Gas Permeation in Polyethersulfone

INTRODUCTION

The permeability of polymers to gases is an important consideration for numerous applications, including barrier materials and membranes for gas separations. This brief report presents experimental gas permeability data for the relatively new high-performance engineering thermoplastic, polyethersulfone, and compares these data with two related engineering thermoplastics, polysulfone and polycarbonate, to better understand the effect of molecular structure on permeation behavior. The comparative data for polysulfone illustrate the effects of melt versus solution formation of film for gas sorption and permeation measurements.

EXPERIMENTAL

Table I lists the three polymers to be compared, their molecular structures, and some physical characteristics. The polyethersulfone (PES) was the commercial product VICTREX 4100 P obtained from Imperial Chemical Industries. Films were prepared by compression molding at 300°C.

The polysulfone (PSF) was the commercial product P-1700 supplied by the Union Carbide Corporation. Unless otherwise specified, the permeabilities for PSF were obtained from a previous study based on melt-extruded films.[1] Solution-cast films were also used to compare their gas sorption and transport properties with the melt-extruded films. Films were cast from dichloromethane on a glass plate floating on mercury. After an initial period of solvent evaporation to produce a solid film, final drying was done in a vacuum oven at 80°C for 1 week.

All the data for polycarbonate (PC) have been reported previously[2] and were obtained on a melt-extruded film of LEXAN supplied by the General Electric Company.
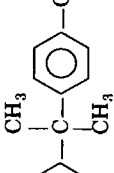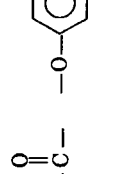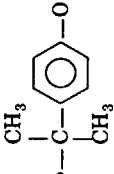
The sorption and permeation measurements were made at 35°C using techniques described previously.[3,4] PSF and PC films were exposed to 20 atm of CO_2 for 1 day to give a uniform conditioning prior to sorption or permeation measurements. The permeabilities of PES were measured using the as-prepared film, that is, without CO_2 conditioning.

Experimental Results

Figures 1 through 3 give the permeability coefficients for helium, methane, and carbon dioxide in each of the three polymers as a function of the upstream driving pressure. Values for helium do not depend on pressure, whereas for both CO_2 and CH_4 the permeabilities for all three polymers decrease as the upstream driving pressure is increased, which is the response normally expected for glassy polymers.[1-5] For each gas the permeabilities for polyethersulfone are lower than those for polycarbonate by a factor of 1.5 for He, 2 for CO_2, and 3 for CH_4. Evidently, the bulky bisphenol A residue facilitates the permeation behavior of both PC and PSF. The more streamlined PES molecule packs more efficiently in the glassy state, resulting in lower transport mobility for gases. These issues are qualitatively shown by the estimates of free volume, $V - V_0$, listed in Table I for each of the polymers. Here, V is the measured specific volume and V_0 is an estimate of specific volume at 0 K (i.e., occupied volume) using a group contribution approach developed for small molecules by Sugden.[6] Rather useful quantitative correlations of permeability with this[7] and other measures of free volume[8] have been developed.

Since glassy polymers do not exist in an equilibrium state, one may expect their properties to depend on prior history, such as fabrication technique. In this work, films of polysulfone were prepared by solvent casting, which can be compared to melt-extruded film. Figures 4 and 5 show data for CO_2 sorption and permeation on films prepared by these two extreme methods. As shown in Figure 4, the sorption of CO_2 is somewhat larger in the cast film than in the melt-extruded

TABLE I
Comparison of the Three Polymers Used in This Study

Characteristic	Polycarbonate	Polysulfone	Polyethersulfone
Abbreviation	PC	PSF	PES
Structure			
T_g (°C)	148	186	225
$V\text{-}V_0$ (cm^3/g)	0.106	0.099	00.089
P_{He}	14.0	11.0	8.0
P_{CO_2}	6.5	4.7	2.8
P_{CH_4}	0.28	0.18	0.10
P_{He}/P_{CH_4}	50	61	80
P_{CO_2}/P_{CH_4}	23	26	28

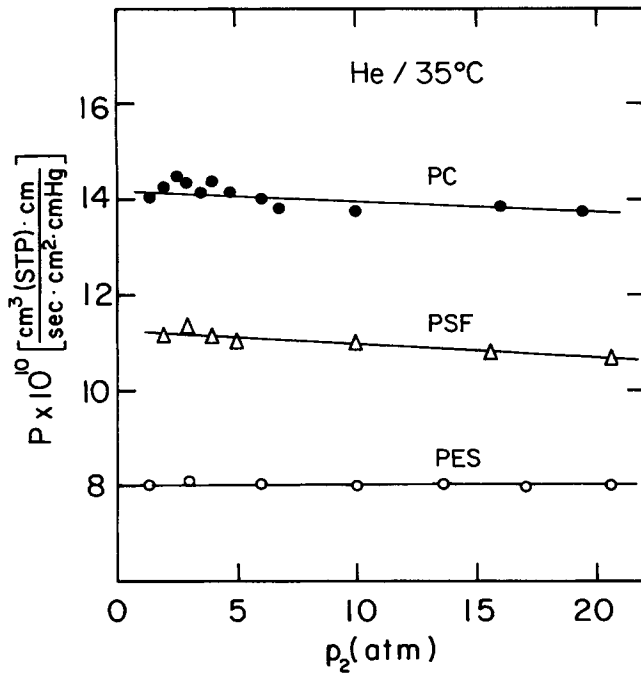[a] Permeability values are for 35°C and 10 atm and are expressed in Barrers.

Fig. 1. Effect of driving pressure on the permeability of helium in polycarbonate (●), polysulfone (△), and polyethersulfone (○) at 35°C.
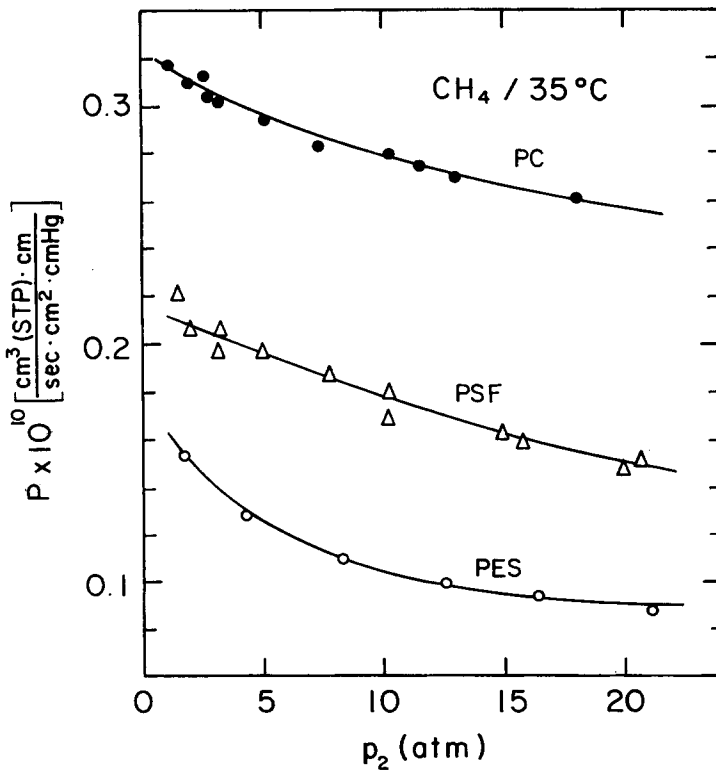

Fig. 2. Effect of driving pressure on the permeability of methane in polycarbonate (●), polysulfone (△), and polyethersulfone (○) at 35°C.
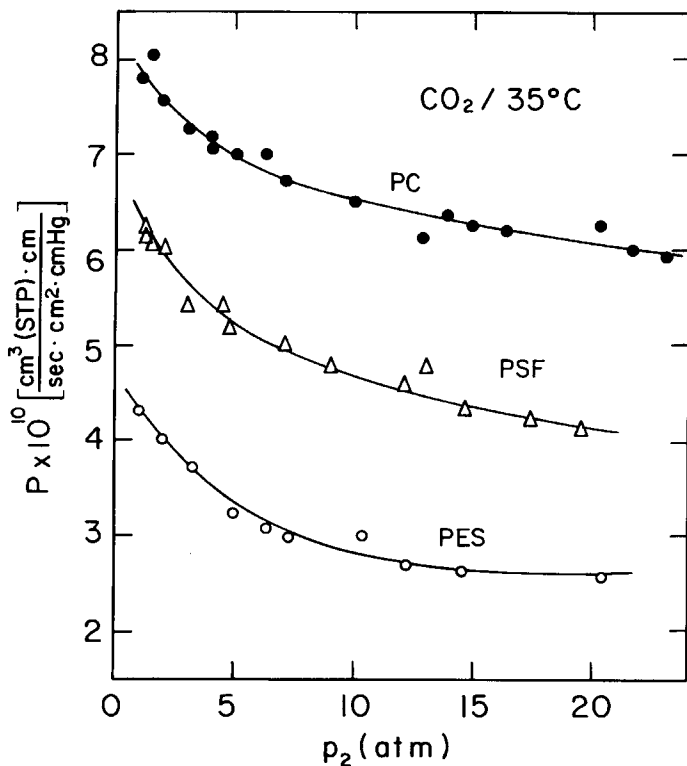
Fig. 3.   Effect of driving pressure on the permeability of carbon dioxide in polycarbonate (●), polysulfone (△), and polyethersulfone (○) at 35°C.
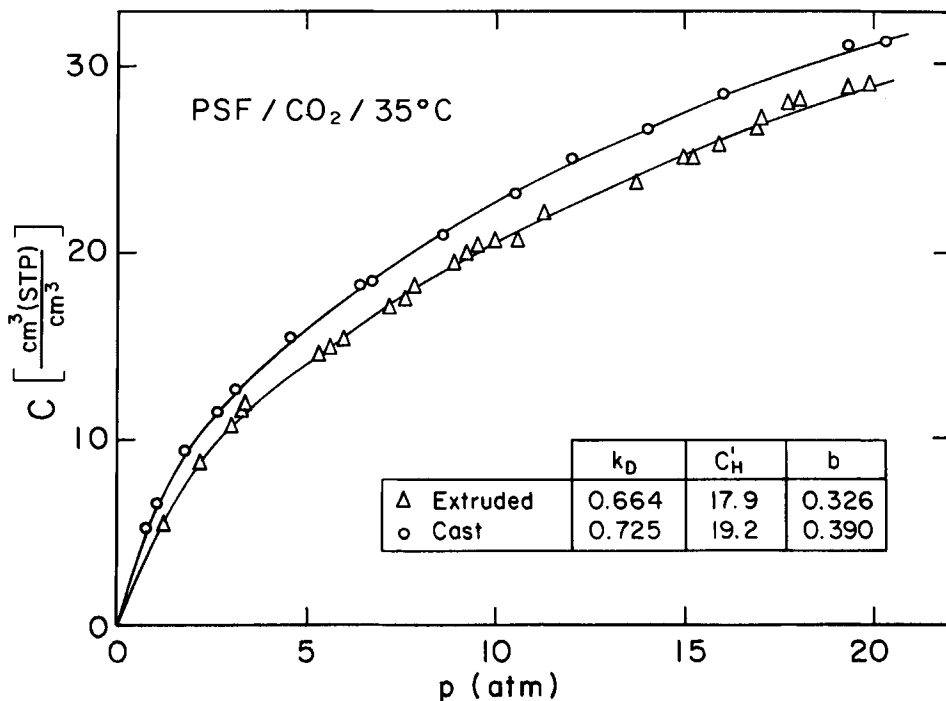

Fig. 4.   Sorption isotherms for CO_2 at 35°C in polysulfone film prepared by solution casting (○) and melt extrusion (△). Dual-sorption model parameters deduced for each isotherm are shown.
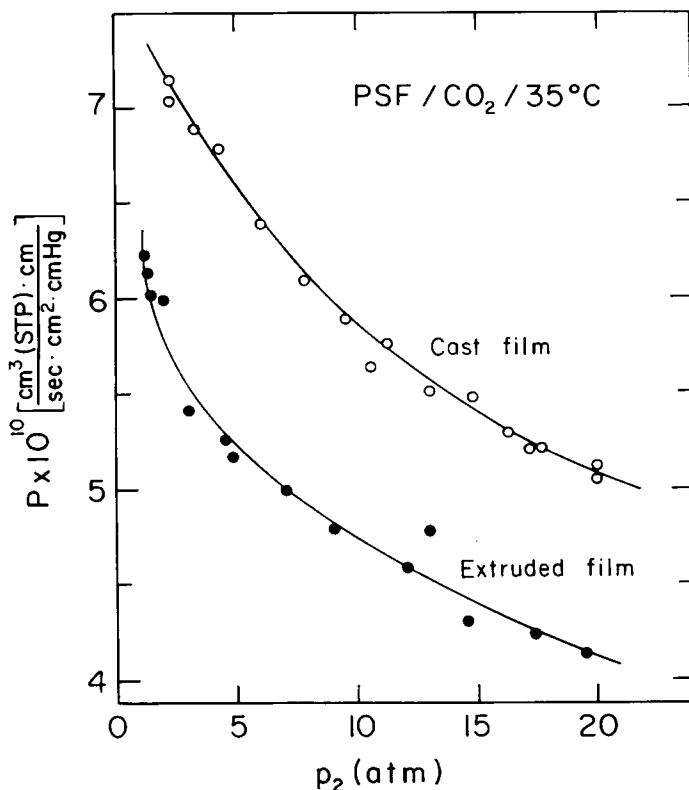
Fig. 5. Permeability of CO_2 in polysulfone film versus driving pressure at 35°C prepared by melt extrusion (●) and solution casting (○).

film. This figure also summarizes the parameters in the dual-sorption model:

$$C = k_D p + \frac{C_H' bp}{1 + bp}$$

which best describe each isotherm. The solid lines are the isotherms calculated with these parameters. Figure 5 shows that the permeability of the extruded film to CO_2 is about 20% less than that for the solution-cast material. Similar results are also observed for permeabilities to He and CH_4. The permeation and the sorption data are consistent with a more open or dilated structure for the solution-cast material than for the melt-extruded material.

SUMMARY

The results shown here indicate that the streamlined chains of polyethersulfone are able to pack more effectively in the glassy state than the related polysulfone with a bisphenol A unit in its structure. One result is that gas molecules permeate more slowly through PES than PSF. The PSF repeat unit is approximately half like that of PC and half like that of PES; thus its transport properties are intermediate.

Table I also shows the ratios of permeabilities for each of the three polymers for the gas pairs He-CH_4 and CO_2-CH_4. These indicate selectivity of transport, which is an important consideration for membrane separation processes. The selectivity for PES is higher than for PC and PSF; however, PES shows lower permeabilities.

References

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