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Specialty Polymeric Membranes. VIII. Separation of Benzene from Benzene/Cyclohexane Mixtures with Nylon 6-*graft*-Poly(Butyl Methacrylate) Membranes

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ABSTRACT

A novel pervaporation membrane was prepared by radical graft polymerization of butyl methacrylate onto nylon 6. The permselectivity toward benzene was increased by the introduction of poly(butyl methacrylate) onto a nylon 6 membrane. From pervaporation and sorption experiments, it was shown that the introduction of poly(butyl methacrylate) onto a nylon 6 membrane leads to the enhancement of permselectivity toward benzene. The solubility data for benzene were described by a combination of simple sorption and specific sorption, while cyclohexane solubility was described by simple sorption.

Key Words. Pervaporation; Graft polymer; Nylon 6; Poly(butyl methacrylate); Membrane; Benzene; Cyclohexane; Permselectivity

INTRODUCTION

Separation carried out by membranes is regarded as one of the most promising processes of energy-saving separation techniques. Our attention has been especially attracted to the membrane separation technique since the energy crisis developed. When membrane separation techniques are used instead of distillation, which consumes much heat energy, a number of organic liquid

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mixtures which are difficult to separate, such as azeotropic mixtures, mixtures with close boiling points structural isomers, or heat-sensitive organic compounds, can separated with ease and with low energy consumption.

Pervaporation is a potential method to separate liquid mixtures wherein a membrane separates an upstream mixture in the liquid state from downstream permeates in the gaseous state and the downstream side is maintained at a reduced pressure to ensure the gaseous state. Pervaporation was named by Kober (1) and suggested by Binning and Lee (2).

For the application of pervaporation in the chemical industry, the following three categories are required:

1. Water removal from water/organic liquid mixtures
2. Removal of organics from water
3. Organic/organic separations

Much attention was focused in the 1980s on category 1, especially the separation of water from aqueous ethanol solutions in connection with the effective production of ethanol (3, 4). More recently, categories 2 and 3 have gained much attention. The former is closely connected with regulations regarding the removal of volatile organic compounds (VOC) (5, 6), and the latter, which has been the least developed up to the present and has the largest potential industrial impact, has gotten attention since early in the 1990s. Category 3 is thought to have the most significant potential application for pervaporation.

The pervaporation separation of olefins from olefins/paraffins mixtures and of aromatics from aromatics/aliphatics mixtures with membranes are interesting subjects to chemical industries, especially in petrochemical industries. The removal of benzene is an interesting and important subject in connection with the environmental issue (7).

Many articles have reported the pervaporation separation of benzene/cyclohexane mixtures, both of which were among the 50 chemicals in 1995 (8), with synthetic polymeric membranes (9–26). From the results reported in these articles, an increase in the solubility of benzene is required so that novel membrane materials for the pervaporation separation of benzene/cyclohexane mixtures might be developed. However, it should be kept in mind that the plasticization effect due to the incremental solubility of benzene often leads to a decrease in the permselectivity of benzene.

In the present report, nylon 6 was adopted as a membrane matrix because polyamides (such as nylon 6, nylon 66, etc.) have been regarded as promising membrane materials due of their excellent strength and commercial availability. The polar amide linkage (—CONH—) in nylon 6 provides high crystallinity (in other words, physical crosslinking) which is expected to show resistance against swelling by permeants during pervaporation. As an atomic group which shows an affinity to benzene, butyl methacrylate was selected (27), and it was introduced onto nylon 6 by radical graft polymerization. As summarized comprehensibly (28), heterogeneous graft polymerization with vinyl and other unsaturated monomers onto polyamides has been investigated ever since the late 1950s. However, we know of only a few successful examples of homogeneous modification of polyamides with free radical methods (26, 29–33). In the present paper, the homogeneous graft polymerization of butyl methacrylate onto nylon 6 is reported.

In the present article, the preparation of nylon 6-*graft*-poly(butyl methacrylate) and the pervaporation separation of benzene/cyclohexane mixtures with membranes from modified nylon 6 are described.

EXPERIMENTAL

Materials

Nylon 6 (N6), UBE NYLON 1022B, was kindly provided by Ube Ind. Ltd. Butyl methacrylate (BMA) (34), potassium persulfate (KPS) (34), and formic acid (35) were purified before use. Methanol (MeOH), 2,2,2-trifluoroethanol (TFE), benzene, cyclohexane, and cyclohexene were used without further purification. Distilled water was employed.

Graft Polymerization

An ampule containing prescribed amounts of N6, BMA, KPS, and formic acid was degassed by three freeze–pump–thaw cycles and sealed off under reduced pressure which was below 10^{-4} mmHg. The sealed ampule was shaken in a water bath at a constant temperature of 80°C for 1 hour. The reaction mixture was poured into a large amount of nonsolvents of N6, such as MeOH, and then the obtained precipitates were purified by dissolving them in TFE and precipitating them with benzene.

Spectroscopic Measurement

IR spectra were taken on a JASCO FT/IR-5300 Fourier Transform Infrared Spectrometer.

The ^{1}H-NMR spectrum was obtained with a Varian Gemini 200 NMR Spectrometer. The spectra were measured at ambient temperature, using a 100 g·dm^{-3} 2,2,2-trifluoroethanol-d_3 solution with tetramethylsilane (TMS) as the internal standard.

Preparation of Membranes

Membranes were prepared from TFE solution (150 $g \cdot dm^{-3}$). The solution was poured onto a glass plate with an applicator (casting thickness, 0.254 mm), and the solvent was allowed to evaporate at ambient temperature for 24 hours. Subsequently the membrane was dried at 50°C for 2 hours. The thicknesses of the membrane used in the present studies were 17–24 μm.

Pervaporation

Permeations of the benzene/cyclohexane and cyclohexene/cyclohexane mixtures were performed by an ordinary pervaporation technique (36). The membrane area in contact with the liquid feed was 17.3 cm^2. The downstream pressure applied was around 267 Pa (2.0 mmHg). Pervaporation experiments were carried out at a constant temperature of 50°C.

Separation analysis was carried out on a Shimadzu GC-8APT gas chromatograph equipped with a 3.0-m long column packed with polyethylene glycol 20M [Chromosorb W (AW-DMCS)].

The separation factor, α, is defined as

$$\alpha = (Y_{\text{benzene}}/Y_{\text{cyclohexane}}) / (X_{\text{benzene}}/X_{\text{cyclohexane}})$$

where the Y_is are the weight fractions in the permeate and the X_is are those in the feed.

Solubility Measurement

Solubility selectivities of N6PBMA-032 and N6 membranes were measured as described previously (37). The solubility selectivity, S_S, is defined as

$$S_S = (Z_{\text{benzene}}/Z_{\text{cyclohexane}}) / (X_{\text{benzene}}/X_{\text{cyclohexane}})$$

where the Z_is are the weight fractions in the membrane and the X_is are those in the solution.

Density Measurement

The densities of N6PBMA-032 and N6 membranes were measured by a floatation method (38). A strip of membrane sample was placed in a solution of sodium chloride at a constant temperature of 50°C. The polymer sample should be initially resting on the bottom of the solution. Saturated aqueous NaCl was added quantitatively while stirring until the membrane strip floated freely in the center of the solution. The mean density of the membrane corresponds to the density of the solution, which was measured with a pycnometer (39).

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RESULTS AND DISCUSSION

Preparation of Membrane Materials

The introduction of BMA onto N6 was confirmed by IR and ^{1}H-NMR spectra of the graft polymers. An example of the IR spectra is shown in Fig. 1. The IR spectrum has a new absorption peak at 1729 cm^{-1}, which is assigned to the C=O stretching band of PBMA, and which can be detected in addition to the characteristic absorption peak at 1638 cm^{-1} assigned to the amide I band. The existence of PBMA in N6 was also confirmed by ^{1}H-NMR measurement. The ^{1}H-NMR spectrum of N6PBMA-048 is shown in Fig. 2. Signals assigned to methylene protons (*f*) in the backbone of PBMA overlap those in N6 (*c*), and methylene protons (*g* and *h*) in the butyl moiety overlap those in N6 (*a* and *b*). After considering overlapping of the ^{1}H-NMR signal, the intensity of methyl protons (*e*), which can be observed at around 1.0 ppm, and the area of methylene protons (*a*, *b*, and *c*) in N6, led to a (PBMA)/(N6) ratio of 0.048. The results of graft polymerization are summarized in Table 1. In the sample code, the last three numbers show the ratio of a unit mole of grafted PBMA to that of N6. The relationship between the ratio of absorbance at 1729 cm^{-1} to that at 1638 cm^{-1} and the chemical composition determined by ^{1}H NMR is shown in Fig. 3. The relationship gave a straight line passing through the origin. From this, it can be said that the correlation shown in Fig. 3 is applicable to the estimation of chemical composition of nylon 6-*graft*-poly(butyl methacrylate). The four kinds of modified N6 thus prepared gave tough membranes like N6.

Pervaporation of Benzene/Cyclohexane through Modified Nylon 6 Membranes

Table 2 summarizes the effect of PBMA content on pervaporation of the benzene/cycylohexane mixture, where the weight faction of benzene in the feed was fixed at 0.5. For convenience, the result for the N6 membrane (26) is also given in the table. The results in Table 2 are also shown in Fig. 4. As expected, modified N6 membranes, having PBMA as a side chain, permeated benzene in preference to cyclohexane from the benzene/cyclohexane mixture. As can be seen in the figure, membrane performance depends on the PBMA content and shows a maximum at a (PBMA)/(N6) ratio of 0.032. This profile might be explained as follows: Permselectivity toward benzene increases through a certain (PBMA)/(N6) ratio with an increase in the concentration of the PBMA unit in the membrane. Above a certain (PBMA)/(N6) value, the effect of membrane swelling surpasses that of permselectivity caused by the introduction of PBMA onto N6. As a result, permselectivity toward benzene decreased with an increase in the (PBMA)/(N6) ratio.

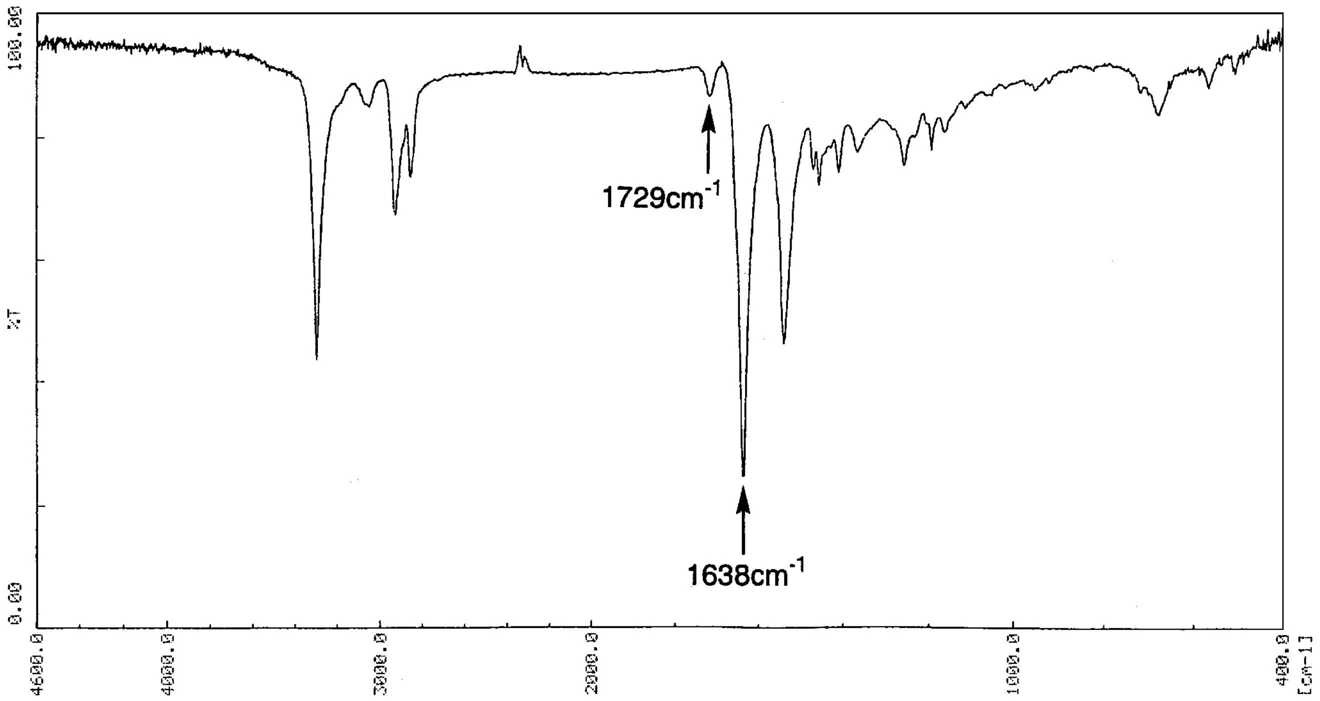

FIG. 1 IR spectrum of N6PBMA-048 [(PBMA)/(N6) = 0.048.]

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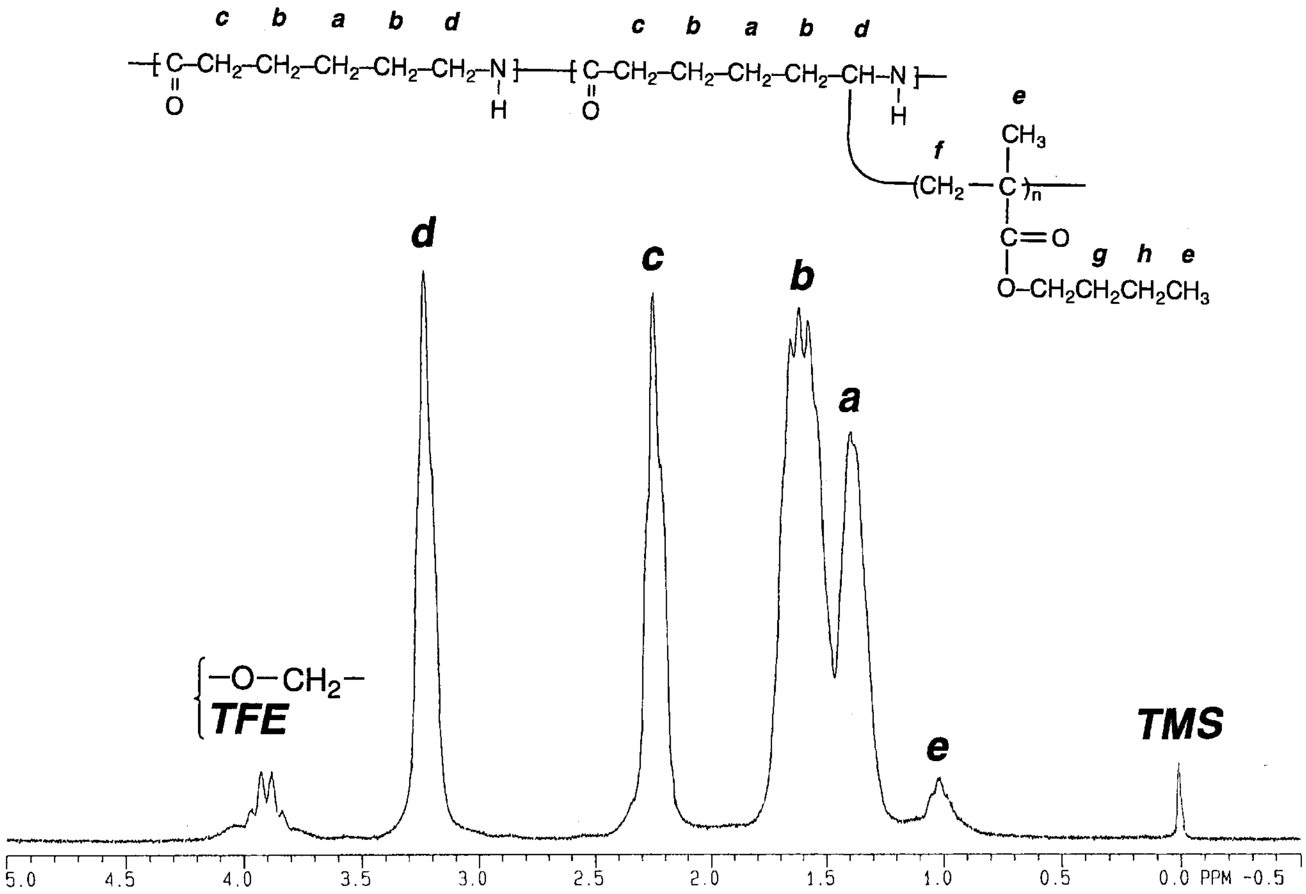

FIG. 2 ^{1}H-NMR spectrum of CF_3CD_2OD solution of N6PBMA-048. [(PBMA)/(N6) = 0.048.]

TABLE 1
Preparation and Characterization of N6-*graft*-PBMA[a]

	Charged amounts				N6-*graft*-PBMA		PBMA fraction	
Sample	N6/g	BMA/g	KPS/g	(BMA)/(N6)[b]	Yield/g	(PBMA)/(N6)[c]	wt	mol
N6PBMA-016	2.66	1.69	0.15	0.5	2.28	0.016	0.020	0.016
N6PBMA-032	2.66	3.34	0.15	1.0	1.72	0.032	0.039	0.031
N6PBMA-040	2.66	6.69	0.15	2.0	2.18	0.040	0.048	0.038
N6PBMA-048	2.66	10.03	0.15	3.0	2.30	0.048	0.057	0.046

[a] Graft polymerization was carried out at 80°C for 1 hour in 40 cm^3 of formic acid.
[b] Ratio of a mole of charged BMA to a unit mole of charged N6.
[c] Ratio of a unit mole of PBMA grafted to that of N6.

Figure 5 shows the results of pervaporation of benzene/cyclohexane mixtures through the N6PBMA-032 and N6 (parent polymer) membranes (26), where the weight fractions of benzene in the permeate are plotted against those in the feed. The vapor–liquid equilibrium curve for benzene/cyclohexane mixtures at 50°C (40) is also given. The results of pervaporation of cyclohexene/cyclohexane mixtures through the N6PBMA-032 membrane, (to be discussed later) are also shown. The N6PBMA-032 membrane gave a good

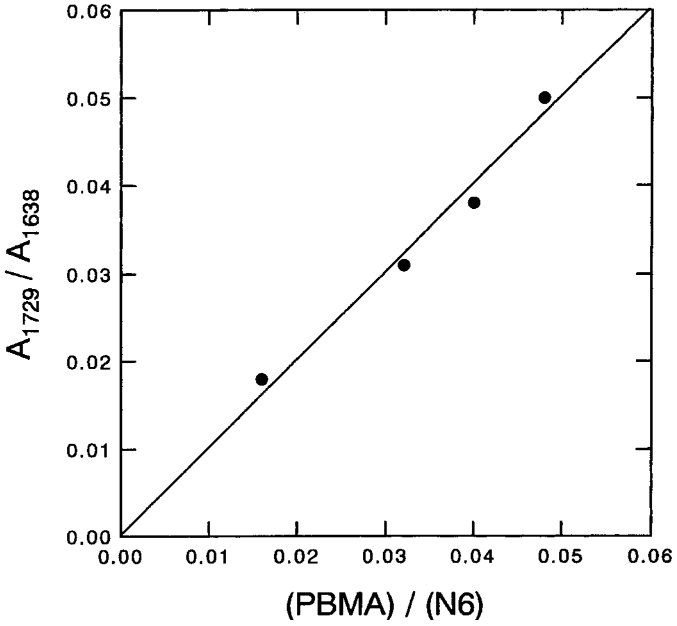

FIG. 3 Relationship between composition of N6-*graft*-PBMA and ratio of absorbance at 1729 cm^{-1} to that at 1638 cm^{-1}.

TABLE 2

Pervaporation of Benzene/Cyclohexane Mixture through N6-*graft*-PBMA Membranes[a]

Membrane	(PBMA)/ (N6)	Thickness/ μm	X_{benzene}[b]	Y_{benzene}[c]	α[d]	$J/g\cdot m^{-2}\cdot h^{-1}$
N6PBMA-016	0.016	18	0.4979	0.9049	9.6	6.7
N6PBMA-032	0.032	24	0.4996	0.9357	14.6	2.2
N6PBMA-040	0.040	17	0.4932	0.7849	3.8	14.6
N6PBMA-048	0.048	21	0.4986	0.7562	3.2	49.0
N6[e]	0	37	0.5002	0.5764	1.4	4.3

[a] Pervaporation was carried out at 50°C; downstream pressure ≈ 267 Pa (2 mmHg).

[b] Weight fraction of benzene in feed.

[c] Weight fraction of benzene in permeate.

[d] $\alpha = (Y_{\text{benzene}}/Y_{\text{cyclohexane}})/(X_{\text{benzene}}/X_{\text{cyclohexane}})$.

[e] Cited from Ref. 26.

membrane performance for permselectivity toward benzene as expected, while the pervaporation data for the N6 membrane is located slightly above the diagonal line in the whole feed fraction range. On the other hand, the feed fraction dependence of the flux value for the N6PBMA-032 membrane resembled that for the N6 membrane (26), and the flux ranged from 0.9 to 7.3 $g\cdot m^{-2}\cdot h^{-1}$.

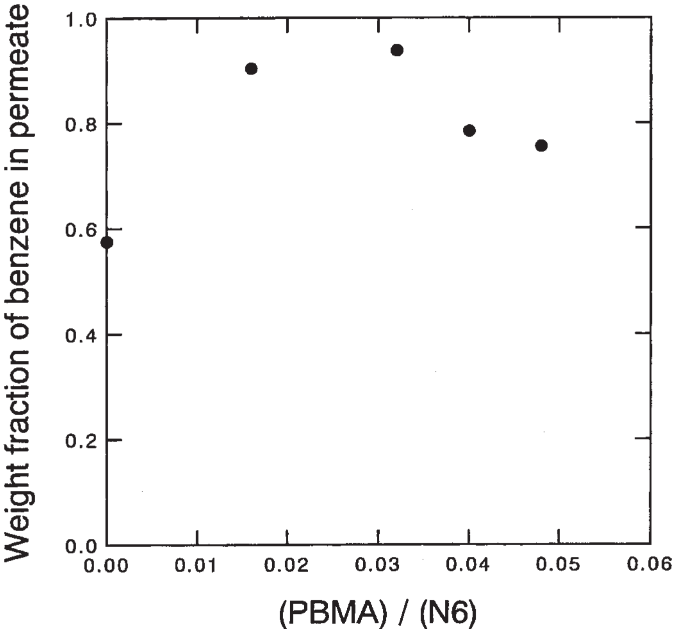

FIG. 4 Effect of composition of N6-*graft*-PBMA on the pervaporation of benzene/cyclohexane mixture. [Weight fraction of benzene in feed, ca. 0.5; operating temperature, 50°C; down stream pressure, ca. 267Pa (2.0 mmHg).]

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Pervaporation of Cyclohexene/Cyclohexane through Modified Nylon 6 Membranes

In order to elucidate the factor which governs the permselectivity, cyclohexene was used instead of benzene as a component of the feed mixture, and pervaporation experiments of cyclohexene/cyclohexane mixtures through the N6PBMA-032 membrane were investigated. The results are given in Fig. 5 together with those of benzene/cyclohexane mixtures. Cyclohexene was permeated in preference to cyclohexane as in the pervaporation of benzene/cyclohexane mixtures, while permselectivity toward cyclohexene was not as high as that of benzene in benzene/cyclohexane separation. The same tendency for the permselectivity between aromatics/aliphatics to be much better than that between olefins/aliphatics was also observed in pervaporation through a cellulose acetate/poly[vinylidene chloride-*co*-styrene(diethyl)phosphonate] alloy membrane (13) and a cellulose acetate/poly[styrene(diethyl)phosphonate] alloy membrane (16). From these results it can be said that π-electrons in benzene play an important role in permselectivity.

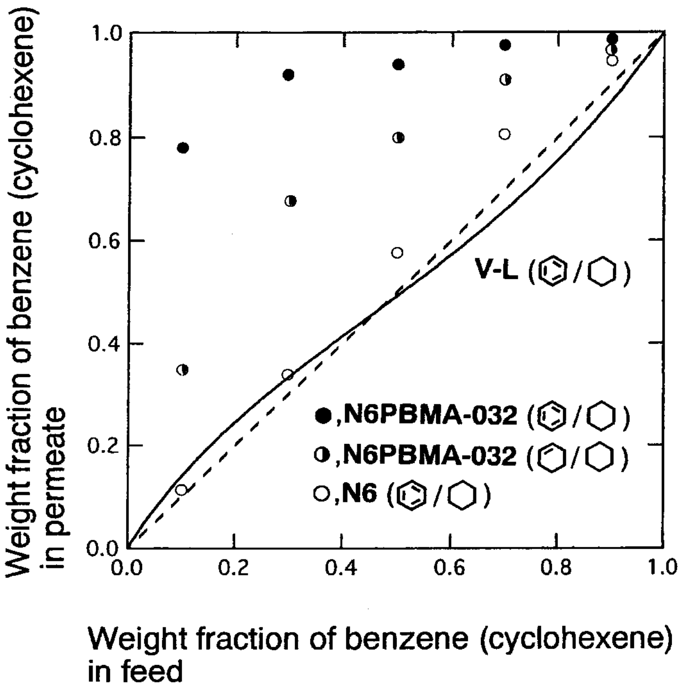

FIG. 5 Effect of feed composition on permselectivity for N6-*graft*-PBMA (N6PBMA-032) and nylon 6 (N6) membranes. (●, benzene/cyclohexane through N6PBMA-032 membrane; ◑, cyclohexene/cyclohexane through N6PBMA-032 membrane; ○, benzene/cyclohexane through N6 membrane.)

Sorption

The amounts of benzene and cyclohexane sorbed in N6PBMA-032 and N6 membranes and the total amounts sorbed in the membranes are shown in Fig. 6. As expected, the amounts of benzene in the N6PBMA-032 membrane were more than those in the N6 membrane. Simultaneously, more cyclohexane was sorbed in the N6PBMA-032 membrane than in the N6 membrane, and the amount of cyclohexane sorbed in the N6PBMA-032 membrane was about one order of magnitude above that in the N6 membrane. The solubility parameter was applied to explain the sorption phenomena (16, 20, 41–44). The solubility parameter (δ_{sp}), which consists of the contributions of dispersion forces (δ_d), dipole forces (δ_p), and hydrogen bonding (δ_h), was calculated for N6 and PBMA, as in the literature (45–47). The space distances between benzene and membrane material (DBM) and between cyclohexane and membrane material (DCM) are defined with the following values: $\delta_{d,B} = 18.3\ \mathrm{J}^{1/2}\cdot\mathrm{cm}^{-3/2}$, $\delta_{p,B} = 1.0\ \mathrm{J}^{1/2}\cdot\mathrm{cm}^{-3/2}$, and $\delta_{h,B} = 2.1\ \mathrm{J}^{1/2}\cdot\mathrm{cm}^{-3/2}$ for benzene (46); and $\delta_{d,C} = 16.7\ \mathrm{J}^{1/2}\cdot\mathrm{cm}^{-3/2}$, $\delta_{p,C} = 0.0\ \mathrm{J}^{1/2}\cdot\mathrm{cm}^{-3/2}$, and $\delta_{h,C} = 0.0\ \mathrm{J}^{1/2}\cdot\mathrm{cm}^{-3/2}$ for cyclohexane (46). The equations are

$$\mathrm{DBM} = [(\delta_d - \delta_{d,B})^2 + (\delta_p - \delta_{p,B})^2 + (\delta_h - \delta_{h,B})^2]^{1/2}$$

$$\mathrm{DCM} = [(\delta_d - \delta_{d,C})^2 + (\delta_p - \delta_{p,C})^2 + (\delta_h - \delta_{h,C})^2]^{1/2}$$

The estimated DBM and DCM values for N6 and PBMA are summarized in Table 3. From these results it can be deduced that the increase in the amount of benzene caused by the introduction of PBMA onto N6 was due to the decrease in DBM. As for DCM, a similar correlation was observed although neither N6 nor PBMA can be dissolved in cyclohexane. It can be said that the increase in the amount of cyclohexane caused by the introduction of PBMA onto N6 was due to swelling of the membrane by benzene sorption rather than to the decrease in DCM.

Each amount of permeant sorbed in N6PBMA-032 and N6 membranes was plotted against the corresponding concentration of solution which was equilibrated with the membrane. The relationship for the N6PBMA-032 membrane is shown in Fig. 7 and that for the N6 membrane in Fig. 8. As for the sorption isotherm of cyclohexane in both membranes, the isotherms are straight lines passing through the origin. This implies that cyclohexane was sorbed into both N6PBMA-032 and N6 membranes without any specific interaction with the membrane. The isotherms for cyclohexane in both membranes are represented by the following equation:

$$C_C = C_{D,C} = k_{D,C}[\mathrm{cyclohexane}]$$

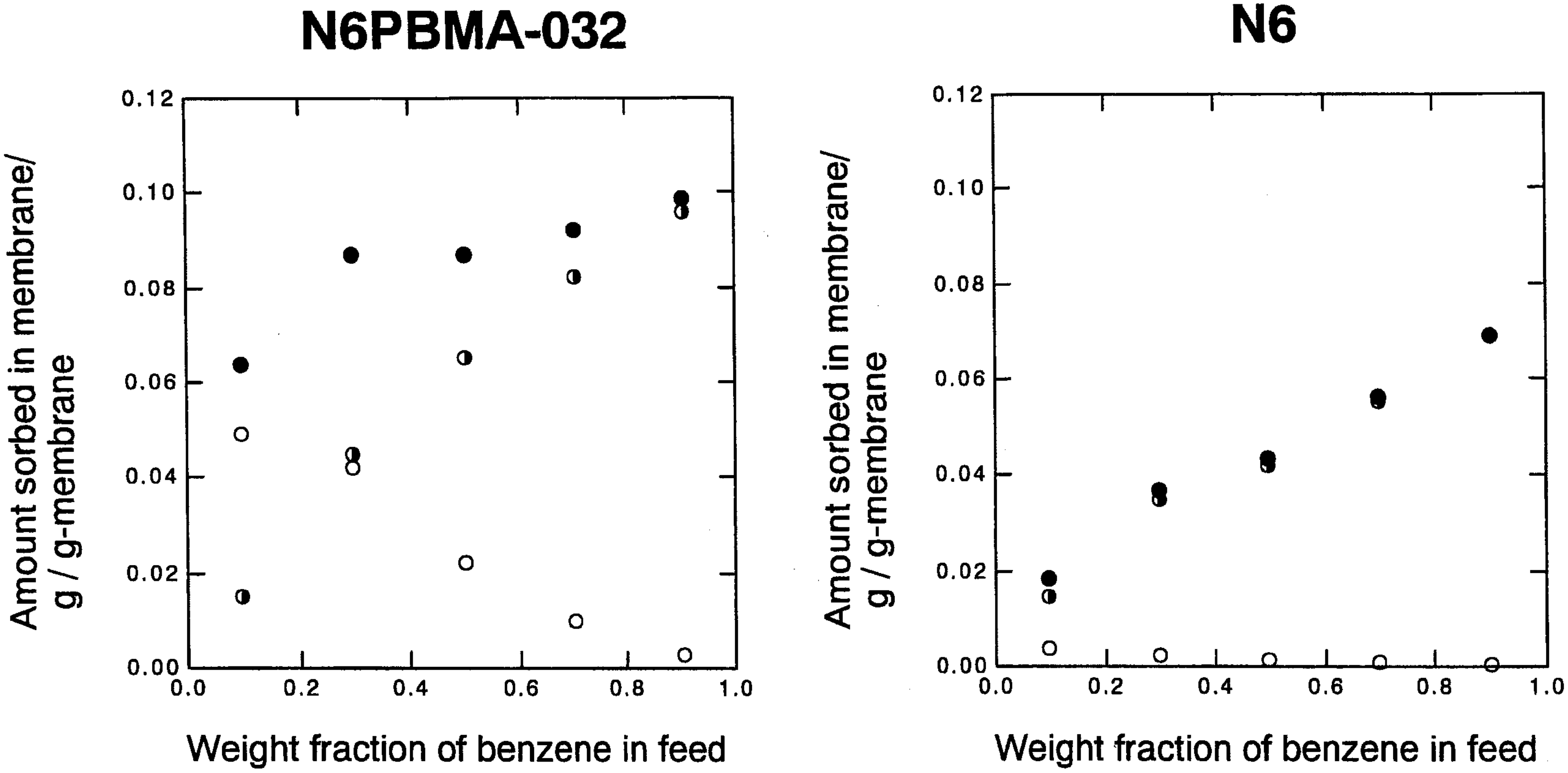

FIG. 6 Effect of feed composition on total and individual sorptions for N6-*graft*-PBMA (N6PBMA-032) and nylon 6 (N6) membranes at 50°C. [(PBMA)/(N6) = 0.032; ●, total; ◑, benzene; ○, cyclohexane.]

TABLE 3
Space Distances between Permeant and Membrane Material

	DBM/$J^{1/2}\cdot cm^{-3/2}$	DCM/$J^{1/2}\cdot cm^{-3/2}$
N6	9.4	11.7
PBMA	6.0	8.0

where C_C = concentration of cyclohexane in membrane, mol/m^3 polymer
$k_{D,C}$ = solubility coefficient for cyclohexane, m^3/m^3 polymer
[cyclohexane] = cyclohexane concentration, mol/m^3

On the other hand, the dependence of the benzene isotherm on benzene concentration in the outer solution exhibits a dual sorption isotherm, which implies that benzene sorption consists of dissolution without specific interaction with the membrane ($C_{D,B}$) and sorption on the specific site of benzene ($C_{H,B}$), similar to the dual sorption of gases (48, 49). The sorption isotherm for benzene in N6 is represented by the following equation:

$$C_{B,N6} = C_{D,B} + C_{H,B} = k_{D,B}[\text{benzene}] + (n_{N6}K_{N6}[N6]_M\,[\text{benzene}])/(1 + K_{N6}[\text{benzene}])$$

where $C_{B,N6}$ = concentration of benzene in N6 membrane, mol/m^3 polymer
$k_{D,B}$ = solubility coefficient for benzene, m^3/m^3 polymer
n_{N6} = the ratio of the maximum amount (mole number) of benzene sorbed in N6 membrane to unit mole of specific binding site in the N6 membrane, mol/mol
K_{N6} = affinity constant between benzene and specific binding site in N6 membrane, m^3/mol
$[N6]_M$ = concentration of constitutional repeating unit of N6 in N6 membrane, mol/m^3 polymer
[benzene] = benzene concentration, mol/m^3

It is possible that the sorption isotherm for benzene in N6PBMA-032 consists of three modes of dissolution: sorption without specific interaction with the membrane ($C_{D,B}$), sorption on the specific site of benzene in the N6 part, and sorption in the PBMA part. Assuming that the additivity of sorption on a specific site of benzene is true, the sorption isotherm for benzene in a modified N6 membrane is represented by the following equation:

$$\begin{aligned}C_{B,N6PBMA} = C_{D,B} + C_{H,B} = k_{D,B}[\text{benzene}] &+ (n_{N6}K_{N6}[N6]_M\,[\text{benzene}]) / (1 + K_{N6}[\text{benzene}])\\ &+ (n_{PBMA}K_{PBMA}[PBMA]_M\,[\text{benzene}]) / (1 + K_{PBMA}[\text{benzene}])\end{aligned}$$

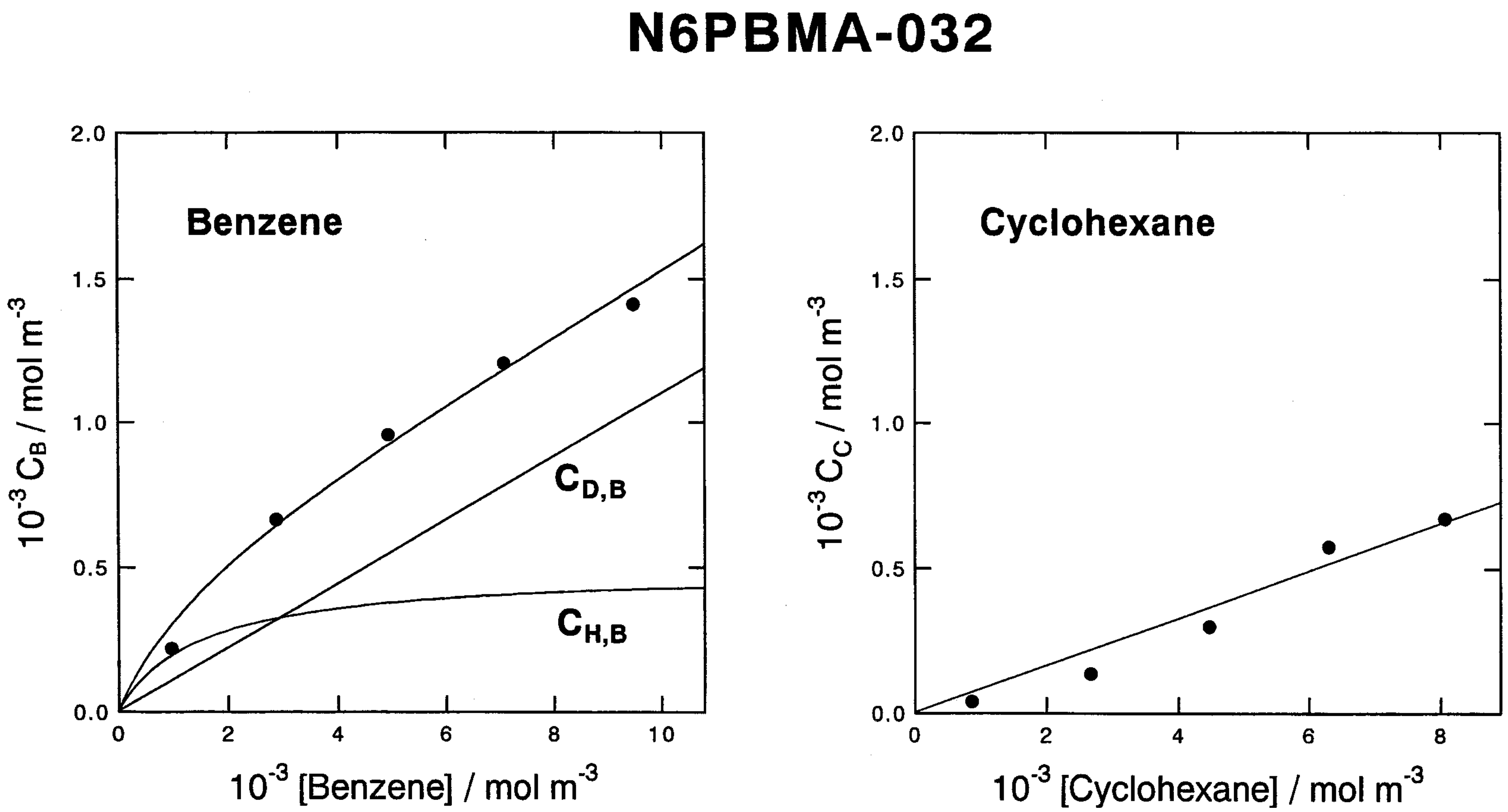

FIG. 7 Effect of feed concentration on sorption of benzene/cyclohexane mixtures in N6-*graft*-PBMA (N6PBMA-032) membrane at 50°C. [(PBMA)/(N6) = 0.032;——, calculated, according to equations, and using the parameters summarized in Table 4.]

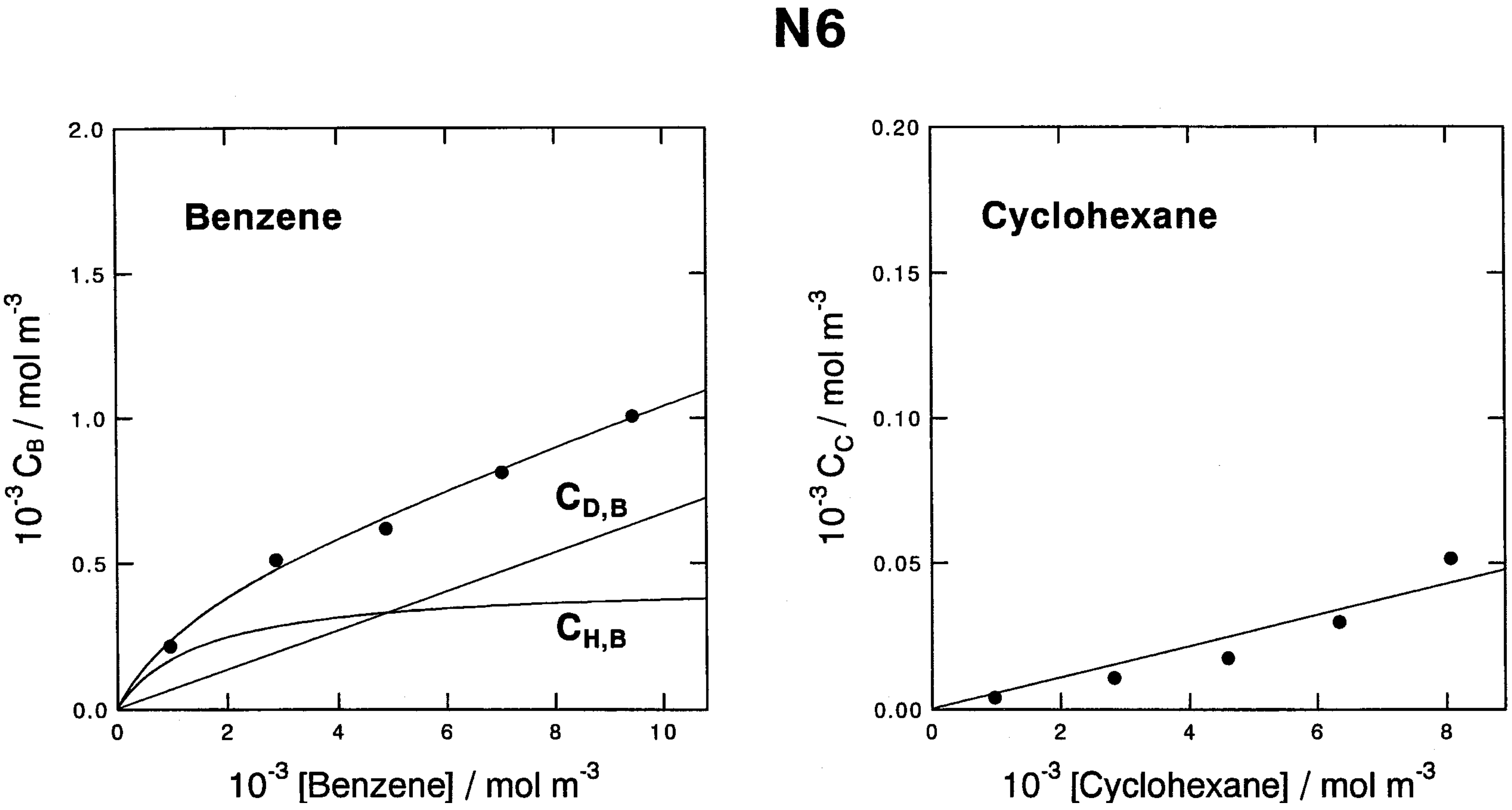

FIG. 8 Effect of feed concentration on sorption of benzene/cyclohexane mixtures in nylon 6 (N6) membrane at 50°C. (——, calculated, according to equations, and using the parameters summarized in Table 4.)

where $C_{B,N6PBMA}$ = concentration of benzene in N6PBMA membrane, mol/m^3 polymer
n_{PBMA} = the ratio of the maximum amount (mole number) of benzene sorbed in PBMA part in N6PBMA membrane to unit mole of PBMA in the N6PBMA membrane, mol/mol
K_{PBMA} = affinity constant between benzene and PBMA part in N6PBMA membrane, m^3/mol
$[PBMA]_M$ = concentration of constitutional repeating unit of PBMA in N6PBMA membrane, mol/m^3 polymer

The five parameters in the equation for benzene sorption and the one parameter for cyclohexane sorption, determined to give the best fit Figs. 7 and 8, are summarized in Table 4. $[N6]_M$ and $[PBMA]_M$ in the equations were provisionally adopted. In the table, the values of $n_{N6}[N6]_M$ and $n_{PBMA}[PBMA]_M$, which imply the maximum amount of benzene sorbed on a specific site in the membrane, have a physical meaning rather than individual values. As for the parameters for benzene sorption, the introduction of PBMA onto N6 led to an increase in the solubility coefficient $k_{D,B}$. The affinity constant between the PBMA part and benzene is higher than that between the N6 part and benzene. As expected, the introduction of PBMA effectively

TABLE 4
Various Parameters for Sorption Isotherms

Membrane	N6PBMA-032	N6
$k_{D,B}$	1.1×10^{-1}	6.7×10^{-2}
K_{N6}/m^3·mol^{-1}	6.5×10^{-4} [a]	6.5×10^{-4}
K_{PBMA}/m^3·mol^{-1}	8.4×10^{-4}	—
n_{N6}	4.3×10^{-2} [b]	4.3×10^{-2}
$[N6]_M$[c]/mol·m^{-3}	9.8×10^3	1.0×10^4
$n_{N6}[N6]_M$/mol·m^{-3}	4.2×10^2	4.3×10^2
n_{PBMA}	6.7×10^{-2}	—
$[PBMA]_M$[d]/mol·m^{-3}	3.2×10^2	—
$n_{PBMA}[PBMA]_M$/mol·m^{-3}	2.1×10^2	—
$k_{D,C}$	8.1×10^{-2}	5.3×10^{-3}

[a] K_{N6} values for N6 membrane were adopted as K_{N6} values for modified N6 membranes.

[b] n_{N6} values for N6 membrane were adopted as n_{N6} values for modified N6 membranes.

[c] Concentration of constitutional repeating unit in N6 membrane.

[d] Concentration of constitutional repeating unit of PBMA in modified N6 membranes.

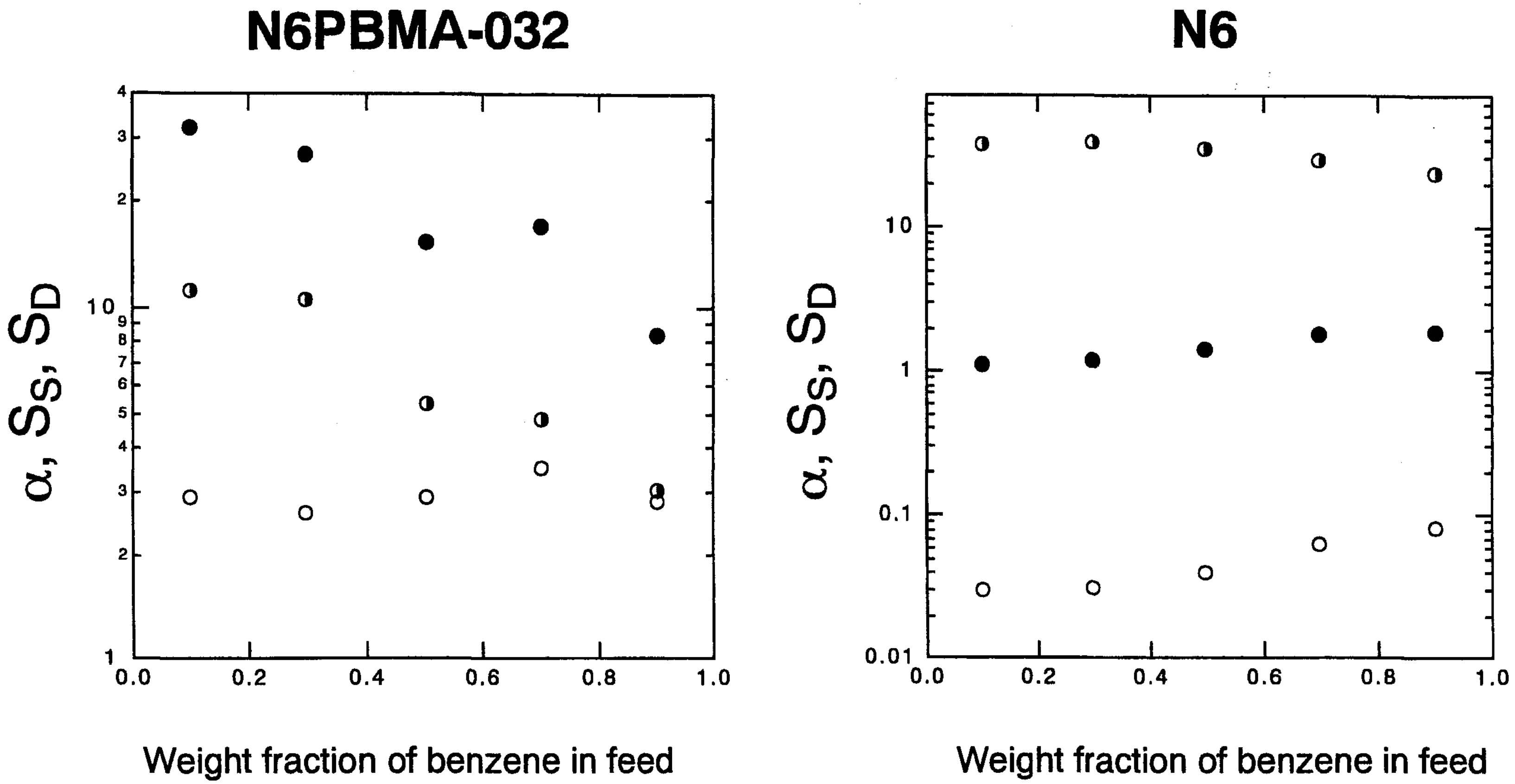

FIG. 9 Effect of feed composition on seperation factor (α) solubility selectivity (S_S) and diffusivity selectivity (S_D) of N6-*graft*-PBMA (N6PBMA-032) and nylon 6 (N6) membranes. [(PBMA)/(N6) = 0.032; ●, α; ◑, S_S; ○, S_D; operating temperature, 50°C; downstream pressure, 267Pa (2.0mmHg).]

increased the solubility of benzene. The solubility coefficient of cyclohexane, $k_{D,C}$, for the N6PBMA-032 membrane was determined to be about 15 times higher than that for the N6 membrane. This might be also due to the introduction of PBMA onto N6. In other words, the increase in benzene solubility led to swelling of the membrane, as a result, the sorption of cyclohexane was enhanced.

By using the sorption data given in Fig. 6, the solubility selectivity, *S*s, was obtained. According to the solution–diffution theory, the diffusivity selectivity, S_D ($= D_{\text{benzene}}/D_{\text{cyclohexane}}$; D_{benzene} and $D_{\text{cyclohexane}}$ are the diffusion coefficients of benzene and cyclohexane, respectively) can be estimated from the separation factor, α, and the solubility selectivity, S_S ($= S_{\text{benzene}}/S_{\text{cyclohexane}}$; S_{benzene} and $S_{\text{cyclohexane}}$ are the solubility coefficients of benzene and cyclohexane, respectively), thus obtained (50). The separation factor, solubility selectivity, and diffusivity selectivity for N6PBMA-032 and N6 membranes are shown in Fig. 9 as a function of the weight fraction of benzene in the feed. As for the N6PBMA-032 membrane, it was concluded that both solubility selectivity and diffusivity selectivity contributed to the permselectivity of benzene. On the other hand, N6 also showed solubility selectivity for benzene. However, the diffusivity selectivity of N6 showed a preference for cyclohexane over benzene. As a result, the N6 membrane did not have as high a permselectivity for benzene as did the N6PBMA-032 membrane.

CONCLUSIONS

From the present study, the following conclusions can be drawn.

1. Nylon 6 is applicable as a membrane matrix for the pervaporation separation of benzene/cyclohexane mixtures.
2. The introduction of poly(butyl methacrylate) onto nylon 6 by radical graft polymerization caused an increase in permselectivity toward benzene.
3. Membranes from nylon 6-*graft*-poly(butyl methacrylate) have potential for applicability to petroleum refining processes.

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REFERENCES

1. P. A. Kober, *J. Am. Chem. Soc.*, *39*, 944 (1917).
2. R. C. Binning and R. J. Lee, US Patent 2,953,502 (1960).
3. H. Strathmann and W. Gudernatsch, in *Pervaporation Membrane Separation Processes* (R. Y. M. Huang, Ed.), Elsevier, Amsterdam, 1991, p. 363.
4. Y. Maeda and M. Kai, *Ibid.*, p. 391.
5. L. H. Keith and W. A. Telliard, *Environ. Sci. Technol.*, *13*, 416 (1979).
6. K. W. Böddeker and G. Bengtson, in *Pervaporation Membrane Separation Processes* (R. Y. M. Huang, Ed.), Elsevier, Amsterdam, 1991, p. 437.
7. E. Browning, *Toxicity and Metabolism of Industrial Solvents*, Elsevier, New York, NY, 1965, p. 3.
8. E. M. Krischner, *C&EN*, p. 16 April 8, (1996).
9. M. Kucharski and J. Stelmaszek, *Int. Chem. Eng.*, *7*, 618 (1967).
10. R. Y. M. Huang and V. J. C. Lin, *J. Appl. Polym. Sci.*, *12*, 2615 (1968).
11. F. P. McCandless, *Ind. Eng. Chem., Process Des. Dev.*, *12*, 354 (1973).
12. F. P. McCandless, D. P. Alzheimer, and R. B. Hartman, *Ibid.*, *13*, 310 (1974).
13. I. Cabasso, J. Jagur-Grodzinski, and D. Vofsi, *J. Appl. Polym. Sci.*, *18*, 2137 (1974).
14. S. Yoshimasu, H. Nomura, K. Komiya, T. Okano, and I. Shinohara, *Nippon Kagaku Kaishi*, p. 1785 (1980).
15. J. Terada, T. Hohjoh, S. Yoshimasu, M. Ikemi, and I. Shinohara, *Polym. J.*, *14*, 347 (1982).
16. I. Cabasso, *Ind. Eng. Chem., Prod. Res. Dev.*, *22*, 313 (1983).
17. H. R. Acharya and S. A. Stern, *J. Membr. Sci.*, *37*, 205 (1988).
18. T. Yamaguchi, S. Nakao, and S. Kimura, *Macromolecules*, *24*, 5522 (1991).
19. T. Yamaguchi, S. Nakao, and S. Kimura, *Ind. Eng. Chem. Res.*, *31*, 1914 (1992).
20. R. Darkow, M. Yoshikawa, T. Kitao, G. Tomaschewski, and J. Schellenberg, *J. Polym. Sci., Polym. Chem.*, *32*, 1657 (1994).
21. N. Tanihara, K. Tanaka, H. Kita, and K. Okamoto, *J. Membr. Sci.*, *95*, 161 (1994).
22. C. K. Park, B.-K. Oh, M. J. Choi, and Y. M. Lee, *Polym. Bull.*, *33*, 591 (1994).
23. S. Sakohara, T. Koshi, and M. Asaeda, *Kobunshi Ronbunshu*, *52*, 155 (1995).
24. F. Sun and E. Ruckenstein, *J. Membr. Sci.*, *99*, 273 (1995).
25. N. Tanihara, N. Umeo, T. Kawabata, K. Tanaka, H. Kita, and K. Okamoto, *Ibid.*, *104*, 181 (1995).
26. M. Yoshikawa and T. Kitao, *Eur. Polym. J.*, *33*, 25 (1997).
27. J. Brandrup and E. H. Immergut, *Polymer Handbook*, 3rd ed., Wiley, New York, NY, 1989.
28. J. Stehlicek, J. Horsky, J. Roda, and A. Moucha, in *Lactam-Based Polyamides, Volume II, Modification, Technology, and Application* (R. Puffr and V. Kubanek, Eds.), CRC Press, Boca Raton, FL, 1991, Chap. 2.
29. W. M. Dziedziela, M. B. Huglin, and R. W. Richards, *Eur. Polym. J.*, *11*, 53 (1975).
30. K. Kosai, T. Higashino, and S. Ohue, *Nippon Kagaku Kaishi*, p. 523 (1975).
31. H.-L. Hu, K. R. Lee, and J. Y. Lai, *J. Macromol. Sci.—Pure Appl. Chem.*, *A30*, 815 (1993).
32. J.-Y. Lai, R.-Y. Chen, and K. R. Lee, *J. Appl. Polym. Sci.*, *47*, 1849 (1993).
33. K.-R. Lee and J.-Y. Lai, *Ibid.*, *57*, 961 (1995).
34. D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, *Purification of Laboratory Chemicals*, 2nd ed., Pergamon Press, Oxford, 1980.
35. J. A. Riddick, W. B. Bunger, and T. K. Sakano, *Organic Solvents*, 4th ed., Wiley, New York, NY, 1986.
36. S. Yamada, *Maku* (*Membrane*), *6*, 168 (1981).
37. M. Yoshikawa, T. Wano, and T. Kitao, *J. Membr. Sci.*, *89*, 23 (1994).

38. J. R. Millar, *J. Chem. Soc.*, p. 1311 (1960).
39. F. Daniels, J. W. Williams, P. Bender, R. A. Alberty, C. D. Cornwell, and J. E. Harriman, *Experimental Physical Chemistry*, International 7th ed., McGraw-Hill Kogakusha, Tokyo, 1970, p. 98.
40. J. Gmehling, U. Onken, and W. Arlt, in *Vapor–Liquid Equilibrium Data Collection, Vol. I, Part 6a*, (D. Behrens and R. Eckermann, Eds.), DECHEMA, Frankfurt, 1980.
41. M. Yoshikawa, T. Ohsawa, M. Tanigaki, W. Eguchi, and N. Ogata, *Sen-i Gakkaishi*, *44*, 551 (1988).
42. M. Yoshikawa, T. Ohsawa, M. Tanigaki, and W. Eguchi, *J. Appl. Polym. Sci.*, *37*, 299 (1989).
43. M. Yoshikawa, S. Kuno, T. Wano, and T. Kitao, *Polym. Bull.*, *31*, 607 (1993).
44. M. Yoshikawa, S. Kuno, and T. Kitao, *J. Appl. Polym Sci.*, *51*, 1021 (1994).
45. C. M. Hansen and B. Beerbower, in *Encyclopedia of Chemical Technology*, *Suppl. Vol. A*, 2nd ed. (A. Standen, Ed.), Wiley-Interscience, New York, NY, 1971, p. 889.
46. D. M. Koenhen and C. A. Smolders, *J. Appl. Polym. Sci.*, *19*, 1163 (1975).
47. T. Matsuura, *Synthetic Membranes and Membrane Separation Processes*, CRC Press, Boca Raton, FL, 1994.
48. W. J. Koros, D. R. Paul, and A. A. Rocha, *J. Polym. Sci.*, *Polym. Phys. Ed.*, *14*, 687 (1976).
49. W. R. Vieth, J. M. Howell, and J. H. Hsieh, *J. Membr. Sci.*, *1*, 177 (1976).
50. C. H. Lee, *J. Appl. Polym. Sci.*, *19*, 83 (1975).

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