Gas Permeability and Selectivity Through Asymmetric Polyimide Membranes

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SYNOPSIS

Permeability and selectivity of CO_2, O_2, N_2, and CH_4 were determined for the asymmetric membrane of aromatic polyimide derived from 2,2'-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) and 3,3'-diaminodiphenylsulfone (m-DDS) at 35°C and at pressure up to 76 cmHg. The average apparent skin layer thickness of all asymmetric membranes measured was 2.6 μm. The selectivities for (O_2/N_2) and (CO_2/CH_4) in the membranes were 11.5 at O_2 permeance of 3.2×10^{-7} and 153 at CO_2 of 6.3×10^{-7} [cm^3(STP)/cm^2 s cmHg], respectively, without the necessity of an additional coating process. The average gas selectivities of the asymmetric membranes were much larger than those determined for the dense membranes. The effect of the microstructure of polyimide on the gas selectivity is discussed. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Aromatic polyimides are a class of high-performance polymers that are highly thermally stable and have high glass transition temperatures and relatively low dielectric constants.[1-3] The various polyimides have become increasingly important in a variety of technological applications, such as semiconductor devices, high-temperature adhesives, and high-performance composite materials. Recently, aromatic polyimides have received considerable attention as gas separation materials because of their surprisingly high gas selectivities to (P_{H_2}/P_{N_2}), (P_{O_2}/P_{N_2}), and (P_{CO_2}/P_{CH_4}).[4-8] There have been many active studies on novel polyimides structurally modified to enhance gas permeability and selectivity. In general, poly(amic acid) precursors, which are soluble in organic solvents, are utilized for the membrane fabrication and are converted into the corresponding polyimides by the thermal imidization process in a solid state. However, most of the aromatic polyimides prepared by the process in a solid state show insolubility due to some branches or crosslinks formed during the high temperature "curing." Ap-

plications of aromatic polyimides to the composite or asymmetric membrane are restricted due to their poor solubility in organic solvents. One approach for preparation of these membranes is to improve the solubility of polyimide in organic solvents. The polyimides prepared by the chemical imidization process at ambient temperature show good solubility because their side reactions do not occur. In addition, the molecular weight decrease observed in a thermal imidization is not shown, because the reverse propagation reaction does not occur during a chemical imidization. Another method to improve the solubility of polyimide is to introduce the flexible groups in the polymer chain. One successful synthesis method is the introduction of hexafluoroisopropylidene groups between the phenyl rings of dianhydride.[9,10]

We synthesized the soluble aromatic polyimides with a chemical imidization. In recent years, we reported that the aromatic polyimide derived from 2,2'-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) and diaminodiphenylsulfone (DDS) shows excellent solubility in organic solvents such as dimethylformamide, dimethylacetamide, N-methylpyrrolidone, dimethylsulfoxide, tetrahydrofuran, methylene chloride, chloroform, and acetone.[11] The soluble aromatic polyimide is advantageous in applications of gas separation materials,

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such as asymmetric membranes with thin and defect-free skin layers, as mentioned above.

We describe herein the preparation and gas transport properties of asymmetric polyimide membranes. The soluble aromatic polyimide derived from 6FDA dianhydride and 3,3'-diaminodiphenylsulfone (m-DDS) was synthesized with a chemical imidization. The asymmetric 6FDA-m-DDS membranes were made by a dry/wet process. The permeances of the membranes to CO_2, O_2, N_2, and CH_4 were determined at 35°C and pressure up to 76 cmHg.

EXPERIMENTAL

Materials

6FDA was purchased from Hoechst Co. (Japan) and purified by sublimation prior to use. m-DDS was purchased from Tokyo Kasei Co. (Japan) and recrystallized twice in ethanol solution prior to use.

Synthesis of 6FDA-m-DDS

6FDA-m-DDS polyimide was synthesized with a chemical imidization as in the literature.[11] The poly(amic acid) derived from 6FDA dianhydride and m-DDS diamine was prepared by solution condensation polymerization at 70°C in dimethylacetamide solution under nitrogen atmosphere. After being stirred at 70°C for 5 h, the poly(amic acid) precursor was converted into the corresponding polyimide by a chemical imidization with acetic anhydride and triethylamine. After a reaction of 15 h, 6FDA-m-DDS was precipitated by methanol, recovered, and filtered. Subsequently, 6FDA-m-DDS was washed with methanol several times and dried in a vacuum oven at 150°C for 24 h. The structure of 6FDA-m-DDS is presented in Figure 1.

Preparation of Dense Membrane

Dense 6FDA-m-DDS membranes were prepared with a solvent-casting method. First, the tetrahydrofuran solutions of the polyimides were carefully cast on the glass plates, and then the plates were placed in a vacuum oven at 40°C for 10 h to slowly remove most of the solvent. The slow drying rate is required to avoid bubble formation and make the polymer surface uniform. After cooling, the membranes were stripped from the plates. The membranes were heated at a rate of 1°C/min to a final thermal treatment of 150 or 250°C and held there in 0.1 mmHg for 15 h.
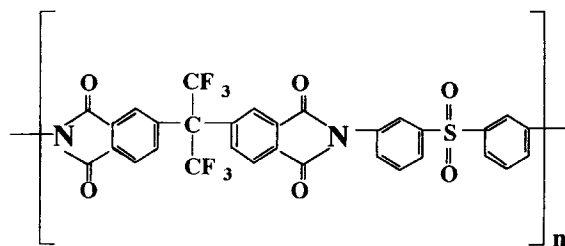

Figure 1 Structure of 6FDA-m-DDS polyimide.

Preparation of Asymmetric Membrane

Asymmetric 6FDA-m-DDS membranes were made by a dry/wet phase inversion technique.[12,13] Compositions of casting solution used for the preparation of asymmetric membranes were 12 wt % polyimide, 58 wt % methylene chloride, 24 wt % 1,1,2-trichloroethane, and 6 wt % butanol. Selection of casting solution for this study was based on the solubility parameters as proposed by Pinnau et al.[12] The polymer solutions were filtered and subsequently degassed. The solutions were cast on glass plates with a knife gap of 250 μm and air-dried there for 30 s. After the evaporation, the membranes were coagulated in methanol, washed for 12 h, air-dried for 24 h, and finally dried in a vacuum oven at 150 or 250°C for 15 h to remove all solvents.

Physical Properties

The molecular weights (M_w and M_n) of 6FDA-m-DDS were determined by gel permeation chromatography (detector Jasco 830-RI monitor) with tetrahydrofuran as the solvent. A flow rate of 1.0 mL/min was used, and the polyimide was dissolved in tetrahydrofuran at a concentration of 0.005 wt %. Molecular weights were estimated by comparing retention times in a column (Shodex KF-805L) to those of standard poly(styrene).

The glass transition temperature (T_g) was determined by differential scanning calorimetry (DSC; Seiko DSC200, SSC/5200H). The samples enclosed in an aluminum pan with a cover were heated at 10°C/min. The thermal behavior of the polyimide under nitrogen atmosphere was evaluated as a 5% weight loss temperature (T_5) by thermogravimetric analysis (TGA; Seiko TG/DTA300, SSC/5200H).

Fluorescence Measurement

The fluorescence spectra of polyimide membranes were measured at ambient temperature in air by using a fluorescence spectrophotometer (Jasco, FR-777). The membranes were set at 45° to both the

a)

b)
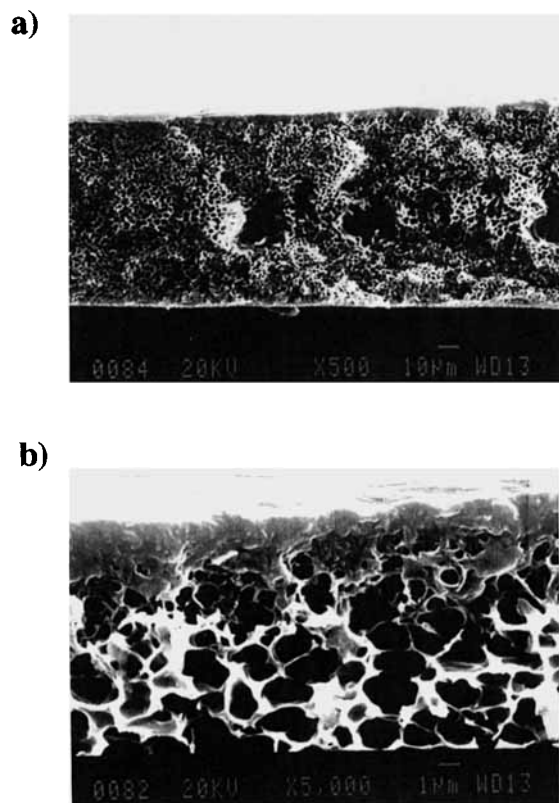
Figure 2 Cross section of asymmetric 6FDA-*m*-DDS membrane: (a) asymmetric membrane and (b) skin layer.

excitation and emission monochrometers and excited at 350 nm.

Permeability Measurement

Carbon dioxide, methane, oxygen, and nitrogen used in this study were represented to be at least 99.9 mol % and were used without further purification.

Asymmetric 6FDA-*m*-DDS membranes were mounted on a permeation cell of 1.0-cm^2 surface area. Gas permeances at pressure up to 76 cmHg were determined with a high vacuum apparatus (Rika Seiki Inc. K-315-H). The pressures on the upstream and the downstream sides were detected

by using a Baratron absolute pressure gauge. The error in the permeance was estimated to be on the order of ±0.1–0.5%. The apparent skin layer thickness of defect-free asymmetric membrane was calculated from the permeability coefficient using

$$L = P/Q \tag{1}$$

where L is the apparent skin layer thickness, P is the gas permeability coefficient measured from the dense membrane, and Q is the gas permeance of the asymmetric membrane.

RESULTS AND DISCUSSION

Characterization of Asymmetric Membrane

A scanning electron micrograph of a typical structure of the asymmetric 6FDA-*m*-DDS membrane is shown in Figure 2. The cross section of the structure consisted of the skin layer and the porous substructure. The substructure was characterized by the presence of a spongelike structure and macrovoids. The structure features of the asymmetric membranes cured at 150 and 250°C were similar.

The results of physical properties for the dense and asymmetric membranes of 6FDA-*m*-DDS are listed in Table I. T_gs of asymmetric membrane determined by DSC were higher than those of the dense membrane. This means that the free volume in the skin layer of the asymmetric membrane is more enhanced than that of the bulk membrane material. Two studies claim that hollow fiber membranes spun from a Lewis acid base complex have a higher T_g than its bulk T_g and possess enhanced free volume, which contributes to their improved gas permeability.[14,15] The dense and asymmetric membranes showed similar decomposition behavior characterized by no weight loss below 450°C under nitrogen. This result indicates that all solvents in the membranes are completely removed. T_5s of asymmetric and dense membranes were in the range 530–570°C.

Table I Physical Properties of 6FDA-*m*-DDS

Polyimide	Membrane Type	M_w	M_w/M_n	T_g (°C)	T_5 (°C)	μ (g/cm^3)
6FDA-*m*-DDS	Dense	44,700	1.54	252	566	1.47
150°C	Asymmetric	44,700	1.54	271	531	—
6FDA-*m*-DDS	Dense	44,700	1.54	263	575	1.48
250°C	Asymmetric	44,700	1.54	272	539	—
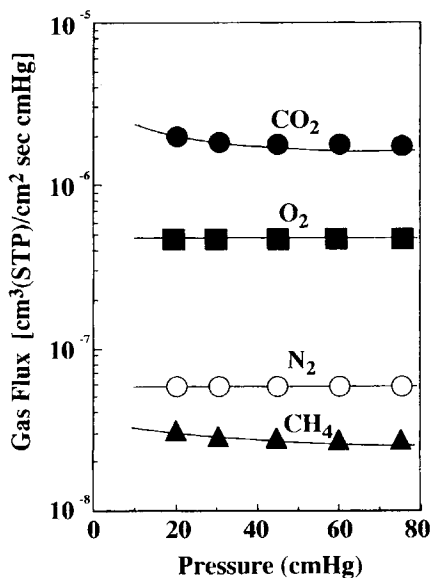
Figure 3 Pressure dependence of permeances for four gases in asymmetric 6FDA-m-DDS membrane at 35°C.

Gas Transport Properties

The permeances of asymmetric 6FDA-m-DDS membranes to CO_2, O_2, N_2, and CH_4 at 35°C are reported in Figure 3 in the form of semilogarithmic plots of the gas permeance, Q, versus the upstream gas pressure. The permeances of CO_2 and CH_4 in the membranes increased with the decreasing pressure of CO_2 and CH_4 in the range from 20 to 76 cmHg, while O_2 and N_2 permeances were constant. The sorption and transport characteristics of glassy polymer membranes are well described by the dual-

mode model.[16-18] The pressure dependences of CO_2 and CH_4 permeances in the asymmetric 6FDA-m-DDS membrane show a typical dual-mode transport behavior, as seen in the dense membrane.[11] On the other hand, O_2 and N_2 permeances in the membrane are independent of the pressures, which may be due to the fact that the dual-mode parameters such as the Langmuir capacity constant and the affinity parameter in O_2 and N_2 are generally significantly smaller than those obtained in CO_2 and CH_4.[18] However, the above arguments require validation by the solubility measurement.

The relationship between the gas permeance and selectivity of polymer membrane is of particular importance for development of a novel gas separation membrane. This relationship is shown in Figures 4 and 5. Figures 4 and 5 present the gas selectivities as a function of the permeances for 10 randomly selected asymmetric membranes. The (O_2/N_2) and (CO_2/CH_4) selectivities of most of the asymmetric membranes were much larger than those measured for the dense membranes. It should be noted that some asymmetric membranes exhibit extremely large (O_2/N_2) and (CO_2/CH_4) selectivities, more than 10 and 130, respectively. The larger selectivities in the asymmetric membranes may be the result of the more efficiently packed polymer chain in the skin layer as mentioned below.

In the solid state, both the structure and dynamics of polymers are, to a large extent, determined by intermolecular and intramolecular interactions between the polymer chains. Because the aromatic polyimides contain an alternating sequence of elec-
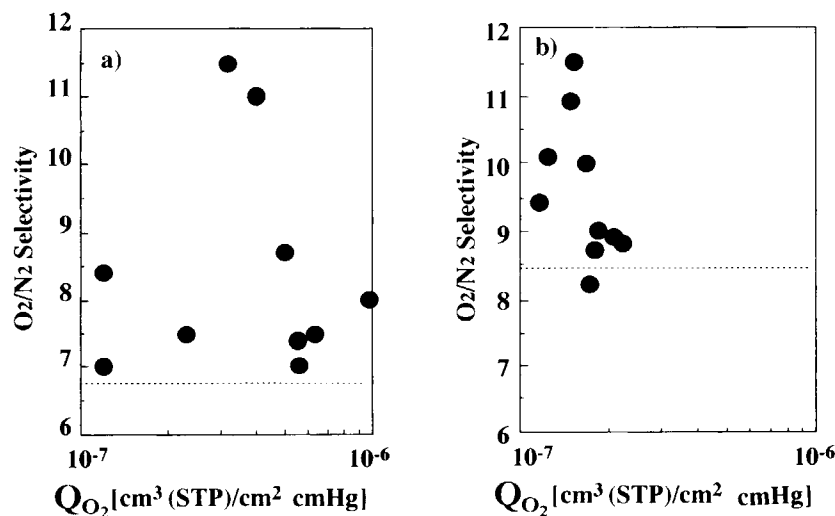
Figure 4 (O_2/N_2) selectivity and Q_{O_2} of asymmetric 6FDA-m-DDS membranes at 35°C and 76 cmHg. Curing temperature: (a) 150°C and (b) 250°C. Broken lines are (O_2/N_2) selectivity calculated from dense 6FDA-m-DDS membrane.
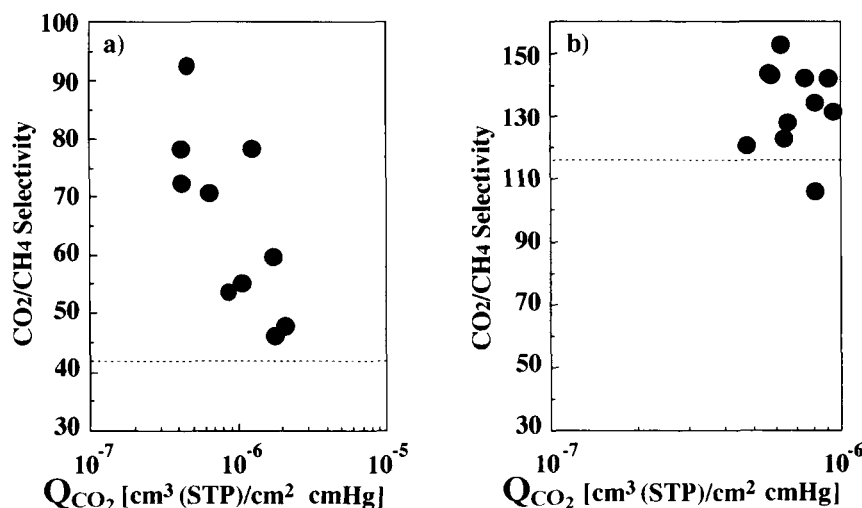
Figure 5   (CO_2/CH_4) selectivity and Q_{CO_2} of asymmetric 6FDA-m-DDS membranes at 35°C and 76 cmHg. Curing temperature: (a) 150°C and (b) 250°C. Broken lines are (CO_2/CH_4) selectivity calculated from dense 6FDA-m-DDS membrane.

tron-rich donor and electron-deficient acceptor molecules, it has been suggested that their physical and microstructural properties are related to intermolecular and intramolecular charge transfer interactions.[19-21] It has been found that the six-membered aromatic rings of electron-rich molecules donate electrons to the five-membered imide rings of electron-deficient molecules. The formation of a charge transfer complex is usually studied by UV-visible or fluorescence spectroscopy. Fluorescence spectroscopy provides an effective method for the study of charge transfer complex formation, and the relationship between the charge transfer fluorescence and the molecular aggregation of polyimides has been investigated in detail.[19,20] Figure 6 gives the results of emission spectra of the dense and asymmetric membranes measured using a fluorescence spectrophotometer. 6FDA-m-DDS membranes had emission spectra bands at 470 nm, when excited at 350 nm. These results support the idea that the charge transfer complex in 6FDA-m-DDS is undoubtedly formed. In addition, the emission intensity for the asymmetric membrane was 10 times larger than that measured for the dense membrane, and the asymmetric membrane cured at 250°C as sub-T_g exhibited a larger intensity than that at 150°C. The gas selectivities of these membranes increase with an increase in the emission intensity. This is evident from Table II that shows the gas permeances and selectivities for the dense and asymmetric membranes. In general, a charge transfer complex in aromatic polyimide is formed when the five- and six-membered rings are able to ap-

proach each other closely enough to allow π-electron density. That is, we believe that the packed polymer structure in the skin layer is formed by the charge transfer complex and provides high size and shape discrimination between the gas molecules. The above results show clearly that the asymmetric 6FDA-m-DDS membranes prepared in this study have excellent gas selectivities.

On the other hand, the smaller selectivities in the asymmetric membranes as compared with the values
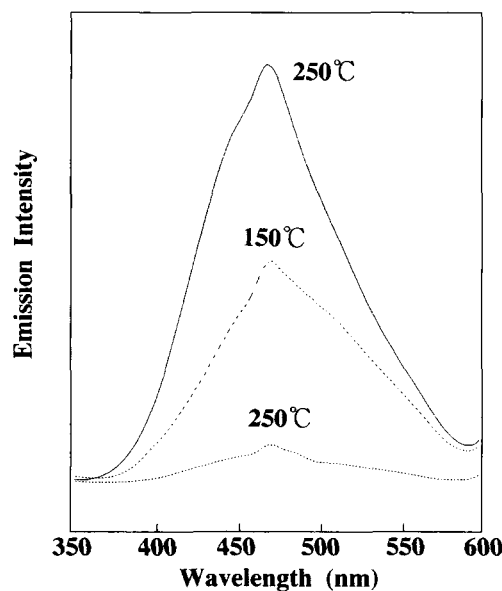
Figure 6   Emission spectra excited at 350 nm for 6FDA-m-DDS membranes. (—), (– – –) Asymmetric membrane, (- - -) dense membrane.

Table II   Average Gas Permeance and Selectivity of 6FDA-*m*-DDS Membranes at 35°C and 76 cmHg

Polyimide	Membrane Type	Q_{O_2}	O_2/N_2	Q_{CO_2}	CO_2/CH_4
6FDA-*m*-DDS	Dense	1.2	6.4	4.8	42
150°C	Asymmetric	41	8.8	131	70
6FDA-*m*-DDS	Dense	0.95	8.5	3.2	116
250°C	Asymmetric	17	9.4	69	136

Q, 10^{-8} [$cm^3(STP)/cm^2$ s cmHg].

obtained for the dense ones may be responsible for the enhanced free volume in the skin layer. It was reported that the acceleration of the coagulation process increases the free volume in the asymmetric hollow fiber membranes, which is reflected by an increase in the T_g.[14] The asymmetric membrane prepared in this study also exhibited a higher T_g than that obtained for the dense one, as shown in Table I. That is, it is believed that an increase in the free volume yields an increase in the gas permeance, and a decrease in the selectivity is accompanied by an increase in the permeance.
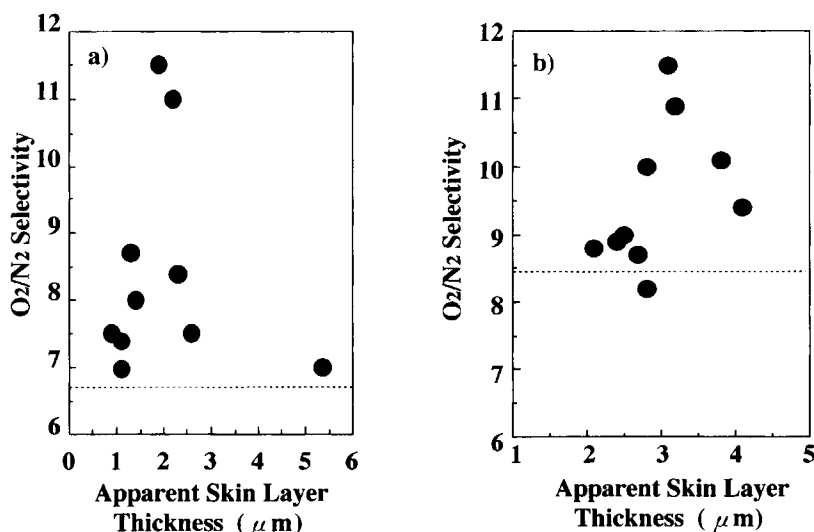
The apparent skin layer thickness of asymmetric membranes is shown in Figure 7. The thickness was determined based on the oxygen permeability coefficient of the dense 6FDA-*m*-DDS membrane. The calculated, average apparent skin layer thickness of the asymmetric membranes measured was 2.6 μm. To achieve the larger gas permeances in the asymmetric membrane, it is necessary to prepare the membrane with a thinner skin layer. The influence

of the coagulation process and solution compositions to the skin layer must be elucidated in a future study.

CONCLUSIONS

Asymmetric 6FDA-*m*-DDS membranes with a thin, selective, and defect-free skin layer were prepared by a dry/wet process. The membranes showed the selectivity of 11.5 for (O_2/N_2) and 153 for (CO_2/CH_4). The obtained gas selectivities of asymmetric membranes were significantly larger than those determined for the dense ones. We suggest that the packed polymer structure formed by the charge transfer complex provides high size and shape discrimination between the gas molecules.

The calculated, average apparent skin layer thickness of the asymmetric membranes was 2.6 μm, without the necessity of an additional coating process. A future study will focus on the formation

Figure 7   (O_2/N_2) selectivity and apparent skin layer thickness of asymmetric 6FDA-*m*-DDS membranes at 35°C and 76 cmHg. Curing temperature: (a) 150°C and (b) 250°C. Broken lines are (O_2/N_2) selectivity calculated from dense 6FDA-*m*-DDS membrane.

mechanism and preparation of an ultrathin skin layer in the asymmetric membrane.

REFERENCES

1. K. Nakagawa, *J. Appl. Polym. Sci.*, **41**, 2049 (1990).
2. G. Xu, C. C. Gryte, A. S. Nowick, S. Z. Li, Y. S. Pak, and S. G. Greenbaum, *J. Appl. Phys.*, **66**, 5290 (1989).
3. C. E. Hoyle and E. T. Anzures, *J. Appl. Polym. Sci.*, **43**, 1 (1991).
4. T. H. Kim, W. J. Koros, G. R. Husk, and K. C. O'Brien, *J. Appl. Polym. Sci.*, **34**, 1767 (1987).
5. S. A. Stern, Y. Mi, and H. Yamamoto, *J. Polym. Sci., Polym. Phys.*, **27**, 1887 (1989).
6. K. Tanaka, H. Kita, M. Okano, and K. Okamoto, *Polymer*, **33**, 585 (1992).
7. K. Matsumoto, P. Xu, and T. Nishikimi, *J. Membr. Sci.*, **81**, 15 (1993).
8. S. A. Stern, *J. Membr. Sci.*, **94**, 1 (1994).
9. M. Gyor, H. C. Wang, and J. R. Faust, *J. Macromol. Sci.*, **A29**, 639 (1992).
10. J. W. Park, M. Lee, M.-H. Lee, J. W. Liu, S. D. Kim, J. Y. Chang, and S. B. Rhee, *Macromolecules*, **27**, 3459 (1994).
11. H. Kawakami, J. Anzai, and S. Nagaoka, *J. Appl. Polym. Sci.*, **57**, 789 (1995).
12. I. Pinnau, J. Wind, and K.-V. Peinemann, *Ind. Eng. Chem. Res.*, **29**, 2028 (1990).
13. I. Pinnau and W. J. Koros, *J. Appl. Polym. Sci.*, **43**, 1491 (1991).
14. A. K. Fritzsche, R. E. Kesting, and M. K. Murphy, *J. Membr. Sci.*, **46**, 135 (1989).
15. R. E. Kesting, A. K. Fritzsche, M. K. Murphy, C. A. Cruse, A. C. Handermann, R. F. Malon, and M. D. Moore, *J. Appl. Polym. Sci.*, **40**, 1557 (1990).
16. W. J. Koros and D. R. Paul, *J. Polym. Sci., Polym. Phys.*, **16**, 1947 (1978).
17. K. Toi, G. Morel, and D. R. Paul, *J. Appl. Polym. Sci.*, **27**, 2997 (1982).
18. C. L. Aitken, W. J. Koros, and D. R. Paul, *Macromolecules*, **25**, 3651 (1992).
19. E. D. Wachsman and C. W. Frank, *Polymer*, **29**, 1191 (1988).
20. M. Hasegawa and I. Mita, *J. Polym. Sci., Polym. Lett.*, **27**, 263 (1989).
21. F. J. Dinan, W. T. Schwartz, R. A. Wolfe, D. S. Hojnicki, T. St. Clair, and J. R. Pratt, *J. Polym. Sci., Polym. Chem.*, **30**, 111 (1992).