

Gas Transport through Integral-Asymmetric Membranes: A Comparison to Isotropic Film Transport Properties

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SYNOPSIS

Pressure-normalized gas fluxes for defect-free integral-asymmetric membranes prepared according to a dry/wet phase inversion process were measured as a function of temperature and pressure and compared to measurements on thick isotropic films. Asymmetric membranes were prepared from polysulfone, polycarbonate, and poly(ester carbonate). The activation energies of permeation for O₂ and N₂ in the range of 25–55°C were higher for the asymmetric polysulfone membranes than for a thick isotropic film. O₂/N₂ selectivities of the asymmetric membranes are higher than those for isotropic films. The asymmetric membranes did not show the typical dual-mode behavior for the CO₂ flux as a function of pressure as determined for thick films. Differences in the free volume and its distribution in the ultrathin skin layer of the asymmetric membranes compared to isotropic films may be responsible for these results. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Asymmetric membranes made from glassy polymers are widely used in industrial gas separations.¹ These membranes consist of a thin skin layer supported by a porous substructure. The thickness of the skin layer is usually on the order of several hundred to several thousand angstroms. The skin layer should be free of defects and as thin as possible to obtain high flux and the maximum permselectivity of the polymer used. It is extremely difficult to prepare such membranes, since the permselectivity is drastically reduced even by a small number of defects allowing pore flow of gases. Recently, a dry/wet phase inversion process for the preparation of ultrathin and simultaneously defect-free asymmetric membranes from glassy polymers has been developed.^{2,3} It was shown that asymmetric membranes with effective skin layer thicknesses of 200–1000 Å can be manufactured.

The properties of glassy polymers depend on their history and the preparation protocol since they are

nonequilibrium materials.^{4–6} The fundamental gas transport properties of polymers are often studied on isotropic films having thicknesses that are orders of magnitude larger than the thickness of the skin layer of asymmetric membranes. The preparation of isotropic films is quite different from the preparation of asymmetric membranes.⁷ Few studies have been reported in the literature that compare the transport properties of asymmetric membranes with those of isotropic films made from the same material, and this is the main objective of this study.

Haraya et al.⁸ compared the selectivities of asymmetric cellulose acetate membranes and isotropic films. The lower gas selectivities of the asymmetric membranes were attributed to pore flow through defects in the skin layer of the asymmetric membranes. The activation energies of permeation for the asymmetric membranes containing defects were much lower than for an isotropic defect-free film from the same material.

Sada et al.⁹ compared the pressure dependence of the permeability coefficient for CO₂ in asymmetric polysulfone (PSF) membranes and isotropic films. The CO₂ permeability coefficient was found to drop, approximated by the behavior of isotropic films. The minimum skin thickness of the asymmetric membranes was 23,000 Å.

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Fritzsche et al. and Kesting et al.¹⁰⁻¹³ suggested that the skin layer of asymmetric PSF hollow fiber membranes may have an increased free volume compared to the bulk membrane material. It was hypothesized that the free volume increase is a result of the extremely rapid quench kinetics of the asymmetric membrane formation process. Evidence for an increase in free volume was based on a higher first heat glass transition temperature (T_g) of asymmetric membranes compared to samples of the bulk membrane material. Fritzsche et al. suggested that the permeability coefficients of the skin layer of asymmetric PSF membranes can be intrinsically higher than those of an isotropic homogeneous film, due to the higher free volume in the asymmetric membrane.

Permeation measurements of defect-free integral-asymmetric membranes prepared according to the dry/wet phase inversion process are presented here and compared to measurements of isotropic films. Our results differ significantly from the prior studies mentioned above. We attempt to rationalize the observed differences in the results in terms of the free volume and the cohesive energy density of glassy polymers.^{14,15}

The skin thicknesses for the integral-asymmetric membranes were estimated from a comparison of the pressure-normalized fluxes of the integral-asymmetric membranes with the permeability (flux normalized with respect to pressure and known thickness) of films made from the same material. This estimation is accurate to within 10–20%; however, these thickness values were of little direct significance to the discussion here. Indeed, the present considerations focus on differences in selectivities and activation energies for asymmetric membranes and isotropic films. Both of these quantities are independent of the thickness of the selective layer, per se. The point of this paper is that the basic morphology of the separating layer in the asymmetric and isotropic media appears to be different.

EXPERIMENTAL

Isotropic Film and Asymmetric Membrane Preparation

Isotropic Film Preparation

A 5 wt % solution of commercial grade bisphenol-A polysulfone (Udel 1700) in chloroform was poured into a stainless-steel ring supported by a glass plate. Solvent was evaporated from the film for 24 h at 24°C. Thereafter, the clear film was removed from

the glass plate and dried in a vacuum oven for 14 days by slowly raising the temperature from 24 to 190°C. Finally, the temperature was held constant at 190°C for 24 h. The thickness of the film, determined with a mechanical thickness gauge, was 100 μm . A DSC run on a dry film sample showed no evidence of residual solvent left in the dried film.

The film preparation procedure for isotropic polycarbonate (PC) and poly(ester carbonate) (PEC) films referred to in this paper is very similar to the procedure given above. Details can be found in Refs. 15 and 16.

Asymmetric Membrane Preparation

Asymmetric polysulfone (PSF), polycarbonate (PC) and poly(ester carbonate) (PEC) membranes were prepared as described elsewhere^{2,3} by the dry/wet phase inversion method using methanol as the quench medium. The same PSF and PEC batches as for the isotropic films were used. DSC runs gave no evidence of residual solvent left in the asymmetric membranes after drying.

Multicomponent membranes were also formed by coating the asymmetric membranes with a thin layer ($\sim 1 \mu\text{m}$) of silicone rubber. The coating solution consisted of 1 wt % prepolymerized silicone (RTV 615 A and RTV 615 B, General Electric Co., Waterford, NY) in *n*-heptane.

The thin silicone rubber layer has a permeability coefficient that is orders of magnitude higher than the permeability coefficient for the glassy material of the asymmetric membrane. The coating will therefore only prevent the hydraulic flux of gas through any defects in the membrane skin, but will not alter the permeation characteristics of the asymmetric membrane material.

Gas Transport Measurements

The two methods employed for the experiments in this paper are described below. We will refer to them throughout the text as *Method I* (vacuum applied to the permeate side, Baratron pressure transducer for flow measurement by pressure rise) and *Method II* (permeate side at atmospheric pressure, soap film bubblemeter for flow measurement).

Variable-Pressure Constant-Volume Method (Method I)

This is the standard variable-pressure constant-volume technique employed in our laboratory.¹⁷ The equipment allows the measurement of gas permeability coefficients from the rate of accumulation of

penetrant in an evacuated downstream volume using a Baratron pressure transducer. The downstream pressure of 10 mmHg or less was always negligible relative to the upstream pressure. The custom-designed high-pressure permeation cell used for measurement of isotropic films was replaced with a commercial test cell for tests of asymmetric membranes.

Constant Pressure–Variable Volume Method (Method II)

Volumetric gas flow rates were determined using soap bubble flowmeters, attached to the permeation cell with a thick-walled rubber hose. The high volumetric flow rates of the asymmetric membranes preclude any backdiffusion of gases or vapors from the bubble flowmeter through the porous substructure of the asymmetric membranes to the active skin layer. Care was taken to fully purge the permeate volume with the gas to be measured. Series of pure gases were always tested in the order of increasing permeability so that any potential residues on the feed side remaining after the usual repeated purge cycles would decrease the pressure-normalized fluxes of the faster gases, thereby decreasing the calculated selectivities and giving a “worst case” value of the selectivity.

Gas-mixture Experiments

The gas-mixture experiments were carried out at 24°C and a feed pressure of 10 atm with certified compressed air (Wilson Oxygen, Austin, TX). The permeate pressure was atmospheric. The ratio of feed gas pressure to permeate pressure of about 10 prevents limitation of the measured separation factor by the pressure ratio. The ratio of permeate flow to retentate flow, i.e., the stage cut, was always less than 1%; hence, the retentate composition was essentially equal to that of the feed mixture. The retentate and the permeate compositions were determined with a Servomex oxygen analyzer 571 (Servomex LTD, Crowborough, Sussex, England). The accuracy of the oxygen analyzer was within 0.3 Vol % of the readout.

The pure gas selectivity or ideal selectivity α is given as

$$\alpha_{A,B} = \frac{P_A}{P_B} = \frac{(P_A/L)}{(P_B/L)} \quad (1)$$

where P_A and P_B are the pure gas permeability coefficients in Barrers [$1 \times 10^{-10} \text{ cm}^3 \text{ (STP) cm/cmHg s cm}^2$] and L is the effective membrane thickness

in cm. The coefficient (P_i/L) is the pressure normalized flux of gas i in [$\text{cm}^3 \text{ (STP)/cmHg s cm}^2$]. The separation factor, β , for a binary mixture and under the assumption of negligible stage cut depends on the pressure ratio of the permeate and the feed and is given by

$$\beta_{A,B} = \frac{Y_{1A} Y_{2B}}{Y_{2A} Y_{1B}} \quad (2)$$

where Y is the mole fraction. The subscript 1 denotes the permeate (low-pressure) side of the membrane, whereas subscript 2 denotes the feed (high-pressure) side of the membrane. The subscripts A and B refer to the components of the binary mixture. The separation factor $\beta_{A,B}$ will be essentially equal to the pure gas selectivity $\alpha_{A,B}$ if the gases do not interact strongly with each other and the membrane material and if the pressure ratio of feed pressure to permeate pressure is sufficiently larger than the pure gas selectivity $\alpha_{A,B}$.¹⁸

RESULTS AND DISCUSSION

Isotropic PSF Film

An isotropic solution-cast PSF film was made from the same batch of material as the asymmetric membranes and measured for reference. The permeability coefficients for N_2 , O_2 , and He in this film were determined over a temperature range of 25–55°C at 3.5 atm pressure difference (3.5 atm Δp), as shown in Figure 1. The data follow the typical linear Arrhenius behavior.

The activation energies of permeation for the isotropic PSF film were calculated from the slope of the Arrhenius plots. The activation energies of permeation were 23,000, 15,000, and 14,900 J/mol for N_2 , O_2 , and He, respectively. The permeability coefficients of N_2 , O_2 , and He at 24°C were 0.165, 1.05 and 11.4 Barrers, respectively. The corresponding O_2/N_2 and He/ N_2 selectivities are 6.4 and 69.1 at 24°C, respectively.

Asymmetric Membranes: Activation Energy and Selectivity

It is shown in Table I that integrally skinned asymmetric PSF membranes and multicomponent asymmetric PSF/silicone rubber membranes made by dry/wet phase inversion can exhibit O_2/N_2 selectivities higher than those of the solvent-cast isotropic PSF film. These results were confirmed with gas-

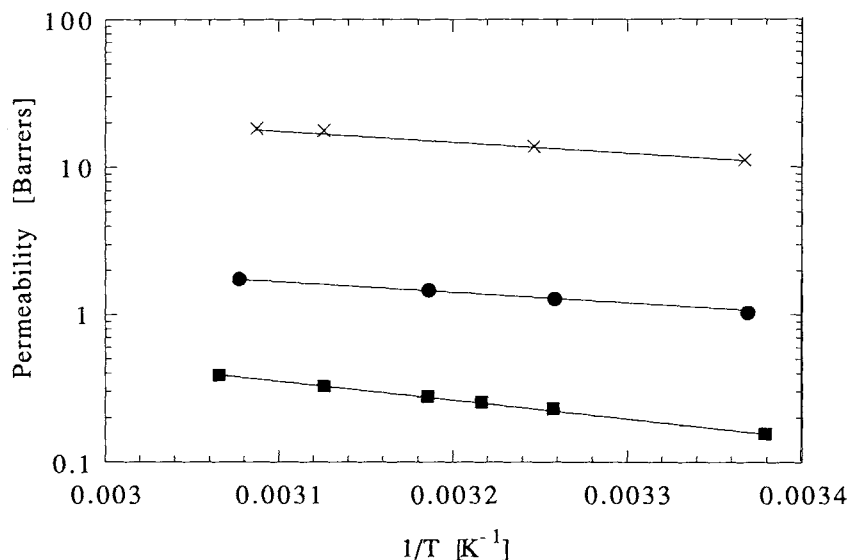


Figure 1 Arrhenius plots of P vs. $1/T$ for a solution-cast isotropic PSF film at 3.5 atm Δp (Method I): (■) N₂; (●) O₂; (×) He.

mixture experiments. Note that, as expected, the selectivities of the coated asymmetric multicomponent membranes appear effectively identical to the defect-free integrally skinned membranes.

The thickness of the skin layer of the asymmetric membranes cannot easily be measured directly. An effective thickness of about 800 Å for the skin of membrane #1 can be estimated by dividing the N₂ permeability coefficient of the isotropic PSF film by the pressure-normalized N₂ flux of the membrane.

The variation of the pressure-normalized N₂ and O₂ fluxes (P/L) with temperature was measured for membrane samples #1 and #4. The absolute values of the permeability coefficients for asymmetric membranes are not measurable because the skin layer thickness cannot be measured explicitly. The

data follow the typical linear Arrhenius behavior as shown in Figure 2.

Asymmetric PSF membrane activation energies of permeation for O₂ and N₂ are noticeably higher compared to those obtained for the isotropic PSF film, as shown in Table II. Similar results were recently reported for integrally skinned asymmetric PEC membranes that showed higher selectivities than did an isotropic PEC film.¹⁵ Results for three materials, comparing isotropic films with asymmetric membranes, are included in Table II to support the proposed differences between asymmetric membranes and isotropic films.

Table II shows that asymmetric membranes made from a variety of materials show increased O₂/N₂ selectivities and activation energies of permeation

Table I Pure Gas Selectivities and Mixed Gas Separation Factor of an Isotropic PSF Film (Method I), Integrally Skinned Asymmetric PSF Membranes (Method II), and Multicomponent PSF/Silicone Membranes (Method II); Conditions: 24°C, 3.5 atm Δp

Sample	Pure Gas Selectivity (α_{O_2/N_2})	Mixed Gas Separation Factor (β_{O_2/N_2})
Film (100 μm)	6.4	—
Integral asymmetric membranes:		
# 1	6.9	6.9
# 2	6.7	6.6
# 3	6.8	6.8
Multicomponent membranes:		
# 4	7.0	6.8
# 5	6.9	6.8
# 6	6.8	6.7

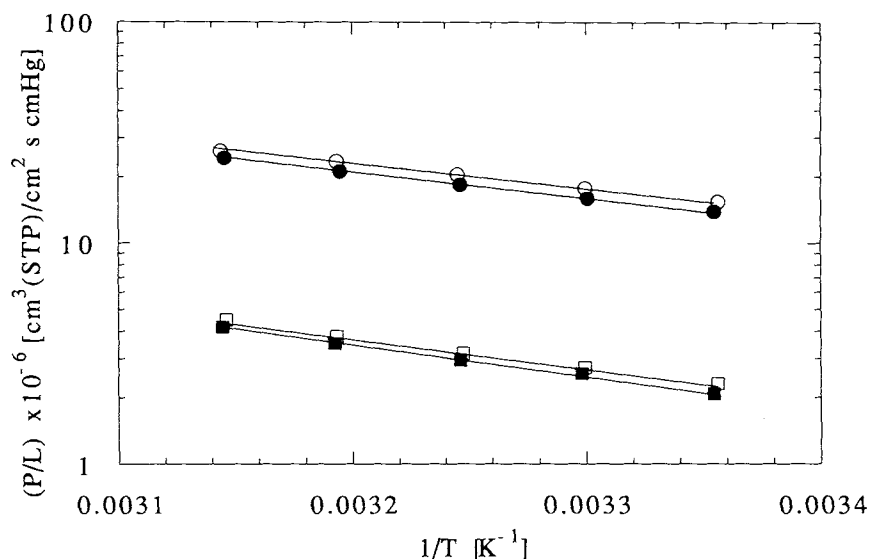


Figure 2 Arrhenius plots of (P/L) vs. $1/T$ for an integrally skinned asymmetric PSF membrane [#1, Method II: (■) N_2 ; (●) O_2] and a multicomponent silicone rubber-coated PSF membrane [#4, Method II: (□) N_2 ; (○) O_2] at 3.5 atm Δp .

when compared with isotropic films made from the same materials.

The temperature-dependent permselectivities in both isotropic PSF films and asymmetric PSF membrane samples were calculated by simply taking the ratio of the Arrhenius expressions for the permeability coefficients, P , or the pressure-normalized fluxes, P/L , respectively. Figure 3 shows that the ideal O_2/N_2 permselectivities are uniformly higher in the asymmetric membranes. Naturally, this im-

plies that the asymmetric membranes were defect-free or else their permselectivities would be lower than those of the corresponding isotropic film, due to flow through pores in the skin layer. Higher permselectivities for the asymmetric membranes could be due to a higher polymer packing density, i.e., lower free volume, in the thin skin layer as a result of the membrane formation procedure. Differences in free volume, cohesive energy density, and possible ordering could be responsible for the ob-

Table II Properties of Isotropic Films and Asymmetric Phase Inversion Membranes Made from Three Polymers

Material	Method	Temp (°C)	Pressure Difference (atm)	α_{O_2/N_2}	Thickness ^a (Å)	E_p (J/mol)	
						N_2	O_2
PSF							
Film	I	24	3.5	6.4	1,000,000	23,000	15,000
Membrane # 1	II	24	3.5	6.9	800	27,600	21,800
Membrane # 4	II	24	3.5	7.0	700	26,400	20,500
PC							
Film ^b	I	35	2	4.8	> 250,000	—	—
Membrane	I	35	4.4	5.4	600	—	—
PEC ^c							
Film	I	35	4.4	4.8	> 250,000	24,300	17,600
Membrane	I	35	4.4	5.7	600	27,200	21,800

^a The effective thickness of the skin layer of the membranes is estimated from permeability data for films of known thickness.

^b Ref. 19.

^c Ref. 15.

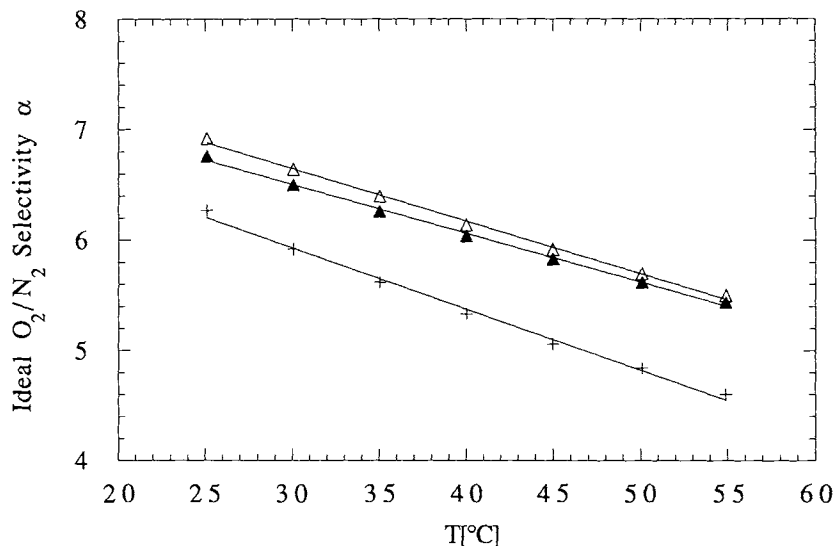


Figure 3 Calculated ideal selectivities α_{O_2/N_2} of a PSF film [(+) Method I], an asymmetric PSF membrane [(▲) #1, Method II], and a multicomponent PSF/silicone membrane [(△) #4, Method II] at 3.5 atm Δp .

served differences between isotropic films and asymmetric membranes.¹⁵

Aging is not the cause of the increased activation energies, since the pressure-normalized fluxes obtained before and after the temperature variation runs for each gas tested were found to agree within $\pm 5\%$.

The differences in the activation energies of permeation and in the selectivity between thick dense films and asymmetric membranes made according to the dry/wet phase-inversion process have been discussed previously for PEC.¹⁵ Increased segmental orientation and reduced average fractional free volume in the thin densified skin region of the asymmetric membranes was suggested to be responsible for the observed differences.

Asymmetric Membranes: CO₂ Permeation

Further indirect evidence for morphological differences between asymmetric membranes and isotropic films is given by considering the pressure dependence of CO₂ permeation. The CO₂ permeability coefficient of a solution-cast PSF film as a function of the upstream pressure is presented in Figure 4.²⁰

As usually observed for amorphous glassy polymers, the CO₂ permeability coefficient of the PSF film decreases with increasing CO₂ upstream pressure.²⁰ It was previously suggested that the sorption of gases in glassy polymers occurs in two different populations, i.e., (i) Langmuir sites and (ii) Henry's

law sites.²¹ The Langmuir sites are believed to represent packing defects in the polymer matrix as a result of the nonequilibrium nature of the glassy membrane material. The high CO₂ permeability coefficient at low upstream pressure has been ascribed to the presence of the Langmuir-type sorption sites.²¹

An asymmetric multicomponent PSF membrane was used to determine the pressure dependence of the CO₂ pressure normalized flux for comparison with the results for isotropic films. The test procedure is outlined in Figure 5.

Pressure-dependent pressure-normalized fluxes were first determined for N₂, O₂, and CO₂ in this sequence, always proceeding from lower to higher pressures for each gas. The normalized N₂ flux was then observed as a function of time after the CO₂ test. Finally, normalized N₂ and O₂ fluxes were again determined for comparison with the values before CO₂ permeation, to assure that the asymmetric membrane was not damaged. Method I was used with a liquid nitrogen trap between the vacuum pump and the permeation system to prevent any backdiffusion of pump oil. The ideal O₂/N₂ selectivity of the asymmetric membrane before and after the entire test sequence was 6.2 at 35°C and 10 atm, indicating that no damage was suffered by exposure to the CO₂ during testing. Figure 6 shows the pressure-normalized fluxes for all gases except CO₂. As expected, there is no significant variation with pressure.

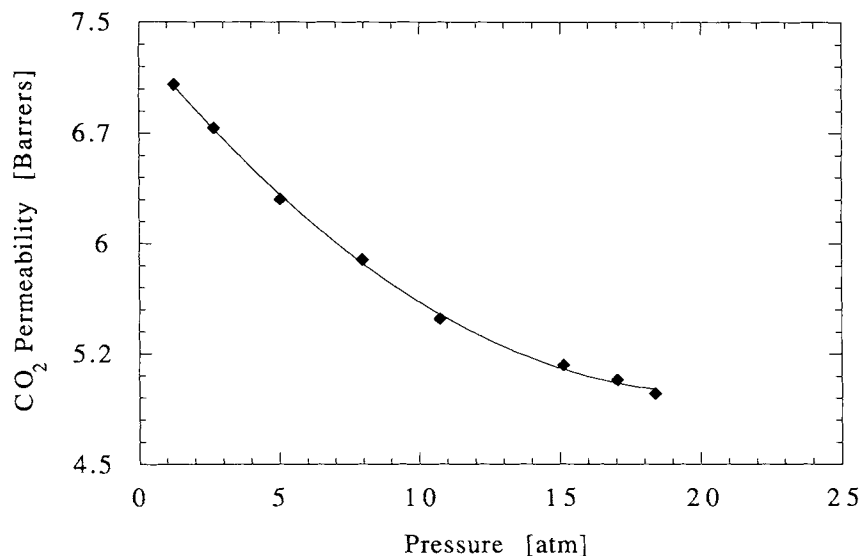


Figure 4 Permeability isotherm for CO₂ in an isotropic PSF film at 35°C (Method I).²⁰

The pressure dependence of the CO₂ flux of this asymmetric multicomponent PSF membrane is shown in Figure 7. The data for the isotropic film (Fig. 4) and the membrane (Fig. 7) were taken on identical test setups as described under Method I in the Experimental section. The data for the asymmetric membrane were taken starting at the lowest CO₂ pressure and then increasing the pressure stepwise without depressurization. Data points were taken after 10 and 20 min of permeation at the given pressure and, in addition, after a longer time at the maximum pressure. It is striking that the pressure-normalized CO₂ flux increases with increasing upstream pressure.

It was the objective to show differences between isotropic thick films and the asymmetric membranes; the time dependence was therefore not studied in depth and does not alter the general trend of the curve. A saturation of the flux increase at the maximum CO₂ pressure was not apparent from our data.

The CO₂ was exchanged without depressurization for N₂ after the data at the maximum CO₂ pressure was taken. The N₂ pressure was lowered to 4.5 atm

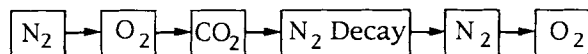


Figure 5 Gas permeation isotherm test sequence for asymmetric PSF membranes. The N₂ pressure-normalized flux decay is measured at constant pressure as a function of time.

and the normalized N₂ flux was observed. Initially, the normalized N₂ flux was increased about 10% when compared to the value before the CO₂ experiment. A protracted flux decay was observed over a period of about 30–45 h to the value before the CO₂ experiment.

The ideal O₂/N₂ selectivity was determined after the N₂ flux had decayed approximately to the level before the CO₂ tests. The selectivity of 6.2 was unchanged, did not depend on pressure in the range tested here, and remained above the value of 5.6 for a thick isotropic film (35°C, see Fig. 3).

The normalized N₂ and O₂ fluxes were both slightly higher than before the CO₂ experiment (see Fig. 6). Thus, both the CO₂ permeability isotherm and the subsequent N₂ flux decay are signs of morphological change in the skin layer of the asymmetric membrane. Opening of defects in the skin of the asymmetric membrane or substructure compaction can be excluded, due to the maintenance of the gas selectivity of the membrane.

Figure 8 shows the increase of the pressure-normalized CO₂ flux with increasing pressure for an asymmetric PC membrane. The procedure as shown in Figure 5 was used. This asymmetric membrane had an initial ideal O₂/N₂ selectivity of 5.4, higher than an isotropic cast film (4.8, see Table II) and is therefore considered to be defect-free. Isotropic PC films show a strong decrease of CO₂ flux with pressure.^{16,19} These opposite results for asymmetric PC membranes when compared to isotropic PC films are qualitatively identical to the comparison of

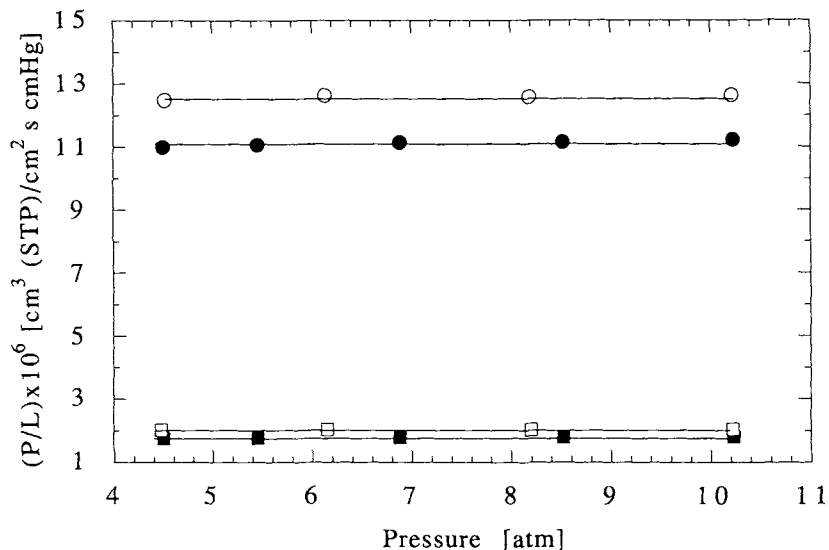


Figure 6 Pressure-normalized flux isotherms for N₂ and O₂ of an integrally skinned multicomponent asymmetric PSF membrane at 35°C (Method I). Before CO₂ permeation/N₂ flux decay: (■) N₂; (●) O₂. After CO₂ permeation/N₂ flux decay: (□) N₂; (○) O₂.

asymmetric PSF membranes and isotropic PSF films shown earlier.

Although there is little time dependence over the observed time span at lower pressures in Figure 8, the time dependence becomes obvious at the highest CO₂ pressure. This seems similar to conditioning behavior reported elsewhere for isotropic PC films, when the polymer is exposed to CO₂ pressures of

about 20 atm or more.^{22,23} Conditioning of asymmetric PC membranes, however, sets in below 8 atm, as shown in Figure 8. Conditioning of PC with CO₂ seems to occur at much lower pressures in asymmetric membranes than in isotropic films. This appears consistent with the existence of a more efficiently packed environment with lower fractional free volume in the skin of the asymmetric mem-

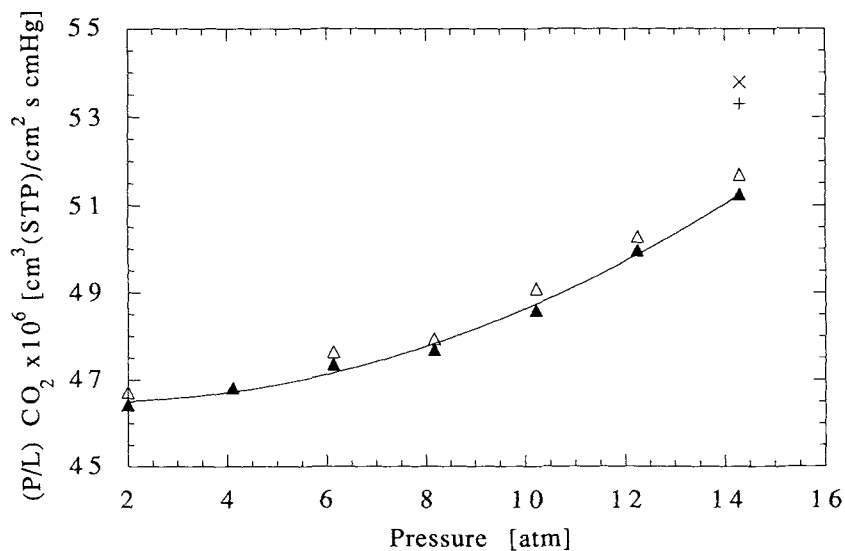


Figure 7 Pressure-normalized CO₂ flux isotherm in an integrally skinned multicomponent asymmetric PSF membrane at 35°C (Method I): (▲) 10 min; (△) 20 min; (+) 43 min; (×) 53 min.

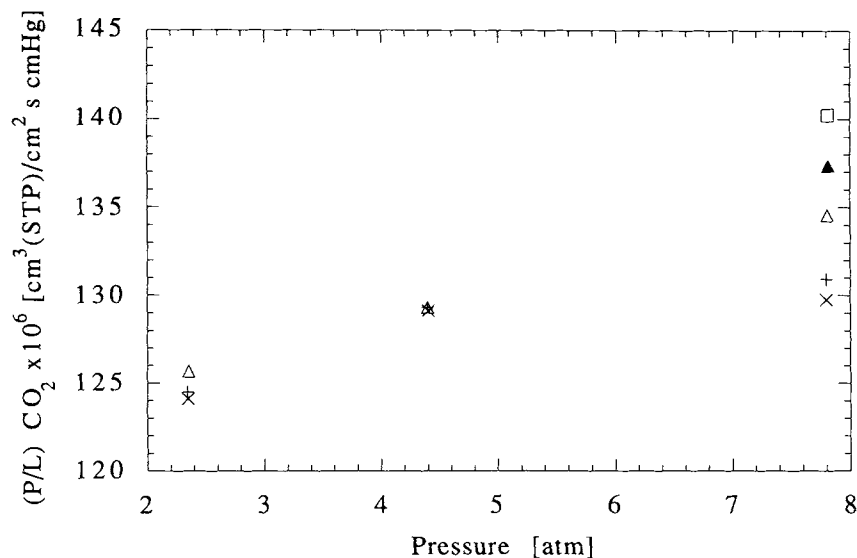


Figure 8 Pressure-normalized CO₂ flux isotherm in an integrally skinned asymmetric PC membrane at 35°C (Method I): (×) 5 min; (+) 10 min; (Δ) 20 min; (▲) 40 min; (□) 68 min.

brane. Lower levels of absorption and swelling of the skin with CO₂ seem to already increase the normalized CO₂ flux of the asymmetric membrane, when compared with thick isotropic films.

Time-dependent flux decay at 4.4 atm N₂ after exchange of CO₂ for N₂ without depressurization occurred over a period of 30–45 h. The initial N₂ flux after the CO₂ experiment was increased over the original value of the asymmetric membrane, but decayed to that original value.

The ideal O₂/N₂ selectivity was 5.4 at 35°C and 4.4 atm before and 5.3 at the same conditions after the CO₂ permeation and the N₂ flux decay. Again, as with the PSF sample, this is still higher than the value of 4.8 for an isotropic film (35°C, see Table II).

Conditioning effects in isotropic films and asymmetric hollow fibers are thought to be semipermanent if a gas exchange without depressurization is performed after exposure of PC to CO₂ of about 20 atm or more.^{22,23} In the asymmetric PC membranes used here, conditioning by CO₂ sets in at much lower pressures, when compared to isotropic PC films, and a loss of the conditioning effect is directly observable after the gas exchange of CO₂ with N₂.

Figure 9 shows the pressure-dependent normalized CO₂ flux for an asymmetric PEC membrane. Again, a striking pressure dependence opposite to what is found for isotropic films¹⁵ is obvious.

The inverted pressure dependence of the nor-

malized CO₂ flux for the asymmetric membranes compared to the isotropic films implies that the number and/or sizes of hypothetical Langmuir sites may be smaller in an asymmetric membrane compared to those present in an isotropic film. The temperature and pressure dependence of the gas transport properties of asymmetric membranes made by dry/wet phase inversion, compared to the properties of isotropic films made from the same material, support the earlier suggestions¹⁵ and allow further tentative conclusions regarding the differences in the behavior of these isotropic films and asymmetric membranes:

- (i) The fractional free volume in the ultrathin skin layer of asymmetric membranes may be lower than that of thick isotropic films of the same material.
- (ii) The free volume distribution may also be different in the skin layer of the asymmetric membranes.
- (iii) Plasticization and conditioning processes may proceed in a different manner in isotropic films and the thin skin of asymmetric membranes.

Orientation of the polymer molecules in the skin could be an additional factor. A qualitative model of the crucial stage of nascent skin layer formation

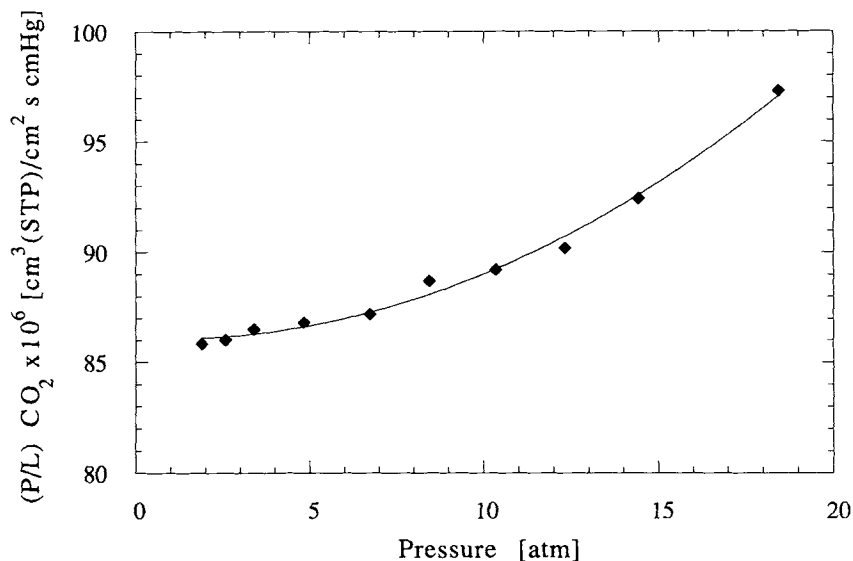


Figure 9 CO₂ permeation isotherm for an asymmetric PEC membrane at 35°C (Method I).

of dry/wet asymmetric membranes was suggested by Pinnau and Koros. Local biaxial orientation of polymer molecules on a scale probed by a gas molecule is thought to occur due to strong capillary forces acting during skin formation.^{2,24}

A combination of the factors mentioned above could explain the increased selectivities and activation energies of permeation, together with the unusual shape and time-dependent behavior of CO₂ permeation isotherms in asymmetric membranes.

SUMMARY AND CONCLUSIONS

The gas transport properties of essentially defect-free asymmetric PSF, PC, and PEC membranes with ultrathin skin layers formed by a dry/wet phase inversion process have been compared to isotropic films from the same polymers. The asymmetric membrane samples exhibited higher permselectivities compared to those determined for the isotropic films. The activation energies of permeation for N₂ and O₂ in PSF were higher in the asymmetric membranes compared to those of the isotropic film. These results suggest that the membrane skin morphology may differ from that of an isotropic film. It is hypothesized that the increase in activation energy implies a higher cohesive energy density, presumably due to a lower free volume in the skin layers of the asymmetric membranes.

The pressure dependence of CO₂ permeation in asymmetric PSF, PC, and PEC membranes was en-

tirely different from that of isotropic films. The *inverted* pressure dependence of the CO₂ flux of the asymmetric membranes compared to isotropic films supports that the skin layer morphology may contain less and/or a different distribution of free volume than that of isotropic films. Time dependence and shape of the CO₂ permeation isotherm and subsequent probing with N₂ shows different plasticization and conditioning behavior for the asymmetric membranes.

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