Gas transport properties of polysulphones: 2. Effect of bisphenol connector groups

J. S. McHattie, W. J. Koros and D. R. Paul*

*Department of Chemical Engineering and Center for Polymer Research,
The University of Texas at Austin, Austin, TX 78712, USA*

The gas sorption and transport properties of a series of polysulphones in which the isopropylidene unit of bisphenol A polysulphone (PSF) has been replaced with another molecular group are reported. Bisphenol A polysulphone is compared to several newly synthesized materials, including hexafluorobisphenol A polysulphone (HFPSF), bisphenol F polysulphone (PSF-F), and bisphenol O polysulphone (PSF-O). These polymers are also compared to Victrex™ polyethersulphone (PES). The effect of the substituents on chain mobility and chain packing has been related to the gas transport properties. Dynamic mechanical thermal analysis and differential scanning calorimetry were used to judge chain mobility, while X-ray diffraction and free volume calculations give information about chain packing. Permeability measurements were made for He, H_2, O_2, N_2, CH_4 and CO_2 at 35°C over a range of pressures up to 20 atm. Sorption experiments were also done for N_2, CH_4 and CO_2 under the same conditions. The permeability coefficients for all gases rank in the order: HFPSF > PSF > PSF-F ≅ PSF-O > PES. With the exception of PES, these permeability trends are in good agreement with the fractional free volume. Possible reasons for this are discussed.

(Keywords: polysulphones; permeation; sorption; diffusion; membranes)

INTRODUCTION

The advent of high surface area, thin skin asymmetric and composite structures was critical to the recent growth of the technology of gas separation by membranes[1-4]. But as module design limits are approached, the continued advancement of this technology depends on new materials with better separation characteristics, i.e. permeability and selectivity. In order to facilitate the search for such materials, an understanding of the structural features that affect gas transport properties is required.

The present work involves the study of a family of polysulphones in which the isopropylidene unit in bisphenol A polysulphone (PSF) has been replaced with another molecular group. The effect of these substitutions on gas transport properties are related to segmental mobility using thermal techniques and to chain packing by free volume analysis. The familiar PSF, which is one of the most widely used materials for gas separation membranes, is compared to several newly synthesized polymers, including hexafluorobisphenol A polysulphone (HFPSF), bisphenol F polysulphone (PSF-F), and bisphenol O polysulphone (PSF-O). These polymers are also compared to Victrex™ polyethersulphone (PES) from ICI Americas Inc., which has been studied previously in this laboratory[5]. Chemical structures and other monomer and synthesis information are presented in *Table 1*.

This paper parallels a similar study of polysulphones with tetramethyl ring substitution[6]. Included in that group are tetramethyl bisphenol A polysulphone (TMPSF), tetramethyl hexafluorobisphenol A polysulphone (TMHFPSF) and tetramethyl bisphenol F polysulphone (TMPSF-F). A third paper deals with the differences between symmetric and asymmetric methyl substitution of polysulphones[7].
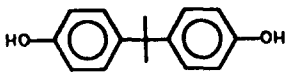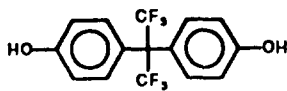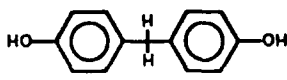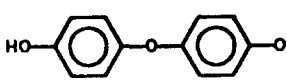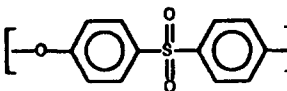
MATERIALS

High molecular weight polysulphones were synthesized by the condensation of the appropriate bisphenol and a dihalogenated diphenyl sulphone in the presence of a base. One of two procedures, described by Johnson et al.[8] and by Mohanty et al.[9-11], was used with only slight modification[7]. *Table 1* lists monomer sources and purification techniques as well as the details of the polymerization reactions. As described elsewhere[7], amorphous films of each of the polymers were prepared by solution casting from methylene chloride on a clean glass plate. PSF-O was not completely soluble in methylene chloride at room temperature, so the solution was heated and cast on a warm glass plate. PES films were compression moulded from the melt state[5]. Cast films were dried thoroughly in a vacuum oven and cooled rapidly from above the glass transition temperature (T_g) to standardize the thermal history. As a measure of molecular weight, the intrinsic viscosity for each polymer was obtained in chloroform at 25°C using a size 25 Cannon-Fenske viscometer.

FREE VOLUME ANALYSIS

The free volume of each of the polymers was obtained by subtracting a calculated occupied volume, V_0, from the measured specific volume, V. The specific volume was measured by flotation of small samples of film in a density gradient column maintained at 30°C. The specific free volume (SFV) and fractional free volume (FFV) are given

Table 1 Monomer and synthesis information for polysulphones

Bisphenols			Synthesis				
Structure	Source	Recrystal- lization	Polymer	Method	Time (h)	T (°C)	$[\eta]$ (dl g^{-1})
HO—⟨O⟩—C—⟨O⟩—OH	Aldrich Chemical Co.	Toluene	PSF[a]	—[b]	4	160	0.40[d]
HO—⟨O⟩—C(CF$_3$)$_2$—⟨O⟩—OH	American Hoechst Corp.	Toluene	HFPSF	—[b]	5	160	0.55[d]
HO—⟨O⟩—CH$_2$—⟨O⟩—OH	Lancaster Synthesis Ltd	Sublimed	PSF-F	—[c]	15	170	0.58[d]
HO—⟨O⟩—O—⟨O⟩—OH	Kennedy and Klim Inc	Sublimed	PSF-O	—[c]	16	160	0.37[e]
[—O—⟨O⟩—SO$_2$—⟨O⟩—][f]	ICI Americas Inc.	–	PES	–	–	–	0.61[e]

[a] [—O—⟨O⟩—C—⟨O⟩—O—⟨O⟩—SO$_2$—⟨O⟩—]
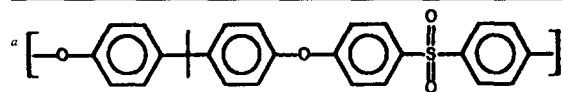
[b] Johnson et al.[8]
[c] Mohanty et al.[9–11]
[d] In chloroform at 25°C
[e] In N-methyl pyrrolidinone (NMP) at 25°C
[f] Polymer repeat unit

Table 2 Characterization of molecular packing for polysulphones

Polymer	Density (g cm^{-3})	d space[a] (Å)	Bondi[12,13]		Sugden[14]	
			$V - V_0$ (cm^3 g^{-1})	$\dfrac{V - V_0}{V}$	$V - V_0$ (cm^3 g^{-1})	$\dfrac{V - V_0}{V}$
PSF	1.240	5.0	0.126	0.156	0.106	0.132
HFPSF	1.427	5.2	0.118	0.168	0.100	0.141
PSF-F	1.282	4.7	0.118	0.151	0.103	0.131
PSF-O	1.330	4.8	0.113	0.150	0.100	0.134
PES	1.370[b]	–	0.111	0.151	0.104	0.143

[a] X-ray diffraction, $\lambda = 1.54$ Å
[b] Chiou et al.[5]

by:

$$SFV = V - V_0 \qquad FFV = \frac{V - V_0}{V} \qquad (1)$$

The group contribution methods of Bondi[12,13] and Sugden[14] can be used to calculate V_0. As a complement to the free volume analysis, wide angle X-ray diffraction measurements were performed on a Phillips X-ray diffractometer with Cu Kα radiation having a wavelength of 1.54 Å. The d spacing, a measure of the most probable intersegmental spacing[15], was calculated from the Bragg equation[16], $n\lambda = 2d \sin \theta$, at the angle of maximum reflective intensity.

The calculated free volume values and the X-ray diffraction d spacing for each polymer are given in *Table 2*. In other studies of polycarbonates[17] and polysulphones[6,7], the best correlation with gas permeability was obtained using FFV based on the Bondi method.

For this group of polymers, the Bondi FFV is reasonably consistent with the d spacing. HFPSF has the highest FFV, 16.8%, and the largest d spacing, 5.2 Å. The Bondi FFVs for PSF-F, PSF-O and PES are all ~15% while this quantity is 15.6% for PSF. The FFV calculated by the Sugden method seems less consistent with other measures of polymer packing efficiency, especially for PES. This may be due to the predicted volume for the sulphone group which makes up a significant portion of the PES repeat unit. There is no clear way to deal with the partial double bond character present in this group. The values given in *Table 2* are based on single S–O bonds. The SFV may not provide an accurate measure of packing efficiency either. Because the SFV is on a mass basis, those materials with relatively heavy substituents tend to be misrepresented. For example, the SFV of HFPSF, calculated by either method, is lower than that of PSF, yet other properties, like gas permeability,

Table 3 Thermal transitions for polysulphones

Polymer	D.s.c.[a]	D.m.t.a. (110 Hz)		
	T_g (°C)	T_α (°C)	T_β (°C)	T_{γ_2} (°C)
PSF	186	193	85	−80 (−100)[b]
HFPSF	192	200	70	−83
PSF-F	179	194	−	−78
PSF-O	181	192	−	−80
PES	225[c]	−[d]	−	−100[b]

[a] Rate: 20°C min⁻¹
[b] Torsion pendulum/1 Hz, Robeson et al.[19]
[c] Chiou et al.[5]
[d] Out of range (>200°C)
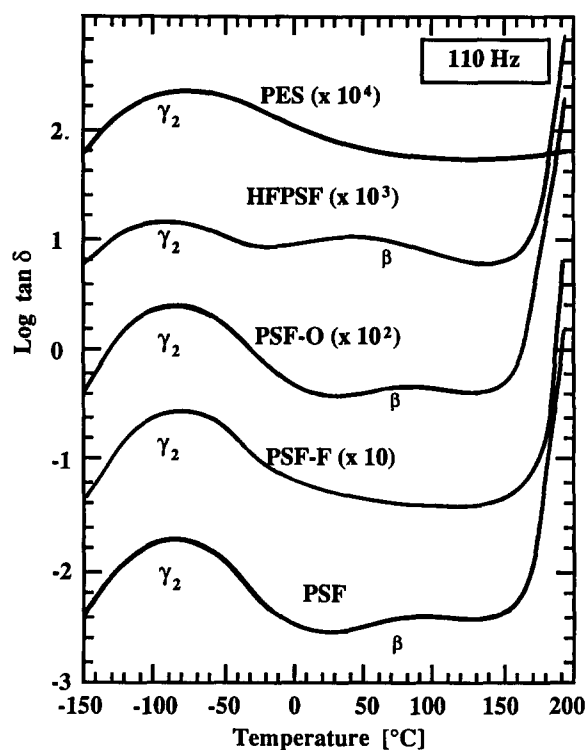
Figure 1 Loss tangent as a function of temperature from dynamic mechanical thermal analysis showing β and γ transitions. Subscript 2 indicates peaks associated with unsubstituted phenylene rings[7]

indicate that HFPSF has a more open structure than PSF.

THERMAL ANALYSIS

The T_g of each polymer was determined by differential scanning calorimetry (d.s.c.) with a Perkin-Elmer DSC-7 at a scanning rate of 20°C min⁻¹. The midpoint of the heat capacity shift on the second scan was taken as the T_g. Low temperature transitions were examined by dynamic mechanical thermal analysis (d.m.t.a.) using the Imass autovibron dynamic mechanical viscoelastometer operated in the tensile mode at 110 Hz and at a heating rate of 1°C min⁻¹. These d.s.c. and d.m.t.a. results are summarized in *Table 3*.

In a previous paper[7], an attempt was made to relate the position of the low temperature γ_2 transition to polymer free volume. The transition occurs at a lower temperature for materials with higher FFV presumably because intermolecularly imposed restraints to small scale molecular motions are reduced. This peak was

ascribed to the motion of the diphenyl sulphone portion of the polymer repeat unit which is the same for each material in this study. The γ relaxation in these types of materials has been attributed to small scale molecular motions about flexible linkages in the polymer chain[18,19]. For polymers which are largely aromatic, like these polysulphones, phenylene motions tend to be the most significant contributors to this transition. Because the polymer modifications of this study are not directly related to the various phenylene units, any differences in behaviour are much more subtle than observed for ring substitutions. Peaks resulting from the bisphenol and diphenyl sulphone portions of the repeat unit tend to overlap one another.

The tan δ curves from the dynamic mechanical spectra of each of the polysulphones are given in *Figure 1*. The curves are offset vertically with a shift of one order of magnitude between each one. The major peak of the γ transition is similar for each polymer in this study because ring mobility has not been affected to a significant extent. The range of free volume among these polymers is only enough to make a change of a few degrees which is difficult to discern due to the broadness of the peaks. The γ transition is clearly not as sensitive to free volume as the gas transport coefficients. A more detailed look at the dynamic mechanical thermal behaviour of these and other polysulphones will be presented in another paper.

GAS SORPTION AND TRANSPORT

Permeation

Pure gas permeability measurements were made at 35°C for He, H_2, O_2, N_2, CH_4 and CO_2 in that order using the standard permeation techniques employed in this laboratory[20,21]. The permeability data were taken by stepping up the upstream pressure from 1 atm with no prior exposure to high pressure gas. Permeability isotherms are presented as a function of upstream pressure in *Figures 2–7*. The relative permeability of the
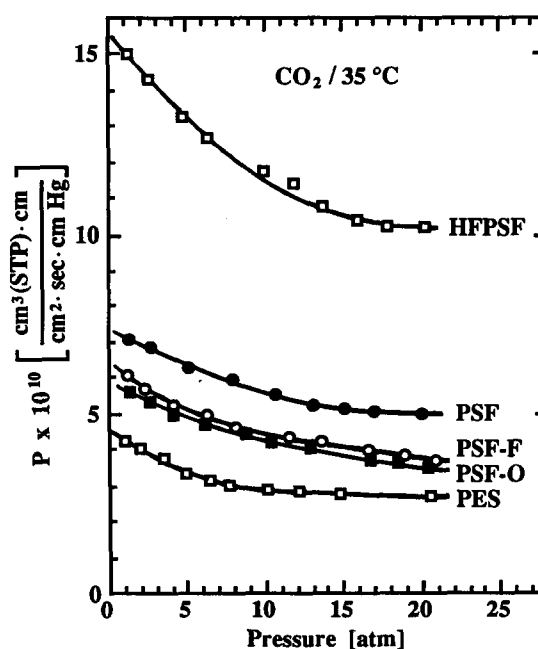
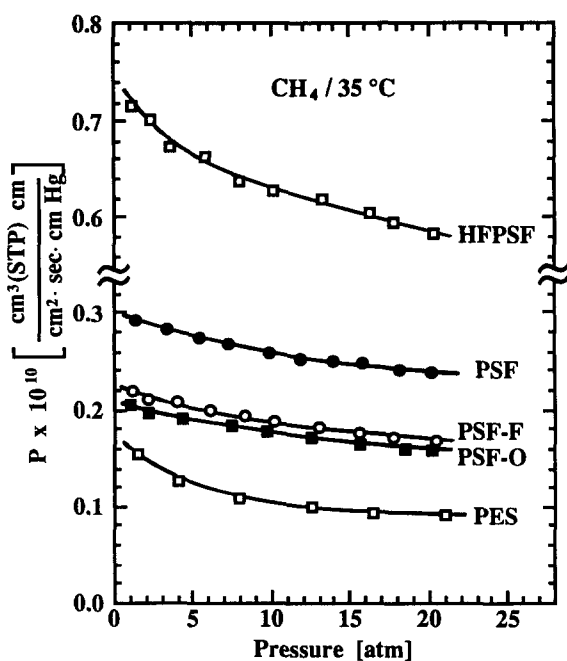**Figure 2** Pressure dependence of CO_2 permeability coefficient at 35°C

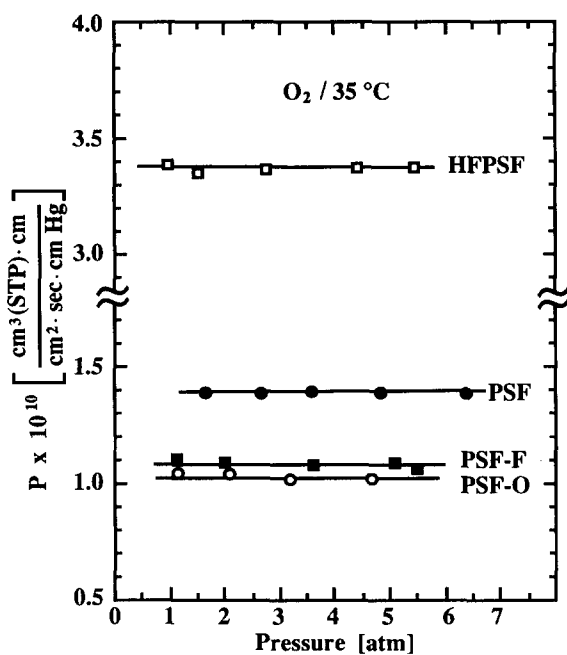**Figure 3** Pressure dependence of CH_4 permeability coefficient at 35°C

Figure 4 Pressure dependence of O_2 permeability coefficient at 35°C

however, it is worth noting other differences. PES has a T_g which is $\sim 45°C$ higher than PSF-F or PSF-O. According to a number of free volume theories[22-31], the process of gas diffusion requires some degree of co-operative polymer chain motion. The stiffer PES chains may be less able to rearrange and allow diffusional jumps to occur than PSF-F and PSF-O chains, even if the average free volume is about the same in each case. This effect is more significant for large penetrant molecules than small ones because more rearrangement is required. As a result, stiff chain polymers may be more selective than flexible chain polymers when all other factors are kept constant[23,32]. Also, the PES film was compression moulded while the other films were solution
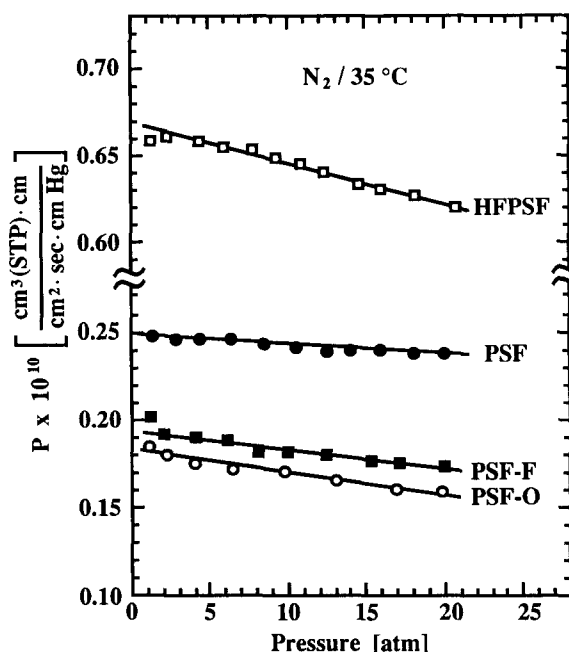
Figure 5 Pressure dependence of N_2 permeability coefficient at 35°C

five polysulphones is:

$$HFPSF > PSF > PSF-F \cong PSF-O > PES$$

With the exception of PES, these permeability values are in agreement with the relative values for the Bondi FFV from *Table 2*. The FFV estimated for PES is approximately the same as that for PSF-F and PSF-O but PES is far less permeable. Several factors need to be mentioned in this connection. First, we indicated earlier the uncertainty in estimating the occupied volume for the sulphone group. For PES, with its relatively short repeat unit, the sulphone group is a more major part of the structure and, therefore, there is more uncertainty in the value of V_0 for this material than the others considered here. The discrepancy may have no other cause than this;

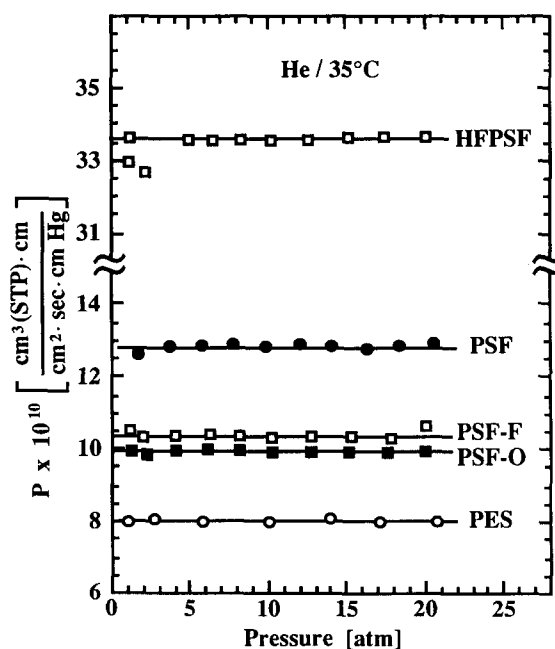**Figure 6** Pressure dependence of He permeability coefficient at 35°C

cast. Orientation imparted during the moulding process can lower permeability[33].

The ideal separation factor, defined as the ratio of the pure component permeabilities:

$$\alpha_{AB}^* = \frac{P_A}{P_B} \tag{2}$$

provides a useful measure of the intrinsic permselectivity of a membrane material for mixtures of A and B for most cases[20]. The permeability coefficients and ideal separation factors for each of the polysulphones at a fixed pressure are shown in *Table 4* for the CO_2/CH_4, O_2/N_2, He/CH_4 and He/H_2 gas pairs. HFPSF is significantly more permeable than PSF with little change in selectivity. The separation factor remains about the same for CO_2/CH_4, decreases for O_2/N_2 and increases for He/CH_4. The steric restrictions of the hexafluoroisopropylidene unit decrease the packing efficiency while increasing the T_g. The open structure leads to high permeability while the rigid chains provide a selective diffusion environment, as discussed above. PSF-F and PSF-O have comparable gas transport properties to one another. Space filling molecular models show that the methylene and ether linkages are similar

in size and mobility. These linkages are smaller and less sterically hindered than the isopropylidene of PSF leading to polymer structures which are less permeable than PSF and only moderately selective. As discussed above, the high degree of chain stiffness for PES leads to high selectivity.

Solubility and diffusivity contributions

Pure gas sorption measurements using a pressure decay sorption cell[34,35] were made for N_2, CH_4 and CO_2 from 1 to 20 atm at 35°C. Again, the data were taken in this order with no previous exposure to high pressure gas. Sorption isotherms for HFPSF, PSF-F and PSF are shown in *Figures 8-10*. The CH_4 sorption levels are similar for each polymer while the CO_2 and N_2 levels are more consistent with the relative free volume values.

For the case of negligible downstream pressure, the permeability coefficient can be written as:

$$P = \bar{D} \times \bar{S} \tag{3}$$

where $\bar{D}$ is a diffusion coefficient averaged across the membrane thickness and $\bar{S}$ is a solubility coefficient obtained from the secant slope of the sorption isotherm at the upstream conditions[36]. An apparent diffusion
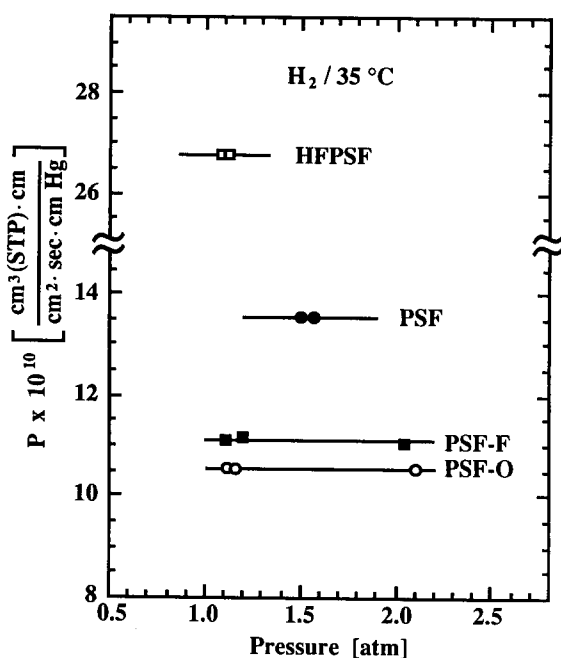

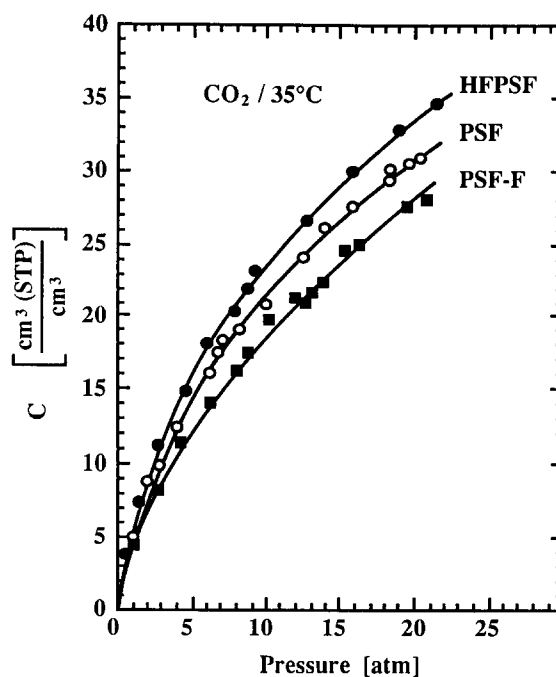**Figure 7** Pressure dependence of H_2 permeability coefficient at 35°C

Figure 8 Sorption isotherms for CO_2 at 35°C

Table 4 Permeability and selectivity for polysulphones at 35°C

Polymer	P_{CO_2}[a]	α_{CO_2/CH_4}^*[a]	P_{O_2}[b]	α_{O_2/N_2}^*[b]	P_{He}[a]	α_{He/CH_4}^*[a]	α_{He/H_2}^*[c]
PSF	5.6	22	1.4	5.6	13	49	0.93
HFPSF	12	22	3.4	5.1	33	63	1.22
PSF-F	4.5	24	1.1	5.5	10	54	0.94
PSF-O	4.3	24	1.1	5.6	10	56	0.96
PES[d]	2.8	28	–	–	8	80	–

P, $\times 10^{10}$ cm³(STP) cm (cm² s cmHg)$^{-1}$
[a] 10 atm
[b] 5 atm
[c] 1 atm
[d] Chiou *et al.*[5]
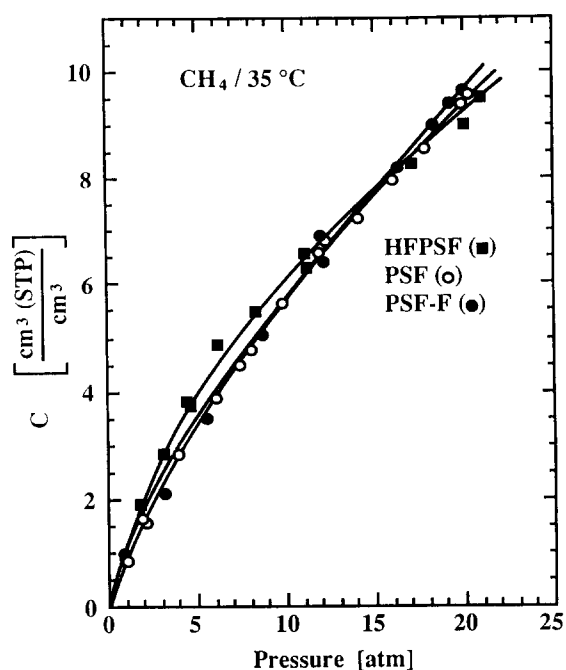
Figure 9 Sorption isotherms for CH_4 at 35°C
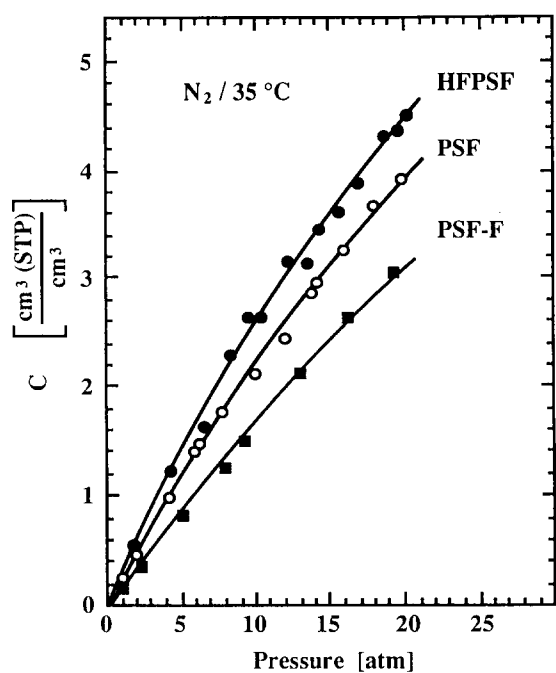
Figure 10 Sorption isotherms for N_2 at 35°C

coefficient can also be estimated from the membrane thickness, l, and the time lag, θ, of a transient permeation measurement[35]:

$$D_{app} = \frac{l^2}{6\theta} \qquad (4)$$

The solubility and diffusivity contributions to the permselectivity of each polymer are given in *Table 5* for the CO_2/CH_4 separation. For HFPSF, diffusive effects are much larger than solubility effects. The CO_2 solubility coefficient of HFPSF is only 20% larger than that of PSF, while the CO_2 diffusion coefficient of HFPSF is almost twice that of PSF. For PSF-F and PSF-O, both solubility and diffusivity are depressed slightly compared to PSF. The separation factor for PSF-F and PSF-O increases relative to PSF because of the large mobility selectivity for each polymer.

Table 6 gives the solubility and diffusivity contributions for the O_2/N_2 gas pair obtained from equation (4). Both solubility and diffusivity effects contribute to the high O_2 permeability for HFPSF, and both the solubility selectivity and mobility selectivity are slightly depressed compared to PSF. For PSF-F and PSF-O, the decrease in free volume compared to PSF results in O_2 solubility and diffusivity coefficients which are lower than those of PSF. With respect to selectivity, the mobility and solubility effects offset one another leaving the separation factor about the same as that of PSF.

Dual mode analysis. Fitting the sorption isotherms from *Figures 8–10* with the dual mode model[37,38]:

$$C = k_D p + \frac{C'_H b}{1 + bp} p \qquad (5)$$

yields the parameters listed in *Table 7*. The parameter k_D is the Henry's law solubility coefficient, C'_H is the

Table 6 Solubility and diffusivity contributions to O_2 and N_2 permselectivity at 5 atm and 35°C

Polymer	P_{O_2}	$\alpha^*_{O_2/N_2}$	S_{appO_2}	$\dfrac{S_{O_2}}{S_{N_2}}$	D_{appO_2} [a]	$\dfrac{D_{O_2}}{D_{N_2}}$
PSF	1.4	5.6	0.24	1.6	4.4	3.6
HFPSF	3.4	5.1	0.41	1.5	6.3	3.5
PSF-F	1.1	5.6	0.20	1.5	4.2	3.7
PSF-O	1.0	5.7	0.21	1.5	4.1	3.7

For units see footnote to *Table 5*
[a] Estimated from permeation time lag

Table 5 Solubility and diffusivity contributions to CO_2 and CH_4 permselectivity at 10 atm and 35°C

Polymer	P_{CO_2}	$\alpha^*_{CO_2/CH_4}$	$\bar{S}_{CO_2}$	$\dfrac{\bar{S}_{CO_2}}{\bar{S}_{CH_4}}$	$\bar{D}_{CO_2}$	$\dfrac{\bar{D}_{CO_2}}{\bar{D}_{CH_4}}$
PSF	5.6	22	2.1 (2.1)	3.7 (3.9)	2.0 (2.0)	5.9 (5.6)
HFPSF	12	22	2.5 (2.8)	4.0 (3.3)	3.6 (3.2)	5.5 (6.7)
PSF-F	4.5	24	1.9 (1.9)	3.6 (4.2)	1.8 (1.8)	6.7 (5.7)
PSF-O	4.3	24	(1.9)	(4.3)	(1.7)	(5.6)

$P \times 10^{10}$ cm^3(STP) cm (cm^2 s cmHg)$^{-1}$; S cm^3(STP) (cm^3 atm)$^{-1}$; $D \times 10^8$ cm^2 s^{-1}
Values in parentheses are estimated from permeation time lag

Table 7 Dual mode parameters for polysulphones at 35°C

Polymer	Gas	k_D [cm³ (STP) (cm³ atm)⁻¹]	C'_H [cm³ (STP) cm⁻³]	b (atm⁻¹)	$D_D \times 10^8$ (cm² s⁻¹)	$D_H \times 10^8$ (cm² s⁻¹)
PSF	CH_4	0.257	6.58	0.0901	0.602	0.131
	CO_2	0.728	19.6	0.260	4.64	0.575
HFPSF	CH_4	0.180	7.32	0.146	1.85	0.154
	CO_2	0.785	21.0	0.285	8.94	1.07
PSF-F	CH_4	0.246	8.84	0.0571	0.368	0.161
	CO_2	0.505	22.6	0.162	4.46	0.763

Langmuir sorption capacity and b is an affinity parameter characterizing the ratio of the rate constants for sorption and desorption. The statistical analysis was carried out using a SAS program with the Marquardt least squares method[39]. According to the dual mobility model[40,41], for the case of negligible downstream pressure, the permeability coefficient can be written as:

$$P = k_D D_D \left[1 + \frac{FK}{1 + bp_2} \right] \quad (6)$$

with

$$K = \frac{C'_H b}{k_D} \quad \text{and} \quad F = \frac{D_H}{D_D}$$

The diffusion coefficient for the Henry's law and Langmuir modes, D_D and D_H, can then be readily calculated from the slope and intercept of an experimental plot of permeability *versus* $1/(1 + bp_2)$. These diffusion coefficients are given in *Table 7*.

CONCLUSIONS

Replacement of the isopropylidene unit of PSF can affect the gas transport properties in a variety of ways depending on the nature of the substituent. The manner in which the substituent affects chain mobility, chain packing and polymer–penetrant interactions is of critical importance. HFPSF is more permeable than PSF with comparable selectivity because the hexafluoroisopropylidene sterically hinders both bond rotation and intersegmental packing. The packing of HFPSF may be further inhibited by intermolecular repulsive forces between fluorine atoms which are areas of high electron density[17]. PSF-F and PSF-O have similar transport properties due to the similarities in size and flexibility of the methylene and ether linkages. PES is less permeable and more selective because of a high degree of chain rigidity.

As observed previously[7], the relative gas transport rates of these materials generally correlate with free volume values calculated from the group contribution method of Bondi[12,13]; however, PES deviates somewhat for possible reasons discussed earlier. In addition, a relationship may exist between the low temperature γ transition and gas transport rate. Because of the nature of the substituents, the differences in low temperature behaviour within this set of polymers are much more subtle than those observed for polysulphones with phenylene ring substitutions[6,7]. The differences in γ transition temperature were only a few degrees.

In designing polymers for gas separations, structural variations which increase chain rigidity while maintaining an open chain packing can result in materials with both high permeability and permselectivity. High free volume is essential to high permeability, while chain stiffness leads to high selectivity.

ACKNOWLEDGEMENTS

REFERENCES

1 Henis, J. M. S. and Tripodi, M. K. *Sep. Sci. Technol.* 1980, **15**, 1059
2 Lundy, K. A. and Cabasso, I. *Ind. Eng. Chem. Res.* 1989, **28**, 742
3 Spillman, R. W. *Chem. Eng. Prog.* 1989, **85**, 41
4 Weber, W. F. and Bowman, W. *Chem. Eng. Prog.* 1986, **82**, 23
5 Chiou, J. S., Maeda, Y. and Paul, D. R. *J. Appl. Polym. Sci.* 1987, **33**, 1823
6 McHattie, J. S., Paul, D. R. and Koros, W. J. *Polymer* in press
7 McHattie, J. S., Paul, D. R. and Koros, W. J. *Polymer* 1991, **32**, 840
8 Johnson, R. N., Farnham, A. G., Clendinning, R. A., Hale, W. F. and Merriam, C. N. *J. Polym. Sci. A1* 1967, **5**, 2375
9 Mohanty, D. K., Hedrick, J. L., Gobetz, K., Johnson, B. C., Yilgor, I., Yilgor, E., Yang, R. and McGrath, J. E. *Am. Chem. Soc., Div. Polym. Chem. Polym. Prepr.* 1982, **23**, 284
10 Mohanty, D. K., Sachdeva, Y., Hedrick, J. L., Wolfe, J. F. and McGrath, J. E. *Am. Chem. Soc., Div. Polym. Chem. Polym. Prepr.* 1984, **25**, 19
11 Mohanty, D. K. *PhD Dissertation* Virginia Polytechnic Institute, 1983
12 Bondi, A. *J. Phys. Chem.* 1964, **68**, 441
13 Bondi, A. 'Physical Properties of Molecular Crystals, Liquids, and Glasses', John Wiley and Sons Inc., New York, 1968
14 Sugden, S. *J. Chem. Soc.* 1927, 1786
15 Alexander, L. E. 'X-ray Diffraction in Polymer Science', John Wiley and Sons Inc., New York, 1969
16 Schwartz, L. H. and Cohen, J. B. in 'Diffraction from Materials', Academic Press, New York, Ch. 3, 1977
17 McHattie, J. S., Koros, W. J. and Paul, D. R. *J. Polym. Sci., Polym. Phys. Edn* 1991, **29**, 731
18 Yee, A. F. and Smith, S. A. *Macromolecules* 1980, **14**, 54
19 Robeson, L. M., Farnham, A. G. and McGrath, J. E. *Midland Macromol. Monogr.* 1978, **4**, 405
20 O'Brien, K. C., Koros, W. J., Barbari, T. A. and Sanders, E. S. *J. Membr. Sci.* 1986, **29**, 229
21 Koros, W. J., Chan, A. H. and Paul, D. R. *J. Membr. Sci.* 1977, **2**, 165
22 Barrer, R. M. *J. Phys. Chem.* 1957, **61**, 178
23 Brandt, W. W. *J. Phys. Chem.* 1959, **63**, 1080

24 Bueche, F. *J. Chem. Phys.* 1963, **21**, 1850
25 Kumins, C. A. and Roteman, J. *J. Polym. Sci.* 1961, **55**, 699
26 Litt, M. *J. Rheol.* 1986, **30**, 853
27 DiBenedetto, A. T. and Paul, D. R. *J. Polym. Sci. A* 1964, **2**, 1001
28 Pace, R. J. and Datyner, A. *J. Polym. Sci., Polym. Phys. Edn* 1979, **17**, 437
29 Pace, R. J. and Datyner, A. *J. Polym. Sci., Polym. Eng. Sci.* 1980, **20**, 51
30 DiBenedetto, A. T. and Paul, D. R. *J. Polym. Sci. A* 1963, **1**, 3459
31 Paul, D. R. and DiBenedetto, A. T. *J. Polym. Sci. C* 1965, **10**, 17
32 Petropoulos, J. H. Seminar given to the Department of Chemical Engineering, The University of Texas at Austin, 1989
33 El-Hibri, M. J. *PhD Dissertation* The University of Texas at Austin, 1986
34 Koros, W. J. and Paul, D. R. *J. Polym. Sci., Polym. Phys. Edn* 1976, **14**, 1903
35 Koros, W. J. *PhD Dissertation*, The University of Texas at Austin, 1977
36 Chern, R. T., Koros, W. J., Hopfenberg, H. B. and Stannett, V. T. *J. Polym. Sci., Polym. Phys. Edn* 1984, **22**, 1061
37 Barrer, R. M., Barrie, J. A. and Slater, J. *J. Polym. Sci.* 1958, **27**, 177
38 Vieth, W. R., Howell, J. M. and Hsieh, J. H. *J. Membr. Sci.* 1976, **1**, 177
39 Marquardt, D. W. *J. Soc. Industr. Appl. Math.* 1963, **2**, 431
40 Koros, W. J. and Paul, D. R. *J. Polym. Sci., Polym. Phys. Edn* 1978, **16**, 1947
41 Petropoulos, J. H. *J. Polym. Sci. A2* 1970, **8**, 1797