

Gas-Permeation Properties of Asymmetric Polycarbonate, Polyestercarbonate, and Fluorinated Polyimide Membranes Prepared by the Generalized Dry–Wet Phase Inversion Process

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SYNOPSIS

Essentially defect-free, ultrathin asymmetric polycarbonate, polyestercarbonate, and 6FDA-IPDA polyimide membranes were prepared by a dry/wet phase inversion process using forced-convective evaporation. The pure gas permeation properties of these membranes were determined for N₂, O₂, He, CO₂, and CH₄. The average apparent skin-layer thicknesses of the membrane samples varied between 330 and 580 Å, which is substantially thinner than for previous defect-free membranes formed by the conventional wet phase inversion process. This study indicates that the dry/wet phase inversion process appears to be universally applicable to form ultrathin, defect-free asymmetric membranes from hydrophobic, glassy polymers. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

It is highly desirable to form ultrathin *and* defect-free asymmetric membranes by a single-step process. Furthermore, the membrane formation process should be applicable to a variety of different membrane-forming polymers and casting conditions. Until now such a universal method has not been reported in the literature. Current casting protocols used for the preparation of asymmetric membranes are generally modifications of the original procedure to form integrally skinned cellulose acetate reverse osmosis membranes, developed more than 30 years ago by Loeb and Sourirajan.^{1,2} However, it was found extremely difficult to successfully apply the same preparation principles to polymers other than cellulose acetate. As a result, most ultrathin asymmetric membranes made by modified Loeb and Sourirajan methods contain skin-layer defects.³⁻⁷

Several methods have been proposed to render defective asymmetric membranes suitable for gas

separation. The most successfully applied post-treatment method was developed by Henis and Tripodi in the late 1970s.⁸ They discovered that skin-layer pores can effectively be sealed with a thin coating of a highly permeable polymer such as silicone rubber, which results in the elimination of any pore-flow contributions to gas transport.^{6,8} The gas-separation properties of the resulting multicomponent asymmetric membranes depend on (i) the skin-layer thickness, (ii) the skin-layer porosity, and (iii) the ratio of the gas-transport resistances of the skin layer and the coating layer.⁸ The method can be applied to a variety of asymmetric membranes made from different membrane materials.⁹⁻¹² However, any posttreatment adds complexity and costs to a membrane production process.

It was recently demonstrated that essentially defect-free asymmetric polysulfone membranes with skin-layer thicknesses as thin as 200 Å could be formed by a dry/wet phase inversion process.¹³ Furthermore, it was shown that the casting formulations and the quench medium could be varied without changing the membrane properties dramatically.¹⁴

The goal of this paper is to demonstrate that the dry/wet phase inversion process seems to be universally applicable to hydrophobic, glassy polymers.

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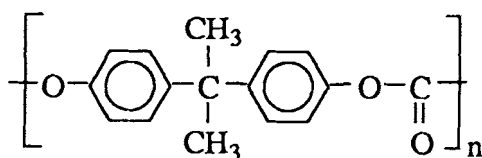


Figure 1 Repeat unit of bisphenol-A polycarbonate.

For this purpose, a crystallizable polymer, i.e., polycarbonate, a copolymer, i.e., polyestercarbonate, and a rigid, highly temperature-resistant polyimide, i.e., poly(hexafluoroisopropylidenedianhydride-isopropylidenedianiline) were selected as the membrane forming materials.

METHODS AND EXPERIMENTS

Materials and Preparation of Dry/Wet Phase Inversion Membranes

Bisphenol-A polycarbonate with a weight-average molecular weight of 32000–36000 g/mol was purchased from Polysciences, Inc., Warrington, PA. The structural unit is shown in Figure 1. Polycarbonate is an amorphous material when formed by melt processing; however, it tends to crystallize in some liquid or vapor environments.^{15,16}

Commercially available polyestercarbonate, Apec 9308, was kindly supplied by Bayer Mobay, Pittsburgh, PA. The polyestercarbonate is an amorphous copolymer of bisphenol-A polycarbonate and bisphenol-A iso/terephthalic acid ester, as shown in Figure 2. Apec 9308 contains 50 wt % ester per repeat unit.¹⁷ The glass transition temperature of Apec 9308 is 170°C, as determined by differential scanning

calorimetry (DSC) at a heating rate of 20°C per minute.¹⁸

The polyimide, poly(hexafluoroisopropylidenedianhydride-isopropylidenedianiline) [6FDA-IPDA], was purchased from Boron Biologicals, Durham, NC. The polymer was synthesized according to the procedure of Husk et al.¹⁹ and shows a weight-average molecular weight of ~ 100,000 g/mol and a glass transition temperature of 310°C.¹⁸ The structural unit of the 6FDA-IPDA polyimide is shown in Figure 3.

The gas-transport properties of polycarbonate,²⁰ polyestercarbonate,²⁰ and 6FDA-IPDA polyimide films²¹ have been studied in great detail. However, only for the polycarbonate material have actual asymmetric gas-permeation results been reported in the literature.²¹

Integrally skinned asymmetric membranes were prepared by the dry/wet phase inversion process using forced-convective evaporation.²² The casting solutions are listed in Table I. All casting formulations were close to the thermodynamic instability limit corresponding to the so-called binodal curve defined by the locus of compositions at which phase separation becomes theoretically possible. The casting formulations used for the preparation of polyestercarbonate and polyimide membranes remained stable for at least 6 months. On the other hand, the polycarbonate solution transferred into a waxlike gel a few hours after the mixing process, similar to solutions used for the preparation of asymmetric poly ether sulfone membranes.²³ The membranes were cast at 24°C on glass plates with a knife gap of 250 μm. Immediately after casting the

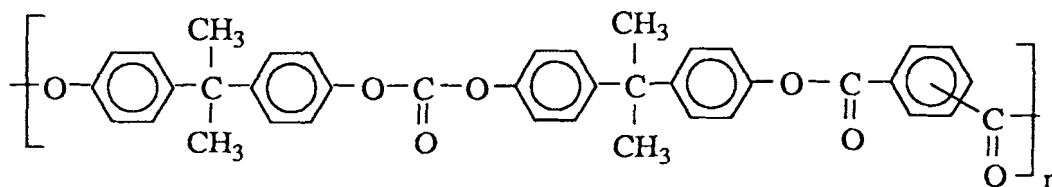


Figure 2 Repeat unit of polyestercarbonate.

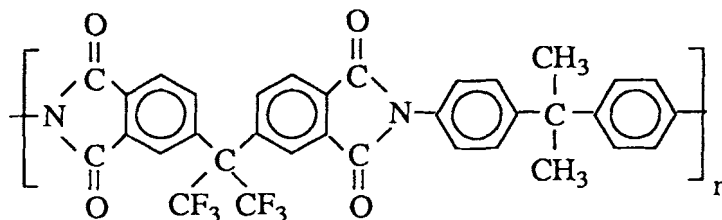


Figure 3 Repeat unit of 6FDA-IPDA polyimide.

Table I Casting Solutions (Wt %) for the Preparation of Membranes Made by Dry/Wet Phase Inversion

Polymer	Solvent	Cosolvent	Nonsolvent	Nonsolvent
12.2 PC	51.0 MTC	22.4 112TCE	—	14.4 2M2B
14.0 PEC	53.0 MC	20.0 112TCE	—	13.0 2M2B
11.9 PI	17.9 MC	23.8 112TCE	23.8 111TCE	22.6 2M2B

PC, polycarbonate; PEC = polyester carbonate; PI = 6FDA-IPDA polyimide; MC = methylene chloride; 112TCE = 1,1,2-trichloroethane; 111 TCE = 1,1,1-trichloroethane; 2M2B = 2-methyl-2-butanol.

films, an air stream was blown across the membrane surface for a period of 10 s. The initially clear, nascent membranes became turbid instantaneously at the onset of the blowing process. After an additional free-standing evaporation period of 15 s, the membranes were quenched in methanol and subsequently washed for a period of 12 h. The membranes were air-dried for 48 h and finally postdried in a vacuum oven at 100°C for at least 4 h. DSC runs on dry samples showed no evidence of residual solvent left in the asymmetric membranes.

Gas-Permeation Experiments

Pure gas pressure-normalized fluxes of N₂, O₂, He, and CO₂ were determined for the asymmetric polycarbonate and polyestercarbonate samples at a test temperature of 35°C. The gas-permeation properties

of the 6FDA-IPDA polyimide membranes were evaluated with N₂, O₂, CH₄, and He at 24°C. The pressure difference was kept constant at 3.5 atm for all gas-permeation tests. Volumetric gas flow rates were determined with soap-bubble flowmeters. The downstream side was always purged with the test gas prior to the permeation measurement. The gas-transport properties of the asymmetric membranes were determined with 20 randomly chosen membrane samples of 12.6 cm² surface area for each polymer.

RESULTS AND DISCUSSION

The pure gas-permeation properties of integrally skinned asymmetric polycarbonate membranes made by the dry/wet phase inversion process are

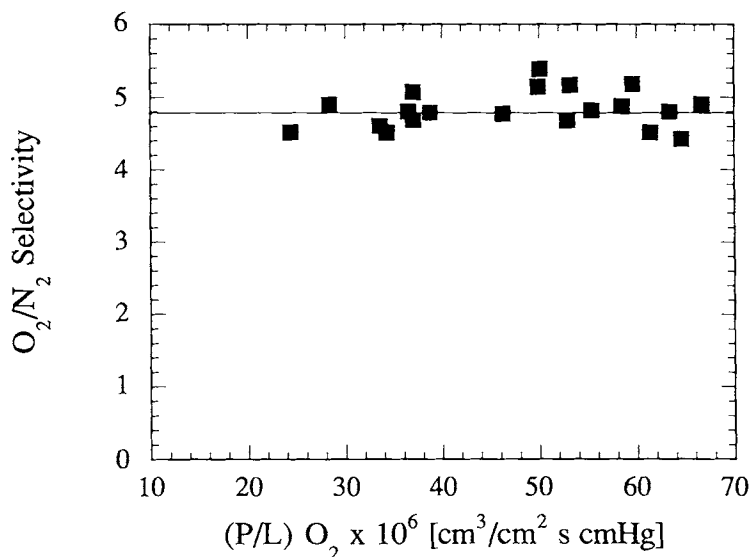


Figure 4 O₂/N₂ selectivities vs. pressure-normalized oxygen fluxes of polycarbonate membranes made by dry/wet phase inversion. *T* = 35°C; Δ*p* = 3.5 atm. The solid line represents the ideal selectivity for dense polycarbonate films under the same testing conditions.

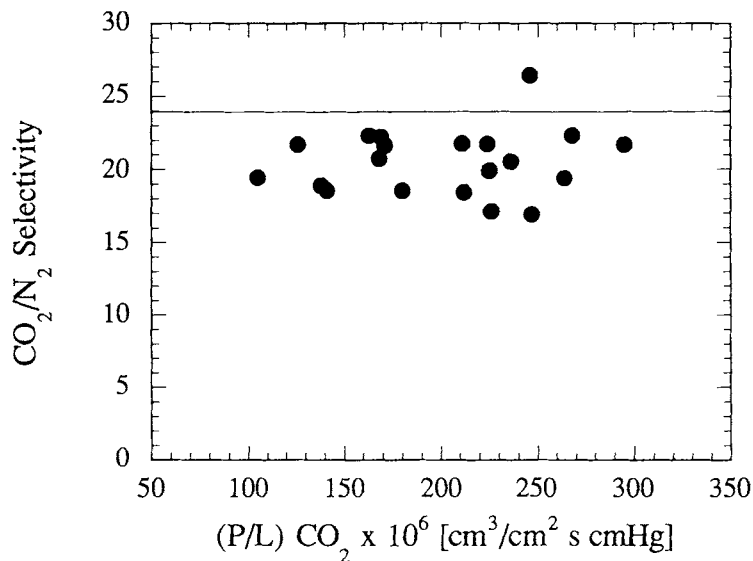


Figure 5 CO₂/N₂ selectivities vs. pressure-normalized carbon dioxide fluxes of polycarbonate membranes made by dry/wet phase inversion. $T = 35^{\circ}\text{C}$; $\Delta p = 3.5$ atm. The solid line represents the ideal selectivity for dense polycarbonate films under the same testing conditions.

shown in Figures 4–6. The average O₂/N₂, CO₂/N₂, and He/N₂ selectivities were 4.8, 21, and 39, respectively. The average selectivities of the asymmetric membrane samples were at least within 85% of the gas selectivities of polycarbonate, as determined for a solution cast film of known thickness.²⁰

These results suggest that the skin layers of the membranes were essentially defect-free. The actual skin-layer thickness cannot be determined explicitly for asymmetric membranes. However, an *apparent* skin layer thickness can be calculated by dividing the permeability coefficient of any chosen gas type

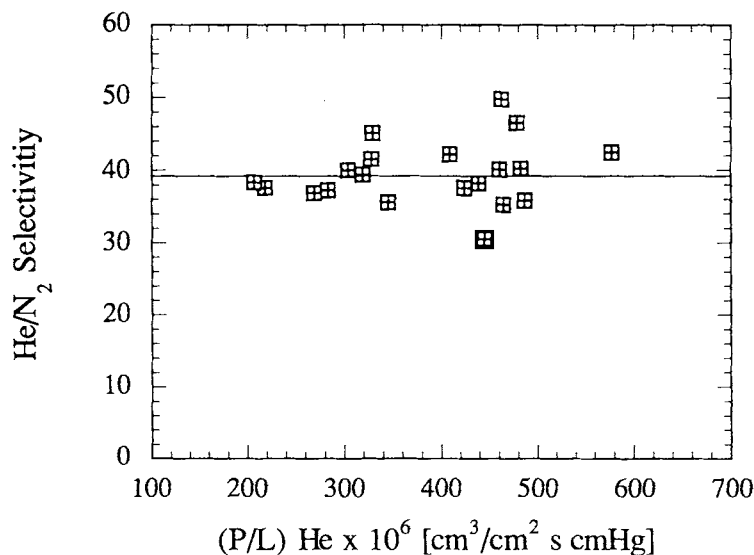


Figure 6 He/N₂ selectivities vs. pressure-normalized helium fluxes of polycarbonate membranes made by dry/wet phase inversion. $T = 35^{\circ}\text{C}$; $\Delta p = 3.5$ atm. The solid line represents the ideal selectivity for dense polycarbonate films under the same testing conditions.

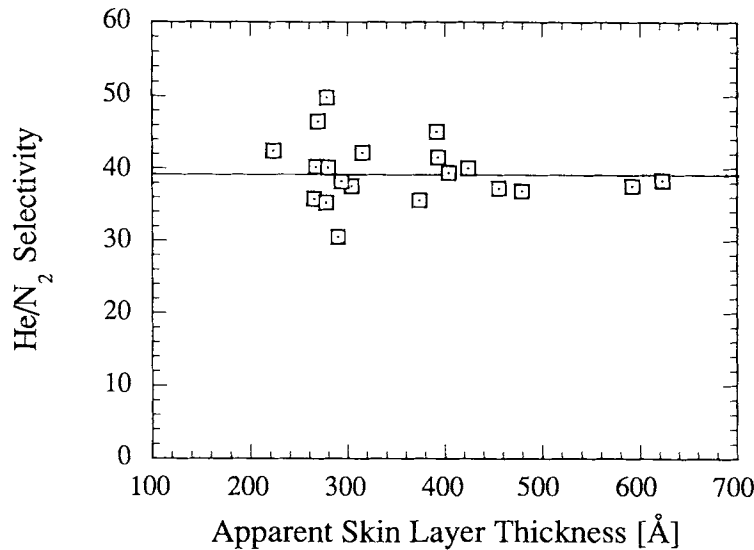


Figure 7 He/N₂ selectivities vs. apparent skin-layer thicknesses of polycarbonate membranes made by dry/wet phase inversion. $T = 35^{\circ}\text{C}$; $\Delta p = 3.5$ atm. The solid line represents the ideal selectivity for dense polycarbonate films under the same testing conditions.

i (say helium) as determined on dense films tested under the same conditions, by the pressure-normalized flux of this same gas in the asymmetric membrane.

The average apparent skin-layer thickness of the polycarbonate samples was 360 Å, based on the pressure-normalized helium fluxes of the asymmetric membrane samples and a helium permeability

coefficient of 12.9×10^{-10} cm³ cm/cm² s cmHg.²⁰ The apparent skin-layer thicknesses of the individual asymmetric membrane samples ranged between 220 and 650 Å, as shown in Figure 7.

Integrally skinned asymmetric polycarbonate membranes previously made by a *wet* phase inversion process using free-standing evaporation showed a pressure-normalized O₂ flux of 0.27×10^{-6} cm³/

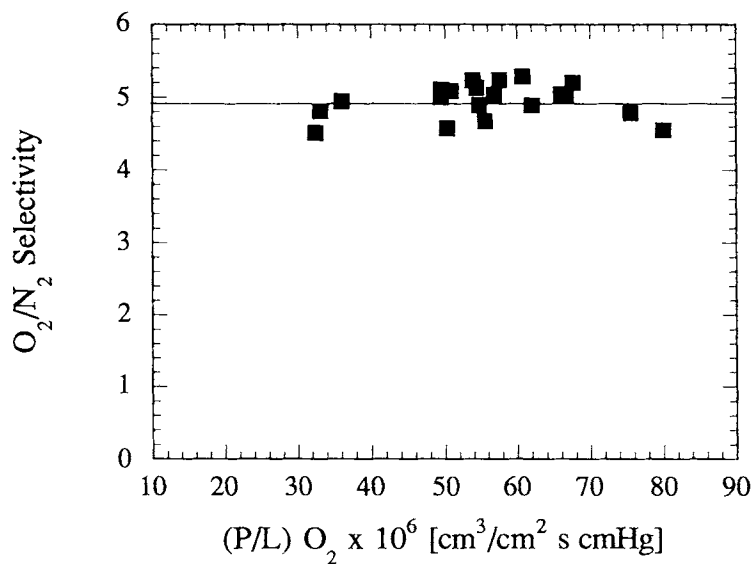


Figure 8 O₂/N₂ selectivities vs. pressure-normalized oxygen fluxes of polyester carbonate membranes made by dry/wet phase inversion. $T = 35^{\circ}\text{C}$; $\Delta p = 3.5$ atm. The solid line represents the ideal selectivity for dense polyester carbonate films under the same testing conditions.

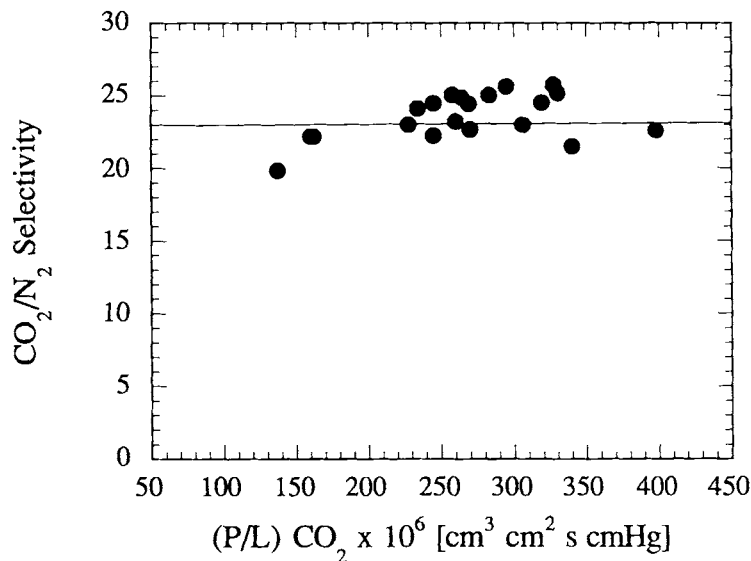


Figure 9 CO_2/N_2 selectivities vs. pressure-normalized carbon dioxide fluxes of polyestercarbonate membranes made by dry/wet phase inversion. $T = 35^\circ\text{C}$; $\Delta p = 3.5$ atm. The solid line represents the ideal selectivity for dense polyestercarbonate films under the same testing conditions.

$\text{cm}^2 \text{ s cmHg}$ and an O_2/N_2 selectivity of 4.5.²⁴ The apparent skin-layer thickness of these membranes was $5.9 \mu\text{m}$ ($59,000 \text{ \AA}$), based on an O_2 permeability coefficient of $1.6 \times 10^{-10} \text{ cm}^3 \text{ cm/cm}^2 \text{ s cmHg}$.²¹ The apparent skin-layer thicknesses of the essentially defect-free asymmetric polycarbonate membranes made by the *dry/wet* phase inversion process dis-

cussed here were two orders of magnitude thinner than those prepared by the conventional wet phase inversion process.

It was previously noted that polyester carbonate shows very similar gas permeabilities and selectivities compared to polycarbonate, as determined on dense film.²⁰ The average O_2/N_2 , CO_2/N_2 , and He/

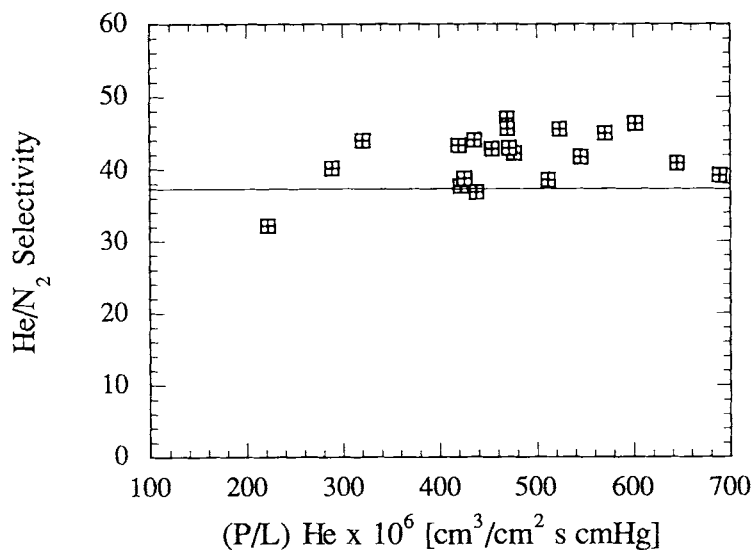


Figure 10 He/ N_2 selectivities vs. pressure-normalized helium fluxes of polyestercarbonate membranes made by dry/wet phase inversion. $T = 35^\circ\text{C}$; $\Delta p = 3.5$ atm. The solid line represents the ideal selectivity for dense polyestercarbonate films under the same testing conditions.

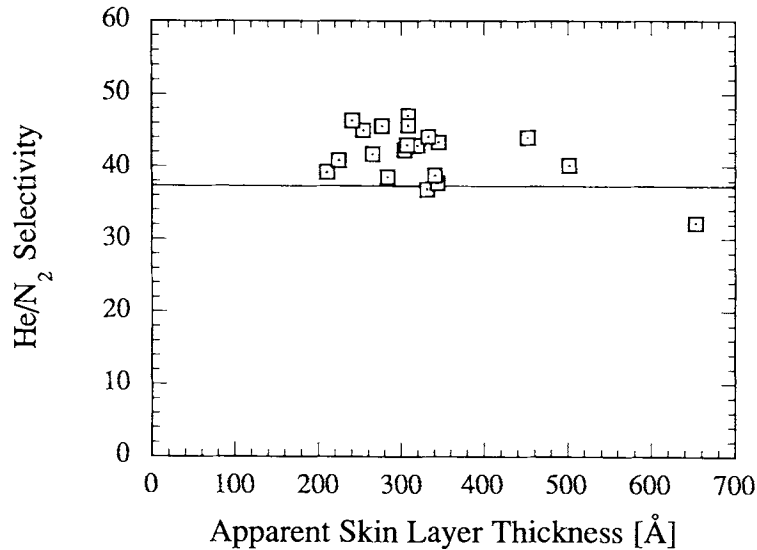


Figure 11 He/N₂ selectivities vs. apparent skin-layer thicknesses of polyestercarbonate membranes made by dry/wet phase inversion. $T = 35^{\circ}\text{C}$; $\Delta p = 3.5$ atm. The solid line represents the ideal selectivity for dense polyestercarbonate films under the same testing conditions.

N₂ selectivities of the asymmetric polyestercarbonate samples were 4.9, 24, and 42, respectively. The selectivities of the integrally skinned asymmetric membranes were essentially equal to those determined for dense PEC films,²⁰ as shown in Figures 8–10. The average apparent skin-layer thickness of the membrane samples was 330 Å, based on a helium

permeability coefficient of 14.5×10^{-10} cm³ cm/cm² s cmHg, as determined on a solution-cast PEC film of known thickness.²⁰ The apparent skin-layer thicknesses of the individual samples varied between 200 and 660 Å, as shown in Figure 11. It appears that the selectivities of the asymmetric PC and PEC membranes were almost equivalent, as expected for

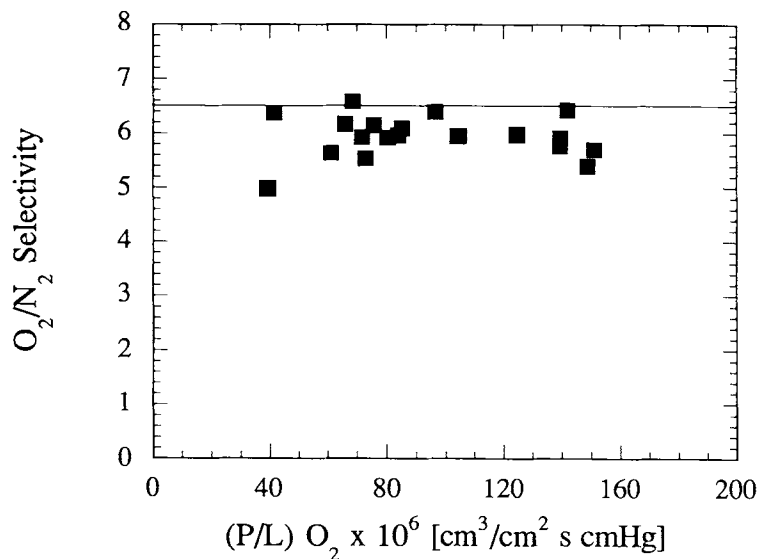


Figure 12 O₂/N₂ selectivities vs. pressure-normalized oxygen fluxes of 6FDA-IPDA polyimide membranes made by dry/wet phase inversion. $T = 24^{\circ}\text{C}$; $\Delta p = 3.5$ atm. The solid line represents the ideal selectivity for dense 6FDA-IPDA polyimide films under the same testing conditions.

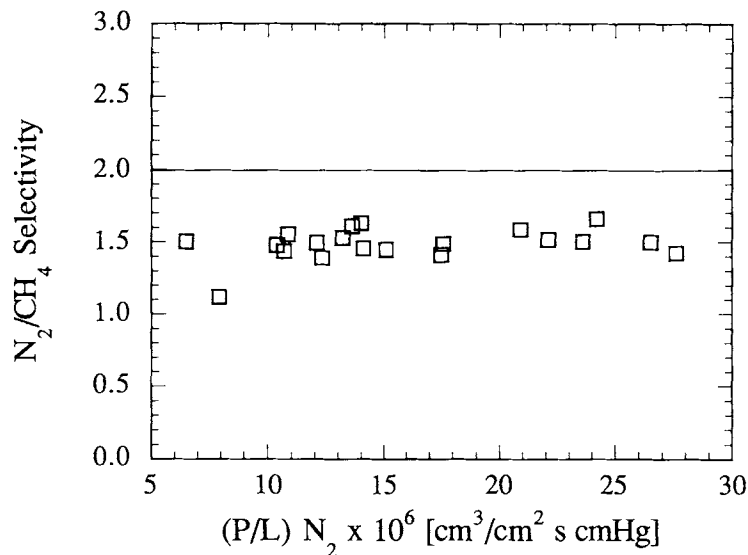


Figure 13 N_2/CH_4 selectivities vs. pressure-normalized nitrogen fluxes of 6FDA-IPDA polyimide membranes made by dry/wet phase inversion. $T = 24^\circ\text{C}$; $\Delta p = 3.5$ atm. The solid line represents the ideal selectivity for dense 6FDA-IPDA polyimide films under the same testing conditions.

defect-free membranes made from these materials.²⁰ It is interesting to point out that several asymmetric membrane samples of both materials exhibited higher selectivities compared to those of the dense films. It has recently been suggested that the molecular polymer packing density in the skin layers

of asymmetric membranes can differ somewhat from that of the bulk membrane material.^{14,18,25}

The gas-transport properties of the 6FDA-IPDA polyimide membranes at 24°C are shown in Figures 12-14. The average O_2/N_2 , N_2/CH_4 , and He/N_2 selectivities of the asymmetric polyimide membranes

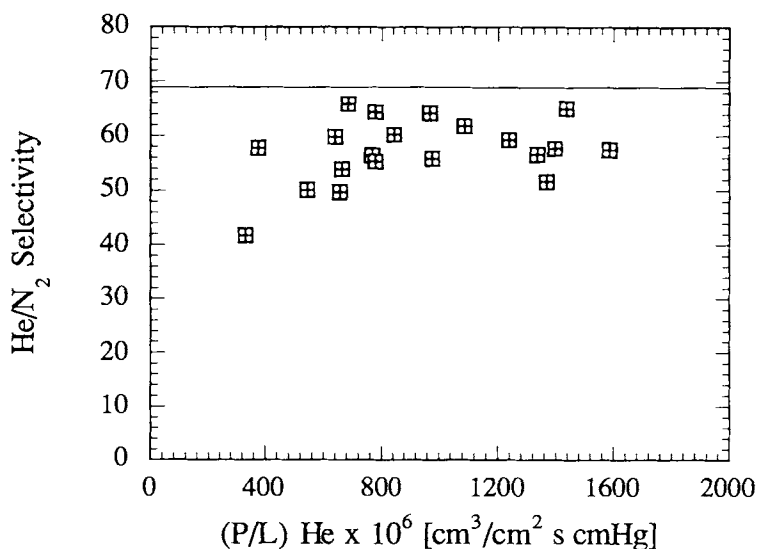


Figure 14 He/N_2 selectivities vs. pressure-normalized helium fluxes of 6FDA-IPDA polyimide membranes made by dry/wet phase inversion. $T = 24^\circ\text{C}$; $\Delta p = 3.5$ atm. The solid line represents the ideal selectivity for dense 6FDA-IPDA polyimide films under the same testing conditions.

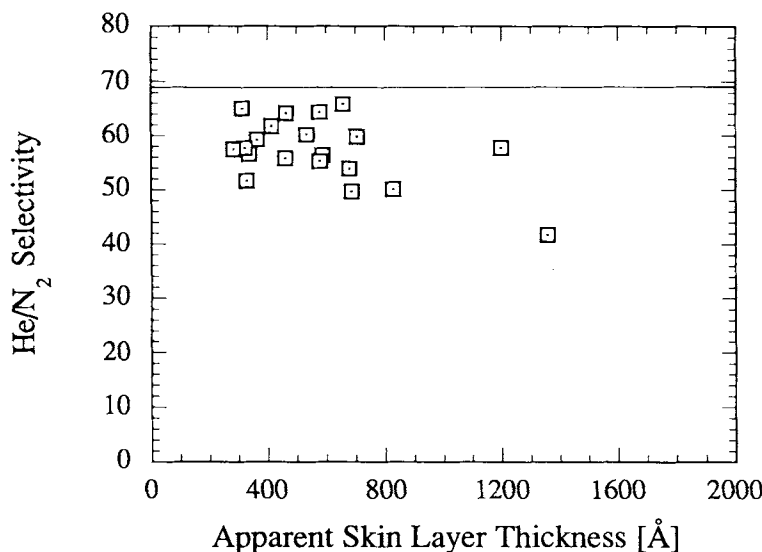


Figure 15 He/N₂ selectivities vs. apparent skin-layer thicknesses of 6FDA-IPDA polyimide membranes made by dry/wet phase inversion. $T = 24^{\circ}\text{C}$; $\Delta p = 3.5$ atm. The solid line represents the ideal selectivity for dense 6FDA-IPDA polyimide films under the same testing conditions.

were 5.9, 1.5, and 58, respectively. Previous gas-permeation studies of dense 6FDA-IPDA films were carried out between 35 and 55°C.²¹ The reported Arrhenius expressions were extrapolated to 24°C to evaluate if the asymmetric membrane samples were essentially defect-free. The O₂/N₂, N₂/CH₄, and He/N₂ selectivities of the dense films at 24°C were estimated to be 6.5, 2.0, and 69, respectively. Hence, the selectivities of the asymmetric membrane samples were at least within 75% of the estimated values of the dense polyimide films. Accordingly, the membranes can be considered to be essentially defect-free. The average skin-layer thickness of the asymmetric membrane samples was 580 Å, based on an estimated helium permeability coefficient of 45.1×10^{-10} cm³ cm/cm² s cmHg at 24°C. The skin-layer thicknesses of the individual polyimide membrane samples varied between 300 and 1400 Å, as shown in Figure 15.

SUMMARY AND CONCLUSIONS

Optimized protocols for the formation of membranes made by the dry/wet phase inversion process resulted in essentially defect-free integrally skinned asymmetric polycarbonate, polyester carbonate, and 6FDA-IPDA polyimide membranes. The average skin-layer thicknesses of these membranes ranged between 330 and 580 Å, which is substantially thin-

ner than for previous membranes formed by the conventional wet phase inversion process. Additional studies demonstrated that the dry/wet phase inversion process is applicable to glassy polymers others than those reported here. These results indicate that the dry/wet phase inversion process seems to be universally applicable to hydrophobic glassy polymers.

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REFERENCES

1. S. Loeb and S. Sourirajan, *Adv. Chem. Ser.*, **38**, 117-132 (1963).
2. S. Loeb and S. Sourirajan, U.S. Pat. 3,133,132 (1964).
3. R. E. Kesting, *Synthetic Polymeric Membranes: A Structural Perspective*, Wiley, New York, 1985, p. 31.
4. R. E. Kesting, A. K. Fritzsche, C. A. Cruse, and M. D. Moore, *J. Appl. Polym. Sci.*, **40**, 1575-1582 (1990).
5. R. E. Kesting, *J. Appl. Polym. Sci.*, **41**, 2739-2752 (1990).
6. J. M. S. Henis and M. K. Tripodi, *J. Membr. Sci.*, **8**, 233-246 (1981).
7. J. van't Hof, PhD Dissertation, University of Twente, The Netherlands, 1988.
8. J. M. S. Henis and M. K. Tripodi, U.S. Pat. 4,230,463 (1980).

9. A. Zampini, U.S. Pat. 4,488,886 (1984).
10. A. Zampini, U.S. Pat. 4,647,297 (1987).
11. R. E. Kesting, C. A. Cruse, A. K. Fritzsche, R. F. Malon, M. K. Murphy, and A. C. Handermann, Eur. Pat. Appl. 0,259,288 (1987).
12. K.-V. Peinemann, U.S. Pat. 4,673,418 (1987).
13. I. Pinnau and W. J. Koros, *J. Appl. Pol. Sci.*, to appear.
14. I. Pinnau, PhD Dissertation, The University of Texas at Austin, 1991.
15. B. J. MacNulty, *J. Mater. Sci.*, **4**, 841-844 (1969).
16. B. J. MacNulty, *J. Mater. Sci.*, **8**, 1495-1504 (1973).
17. Dr. Winfried Paul, Bayer Mobay, Personal communication, 1989.
18. I. Pinnau, M. W. Hellums, and W. J. Koros, *Polymer*, to appear.
19. G. R. Husk, P. E. Cassidy, and K. L. Gebert, *Macromolecules*, **21**, 1234-1238 (1988).
20. M. W. Hellums, PhD Dissertation, The University of Texas at Austin, 1990.
21. T. H. Kim, PhD Dissertation, The University of Texas at Austin, 1988.
22. I. Pinnau and W. J. Koros, U.S. Pat. 4,902,422 (1990).
23. I. Pinnau, J. Wind, and K.-V. Peinemann, *Ind. Eng. Chem. Res.*, **29**, 2028-2032 (1990).
24. S. G. Kimura, U.S. Pat. 3,709,774 (1973).
25. A. K. Fritzsche, M. K. Murphy, C. A. Cruse, R. F. Malon, and R. E. Kesting, *Gas Sep. Pur.*, **3**, 106-118 (1989).

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