Gas transport through homogeneous and asymmetric polyestercarbonate membranes

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Permeabilities, solubilities and diffusivities of N_2, O_2, CO_2 and H_2 are reported for a polyestercarbonate at 35°C and 4.4 atm. Constant activation energies of permeation were determined for dense films and defect-free asymmetric polyestercarbonate membranes over a temperature range of 25–55°C. Activation energies of permeation were 10 and 20% higher for N_2 and O_2, respectively, in the asymmetric membrane samples as compared to the dense films. Permselectivities for the gas pairs O_2/N_2, H_2/N_2 and CO_2/N_2 were found to be higher in the asymmetric membranes compared to those of the dense films. The detailed cause of the higher permselectivities and activation energies in the asymmetric membranes is currently not known. Possible orientation-induced increases in segmental packing density in the asymmetric membrane skin is discussed as a potential explanation for the differences between the asymmetric and dense films.

(Keywords: polyestercarbonate; gas permeability; homogeneous film; asymmetric membrane; activation energy; membrane structure)

INTRODUCTION

Fundamental gas transport properties of polymeric materials are generally studied on homogeneous films of known thickness. On the other hand, asymmetric membranes are most commonly utilized for industrial membrane gas separation. An asymmetric membrane consists of a thin, selective skin layer supported by a microporous substructure. The transport properties of asymmetric membranes are determined primarily by the properties of the skin layer. Optimum asymmetric gas separation membranes should provide a defect-free skin layer to assure that permeation is exclusively controlled by a solution/diffusion mechanism to achieve maximum permselectivity[1]. Furthermore, the skin layer should be as thin as possible to maximize the membrane productivity. However, defect-free skin layers are extremely difficult to obtain for asymmetric membranes made by the conventional wet phase inversion process[2,3]. Pores or defects on the order of 5–10 Å over an area fraction of only a few parts per million reduce the membrane permselectivity drastically[4].

It has long been known that polymeric glasses are non-equilibrium materials whose film properties can be significantly dependent on history and preparation protocols[5–7]. Surprisingly, very few studies have been carried out to explore the relationship between the permeation properties of homogeneous films and those of asymmetric membranes. Haraya *et al.* investigated the permeation of various gases through asymmetric cellulose acetate membranes[8]. In their study the selectivities of the asymmetric membranes were lower compared to those of homogeneous cellulose acetate films. The differences in selectivity were attributed to pore flow through skin defects in the asymmetric membranes. Furthermore, it was shown that the temperature dependence of gas transport through the defective asymmetric membranes showed significant deviations from the typical linear Arrhenius behaviour.

Sada *et al.*[9] studied the permeation of CO_2 through homogeneous and asymmetric polysulphone membranes. This investigation suggested that the pressure dependence of the mean permeability coefficient in an asymmetric membrane is essentially equal to that in a homogeneous film. It was concluded that the sorption and diffusion behaviour for the thin skin layer in the asymmetric membrane can be approximately simulated by the behaviour of a homogeneous dense membrane.

On the other hand, Fritzsche *et al.*[10] propose that the molecular skin structure of asymmetric polysulphone hollow fibre membranes exhibit a higher 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 membrane samples compared to samples of the bulk membrane material. Fritzsche *et al.* suggested that the permeabilities of the skin layer of asymmetric polysulphone membranes can be intrinsically higher than those of a dense homogeneous film, due to the higher free volume in the membrane.

A dry/wet phase inversion process to prepare simultaneously ultrathin and essentially defect-free asymmetric membranes from glassy polymers was recently developed by Pinnau and Koros[11]. It was demonstrated that

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defect-free ultrathin asymmetric membranes with effective skin layer thicknesses of 200–1000 Å could be formed. Optimized membranes formed by this process have shown selectivities equal to or in some cases higher than those determined for dense homogeneous films. These results prompted the investigation of possible differences in the gas permeation behaviour of asymmetric membranes made using this process and dense homogeneous films made from polyestercarbonate (PEC).

EXPERIMENTAL

Materials

Commercially available PEC, APEC DP9-9308, was used to explore the relationships between film and asymmetric membrane properties. The PEC is a copolymer of bisphenol-A polycarbonate (PC) and bisphenol-A iso/terephthalic acid ester, as shown in *Figure 1*. The copolymer contains 50 wt% ester per repeat unit. The material is an amorphous polymer with a T_g of 170°C measured by differential scanning calorimetry (d.s.c.) at a heating rate of 20°C min^{-1}. All solvents used for this study were of reagent grade and used without further purification.

Dense film preparation

A 5 wt% solution of PEC in methylene chloride was poured into a stainless steel ring supported by a glass plate. Solvent was evaporated from the film over a period of 24 h at 25°C. Then the clear film was removed from the glass plate and dried in a vacuum oven for 3 days by slowly raising the temperature from 25 to 180°C. Finally the temperature was held at 180°C for 12 h. A d.s.c. run on a dry film sample showed no evidence of residual solvent left in the dried film.

Asymmetric membrane preparation

Asymmetric PEC membranes were prepared by a modified dry/wet phase inversion process[11]. Casting solutions consisted of 14 wt% PEC, 53 wt% methylene chloride, 20 wt% 1,1,2-trichloroethane and 13 wt% 2-methyl-2-butanol. The membranes were cast at 25°C on glass plates with a knife gap of 250 μm. Immediately after casting the membranes, a water vapour saturated air stream was blown across the membrane surface for a period of 10 s. The initially clear, nascent membrane became turbid instantaneously at the onset of the blowing process. After an additional free convection period of 10 s, the membranes were quenched in methanol and subsequently washed for a period of 6 h. The membranes were air-dried for 24 h and finally post-dried in a vacuum oven at 100°C for 4 h. D.s.c. runs on dry samples showed no evidence of residual solvent left in the membranes.

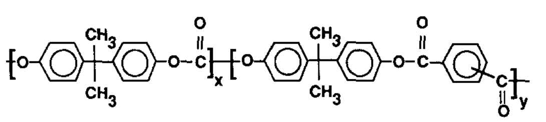

Figure 1 Structure of PEC

Gas permeation measurements

The permeabilities and gas solubilities of H_2, N_2, O_2 and CO_2 were measured in the solution cast PEC film. The permeation data were taken using the standard permeation techniques employed in our laboratory[12]. The equipment allows the measurement of gas permeability coefficients from the rate of accumulation of penetrant in an evacuated downstream volume using a sensitive Baratron® pressure transducer. The downstream pressure at 10 mmHg or less was always negligible relative to the upstream pressure.

The sorption measurements were made with a pressure decay sorption cell as described previously by other authors from our laboratories[13,14].

RESULTS AND DISCUSSION

Dense films

The permeabilities, solubilities and diffusivities measured for PEC are compared to standard PC in *Tables 1–3*. The transport properties of solution cast PEC were found to be very similar to those of conventional solution cast PC[15]. The PEC has ~15% higher gas permeabilities and roughly the same permselectivities relative to PC. The higher permeabilities in the PEC occur due to the slightly higher diffusion coefficients for gases in PEC relative to PC. Solubilities of gases are virtually the same in the two materials.

Permeability coefficients for N_2, O_2, H_2 and CO_2 of PEC films were measured over a temperature range of 25–55°C, as shown in *Figure 2*. The data follow the typical linear Arrhenius behaviour. Activation energies of permeation for dense PEC films were calculated from the slope of the Arrhenius plots, as shown in *Table 4*. Muruganandam[16] determined activation energies of permeation of 3940 and 5160 cal mol^{-1} for O_2 and N_2, respectively, in dense PC films. These results are close to the values obtained for the PEC in this study.

Asymmetric membranes

A similar set of permeation experiments was carried out on asymmetric PEC membranes. In these experiments the variation of the pressure-normalized flux (permeability divided by effective skin thickness), P/L, with temperature was measured for the various gases. The absolute values of permeabilities for asymmetric membranes are not measurable because the skin thickness cannot be measured explicitly. The data follow the typical linear Arrhenius behaviour as shown in *Figure 3*.

Table 1 Permeabilities (P), solubilities (S) and diffusivities (D) of CO_2 and N_2 in PEC and PC at 35°C and 4.4 atm

Polymer	P_{CO_2} (barrer)[a]	$\frac{P_{CO_2}}{P_{N_2}}$	S_{CO_2} (cm^3 (STP) cm^{-3} atm^{-1})	$\frac{S_{CO_2}}{S_{N_2}}$	D_{CO_2} (10^{-8} cm^2 s^{-1})	$\frac{D_{CO_2}}{D_{N_2}}$
APEC® 9308	9.1	23	2.2	13	3.1	1.8
PC	7.9	24	2.1	15	2.9	1.6

[a] 1 barrer = 10^{-10} cm^3 (STP) cm (cm^2 s cmHg)$^{-1}$

Table 2 Permeabilities, solubilities and diffusivities of H_2 and N_2 in PEC and PC at 35°C and 4.4 atm

Polymer	P_{H_2} (barrer)	$\frac{P_{H_2}}{P_{N_2}}$	S_{H_2} (cm^3 (STP) cm^{-3} atm^{-1})	$\frac{S_{H_2}}{S_{N_2}}$	D_{H_2} (10^{-8} cm^2 s^{-1})	$\frac{D_{H_2}}{D_{N_2}}$
APEC® 9308	15	38	0.081	0.48	140	79
PC	13	40	0.075	0.54	135	74

Table 3 Permeabilities, solubilities and diffusivities of O_2 and N_2 in PEC and PC at 35°C and 4.4 atm

Polymer	P_{O_2} (barrer)	$\frac{P_{O_2}}{P_{N_2}}$	S_{O_2} (cm^3 (STP) cm^{-3} atm^{-1})	$\frac{S_{O_2}}{S_{N_2}}$	D_{O_2} (10^{-8} cm^2 s^{-1})	$\frac{D_{O_2}}{D_{N_2}}$
APEC® 9308	1.85	4.8	0.23	1.3	6.1	3.7
PC	1.60	4.8	0.21	1.5	5.8	3.2

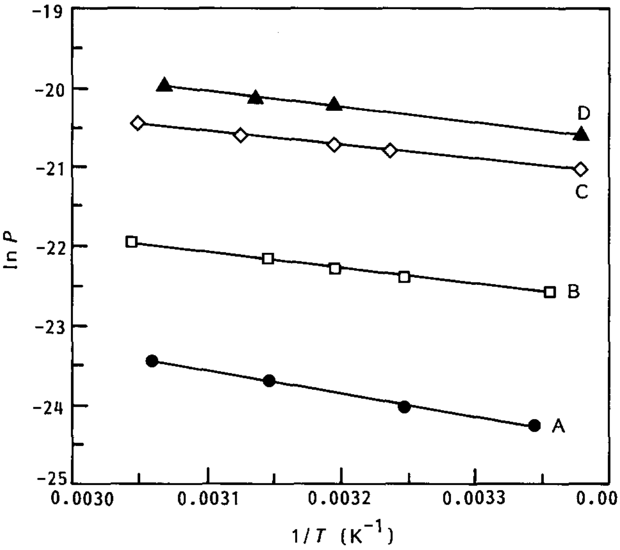

Figure 2 Arrhenius plot of ln *P versus* 1/*T* for (A) N_2, (B) O_2, (C) H_2 and (D) CO_2 in a homogeneous PEC film at 4.4 atm upstream pressure

Table 4 Activation energies (cal mol^{-1}) of permeation for homogeneous PEC films and asymmetric PEC membranes at 4.4 atm

	N_2	O_2	H_2	CO_2
PEC film	5782	4187	3861	3552
Membrane 1	6506	5191	3931	–
Membrane 2	6548	5177	–	3559

Asymmetric PEC membrane activation energies of permeation for O_2 and N_2 are noticeably different from those obtained for the dense PEC films as shown in *Table 4*. The membranes show 10 and 20% higher activation energies for N_2 and O_2, respectively. For CO_2 and H_2 the activation energies are virtually the same for the film and the membranes; however, the order of activation energies for the various gases follow $N_2 > O_2 > H_2 > CO_2$ in both the films and the membranes. This is the same order demonstrated for other glassy polymers[16,17].

The temperature-dependent permselectivities in both dense and asymmetric membrane samples were calculated by simply taking the ratio of the Arrhenius expressions for the permeabilities or *P*/*L*, respectively. *Figures 4–6* show that the permselectivities are uniformly higher in the asymmetric membranes for the gas pairs O_2/N_2, H_2/N_2 and CO_2/N_2. Naturally this implies that the asymmetric membranes are defect-free or their permselectivities would be lower than those of the corresponding dense films, due to flow through pores in the skin layer. Higher permselectivities for the asymmetric membranes could be due to a higher chain packing density, i.e. lower free volume, in the thin skin layers as a result of the membrane formation procedure.

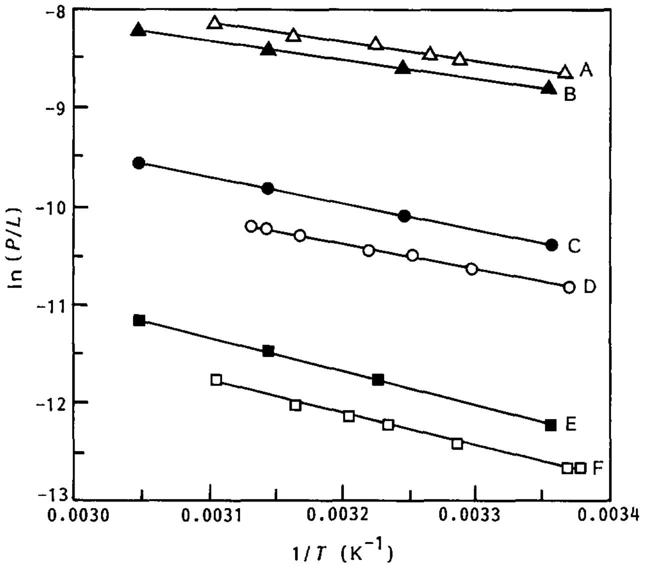

Figure 3 Arrhenius plot of ln (*P*/*L*) *versus* 1/*T* for N_2, O_2, H_2 and CO_2 in asymmetric PEC membranes at 4.4 atm upstream pressure: (A) membrane 1 (H_2); (B) membrane 2 (CO_2); (C) membrane 2 (O_2); (D) membrane 1 (O_2); (E) membrane 2 (N_2); (F) membrane 1 (N_2)

Asymmetric membranes are subject to physical ageing in which the flux tends to decline as a function of time. This phenomenon has been attributed to a slow consolidation or densification of the ultrathin selective skin layer of the membrane[1]. Careful experimental protocols guaranteed that membrane ageing could not have caused the observations noted here. Permeation studies on asymmetric membranes were carried out while raising the temperature in increments from 25 to 55°C. Therefore, ageing phenomena would lead to a decrease of pressure-

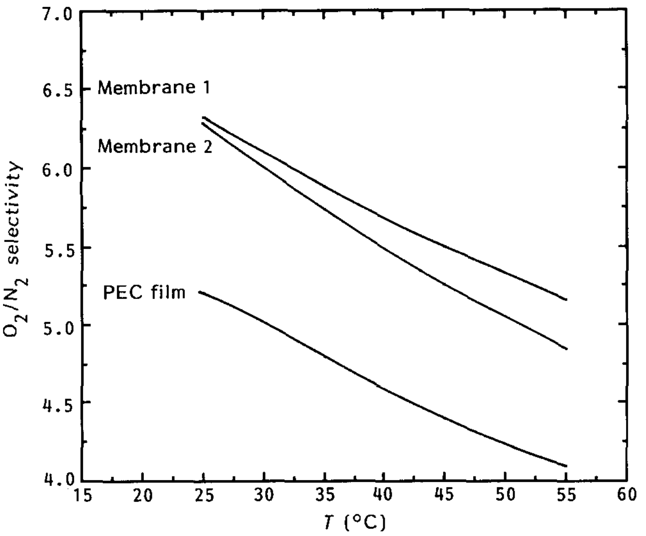

Figure 4 Oxygen/nitrogen selectivities of a PEC film and asymmetric PEC membranes 1 and 2

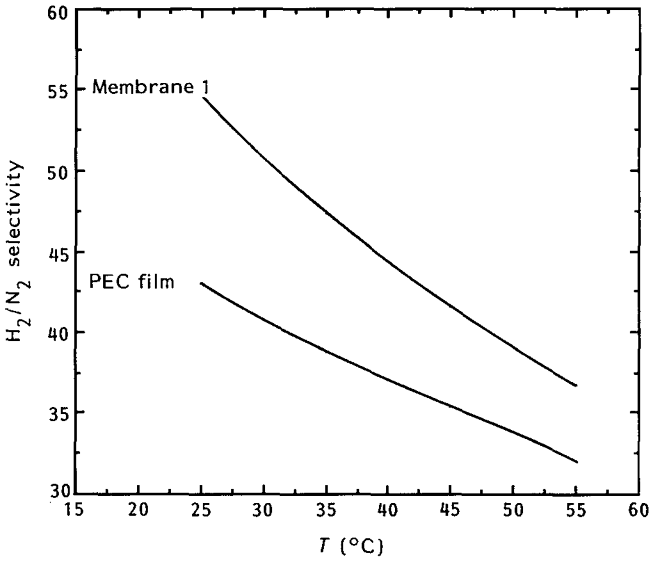

Figure 5 Hydrogen/nitrogen selectivities of a PEC film and asymmetric PEC membrane 1

normalized gas fluxes in the higher temperature experiments as compared to unaged samples. In this case, ageing phenomena would tend to cause the activation energies to be lower, rather than higher compared to those of the dense film in contrast to the observed behaviour. Furthermore, the initial P/L values obtained at 25°C were found to agree within $\pm 5\%$ after the temperature runs for each gas tested.

Effective skin thicknesses of defect-free asymmetric membranes can be calculated by dividing the permeability coefficient of gas i, as determined on dense films, by the P/L of gas i in the asymmetric membrane. The effective skin layer thickness of membrane sample 1 was calculated based on N_2, O_2, and H_2 permeability coefficients as shown in *Figure 7*. Clearly, the effective skin layer thicknesses based on N_2 and O_2 permeabilities depend on temperature due to the variation in activation energies of permeation between the asymmetric membranes and the dense film. These results suggest that the microscopic skin structure of defect-free asymmetric PEC membranes can differ somewhat from that of dense PEC films.

Although the reasons for the higher activation energies and higher permselectivities in the asymmetric membranes are not well understood a few qualitative arguments can be made to explain the results. El-Hibri[18] considered the effects of orientation on the permeability and activation energies of gases in glassy polymers. Gas permselectivity tended to increase while permeability tended to decrease with degree of orientation. Furthermore, the activation energy of permeation for argon in poly(vinyl chloride) (PVC) was shown to increase upon orientation. The changes in argon activation energy of permeation ($\Delta E_p = \Delta E_d + \Delta H_s$) were due to an increase in the enthalpy of sorption (ΔH_s) while the activation energy for diffusion (ΔE_d) was essentially unchanged. Clearly, in the present asymmetric membrane case, enthalpies of sorption and diffusion cannot be measured in the ultrathin membrane skin for comparison to the dense film case to test for

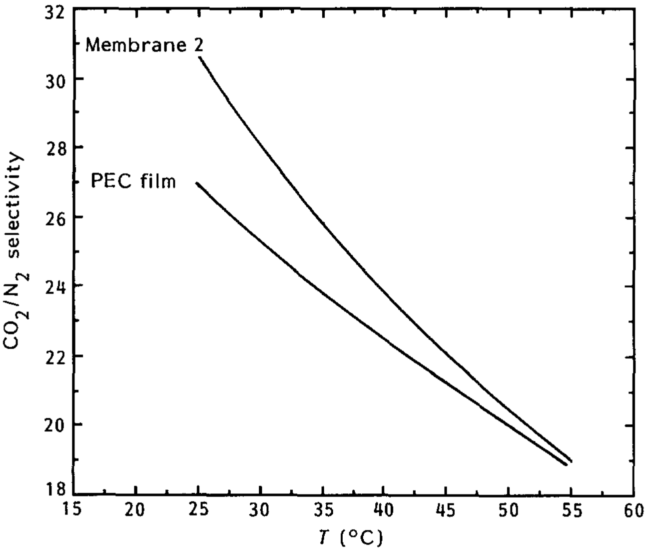

Figure 6 Carbon dioxide/nitrogen selectivities of a PEC film and asymmetric PEC membrane 2

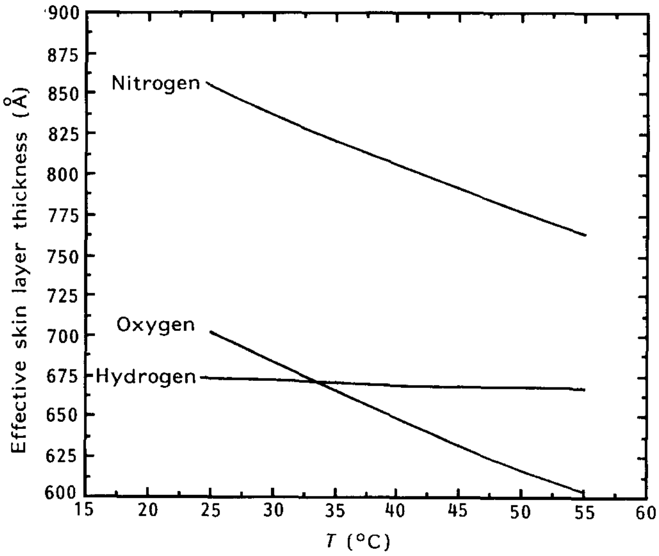

Figure 7 Effective skin thickness of asymmetric PEC membrane 1 based on N_2, O_2 and H_2 PEC permeability coefficients

differences in these parameters. Therefore unlike the PVC example cited above, the alternative possibility involving differences in the activation energy of diffusion between the dense film and asymmetric membrane skin must also be considered in the present case. In fact, as noted below, this appears to be a likely cause of the observed differences between the dense and asymmetric samples.

The simple expression suggested by Meares[19] to relate the cohesive energy density, *CED*, to ΔE_d and the volume of one mole of cylindrical activated cavities is useful in pursuing this matter. The cavities are assumed to have a length of λ and a diameter, d, equal to that of the diffusing molecule:

$$\Delta E_d = CED d^2 \pi \lambda / 4 \qquad (1)$$

Based on this expression, the higher activation energy of permeation for the asymmetric membranes could reflect a higher value of ΔE_d due to either a higher cohesive energy density or a higher penetrant jump length. For the physically similar O_2 and N_2 gas pair, higher permeation activation energies and higher permselectivities are observed in the asymmetric membranes. Since the permselectivity of the asymmetric membrane is higher than that for the dense film, it seems unlikely that a larger jump length is occurring in the more selective medium. Thus, any increase in ΔE_d would presumably be due to an increase in *CED*.

In addition to ΔE_d the cohesive energy density can influence ΔH_s, and thereby have an additional effect on ΔE_p. To accommodate a penetrant in its 'sorbed cage' the polymer matrix must be dilated by an amount equivalent to the sorbed cage volume of the penetrant. This process entails overcoming the *CED* of the polymer. The contribution to the sorption enthalpy by the endothermic 'cavity term', equal to the product of the *CED* times the sorbed cage volume of the penetrant, would also be increased in the asymmetric samples having higher *CED*. Such an effect is also consistent with these asymmetric membrane samples having higher observed permeation activation energies. Therefore, we favour an explanation based predominantly on an increase in *CED* in the asymmetric membrane skin.

Intuitively, a higher cohesive energy density is consistent with more efficient chain packing in the selective skin, possibly resulting from chain orientation present in the rapidly solidified asymmetric membrane structures. Moreover, a more tightly packed matrix resulting from the higher cohesive energy density in the membranes might be expected to have a narrower distribution of transient gap sizes available for diffusion, thereby leading to improved size selection between gas molecules in the membranes.

Direct measurement of the orientation in the thin (<0.1 μm) selective skin layer in the asymmetric membrane is not feasible, so the hypotheses related to reduced free volume due to orientation cannot be tested directly. If the above explanation is correct for O_2 and N_2, one might expect a similar tendency for the activation energy of permeation for CO_2 and H_2. However, *Table 4* shows that activation energies of permeation for CO_2 and H_2 are similar for the asymmetric membranes and the dense films. We suggest that this discrepancy for both gases might be due to their substantially different condensibility and/or size compared to O_2 and N_2, thereby complicating exothermic contributions to the sorption enthalpy term in ΔE_p.

Recently, Fritzsche *et al.*[10] reported that the skin layers of polysulphone membranes prepared by a wet phase inversion process show higher free volume relative to dense polysulphone films. The membrane samples studied by Fritzsche *et al.* were found to give higher first heat T_g values by d.s.c. characterization. On the contrary, the first T_gs measured for the PEC membranes and dense films used in this study were found to agree within ±1°C. The differences between the dry/wet phase inversion process used here and the wet phase inversion process of Fritzsche *et al.* may account for the different d.s.c. findings in both studies.

CONCLUSIONS

The present study showed that PEC displays similar gas transport properties compared to those of PC. Defect-free asymmetric PEC membranes can be prepared by a dry/wet phase inversion process. The membrane samples employed in this study exhibited slightly higher permselectivities compared to those determined for the dense film. Higher permselectivities for asymmetric PEC membranes compared to those of dense PEC films could be a result of some orientation of the chains in the skin layer due to the very different formation methods. The activation energies of permeation for N_2 and O_2 were 10 and 20% higher in the asymmetric membranes, respectively. The results suggest that the membrane skin morphology may differ somewhat from that of the bulk material. 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. Additional investigations between film and asymmetric membrane properties based on temperature–permeation relationships are warranted in order to improve the fundamental understanding of asymmetric membrane skin structure and formation methods.

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