Separation of Aqueous Phenol through Polyurethane Membranes by Pervaporation. III. Effect of the Methylene Group Length in Poly(alkylene glycols)

MASARU HOSHI,[1] MUNENORI IESHIGE,[2] TAKANORI SAITOH,[3] TSUTOMU NAKAGAWA[2]

[1] Laboratory of Healthcare Products, LINTEC Corporation, Nishikicho, Warabi, Saitama 335-0005, Japan

[2] Department of Industrial Chemistry, Meiji University, Higashimita, Tamaku, Kawasaki, Kanagawa 214-0033, Japan

[3] Research and Development Division, LINTEC Corporation, Nishikicho, Warabi, Saitama 335-0005, Japan

ABSTRACT: Separation of phenol from dilute aqueous solution through polyurethane membranes by pervaporation was investigated. The effect of the methylene group length in poly(alkylene glycols) on permselectivity and solubility of phenol was studied. The poly(alkylene glycols) were obtained by polycondensation of 1,6-hexanediol, 1,8-octanediol, and 1,10-decanediol with a sulfuric acid catalyst. Polyethyleneglycol and polytetramethyleneglycol were commercially available. Progress of the polymerization in the poly(alkylene glycols) was confirmed by FTIR, ^{1}H-NMR analysis, and SEC measurement. The polyurethanes were obtained by polyaddition reaction of 1,6-hexamethylenediisocyanate and the poly(alkylene glycol), and were confirmed by FTIR analysis and SEC measurement. The phenol concentration in a permeate liquid increased from 25.1 to 36.2 wt %, and the phenol partial flux also increased from 49.3 to 68.9 g $\cdot$ m^{-2} $\cdot$ h^{-1} with increasing the methylene group length in the poly(alkylene glycols), whereas the water partial flux slightly decreased. As a result of sorption measurements, the change in the degree of swelling was small, and the phenol concentration in the membrane increased from 42.1 to 70.8 wt %. The increase in the methylene group length of the poly(alkylene glycols) should contribute to an increase in the hydrophobicity of the polyurethane so that the solubility of phenol to the membrane should increase. The phenol concentration in the permeate liquid and the phenol partial flux increased with an increase in the methylene group length of the poly(alkylene glycols) due to the increase in the phenol solubility for the polyurethane membranes. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 654–664, 2000

Key words: pervaporation; polyurethane; poly(alkylene glycol); phenol

INTRODUCTION

Recently, attention has been focused on environmental pollution by chlorinated hydrocarbons and other organics. To prevent the pollution, these organics have to be separated from waste water and exhaust gases before release to rivers and air.[1]

Membrane separation processes have been studied as an efficient method for liquid mixture separation.[2] Pervaporation, which is one of the membrane separation processes, has been investigated for alcohol dehydration, recovery of useful aroma compounds, and organic solvent separation from dilute aqueous solutions.[3–8] Polyvinylalcohol, polydimethylsiloxane, poly[1-trimethylsilyl-1-propyne], polyacrylate, polyether-*block*-polyamide, and polyurethane have been reported as pervaporation membrane materials.[9–22]

The organic solvent is a minor component in dilute aqueous solutions. Therefore, it is more effective to preferentially permeate the organic

solvent in the case of the organic solvent separation from its dilute aqueous solution. The permeability of pervaporation is expressed by the product of the diffusivity and solubility.[6,23] In general, the molecular size of the organic solvent is larger than that of water, and the diffusivity should be favorable for water. Consequently, it required high affinity (=solubility) and low diffusion resistance of organic solvent to the membrane material in the organic solvent separation.

The polyurethane has unique polymer chain structures. They are formed with a flexible soft segment (polyether diol or polyester diol) and a rigid hard segment diisocyanate. The flexible soft segment reduces the diffusion resistance of the organic solvent. The affinity of specific organic solvent should be increased by selection of the diol compound. Furthermore, the mechanical strength of the membrane is held by the hard segment that is based on a hydrogen bond of the urethane groups. Therefore, the polyurethanes are considered as good membrane material, due to the polyurethanes having various structure and property by choosing a combination of diisocyanate and diol compounds.

In previous work, we have reported polyurethane membranes for the separation of phenol from dilute aqueous solutions.[24,25] The polyurethane, which was made from polytetramethyleneglycol (PTMG), showed a good phenol permselectivity. The phenol concentration in the permeate solution increased from 0 to 65 wt %, and the total flux also increased up to $930 \ g \cdot m^{-2} \cdot h^{-1}$ with increasing the feed concentration of phenol from 0 to 7 wt % for the polyurethane of 1,6-hexamethylenediisocyanate (HMDI)–PTMG. In the sorption measurement at 60°C and 1 wt % phenol aqueous solution, the concentration of phenol in the membrane was 68 wt %, which was higher than that of the permeate solution. It is considered that a good phenol permselectivity was based on high solubility of phenol to the polyurethane membranes. PTMG is soluble in phenol, so that the affinity of PTMG to the phenol should be contributed to the high phenol solubility of the polyurethane.

Comparing phenol and water, the hydrophobicity of phenol should be greater than that of water. Therefore, it is anticipated that the phenol selectivity is going to become higher by increasing the hydrophobicity of the diol compound. PTMG has four methylene groups and one oxygen in a repeating unit. It is thought that the hydrophobicity

of diol increases with increasing the number of methylene groups in the repeating unit.

In this study, the poly(alkylene glycols) that have 6, 8, and 10 methylene groups were synthesized, and polymerized with HMDI. In addition, the polyurethanes using PEG and PTMG were also synthesized. An effect of methylene group length in the polyurethanes were investigated for the separation of phenol from dilute aqueous solution by the pervaporation method.

EXPERIMENTAL

Synthesis of Poly(alkylene glycols)

Poly(alkylene glycols) were synthesized by condensation polymerization.[26] One hundred grams of 1,6-hexanediol (Tokyo Kasei Kogyo) was placed in a flask and heated under vacuum (0.1 mmHg, 100°C) for 1 h to remove the volatiles, water, and other gases. After 1,6-hexanediol was cooled below 50°C, it was placed in a separable reaction flask, which was equipped with a distilling trap with condenser, stirring motor, and calcium dichloride ($CaCl_2$) drying tube. The reaction flask was purged with dry nitrogen, and concentrated sulfuric acid (1.1 mL) was dropped in with stirring. The reaction mixture was heated at 170°C with a temperature-controlled mantle heater. The polymerization reaction was carried out for 8, 10, and 12 h, respectively. The reaction mixture was then slowly poured into a warm, saturated calcium hydroxide aqueous solution to neutralize the sulfuric acid. The mixture was cooled to room temperature with stirring, and a precipitate was filtered and thoroughly washed with water. The precipitate was dried in a vacuum oven at 45°C for 48 h. The dried polymer was dissolved in hot ethanol and filtered to remove residual calcium sulfate. The filtrate was purified by recrystallization from 70/30 (v/v) mixture of ethanol and water, and the precipitate was dried in a vacuum oven at 45°C for 48 h. For the preparation of poly(octamethylene glycol) (POMG) and poly(decamethylene glycol) (PDMG), a similar experimental procedure was carried out in poly(hexamethylene glycol) (PHMG) except for the purification procedure. The purification procedure of POMG and PDMG was carried out as follows.

After completion of the polymerization reaction, the reaction mixture was poured into a warm, saturated calcium hydroxide aqueous solution. The solution was cooled to room tempera-

ture with stirring. A precipitate was filtered and sufficiently washed with water. The precipitate was dried in the vacuum oven at 45°C for 48 h. The dried polymer was dissolved in hot ethanol. The solution was decanted, and the residual material was dissolved with hot ethanol. The decantation and dissolution in hot ethanol were carried out two or three times. The decanted solution was filtered under hot conditions and recrystallized from ethanol. The polymer was dried in the vacuum oven at 45°C for 48 h. The polymerization reaction time in 1,8-octanediol (Tokyo Kasei Kogyo) was 8 and 10 h, and that of 1,10-decanediol (Tokyo Kasei Kogyo) was 6, 8, 10, and 12 h.

Synthesis of Polyurethanes

Into a 500-cm^3 flask equipped with a stirring motor and a reflux condenser with a CaCl$_2$ drying tube, approximately 30 g of poly(alkylene glycol) ($M_w = 4500$), dibutyltindilaurate (DBTDL) as a catalyst, and ethylacetate were placed in an oil bath at 70°C under a dry nitrogen atmosphere and stirred. The concentration of mixture was 70–80 wt %. After 1 h, 1,6-hexamethylenediisocyanate (HMDI) in an amount that was 1.02 times the molar quantity in poly(alkylene glycol) was added, and the mixture was stirred 8 h at the same temperature. The quantity of DBTDL was 0.005% of the total weight in poly(alkylene glycol) and HMDI, and added as 1 wt % ethyl acetate solution. When the viscosity of the solution became high and could not be sufficiently stirred, the solution was diluted with ethylacetate. After 8 h, 1-propanol that amount of 20 mol % of HMDI was added and stirred for 15 min to react the residual isocyanate group and to stop the polyaddition reaction. Thus, polyurethane was obtained. The remnant isocyanate was confirmed by a Fourier transform infrared (FTIR) spectrometer.

In this study, HMDI (Tokyo Kasei Kogyo) as a diisocyanate compound, polyethyleneglycol (PEG, Aldrich), PTMG (BASF), PHMG, POMG, and PDMG as diol compounds were used. HMDI, DBTDL, ethylacetate, and 1-propanol were used without further purification. PEG and PTMG were under vacuum before use to remove water and other gases.

For example, the polyurethane, which was made from HMDI and PTMG (4500 of number-average molecular weight) is represented as HMDI–PTMG(4500).

Size-Exclusion Chromatography

The molecular weight of poly(alkylene glycols) and polyurethanes was measured by size-exclusion chromatography [SEC, HLC-2000 (Tosoh)]. SEC measurements were carried out under the following conditions: detector; RI, carrier; tetrahydrofuran, 1 mL/min, temperature; inlet 35.0°C, column 40.0°C, RI detector 35.0°C, and standard polystyrene.

FTIR, ^{1}H-NMR, and DSC Analysis

FTIR analysis was carried out with SPECTRUM 2000 (Perkin-Elmer). The poly(alkylene glycol) and the polyurethane were deposited on a KBr plate as a thin film. ^{1}H-NMR (400 MHz) spectra were measured with JNM-A400S (JEOL) at room temperature from CDCl$_3$ solution. Differential scanning calorimetric (DSC) measurements were performed by DSC22 (Seiko Instruments Inc.) with a 10°C/min heating rate. A sample weight of about 10 mg was used.

Membrane Preparation

A membrane was prepared in the same way as in the previous work.[17,24] An ethylacetate solution containing 20–30 wt % polyurethane was coated on an exfoliate-treated polyethyleneterephthalate (PET) film, and then dried at 100°C for 5 min. The polyurethane membrane was laminated with a porous polypropylene sheet (Celgard® 2500), and the PET film was displaced with a porous polypropylene sheet. Thus, a sandwiched-type composite membrane was prepared. The membrane thickness was from 60 to 90 μm.

Pervaporation Measurement

Pervaporation measurements were carried out with an apparatus that was reported in a previous work.[25] A permeation cell was assembled from two half-cells of stainless steel and fastened together by bolted clamps. A Viton® O-ring was used between the pervaporation cell's upper compartment and the membrane. The membrane was supported on a sintered stainless steel plate with holes, and the effective membrane area was 14.55 cm^2. The feed liquid (1000 cm^3) was circulated using a microtube pump. The downstream pressure was kept below 0.1 mmHg, and the upstream pressure was maintained at atmospheric pressure. The permeate vapor was collected in a cold trap surrounded by liquid nitrogen.

The experimental procedure was as follows: the pervaporation cell, after setting the membrane, was placed in a constant-temperature water bath maintained at 60°C. The downstream side of the membrane was under vacuum, and the feed liquid was circulated. After reaching a steady-state condition, the permeate vapor was collected. The phenol concentration in the feed liquid was measured by gas chromatographic analysis at the start and the end of the pervaporation measurements. The concentration of the phenol and water in the permeate liquid and the flux were determined by gas chromatographic analysis and by measuring the weight of the collected sample, respectively. The concentration of the phenol in the permeate liquid was high, so that the permeant separated into two phases. The gas chromatographic analysis was then carried out by adding ethanol to make a uniform solution.

For each condition, the previous pervaporation measurements were conducted three times, and it was confirmed that the flux and the concentration of the phenol and water in the permeate liquid were constant.

The flux was calculated from the following equation:

$$\text{Flux (g·m}^{-2}\text{·h}^{-1}) = \frac{Q}{A \cdot t} \qquad (1)$$

The separation factor of permeation was expressed as follows:

$$\text{Separation factor}_{\text{(phenol/water)}} = \frac{C^2_{\text{phenol}}/C^2_{\text{water}}}{C^1_{\text{phenol}}/C^1_{\text{water}}} \qquad (2)$$

Sorption and Degree of Swelling Measurement

The polyurethane membrane without a porous substrate was prepared by the same method as the pervaporation membrane. The polyurethane membrane piece, whose weight was previously measured, was immersed in the aqueous phenol solution for 48 h at 60°C. The solution on the membrane surface was wiped off, and the weight of the membrane was measured. The polyurethane piece was sandwiched between polyethyleneterephthalate mesh sheets for the swelling measurement because of the adhesiveness of the polyurethane.

The degree of swelling was calculated as follows:

$$\text{Degree of swelling (\%)} = \frac{W_W - W_D}{W_D} \times 100 \qquad (3)$$

The concentration of the absorbate was measured with an apparatus that was previously reported.[25]

After weighing the swollen membrane for the degree of swelling measurement, the membrane piece was frozen in a glass vessel with liquid nitrogen. The glass vessel and a cold trap were under vacuum, and the glass vessel was then heated after removing the liquid nitrogen. The absorbate was vaporized and collected in the cold trap with liquid nitrogen. The pressure of the glass apparatus was made atmospheric by opening a leak cock attached to a $CaCl_2$ drying tube. The concentration of the phenol and water was determined by measuring the collected liquid in the same way as for the pervaporation.

RESULTS AND DISCUSSION

Synthesis of Poly(alkylene glycols)

The number-average molecular weight (M_n) and the weight-average molecular weight (M_w) in the poly(alkylene glycols) for each reaction time with SEC are summarized in Table I. The yields are also summarized in Table I. The poly(alkylene glycols) after purification were used for the characterization and the calculation of yields.

The M_n of PHMG increased progressively from 4.37×10^3 to 1.12×10^4 with increasing reaction time; that of POMG and PDMG slightly increased from 4.21×10^3 to 5.51×10^3, and from 3.84×10^3 to 5.12×10^3, respectively. In the polycondensation reaction of the diol compound, a cyclic compound as a byproduct was obtained by intramolecular reaction.[26] The intramolecular reaction in the 1,10-decanediol should be more progressive than that of the 1,6-hexanediol due to flexibility and length of the molecular chain. Therefore, it is thought that the dependence of the reaction time on the molecular weight was different from the increase in the intramolecular reaction with increasing the methylene group length.

The yields of poly(alkylene glycol) were from 30.4 to 38.5%. The polydispersity index was less than 1.5, and was relatively narrow. Because the low molecular weight compounds were removed by the purification procedure, the yields should become low, and the polydispersity index should be narrow. The poly(alkylene glycol) where the

Table I Molecular Weight by SEC and Yield of Poly(alkylene glycols)

	Reaction Time (h)	M_n (×10³)	M_w (×10³)	M_w/M_n	Yield (%)
1,6-Hexanediol	8	4.37	5.98	1.37	30.4
	10	9.34	12.0	1.29	35.6
	12	11.2	13.9	1.24	34.7
1,8-Octanediol	8	4.21	5.50	1.31	33.4
	10	5.51	7.65	1.39	35.0
1,10-Decanediol	6	3.84	3.99	1.04	32.0
	8	4.91	5.70	1.16	38.5
	10	4.53	4.83	1.07	33.5
	12	5.12	5.86	1.15	35.2

M_n was ca. 4500 was used for the polyurethane synthesis (reaction time; PHMG: 8 h, POMG: 8 h, PDMG: 10 h).

Figure 1 shows the FTIR spectrum of 1,6-hexanediol and PHMG. A broad strong band in the 3600–3200 cm^{-1} region (—OH:O; stretching) and a wide band of medium intensity between 750–400 cm^{-1} (—OH:O; out-of-plane hydrogen defor-
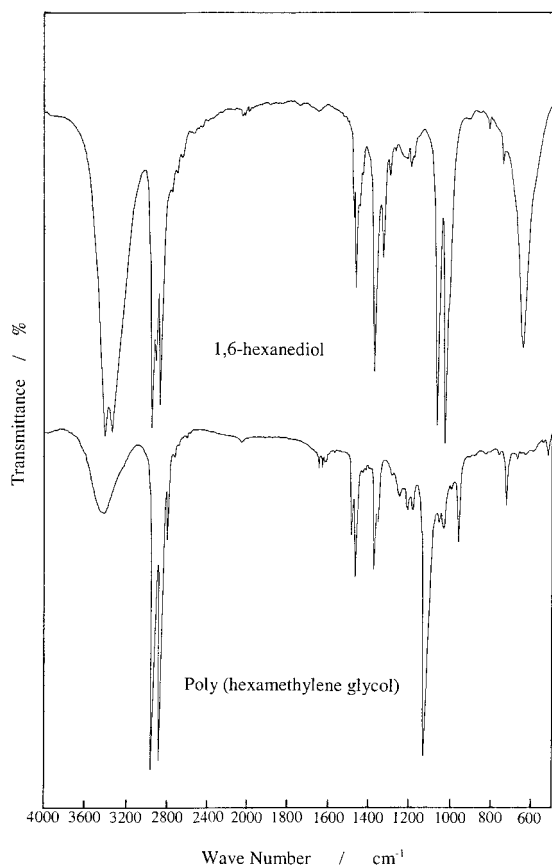

Figure 1 FTIR spectrum of 1,6-hexanediol and poly-(hexamethylene glycol).

mation of intermolecularly hydrogen bonded groups) due to hydrogen bonding of alcoholic hydroxyl groups of 1,6-hexanediol became weak in PHMG. A strong band in the 1150–950 cm^{-1} region due to C—O—C stretching vibration appeared in PHMG.[27] It is considered that the number of hydroxyl groups of 1,6-hexanediol were decreased and increased the ether bonding by polymerization. The same changes of peaks in 1,8-octanediol–POMG and 1,10-decanediol–PDMG were observed.

The ¹H-NMR spectrum of PHMG is shown in Figure 2. The assignments were on the basis of the chemical shift values and the signal areas.[26] The ¹H-NMR spectrum of PHMG showed the signals at δ 1.36 [m, —CH₂CH₂(CH₂)₂CH₂CH₂—], 1.57 (m, —O—CH₂CH₂—), 3.39 (t, —O—CH₂—), and 3.64 ppm (t, HO—CH₂—). The ¹H-NMR signals at δ 1.29, 1.53, 3.37, and 3.61 ppm in the POMG were observed, and the signals at δ 1.31, 1.56, 3.38, and 3.63 ppm were observed in the PDMG.

As a result of the previous analysis, it is thought that the polymerization reaction progressed sufficiently.

Figure 3 shows the DSC thermograms for poly-(alkylene glycols), and the thermal transitions are summarized in Table II.

These poly(alkylene glycols) were very crystalline.[28] The thermal transition in Figure 3 (T_{m1}) was thought to be the melting temperature of a crystalline structure of the poly(alkylene glycol). The T_{m1} was increased from 25.2 to 63.1°C with increasing the methylene group length.

Synthesis of Polyurethane

The FTIR spectrum of HMDI–PHMG(4500) is shown in Figure 4. A strong absorption in the 2260–2280 cm^{-1} region of HMDI (asymmetric
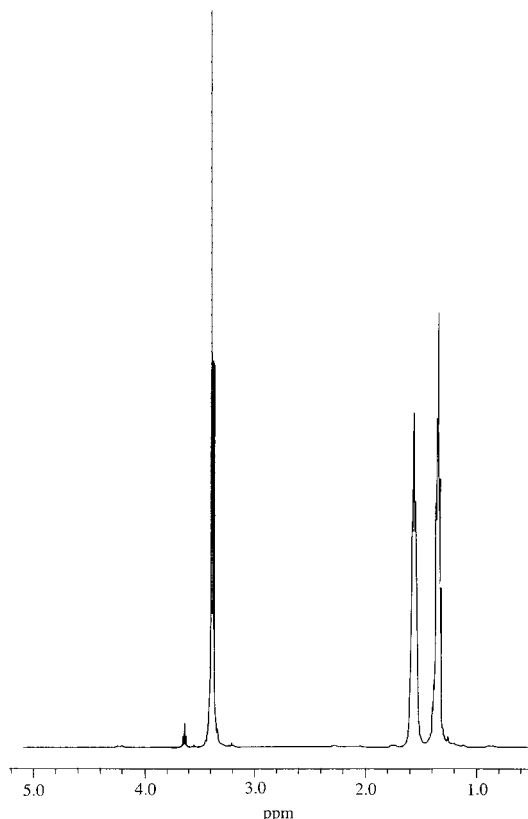
Figure 2 ^{1}H-NMR spectrum (400 MHz) of purified PHMG.

Figure 3 DSC thermograms for purified poly(alkylene glycols).

—N═C═O stretch) was not observed. A peak near the 1720 cm^{-1} of the C═O stretch or Amide I appeared.[29] This peak was not observed for HMDI or PHMG(4500). A similar spectrum was obtained on the other polyurethanes.

The M_n, M_w, and polydispersity index of the polyurethanes are summarized in Table III. The M_w was over 1.0×10^5, and it was sufficient to prepare the membrane. The polydispersity index was from 1.65 to 2.36. It is considered that the dispersity was the usual distribution, and there was little chain branching. The polyaddition reaction should progress sufficiently as a result of the FTIR analysis and the molecular weight by SEC.

Figure 5 shows the DSC thermograms of the polyurethanes, and the thermal transitions are summarized in Table II. The glass transition temperature (T_g) for various polyurethanes was nearly equal.

The polyurethanes, which were synthesized from a 4,4′-methylenediphenyldiisocyanate (MDI), 1,4-butanediol (BD), and poly(alkylene glycol), showed different T_g with an increase in the meth-
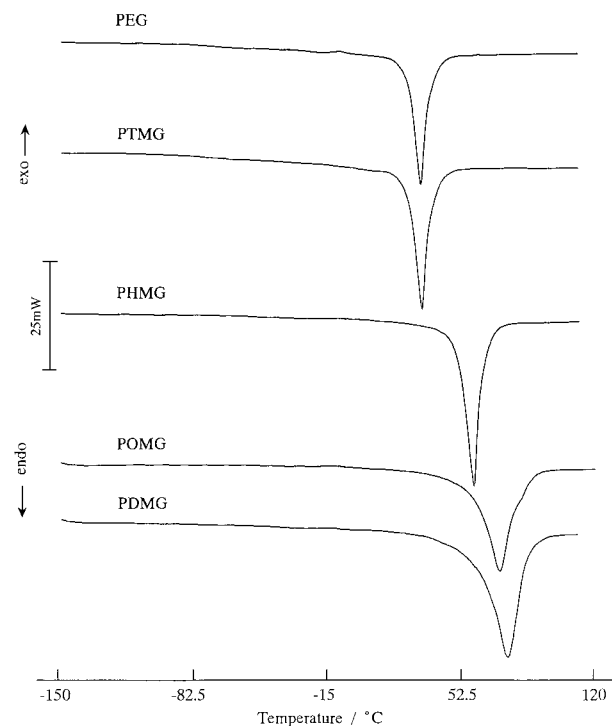
ylene group length of the poly(alkylene glycols).[28] These polyurethanes were linear segmented polymers with a hard segment (MDI and BD)–soft segment [poly(alkylene glycol)] type structure (HS type), and had two T_gs of the soft segment and the hard segment. The T_g below room temperature indicated that of a soft segment. Therefore, the HS-type polyurethanes where the soft segment was a different poly(alkylene glycol) showed different T_gs in the low temperature region. The polyurethanes in this study were an

Table II   Thermal Transitions of Polyurethanes and Poly(alkylene glycols) by DSC

	Poly(alkylene glycol)	Polyurethane[a]	
	T_{m1} (°C)	T_g (°C)	T_{m2} (°C)
PEG	25.2	−82.9	18.2
PTMG	25.3	−83.2	19.6
PHMG	50.6	−81.6	12.0
POMG	58.4	−82.4	13.0
PDMG	63.1	−80.5	9.8

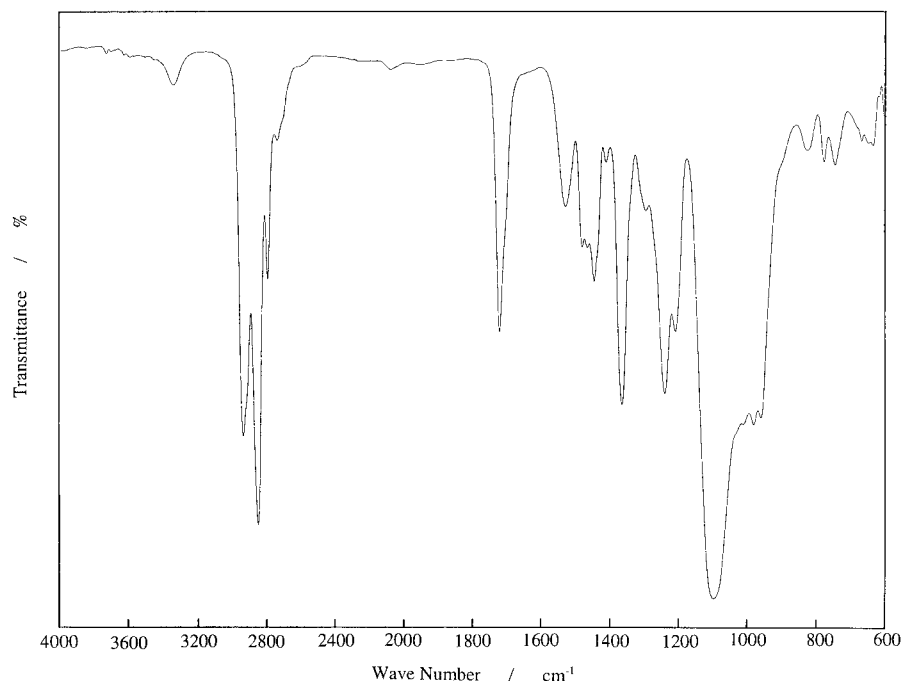[a] Polyurethane: HMDI–poly(alkylene glycol)(4500).

Figure 4   FTIR spectrum of HMDI–PHMG(4500).

alternate structure of HMDI and poly(alkylene glycol). It is thought that these did not have a definite HS-type structure. Consequently, the original properties of poly(alkylene glycols) diminished, and the different behavior of T_g in the low-temperature region should be observed.

Although the T_{m1} increased with increasing the methylene group length of poly(alkylene glycols), the peaks from 10 to 20°C (T_{m2}), which was attributed to the melting temperature of a crystalline structure in the poly(alkylene glycol) segment, were decreased. Furthermore, the difference between T_{m1} and T_{m2} of the poly(alkylene glycol) that had a long methylene group was greater than that of the short one. PTMG as a homopolymer is a crystalline substance having a melting point at about 45°C. However, in polyure-
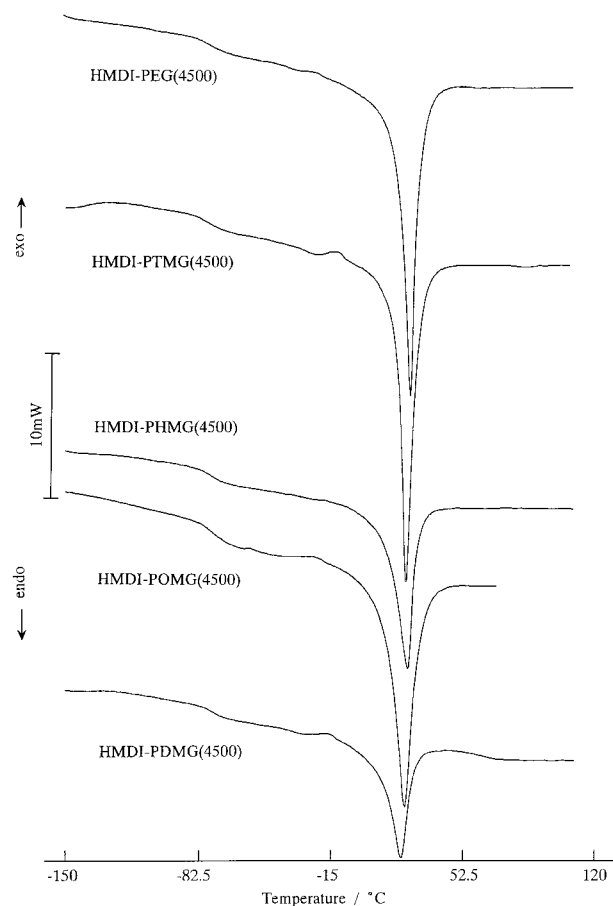
Table III   Molecular Weight of Polyurethanes by SEC

Polyurethane	M_n ($\times 10^4$)	M_w ($\times 10^5$)	M_w/M_n
HMDI–PEG(4500)	8.98	1.48	1.65
HMDI–PTMG(4500)	7.09	1.44	2.04
HMDI–PHMG(4500)	7.60	1.54	2.02
HMDI–POMG(4500)	14.9	3.52	2.36
HMDI–PDMG(4500)	16.2	3.24	2.00

Figure 5   DSC thermograms for polyurethanes of HMDI–poly(alkylene glycol).

phenol concentration in the permeate liquid increased from 25.1 to 36.2 wt % with an increase in the methylene group length of the poly(alkylene glycol). The phenol partial flux also increased from 49.3 to 68.9 $g \cdot m^{-2} \cdot h^{-1}$, and the water partial flux slightly decreased.

Figure 7 shows the results of sorption and degree of swelling measurements at 60°C and 1 wt % phenol aqueous solution for the various polyurethane. The phenol concentration in the membrane increased from 42.1 to 70.8 wt % as well as the phenol concentration in the permeate liquid. The degree of swelling was around 90%, and the dependence of the methylene group length of poly(alkylene glycol) was small.

For the polyurethanes of HMDI–PTMG, the degree of swelling in 1 wt % phenol aqueous solution increased with increasing the molecular weight of the PTMG.[25] The distance of urethane groups in the polymer chain becomes long, and a physical crosslinking density by a hydrogen bond of urethane groups decreased in the polyurethane consisting of the high molecular weight of the PTMG. The molecular weight of poly(alkylene glycols) was nearly equal (ca. M_n = 4500), so that the physical crosslinking density of polyurethanes should also be equal. The crosslinking density relates to the degree of swelling.[25] It is considered that the change in the degree of swelling was small. Furthermore, the diffusivity should not be the degree of swelling dependence, but it should be a concentration dependence.

For the unit molecular weight, a number of hydrophobic methylene groups in PDMG is
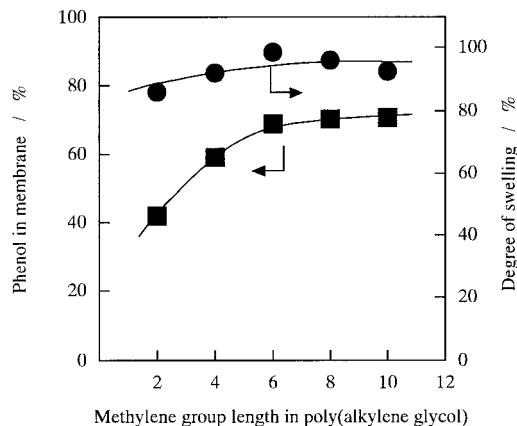

Figure 6 Effect of methylene length in poly(alkylene glycols) on the separation of phenol through HMDI–poly(alkylene glycol) membranes. Pervaporation conditions: feed solution, 1 wt % phenol aqueous solution; temperature, 60°C; downstream pressure, below 1 mmHg.

thanes, the PTMG soft segment loses its ability to crystallize when the segment length is short enough, due to steric hindrance.[30] It is thought that the crystallization of the poly(alkylene glycol) segment in the polyurethane was inhibited by the polyaddition of HMDI. The steric hindrance should influence the crystallization ability of the poly(alkylene glycol) that had long methylene groups. Therefore, it is considered that the T_{m2} was decreased with increasing the methylene group length, and the difference between T_{m1} and T_{m2} in the poly(alkylene glycol) of the long methylene group was greater than that of the short one.

Pervaporation and Sorption Measurement

The results of pervaporation measurements at 60°C and 1 wt % phenol aqueous solution for the various polyurethanes are shown in Figure 6. The

Figure 7 Effect of methylene length in poly(alkylene glycols) on the sorption and swelling for HMDI–poly-(alkylene glycol) membranes at 60°C, 1 wt % phenol aqueous solution.
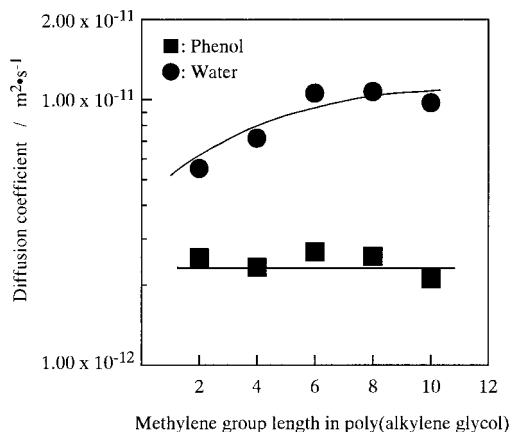
Figure 8 Effect of methylene length in poly(alkylene glycols) on the apparent mean diffusion coefficient for HMDI–poly(alkylene glycol) membranes at 60°C, 1 wt % phenol aqueous solution.

greater than PEG, whereas a number of ether groups, which are more hydrophilic than the methylene group, in PEG is greater than PDMG. In the unit molecular weight, the hydrophobicity of the poly(alkylene glycol) that has a long methylene group should become greater than that of the short methylene group one. Thus, it is considered that the concentration of phenol in the membrane increased with increasing the methylene group length in poly(alkylene glycols). The increase in the solubility of phenol should contribute to the phenol permselectivity.

Under the pervaporation conditions, it is thought that a concentration gradient through the membrane is not constant.[31,32] Therefore, a diffusion coefficient that is calculated by the following equations is thought to be an apparent mean diffusion coefficient.[24,25]

$$J_i = \frac{P_i}{l} C_i^1 \qquad (4)$$

$$P_i = D_i \cdot K_i \qquad (5)$$

$$K_i = \frac{C_i^3}{C_i^1} \qquad (6)$$

Figure 8 shows the influence of the methylene group length in poly(alkylene glycols) on the apparent mean diffusion coefficient of the phenol (D_{phenol}) and the water (D_{water}) that was calculated by eqs. (4), (5), and (6). The D_{phenol} was practically constant, whereas the D_{water} in-

creased with increasing the methylene group length in the poly(alkylene glycols).

The melting temperature of the poly(alkylene glycol) segment in the polyurethane (T_{m2}) that had a long methylene group was lower than that of the shorter one. Consequently, the flexibility of the poly(alkylene glycol) segment that had a long methylene group should be greater than that of the short one at the experiment temperature. However, the level of the increase in poly(alkylene glycol) segments (i.e., polymer chain) flexibility should be affected on the water molecule diffusivity, and should have little influence on the phenol molecule diffusivity because the molecular size of the phenol is larger than that of the water. For example, van der Waals volume of phenol is 53.9 cm^3/mol, and that of water is 11.6 cm^3/mol.[33,34] Therefore, it is considered that the water diffusivity increased, and that of the phenol was practically constant.

The permeability of pervaporation is thought as a product of the diffusivity and solubility.[6,23] Thus, the phenol concentration in the permeant and the phenol partial flux should be increased due to the increase in the solubility of phenol to the membrane and the constant diffusivity. On the other hand, the water concentration in the membrane decreased. Because the dependence of the methylene group length on the degree of swelling was small and the water concentration in the membrane decreased, it is considered that the water solubility to the polyurethane membrane decreased with increasing the methylene group length. The diffusivity of water increased, whereas the solubility of that remarkably decreased with increasing the methylene group length. Therefore, it is considered that the water partial flux decreased due to the behavior of the diffusivity and solubility.

CONCLUSIONS

Poly(alkylene glycols) were synthesized by polymerization of 1,6-hexanediol, 1,8-octanediol, and 1,10-decanediol using a sulfuric acid catalyst. The M_n of these poly(alkylene glycols) increased with increasing reaction time. As a result of FTIR, ^{1}H-NMR analysis, and SEC measurement, the polymerization reaction should sufficiently progress.

Polyurethanes were synthesized by polyaddition reaction of poly(alkylene glycols) (polyethyleneglycol, polytetramethyleneglycol, polyhexa-

methyleneglycol, polyoctamethyleneglycol, and polydecamethyleneglycol), and 1,6-hexamethylenediisocyanate (HMDI) using a dibutyltindilaurate catalyst. The progress in the polyaddition reaction was confirmed with FTIR analysis and SEC measurements. These polyurethanes had sufficient strength to prepare pervaporation composite membranes with porous substrate. The glass transition temperature for various polyurethanes was nearly equal. The peaks that were thought of as the melting temperature of the crystalline structure in the poly(alkylene glycol) segment for the polyurethane (T_{m2}) were decreased with increasing the methylene group length. Furthermore, the difference between the melting temperature of poly(alkylene glycol) and T_{m2} in the long methylene group was greater than that of the short one. It is thought that the crystallization of the poly(alkylene glycol) segment in the polyurethane was inhibited by polyaddition with HMDI.

The phenol permselectivity (the phenol concentration in the permeate liquid and the phenol partial flux) increased with increasing the methylene group length in the poly(alkylene glycol), and the water partial flux was slightly decreased. The apparent mean diffusion coefficient of phenol that was calculated from the results of pervaporation and sorption measurement was practically constant, and that of water increased. Though the flexibility of the polymer chain should be increased with increasing the methylene group length, it is considered that the level of flexibility increase affected on the water molecule diffusivity, and did not affect on that of the phenol. The difference in the behavior of the phenol and water diffusivity was assumed to be the difference in molecular size between the phenol and water. Because of the increase in the hydrophobicity of the poly(alkylene glycol) chain with increasing the methylene group length and the behavior of diffusivity, it is thought that the phenol concentration in the permeate liquid and the phenol partial flux increased, and the water partial flux slightly decreased.

NOMENCLATURE

A effective membrane area
C concentration
D diffusion coefficient
J flux
K partition coefficient
l membrane thickness
P permeability coefficient
Q weight of permeate liquid
t measurement time
W_D dried membrane weight
W_W swollen membrane weight

Superscripts

1   quantities concerning the bulk feed solution
2   quantities concerning the downstream side of membrane
3   quantities concerning the membrane interior

Subscripts

i component i
phenol   concerning phenol
water   concerning water

REFERENCES

1. Mulder, M. In Membrane Processes in Separation and Purification; Kluwer Academic Publishers: Dordrecht, 1994, p. 229.
2. Mulder, M. In Basic Principles of Membrane Technology; Kluwer Academic Publishers: Dordrecht, 1996, p. 7.
3. Néel, J. In Pervaporation Membrane Separation Processes; Elsevier: Amsterdam, 1991, p. 1.
4. Yamaguchi, T.; Yamahara, S.; Nakao, S.; Kimura, S. J Membr Sci 1994, 95, 39.
5. Matsuura, T. In Synthetic Membranes and Membrane Separation Processes; CRC Press: Boca Raton, FL, 1994, p. 431.
6. Zhang, S.; Drioli, E. Sep Sci Technol 1995, 30, 1.
7. Baudot, A.; Marin, M. J Membr Sci 1996, 120, 207.
8. Börjesson, J.; Karlsson, H. O. E.; Trägårdh, G. J Membr Sci 1996, 119, 229.
9. Néel, J.; Aptel, P.; Clément, R. Desalination 1985, 53, 297.
10. Huang, R. Y. M.; Jarvis, N. R. J Appl Polym Sci 1970, 14, 2341.
11. Blume, I.; Baker, R. In Proceedings of Second International Conference on Pervaporation Processes in the Chemical Industry, Bakish Materials Corp., Englewood, 1987, p. 111.
12. Favre, E.; Nguyen, Q. T.; Bruneau, S.; Néel, J. In Proceedings of Seventh International Conference on Pervaporation Processes in the Chemical Industry, Bakish Materials Corp., Englewood, 1995, p. 229.
13. Nakagawa, T.; Yoshida, T.; Higuchi, A. Polym Mater Sci Eng 1992, 67, 264.
14. Nagase, Y.; Ishihara, K.; Matsui, K. J Polym Sci Part B 1990, 28, 377.

15. Hoshi, M.; Saito, T.; Higuchi, A.; Nakagawa, T. Sen-i Gakkaishi 1991, 47, 644.
16. Nakagawa, T.; Hoshi, M.; Higuchi, A. In Proceedings of Fifth International Conference on Pervaporation Processes in the Chemical Industry, Bakish Materials Corp., Englewood, 1991, p. 88.
17. Hoshi, M.; Kobayashi, M.; Saitoh, T.; Higuchi, A.; Nakagawa, T. J Appl Polym Sci 1998, 69, 1483.
18. Böddeker, K. W.; Bengtson, G.; Bode, E. J Membr Sci 1990, 53, 143.
19. Meckl, K.; Lichtenthaler, R. N. J Membr Sci 1996, 113, 81.
20. Ji, W.; Sikdar, S. K.; Hwang, S.-T. J Membr Sci 1994, 93, 1.
21. Ohst, H.; Hildenbrand, K.; Dhein, R. In Proceedings of Fifth International Conference on Pervaporation Processes in the Chemical Industry, Bakish Materials Corp., Englewood, 1991, p. 7.
22. Cipriano, M. M.; Diogo, A.; de Pinho, M. N. J Membr Sci 1991, 61, 65.
23. Böddeker, K. W. J Membr Sci 1990, 51, 259.
24. Hoshi, M.; Kogure, M.; Saitoh, T.; Nakagawa, T. J Appl Polym Sci 1997, 65, 469.
25. Hoshi, M.; Ieshige, M.; Saitoh, T.; Nakagawa, T. J Appl Polym Sci 1999, 71, 439.
26. Gunatillalke, P. A.; Meijs, G. F.; Chatelier, R. C.; McIntosh, D. M.; Rizzardo, E. Polym Int 1992, 27, 275.
27. Nyquist, R. A. In The Infrared Spectra Atlas of Monomers and Polymers; Sadtlar Research Laboratories: Philadelphia, PA, 1980, p. 245.
28. Martin, D. J.; Meijs, G. F.; Renwick, G. M.; Gunatillake, P. A.; McCarthy, S. J. J Appl Polym Sci 1996, 60, 557.
29. Nyquist, R. A. In The Infrared Spectra Atlas of Monomers and Polymers; Sadtlar Research Laboratories: Philadelphia, PA, 1980, p. 203.
30. Petrović, Z. S.; Simendić, J. B. Rubber Chem Technol 1985, 58, 685.
31. Nakagawa, T. In Membrane Science and Technology; Dekker: New York, 1992, p. 239.
32. Mulder, M. In Basic Principles of Membrane Technology; Kluwer Academic Publishers: Dordrecht, 1996, p. 325.
33. Shibusawa, T. Sen-i Gakkaishi 1987, 43, 401.
34. Bondi, A. J Phys Chem 1964, 68, 441.