

Synthesis and Characterization of Poly(hydroxyether). II. Poly(hydroxyethers) Based on Various Bisphenols and 2,2-Bis(4-hydroxyphenyl)hexafluoropropane

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ABSTRACT: Several kinds of linear copoly(hydroxyethers) (CPHEs) were prepared by the base-induced condensation of bisphenol with epichlorohydrin in a polar mixed solvent. The CPHEs were based on bisphenol AF [2,2-bis(4-hydroxyphenyl)hexafluoropropane], and the composition ratio of bisphenol AF and bisphenol was 50 : 50 mol/mol. The CPHEs and the corresponding homopoly(hydroxyethers) (HPHEs) were characterized in terms of reduced viscosity, NMR, differential scanning calorimetry (DSC), solubility, and contact angle. NMR results indicated that the compositions of the copolymers were in good agreement with the feed compositions in the preparation. DSC analysis revealed that the CPHEs and HPHEs were amorphous polymers. The incorporation of bisphenol AF into the HPHE increased the solubility in many kinds of organic solvents when the CPHEs were compared with the corresponding HPHE. In the measurement of contact angles of water and plasma for poly(hydroxyethers) (PHEs) and common hydrophobic polymers, the peculiar phenomenon that the contact angles of plasma were higher than that of water was observed only in the case of PHEs. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1697–1709, 2001

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

INTRODUCTION

Synthetic membranes have been applied to many fields such as desalination, gas separation, dehydration of organic solvents, and medical devices. Many kinds of polymers have been investigated to prepare the high-performance membranes. Concerning membranes for medical devices, especially membranes for oxygenators, most of the commercialized membranes are prepared from hydrophobic polyolefins. They have porous struc-

tures with a pore size of 0.01–0.1 μm , ideally suitable for the high performance of gas exchange.¹ These oxygenators, however, sometimes have some problems in clinical use (e.g., during the long-term extracorporeal circulation treatment), typically reduced gas-exchange efficiency and plasma leakage, which problems are induced by the occupation of the membrane pore by plasma or water from the blood. Therefore, it is deduced that an asymmetric and highly hydrophobic membrane with a skin layer-like ultrafiltration membrane is an ideal oxygenator membrane. Because proteins or water cannot penetrate the pores in the membrane, however, because such polyolefins are semicrystalline polymers and do not dissolve in common solvents, it is

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difficult for them to yield a membrane like the ultrafiltration membrane prepared by the phase-inversion method.

Recently, Kawakami et al. reported the asymmetric oxygenator membrane prepared from the fluorinated polyimide by the phase-inversion method.^{2,3} They showed that the membrane had a nonporous top surface, good gas-exchange performance, and excellent blood compatibility. It seems that their membrane has the ideal structure of the oxygenator membrane. In our opinion, a polymer suitable for the oxygenator membrane has to have good solubility in water-soluble organic solvents, high hydrophobicity, and low cost. In our investigation of membrane materials, we focused attention on an epoxy resin that has a linear chain structure, poly(hydroxyether) (PHE). In a companion study,⁴ we prepared copoly(hydroxyethers) (CPHEs) based on 2,2-bis(4-hydroxyphenyl)hexafluoropropane (bisphenol AF) and 2,2-bis(4-hydroxyphenyl)propane (bisphenol A) in various compositions and characterized them in terms of their chemical structure, monomer sequence, thermal property, and contact angle. It was found that PHE had good properties in mechanical strength and solubility in water-soluble organic solvents, features that will satisfy the demand for the membrane material as oxygenator. In this study we characterized several kinds of CPHEs and the corresponding homopoly(hydroxyethers) (HPHEs) in terms of their chemical structure, monomer sequence, thermal property, and the behavior of the contact angle, depending on the media, water, and serum. These results are reported in this study, where the CPHEs were prepared by the base-induced condensation of bisphenol mixture (composed of bisphenol and bisphenol AF with the ratio of 50 : 50 mol/mol) with epichlorohydrin.

EXPERIMENTAL

Materials

Epichlorohydrin was purchased from Nakarai Tesque (Japan). The bisphenols summarized in Table I were used. Biphenol (4,4'-bisphenol) (**1**), bisphenol F [2,2-bis(4-hydroxyphenyl)methane] (**2a**), ethylidene-bisphenol (**2b**), bisphenol A [2,2-bis(4-hydroxyphenyl)propane] (**2c**), 1,1-bis(4-hydroxyphenyl)cyclohexane (**2d**), 2,2-bis(4-hydroxy-3-methylphenyl)propane (**3a**), and 2,2-bis(4-hydroxy-3,5-dimethylphenyl)propane (**3b**) were

purchased from Tokyo Kasei Kogyo (Japan). Bisphenol AF [2,2-bis(4-hydroxyphenyl)hexafluoropropane] (**4**) was purchased from Riedel-de-haën Aktiengesellschaft (Germany). Dimethylsulfoxide (DMSO) and *N,N*-dimethylacetamide (DMAc) were purchased from Toray Fine Chemicals (Japan) and Kokusan Chemical Works (Japan), respectively. These reagents and solvents were used without further purification.

Polymerization

The abbreviations of HPHEs and CPHEs synthesized are summarized in Table I. The typical preparation method of the copolymer based on bisphenol F (**2a**) and bisphenol AF (**4**) is described below as an example. Under nitrogen atmosphere, 5.00 g (25 mmol) of bisphenol F, 8.41 g (25 mmol) of bisphenol AF, and 4.63 g (50 mmol) of epichlorohydrin were added into a mixed solvent [DMSO (8.68 g) and DMAc (8.68 g)]. After the mixture was dissolved by stirring for 30 min at room temperature, 53 mmol of sodium hydroxide (as 50 wt % aqueous solution) was added to the solution, and the solution was stirred for 30 min at room temperature. The reaction solution was then heated to 70°C and was kept at that temperature for 20 h with vigorous stirring. The viscous white reaction solution thus obtained was filtered and dropped into excess water to precipitate a polymer. The polymer obtained was repeatedly washed with hot water (~ 70°C) and was dried *in vacuo* at 100°C overnight.

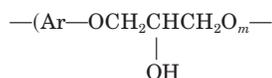
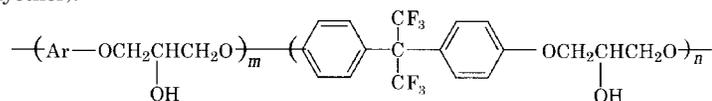
In the preparation of the copolymer, the homopolymer based on each bisphenol was also prepared. The precipitation from the polymerization solution and the subsequent wash with hot water did not involve the removal of the homopolymers from the copolymer; moreover, it would be very difficult to remove the homopolymer. Therefore, the latter investigation was carried out without further purification.

Characterization

Proton NMR spectra of the PHEs were recorded at 400 MHz on a Varian Unity Plus 400 Spectrometer (Varian Associates, Palo Alto, CA) in DMSO-*d*₆ at room temperature. Differential scanning calorimetry (DSC) was carried out by a DSC-50A (Shimadzu, Japan) under nitrogen atmosphere at the heating rate of 10°C/min. The reduced viscosities of the polymers were measured

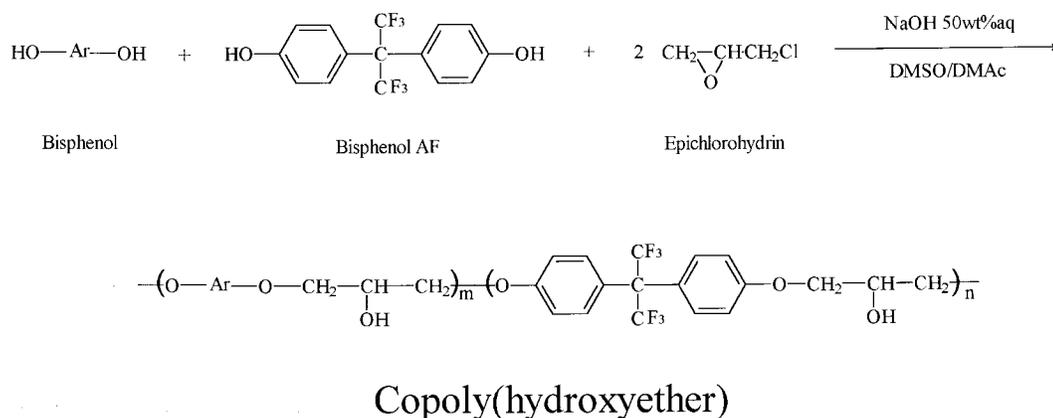
Table I Abbreviation of Monomer, Homopoly(hydroxyether), and Copoly(hydroxyether)

| Bisphenol No. ^a | HO—Ar—OH | HPHE ^a | CPHE ^b |
|----------------------------|----------|-------------------|-------------------|
| 1 | | (H1) ^c | C2aC1 |
| 2a | | H2a | C2a |
| 2b | | H1b | C2b |
| 2c | | H2c | C2c |
| 2d | | H2d | C2d |
| 3a | | H3a | C3a |
| 3b | | H3b | C4b |
| 4 | | H4 | — |

^a HPHE = Homopoly(hydroxyether).^b CPHE = Copoly(hydroxyether).^c H1 could not be prepared.

with an Ubbelohde viscometer in DMAc at $25.0 \pm 0.1^\circ\text{C}$. The contact angles of water and bovine plasma on the PHE were measured at room temperature ($\sim 23^\circ\text{C}$) using solvent-cast films, which were prepared as follows. The polymer was dis-

solved 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 overnight.



Scheme 1 Synthesis of copoly(hydroxyether) based on bisphenol and bisphenol AF.

RESULTS AND DISCUSSION

Polymer Synthesis

The polycondensation scheme for the preparation of PHE is shown in **Scheme 1**. Preparation of seven HPHEs and seven CPHEs was performed using eight kinds of bisphenols listed in Table I. The feeding molar ratios of bisphenol : epichlorohydrin in the preparation of the HPHEs were 1 : 1, and those of bisphenol : bisphenol AF : epichlorohydrin in the case of CPHEs were 1 : 1 : 2. Polymerization was conducted in DMSO/DMAc = 1 : 1 (w/w) mixture. The amount of sodium hydroxide added to the reaction mixture was 1.06-fold that of epichlorohydrin. Unfortunately, preparation of HPHE (**H1**) based on biphenol (**1**) was unsuccessful, because the insoluble compound precipitated from the reaction solution on addition of sodium hydroxide to the monomer solution. The compound was insoluble in any kinds of solvents and seemed to be an oligomer. The fail-

ure is attributed to the strong intermolecular interaction of biphenylene units. Other HPHEs and CPHEs were prepared with good results, as listed in Table II. The viscosities of the homopolymers and copolymers were in the range of 0.57–0.95. The films prepared by the solvent-cast method were tough. By these results we conclude that these polymers have sufficient molecular weights to yield membrane.

As mentioned earlier, the obtained copolymer might contain the homopolymers based on each bisphenol. However, because the sequence distribution analysis described later indicates that the polymerization proceeds at random, the copolymer will contain little or no homopolymer.

NMR Analysis

The structures of these polymers were confirmed by $^1\text{H-NMR}$. The representative spectra are shown in Figure 1, where the samples are HPHEs (**H2a** and **H4**) and CPHE (**C2a**) based on bisphe-

Table II Characterizations of Homopoly(hydroxyether) and Copoly(hydroxyether)

| HPHE | H1 ^a | H2a | H2b | H2c | H2d | H3a | H3b | H4 |
|----------------------------|------------------------|------------|------------|------------|------------|------------|------------|------------|
| η (dl/g) ^b | — | 0.53 | 0.42 | 0.80 | 0.41 | 0.61 | 1.22 | 0.85 |
| T_g (°C) ^c | — | 74 | 83 | 100 | 120 | 89 | 123 | 124 |
| CPHE | C1 | C2a | C2b | C2c | C2d | C3a | C3b | C3b |
| η (dl/g) ^b | 0.69 | 0.63 | 0.95 | 0.89 | 0.72 | 0.62 | 0.86 | |
| T_g (°C) ^c | 125 | 103 | 107 | 114 | 124 | 104 | 128 | |

^a **H1** could not be prepared.

^b Reduced viscosity in DMAc at $25.0 \pm 0.1^\circ\text{C}$.

^c Glass-transition temperature.

nol F (**2a**) and bisphenol AF (**4**). In homopolymer **H2a**, aromatic eight protons on the phenylene ring appear at 6.84 and 7.07 ppm as two doublet peaks. The protons appearing at the higher field are assigned to the protons of 3, 3', 5, and 5' positions on the bisphenol unit (Hb protons), and the protons appearing at the lower field are assigned to protons of 2, 2', 6, and 6' positions on the bisphenol unit (Ha protons), respectively, as shown in Figure 1(a). Methylene protons between the phenylene groups are observed at 3.77 ppm as a singlet peak. Methylene, methine, and hydroxyl protons of the oxy-(2-hydroxytrimethylene)oxy group appear as a multiplet peak at 3.9–4.0 ppm, a multiplet peak at 4.10 ppm, and a doublet peak at 5.33 ppm, respectively. In homopolymer **H4**, aromatic eight protons on the phenylene rings appear at 7.05 and 7.23 ppm. Methylene, methine, and hydroxyl protons derived from the oxy-(2-hydroxytrimethylene)oxy group appear as a multiplet peak at 4.0–4.1 ppm, a multiplet peak at 4.19 ppm, and a doublet peak at 5.47 ppm, respectively. From these results it is found that these peaks of **H4** shift to the lower field as a result of the strong electron drawing group, trifluoromethyl group, when compared with those of **H2a**.

In the case of CPHE **C2a**, aromatic protons are observed as three peaks at 6.8–7.2 ppm, although it has four kinds of aromatic protons, which can be explained by the fact that the peak of proton Ha, of the bisphenol F unit, overlaps with the peak of proton Hb, of the bisphenol AF unit. The singlet peak at 3.77 ppm is assigned to the methylene proton between the phenylene groups. The methylene and methine peaks of oxy-(2-hydroxytrimethylene)oxy group are observed at 3.9–4.2 ppm as a multiplet peak. For the hydroxyl proton peak of **C2a**, three doublet peaks are observed at 5.3–5.5 ppm, whereas those of **H2a** and **H4** show a doublet peak. This is the evidence that there are three types of hydroxyl protons in the CPHE. On the basis of the peak intensity ratio of the hydroxyl protons the sequence of the repeating units $[-\text{BisF}-\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2\text{O}-$ and $-\text{BisAF}-\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2\text{O}-]$ in the copolymer can be estimated as reported in the previous study,⁴ in which BisF and BisAF are the bisphenol F unit and the bisphenol AF unit, respectively. The peak appearing at the higher field is derived from the oxy-(2-hydroxytrimethylene)oxy group sandwiched between the bisphenol F units. The peak in the middle is assigned to the hydroxyl proton on the group existing between the bisphenol F

(**2a**) unit and the bisphenol AF (**4**) unit, and the peak appearing at the lower field is assigned to hydroxyl protons existing between bisphenol AF (**4**) units. The intensity ratio of the three peaks is 1.00 : 1.89 : 1.03. In that the calculated ratio, on the assumption that the polymer has random composition, is 1 : 2 : 1, the result strongly indicates that **C2a** has a random structure.

Next, the characterization of other PHEs by NMR is discussed. The NMR results of HPHEs were similar to that of **H2a** and are summarized in Table III. The proton peaks of methylene, methine, and hydroxyl groups derived from oxy-(2-hydroxytrimethylene)oxy group in the HPHEs appear at 3.7–4.2, 4.1–4.2, and 5.3–5.5 ppm, respectively, and two types of aromatic protons are observed in the range of 6.8–7.5 ppm, except for **H3b**. The NMR results of the other CPHEs were also similar to that of **C2a**. In the NMR spectra of **C1**, **C2a**, **C2c**, and **C3b** three aromatic proton peaks were apparently observed. This is because the proton peak based on the bisphenol overlaps with that based on bisphenol AF, as mentioned in the case of **C2a**. On the other hand, four aromatic peaks were observed for **C2b**, **C2d**, and **C3a** in the range of 6.8–7.5 ppm. From the intensity of the aromatic proton peaks, the composition ratio of bisphenol AF unit to bisphenol unit in each copolymer could be calculated in a similar manner as mentioned in the case of **C2a**, results of which are shown in Table IV. The composition ratios observed for all the CPHEs are in good agreement with the feed ratio of bisphenol AF unit to bisphenol unit, 50 : 50 mol/mol. The hydroxyl proton of the oxy-(2-hydroxytrimethylene)oxy group is described below. The three hydroxyl proton peaks of CPHEs (except **C1**) were observed in the range of 5.3–5.5 ppm, as described in the analysis of **H2a**, **H4**, and **C2a**. These three peaks are based on the difference of the circumstance of the oxy-(2-hydroxytrimethylene)oxy group as mentioned earlier. In the case of **C1**, the hydroxyl proton was observed as one broad peak at 5.4–5.5 ppm. This is explained by the overlapping of the each hydroxyl proton peak. The peak intensity ratios of the three hydroxyl protons for CPHEs are listed in Table IV. The values are close to 1 : 2 : 1, calculated from the assumption that they have random structure. Therefore, it is concluded that the CPHEs have random composition in terms of the repeating units, $-\text{Ar}-\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2\text{O}-$ and $-\text{BisAF}-\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2\text{O}-$, where Ar is the bisphenol unit.

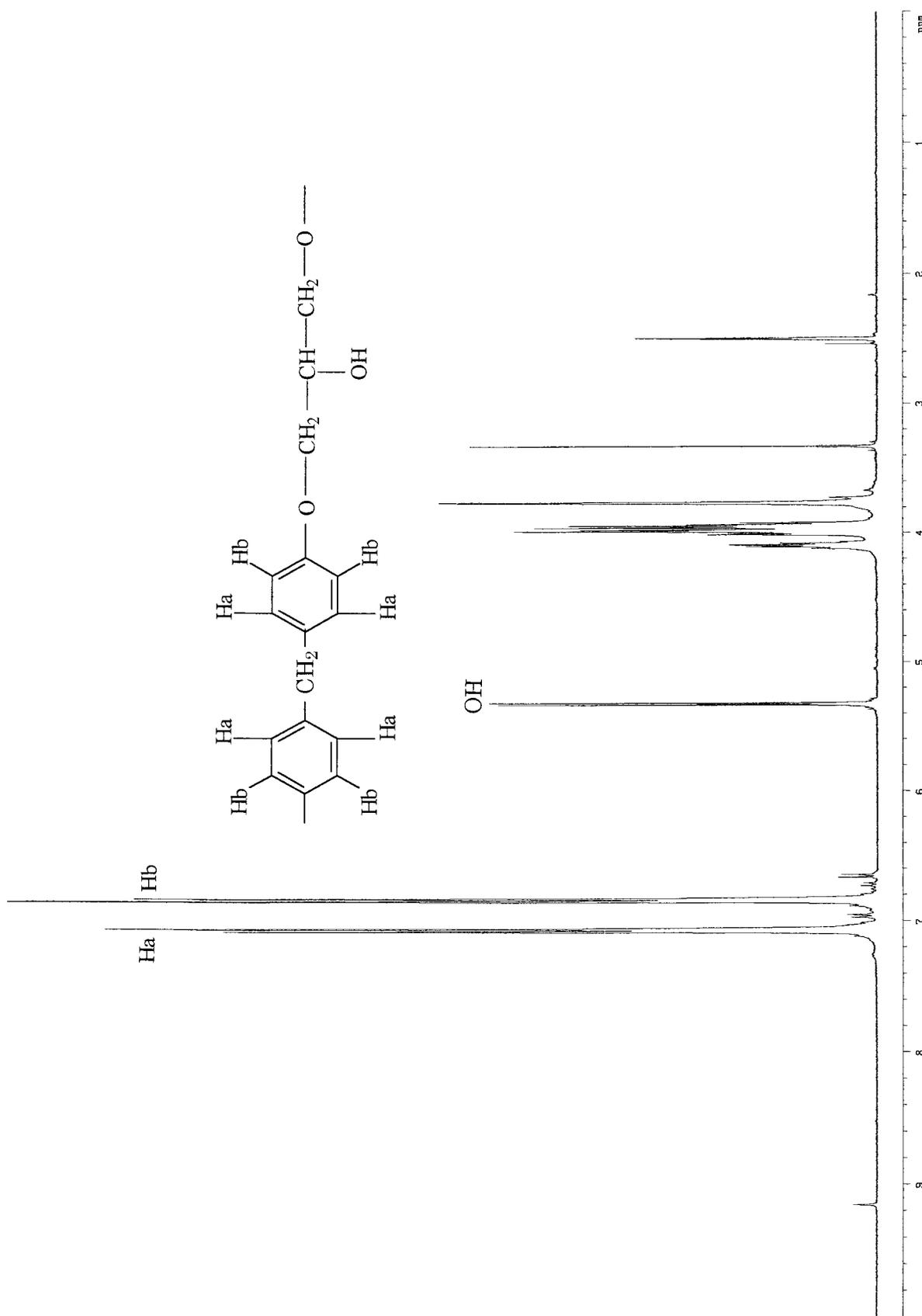


Figure 1 H2a Representative ¹H-NMR spectra of poly(hydroxyethers). **H2a**: homopoly(hydroxyether) based on bisphenol F; **H4**: homopoly(hydroxyether) based on bisphenol AF; **C2a**: copoly(hydroxyether) based on bisphenol F and bisphenol AF.

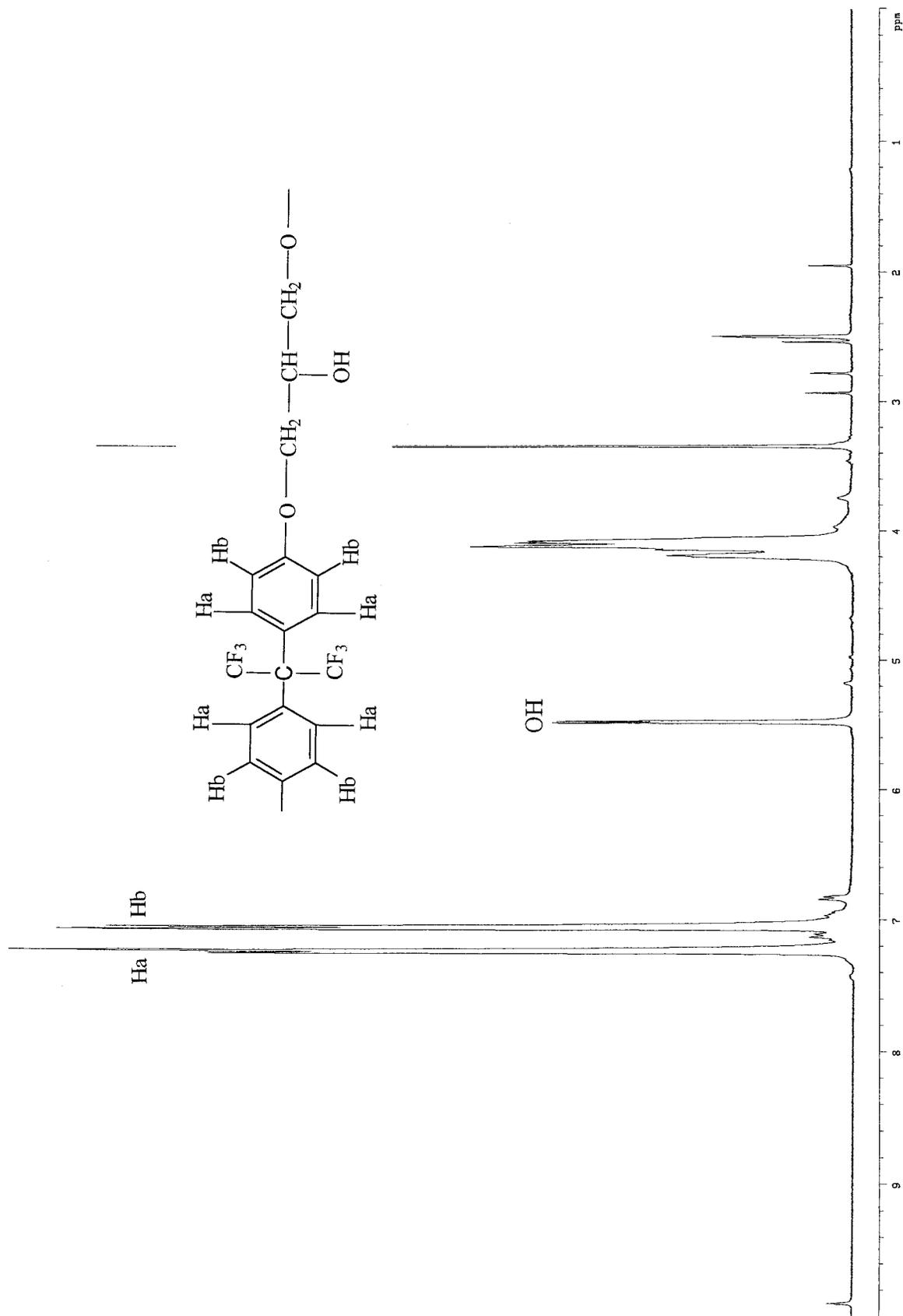


Figure 1 H4 (Continued from the previous page)

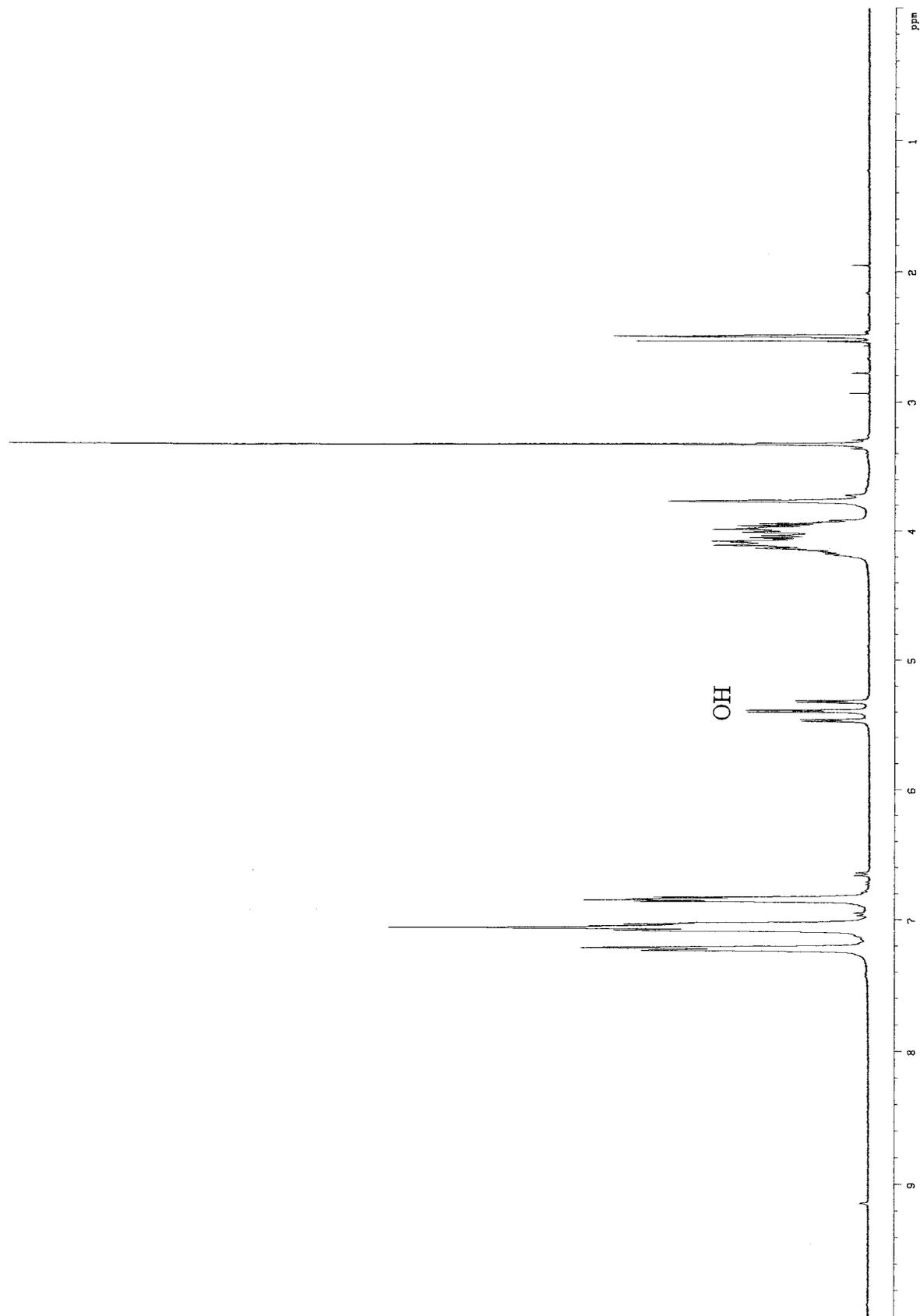


Figure 1 C2a (Continued from the previous page)

Table III Assignment of Homopoly(hydroxyether) by $^1\text{H-NMR}$

| HPHE | Proton Number and Chemical Shift | | | | | | | |
|------------|----------------------------------|--------|--------------------|----------------|--|--------|--------------------|----------------|
| | Bisphenol Unit | | | | —OCH ₂ CH(OH)CH ₂ O— | | | |
| | Group | Calcd. | Obsd. ^a | Chemical Shift | Group | Calcd. | Obsd. ^a | Chemical Shift |
| H1 | | | — ^b | | | | — ^b | |
| H2a | Aromatic | 8H: | 8.29H | 6.84, 7.07 ppm | Hydroxyl | 1H: | 1.00H | 5.33 ppm |
| | Methylene | 2H: | 2.14H | 3.77 ppm | Methylene | 4H: | 4.12H | 3.9–4.0 ppm |
| | | | | | Methine | 1H: | 1.09H | 4.10 ppm |
| H2b | Aromatic | 8H: | 7.93H | 6.83, 7.10 ppm | Hydroxyl | 1H: | 1.00H | 5.32 ppm |
| | Methyl | 3H: | 2.87H | 1.48 ppm | Methylene | 4H: | 4.98H ^c | 3.9–4.0 ppm |
| | Methine ^c | 1H: | — | 3.9–4.0 ppm | Methine | 1H: | 1.00H | 4.10 ppm |
| H2c | Aromatic | 8H: | 8.43H | 6.82, 7.07 ppm | Hydroxyl | 1H: | 1.00H | 5.34 ppm |
| | Methyl | 6H: | 6.22H | 1.55 ppm | Methylene | 4H: | 4.27H | 3.9–4.0 ppm |
| | | | | | Methine | 1H: | 1.07H | 4.11 ppm |
| H2d | Aromatic | 8H: | 8.65H | 6.80, 7.12 ppm | Hydroxyl | 1H: | 1.00H | 5.31 ppm |
| | Methylene | 6H: | 6.05H | 1.40 ppm | Methylene | 4H: | 4.20H | 3.9–4.0 ppm |
| | Methylene | 4H: | 4.10H | 2.18 ppm | Methine | 1H: | 1.11H | 4.08 ppm |
| H3a | Aromatic | 6H: | 6.08H | 6.79, 6.93 ppm | Hydroxyl | 1H: | 1.00H | 5.27 ppm |
| | Methyl | 6H: | 6.21H | 1.52 ppm | Methylene | 4H: | 4.03H | 3.9–4.0 ppm |
| | Methyl ^d | 6H: | 6.04H | 2.07 ppm | Methine | 1H: | 1.10H | 4.15 ppm |
| H3b | Aromatic | 4H: | 4.09H | 6.83 ppm | Hydroxyl | 1H: | 1.00H | 5.25 ppm |
| | Methyl | 6H: | 5.57H | 1.52 ppm | Methylene | 4H: | 4.00H | 3.7–3.8 ppm |
| | Methyl ^d | 12H: | 11.93H | 2.16 ppm | Methine | 1H: | 1.10H | 4.10 ppm |
| H4 | Aromatic | 8H: | 8.32H | 7.05, 7.23 ppm | Hydroxyl | 1H: | 1.00H | 5.47 ppm |
| | | | | | Methylene | 4H: | 4.10H | 4.0–4.1 ppm |
| | | | | | Methine | 1H: | 1.08H | 4.19 ppm |

^a Observed proton numbers were determined on the basis that hydroxyl proton observed was one proton.

^b **H1** could not be prepared.

^c The resonance peak of methine proton of bisphenol unit overlapped with the peak of the methylene proton of oxy-(2-hydroxytrimethylene)oxy group. Therefore, the observed protons were the sum of the one proton of the methine and four methylene protons.

^d Methyl group on the phenylene group.

DSC Analysis

The thermal analysis of HPHEs and CPHEs was carried out using DSC. The DSC curves for all the PHEs showed no end-thermal peak based on the melt of the crystalline, and only the glass-transition point (T_g) was observed. These results indicate that the PHEs are amorphous. The T_g 's of the polymers are listed in Table II. In the polymer series, from **H2a** to **H2c**, the effect of incorporation of the methyl group into the methylene part of the bisphenol unit (—Ph—CH₂—Ph—) on the T_g was investigated. The incorporation of the methyl group produced an increase in T_g from 74 to 100°C, which is attributed to the suppression of rotational mobility around the phenylene-carbon-phenylene (—Ph—C—Ph—) by the steric hindrance of methyl group incorporated. This steric

effect appears more strongly when the pentamethylene group is substituted for two methyl groups (**H2d**). That is, the T_g increases from 100°C (**H2a**) to 120°C (**H2d**). The substitution of the methyl group for the aromatic proton in the phenylene group of the bisphenol A unit also produces an increase in T_g from 89 to 123°C (**H3a** and **H3b**, respectively), which is also explained by the steric hindrance.

Next, the effect of trifluoromethyl group is discussed. When the T_g of **H4** (the homopolymer based on bisphenol AF) is compared with that of **H2c** (the corresponding homopolymer based on bisphenol A), the T_g of **H4** is higher than that of **H2c**. It was reported in detail in a companion study that the T_g of the CPHE prepared from bisphenols **2c** and **4** increased with an increase in

Table IV $^1\text{H-NMR}$ Characterization of Copoly(hydroxyether) (CPHE)

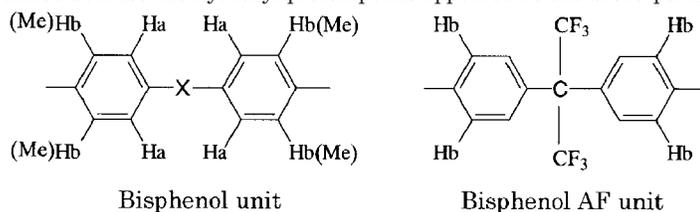
| CPHE | Aromatic Proton in Bisphenol Unit | | Composition Ratio (mol/mol) ^a | |
|------------|-----------------------------------|-------------------------------------|--|--|
| | Chemical Shift (ppm) | Observed Proton Number ^b | (bisphenol AF : bisphenol unit) | Sequence Ratio of Monomer ^c AF—OH—AF/AF—OH—BP/BP—OH—BP |
| C1 | Ha: 7.52 | 3.82 | 51.2 : 48.8 | — ^d |
| C2a | Hb: 6.84 | 3.76 | 51.5 : 48.5 | 1 : 1.89 : 1.03 |
| C2b | Hb: 6.84 | 4.21 | 48.7 : 51.3 | 1 : 2.00 : 1.12 |
| C2c | Hb: 6.83 | 3.95 | 50.3 : 49.7 | 1 : 2.00 : 1.00 |
| C2d | Hb: 6.84 | 4.00 | 50.0 : 50.0 | 1 : 2.25 : 1.09 |
| C3a | Ha: 6.93 | 3.85 | 52.2 : 47.8 | 1 : 1.77 : 0.93 |
| C3b | Ha: 6.82 | 3.89 | 50.5 : 49.5 | 1 : 1.53 : 0.91 |

^a Composition ratio was calculated from the peak strength of the aromatic protons. The feed ratio of bisphenol (Ar) was 50 : 50 (mol/mol).

^b The observed number was calculated on the basis that the Hb proton peak strength (7.20–7.23 ppm) of bisphenol AF unit was four protons.

^c AF = bisphenol AF unit; OH = oxy-(2-hydroxytrimethylene)oxy group; BP = bisphenol unit.

^d The ratio could not be calculated because the hydroxyl proton peaks appeared as one broad peak.



the composition ratio of the bisphenol AF (4) unit.⁴ There are the same cases in which the substitution of the trifluoromethyl group for the methyl group in the base polymer produced an increase in T_g .^{5,6}

The resulting values of T_g 's of CPHEs are mentioned below. As shown in Table II the T_g of CPHE is influenced by the same steric hindrance effect by the methyl or pentamethylene groups with that of HPHE. One can notice that T_g of **C1** is significantly high when compared with that of **C2a**, which is attributed to the rigid structure of the biphenylene unit. We reported the relationship between the composition of the repeating unit and the T_g using the copoly(hydroxyether) based on bisphenol A and bisphenol AF in the previous investigation,⁴ in which the experimental data were in good agreement with the Fox equation, and we concluded that there was no sequence distribution effect on the T_g of the copolymer. In this study, the relationship of T_g between the various CPHEs and the corresponding HPHEs is discussed. The T_g 's of the PHEs are plotted according to the Fox equation (eq. 1),⁷ the results of which are shown in Figure 2.

$$1/T_g = w_1/T_{g1} + w_2/T_{g2} \quad (1)$$

where w_1 and w_2 are the weight fractions of the two repeating units, and T_{g1} and T_{g2} are glass-transition temperatures of the corresponding ho-

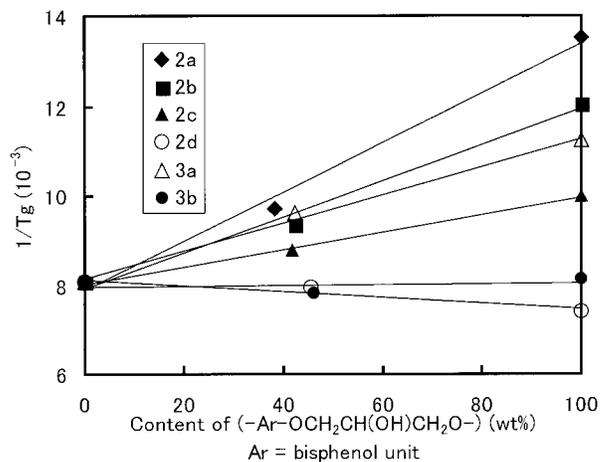


Figure 2 Dependence of T_g on composition of poly(hydroxyethers).

Table V Solubility of PHE in Organic Solvent

| PHE | MeOH | EtOH | Acetone | Chloroform | THF | DMSO | DMAc | DMF | Formic Acid |
|------------------------|------|------|---------|------------|-----|------|------|-----|-------------|
| H1 ^a | — | — | — | — | — | — | — | — | — |
| H2a | Is | Is | Is | Is | Sw | Ds | Ds | Ds | Is |
| H2b | Sw | Sw | Sw | Ds | Ds | Ds | Ds | Ds | Is |
| H2c | Sw | Sw | Sw | Ds | Ds | Ds | Ds | Ds | Is |
| H2d | Is | Is | Sw | Ds | Ds | Ds | Ds | Ds | Is |
| H3a | Sw | Sw | Ds | Ds | Ds | Ds | Ds | Ds | Is |
| H3b | Is | Sw | Ds | Ds | Ds | Ds | Ds | Ds | Is |
| C1 | Is | Is | Sw | Sw | Sw | Ds | Ds | Ds | Is |
| C2a | Sw | Sw | Ds | Ds | Ds | Ds | Ds | Ds | Is |
| C2b | Sw | Sw | Ds | Ds | Ds | Ds | Ds | Ds | Is |
| C2c | Sw | Sw | Ds | Ds | Ds | Ds | Ds | Ds | Is |
| C2d | Sw | Sw | Ds | Ds | Ds | Ds | Ds | Ds | Is |
| C3a | Sw | Sw | Ds | Ds | Ds | Ds | Ds | Ds | Is |
| C3b | Sw | Sw | Ds | Ds | Ds | Ds | Ds | Ds | Is |
| H4 | Ds | Ds | Ds | Ds | Ds | Ds | Ds | Ds | Is |

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

^a **H1** could not be prepared.

mopolymers. In this case the repeating units referred to by subscripts 1 and 2 are $-\text{BisAF}-\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2\text{O}-$ (**H4**) and $-\text{Ar}-\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2\text{O}-$ (HPHE), respectively. T_{g1} and T_{g2} are T_g 's of **H4** and the HPHE based on the corresponding bisphenol, respectively. Figure 2 shows that a linear relationship is observed among the T_g 's of HPHE, the corresponding CPHE, and **C4**. Therefore, it is concluded that there is no sequence distribution effect on the T_g of CPHEs.

Solubility of Polymers in Organic Solvent

The solubilities of the homopolymers and copolymers in organic solvents were investigated at room temperature. The solvents used were methanol (MeOH), ethanol (EtOH), acetone, chloroform, tetrahydrofuran (THF), DMSO, DMAc, dimethylformamide (DMF), and formic acid. The results are summarized in Table V. In the **H2** and **H3** series it is suggested that the introduction of either the methyl or the pentamethylene group into the diphenylmethane part in the polymer increases the solubility in organic solvent. That is, **H2b**, **H2c**, and **H2d** can dissolve in THF and chloroform, and **H3a** and **H3b** are soluble in acetone as well as in THF and chloroform, whereas **H2a**, which has no substituent group in the bisphenol unit, cannot dissolve in these solvents. **H4**, the homopolymer based on bisphenol AF, is soluble in all the solvents investigated, except formic

acid. This excellent solubility of **H4** is attributed to the small intermolecular interaction derived from the trifluoromethyl group. Next, the solubility of CPHE is described. The solubility of CPHEs (except **C1**) increases, when compared with each corresponding HPHE, and they dissolve in acetone, chloroform, THF, and aprotic polar solvents, and swell in alcohols. The increase of the solubility in the various solvents by the copolymerization of bisphenol AF is attributed to the trifluoromethyl group. **C1**, the copolymer based on 4,4'-biphenol, shows poor solubility and dissolves only in aprotic polar solvents, DMSO, DMAc, and DMF. Because the homopolymer **H1** could not be synthesized (because of the precipitation of the oligomer as mentioned earlier), it is clear that the increase in solubility is the result of copolymerization.

Contact Angles

To develop the oxygenator membrane, the wettability of the membrane surface is a very important factor, and a high hydrophobic surface is critically necessary, as mentioned earlier. From this point, we investigated the static contact angles of water and bovine plasma on the homopolymer and copolymer films prepared by the solvent-cast method. The results are shown in Figure 3. The contact angles of water on the HPHEs are in the range of 76–82°, except for **H4**, the bisphenol

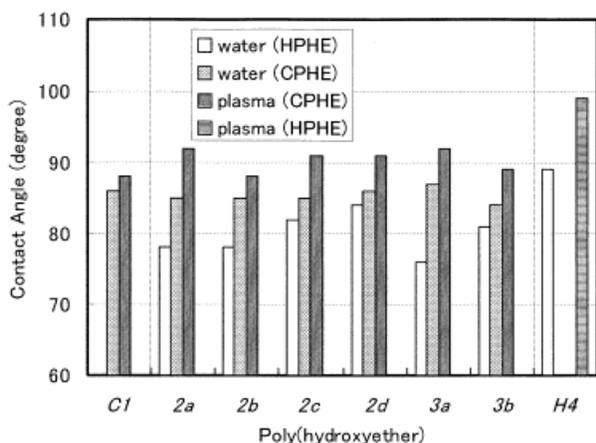


Figure 3 Contact angles of water and bovine plasma on poly(hydroxyethers).

AF-based HPHE. **H4** shows the highest contact angle (89°), and this high hydrophobicity is attributed to the trifluoromethyl group. As predicted from the result of **H4**, the increase in the contact angle of water was observed for all of the CPHEs when compared with the corresponding HPHE, which are in the range of 83 – 87° . Next, the wettability of the PHE surface for bovine plasma is described. It has been considered that the contact angle on the hydrophilic polymer is reduced when the liquid is changed from water to protein solution because of the surfactant effect of the proteins. However, the contact angles of bovine plasma on the CPHEs and **H4** were found to be larger than those of water and they are in the range of 88 – 99° (as shown in Fig. 3), a phenomenon that is very peculiar.

To investigate the phenomenon further, we compared each behavior of the contact angle on **H4**, polypropylene (PP), and silicone films, using water, bovine plasma, and synthetic polymer solution [polyvinylpyrrolidone (PVP)]. The results

are listed in Table VI. This table indicates that the contact angles of the bovine plasma on the common hydrophobic polymers such as PP and silicone are smaller than those of water. This result agrees with the prediction for the contact angle of the protein solution mentioned earlier. The contact angles of the PVP solution on the PP and silicone surfaces are close to that of the plasma on them, behavior that is based on the surfactant effect of PVP. On the other hand, in the case of the **H4** surface, the contact angle of the PVP solution is 86° , whereas that of the plasma is 99° . These results indicate that the extraordinary phenomenon appears only in the case of the combination of the PHEs and the plasma, the reason for which has not yet been clarified, although studies are now in progress. We consider that a specific interaction between the polymer structure and the plasma protein plays an important role in the appearance of this phenomenon.

CONCLUSIONS

Several kinds of CPHEs based on various bisphenols and bisphenol AF, and corresponding homophes were prepared and characterized. The polymers were synthesized by the polycondensation of various bisphenols with epichlorohydrin in DMSO/DMAc mixed solvent. NMR analysis suggested that CPHEs had random structures when the repeating units in the copolymer were considered to be $-\text{Ar}-\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2\text{O}-$ and $-\text{PhC}(\text{CF}_3)_2\text{Ph}-\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2\text{O}-$. When the properties of CPHEs were compared with those of corresponding HPHEs, the CPHEs were more soluble in many kinds of organic solvents and had higher T_g 's. The contact angles of water and bovine plasma on the PHE films were investigated and a peculiar phenomenon was observed. The contact angles of plasma on PHE films were

Table VI Contact Angles on Various Polymer Surfaces

| Liquid | Viscosity (cP) ^a | Contact Angle | | |
|---------------------------|-----------------------------|------------------|---------------|-----------------|
| | | HPHE = H4 | Polypropylene | Silicone Rubber |
| Water | 1.1 | 89° | 97° | 105° |
| Bovine plasma | 3.8 | 99° | 94° | 100° |
| PVP solution ^b | 4.8 | 86° | 94° | 99° |

^a Measured by rotary viscometer at 25.0°C .

^b 1 wt % of polyvinylpyrrolidone solution (PVP-K90, BASF; Germany).

higher than those of water, whereas in common polymers such as polypropylene the former was smaller than the latter. This phenomenon might be brought about by the plasma proteins.

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