum of the copolymer [Fig. 1(c)] one can recognize three doublet peaks at 5.33, 5.40, and 5.47 ppm, which will be assigned to it. When the monomer sequence is considered, there can be three types of hydroxyl protons on the group as shown in Figure 2. The analysis of homopolymers shows that the peak observed at 5.33 ppm is assigned to the hydroxyl proton of the oxy-(2-hydroxytrimethylene)oxy group between bisphenol A units (Fig. 2, A-A), and that the peak at 5.47 ppm is assigned to that between bisphenol AF units (Fig. 2, AF-AF). We assigned the new peak at 5.36 ppm in CPHEs to the hydroxyl proton between the bisphenol A unit and the bisphenol AF unit (Fig. 2, A-AF). From the ratios of these three peak intensities, we could estimate the sequence distribution of the constitutional repeating unit in the copolymers, where the repeating unit was composed of bisphenol and oxy-(2-hydroxytrimethylene)oxy group, $-\text{Ar}-\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2\text{O}-$. The results are listed in Table III together with the theoretical values calculated on the assumption that the repeating unit sequence in the co-

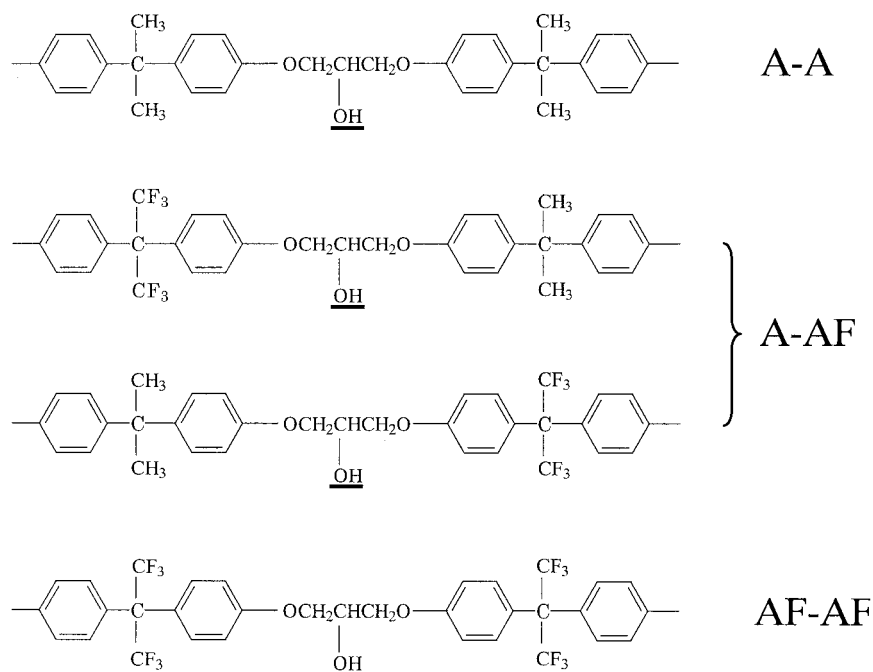


Figure 2 Circumstance of oxy-(2-hydroxytrimethylene)oxy group in copoly(hydroxyether).

polymer is random. The table reveals that the experimental results are in good agreement with the calculated ones within the whole range of the composition ratio of the bisphenol unit. Therefore, it is concluded that the copolymers have random compositions. This conclusion does not coincide with the above-mentioned prediction from the difference of the nucleophilicity of phenolate anion. Indeed, the nucleophilicity of the phenolate anion derived from bisphenol A may be larger than that from bisphenol AF. This difference, however, will be small, and the apparent reactivities of both the

phenolate anions toward epichlorohydrin and/or the epoxide will be equal. Consequently, the polymerization proceeds at random.

Thermal Properties

The thermal property of the PHEs was investigated in the range of 50–200°C using DSC. The thermograms of HPHE-A, HPHE-AF, and CPHEs showed only the glass-transition point (T_g) and no endothermic peak resulting from the fusion of crystalline, which means that the PHEs are an

Table III Sequencing Result of Copoly(hydroxyether)

Composition ^a (Bisphenol AF/A Units)	Calculated Sequence Ratio			Observed Sequence Ratio		
	A-A ^b	A-AF ^b	AF-AF ^b	A-A ^b	A-AF ^b	AF-AF ^b
0 : 100	100	0	0	100	0	0
21 : 79	64	32	4	61	32	7
42 : 58	36	48	16	36	47	17
50 : 50	25	50	25	25	50	25
61 : 39	16	48	36	17	45	38
80 : 20	4	32	64	4	29	67
100 : 0	0	0	100	00	0	100

^a The observed ratio in the copolymer (mol/mol).

^b Abbreviation refers to Fig. 2.

Table IV Glass Transition Point of Copoly(hydroxyether)

Composition ^a (bisphenol AF/A units)	0 : 100	21 : 79	42 : 58	50 : 50	61 : 39	80 : 20	100 : 0
T_g (°C)	100	104	111	113	114	118	124

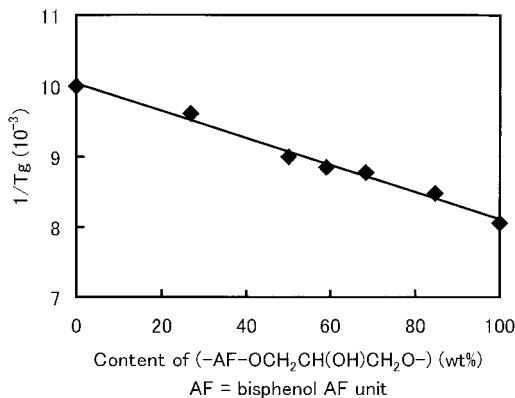
^a The observed ratio in the copolymer (mol/mol).

amorphous polymer. The T_g 's of the PHEs are listed in Table IV. The T_g of HPHE-AF is higher than that of HPHE-A by 24°C and the T_g of CPHE increases monotonously with an increase in the content of the bisphenol AF unit in CPHE. Most of fluorinated aromatic condensation polymers have lower T_g 's than those of the corresponding nonfluorinated polymers.⁹ Our result is thus a peculiar case. A similar tendency that the substitution of the trifluoromethyl group for the methyl group in base polymer brings about the rise of T_g was reported for poly(aryl ether ketone)³ and polycarbonate.⁹

It is well known that the relationship between the T_g of the copolymer and the composition ratio of the monomers is described by some equations.^{10,11} One equation in Johnston¹¹ is expressed here by eq. (1):

$$1/T_g = \sum_{i,j} W_i P_{ij} / T_{gij} \quad (1)$$

which takes the sequence distribution of the copolymer into consideration and where $T_{gij} = T_g$ contributions of different repeating unit diads, ij , ji , jj , and P_{ij} is the probability that the growing macromolecule having i or j repeating unit moiety at the end of the molecular chain adds i or j unit.

**Figure 3** Fox plot of glass-transition temperature of copoly(hydroxyether).

If there is no sequence distribution effect, eq. (1) reverts back to the equation in Fox,¹² eq. (2):

$$1/T_g = \sum_i W_i / T_{gi} \quad (2)$$

where W_i is the weight fraction of the repeating units and $T_{gi} = T_g$ of homopolymer.

In our experiments, the repeating units in the copolymer are $-\text{PhC}(\text{CH}_3)_2\text{Ph-OCH}_2\text{CH}(\text{OH})\text{CH}_2\text{O}-$ derived from bisphenol A, and $-\text{PhC}(\text{CF}_3)_2\text{Ph-OCH}_2\text{CH}(\text{OH})\text{CH}_2\text{O}-$ derived from bisphenol AF. On the basis of the T_g data shown in Table IV, the T_g 's of the copolymers were plotted according to Fox eq. (2) (Fig. 3). It is clear from the figure that the experimental data are in very good agreement with the equation. Therefore, it is concluded that there is no sequence distribution effect on the T_g of CPHE.

Contact Angles

The static contact angles of water on the PHEs were investigated using the solvent-cast films. The results are shown in Figure 4, where the contact angle is plotted against the feed ratio of bisphenol AF in the preparation of the polymer. The contact angle tends to increase simply between those of the two homopolymers PHE-A and

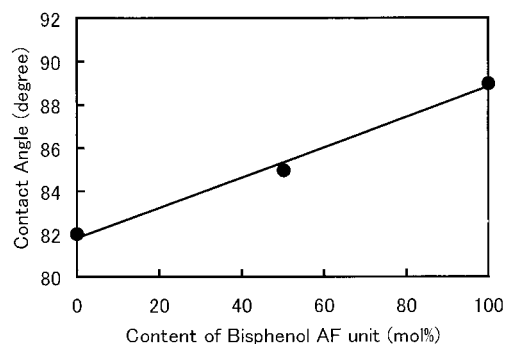
**Figure 4** Relationship between contact angle and composition of poly(hydroxyether).

Table V Solubility of Poly(hydroxyether) in Organic Solvent

Solvent	HPHE-AF	CPHE ^a	HPHE-A
Dimethylsulfoxide	Ds	Ds	Ds
<i>N,N</i> -Dimethylformamide	Ds	Ds	Ds
<i>N,N</i> -Dimethylacetamide	Ds	Ds	Ds
Chloroform	Ds	Ds	Ds
Tetrahydrofuran	Ds	Ds	Ds
Acetone	Ds	Ds	Is
Methanol	Ds	Sw	Is
Ethanol	Ds	Sw	Is
Formic acid	Is	Is	Is

Ds, dissolved; Sw, swelled; Is, insoluble.

^a Composition ratio of bisphenol AF unit to bisphenol A unit = 50 : 50 mol/mol.

PHE-AF, whose contact angles are 82 and 89°, respectively.

Solubility of Polymers in Organic Solvent

The solubilities of the HPHEs and CPHE (AF : A = 50 : 50 mol/mol) in organic solvents were investigated using methanol (MeOH), ethanol (EtOH), acetone, chloroform, tetrahydrofuran (THF), DMSO, DMAc, *N,N*-dimethylformamide (DMF), and formic acid at room temperature. The results are summarized in Table V. HPHE-A dissolved in aprotic polar solvents (DMSO DMAc and DMF), THF, and chloroform, but was not soluble in acetone and the alcohols. The incorporation of the bisphenol AF unit into the HPHE-A improved the solubility, and the CPHE could dissolve in acetone. HPHE-AF could be soluble in all the organic solvents investigated except formic acid. The improvement of the solubility by the incorporation of the bisphenol AF unit results from the decrease in the intermolecular interaction by the CF₃ group.

CONCLUSIONS

The preparation and characterization of the linear homopoly(hydroxyethers) (HPHEs) and copoly(hydroxyethers) (CPHEs) based on bisphenol A and bisphenol AF were carried out. Polymers having the high reduced viscosity could be prepared by the base-induced condensation of bisphenol with epichlorohydrin in a polar mixed sol-

vent. The NMR analysis of the PHEs showed that the composition of the copolymer agreed with the feed ratio of bisphenol A to bisphenol AF in the polymer preparation. Moreover, NMR analysis revealed that there were three kinds of proton resonance peaks assigned to the hydroxyl proton of the oxy-(2-hydroxytrimethylene)oxy group in the polymer as a result of the difference of the sequence of the repeating unit. The sequence was estimated from the intensity ratio of the three peaks, and it was concluded that the copolymer had a random structure within the whole range of copolymerization compositions. DSC analysis revealed that the PHEs were an amorphous polymer and that the T_g of PHE increased from 100°C (for PHE-A) to 124°C (for PHE-AF) according to the Fox equation. The additional properties of PHEs, the solubility in organic solvent, and contact angle of water were investigated and they increased with an increase in the amount of bisphenol AF unit because of two strong hydrophobic CF₃ groups in the bisphenol AF unit.

REFERENCES

- Sorenson, W. R.; Campbell, T. W. *Preparative Methods of Polymer Chemistry*; Wiley: New York, 1961.
- Rokicki, G.; Kuran, W.; Nowiński, A. *Makromol Chem* 1978, 179, 1661.
- Cassidy, P. E.; Aminabhavi, T. M.; Farley, J. M. *J Macromol Sci Rev Macromol Chem Phys* 1989, C29, 365.
- Gao, J.; Zhao, M.; Yang, L. *J Appl Polym Sci* 1997, 63, 1137.
- Batzer, H.; Zahir, S. A. *J Appl Polym Sci* 1977, 21, 1843.
- Silvis, H. C.; White, J. E.; Crain, S. P. *J Appl Polym Sci* 1992, 44, 1751.
- Shih, W.-C.; Ma, C.-C. M. *J Appl Polym Sci* 1999, 73, 2369.
- Livshits, B. R.; Vasil'ev, V. I.; Knunyants, I. L.; Vinogradova, S. V. *Zh Vses Khim Obshch* 1968, 13, 465.
- Saegusa, Y.; Kuriki, M.; Kawai, A.; Nakamura, S. *J Polym Sci Part A: Polym Chem* 1990, 28, 3327.
- Johnston, N. W. *J Macromol Sci Rev Macromol Chem* 1976, 14B, 215.
- Barton, J. M. *J Polym Sci C* 1970, 30, 573.
- Fox, T. G. *Bull Am Phys Soc* 1956, 1, 123.