

# Gas transport properties of a series of poly(ether ketone) polymers

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The gas sorption and transport properties of a series of poly(aryl ether ketone) materials are reported. In this series, the isopropylidene groups ( $-\text{C}(\text{CH}_3)_2-$ ) in the backbone are systematically replaced with a hexafluoroisopropylidene group ( $-\text{C}(\text{CF}_3)_2-$ ). Dynamic mechanical analysis and differential scanning calorimetry were used to show that the substitution of  $-\text{C}(\text{CF}_3)_2-$  for  $-\text{C}(\text{CH}_3)_2-$  units results in a stiffer polymer chain. Free-volume calculations show that the substitution opens up the polymer structure and leads to an increase in diffusion coefficients. Methane and carbon dioxide sorption measurements were made to examine the solubility and diffusivity contributions to the permeability. The permeability increases as  $-\text{C}(\text{CF}_3)_2-$  units replace the  $-\text{C}(\text{CH}_3)_2-$  groups and, in general, it is the increase in diffusivity that accounts for the permeability increase. Along with the increase in permeability is an increase in the selectivity for gas pairs like helium/methane and carbon dioxide/methane. This simultaneous increase in permselectivity and permeability when  $-\text{C}(\text{CF}_3)_2-$  units replace  $-\text{C}(\text{CH}_3)_2-$  units seems to be a general trend, as it has been observed for polycarbonate and polysulphone materials as well.

(Keywords: poly(ether ketone); membranes; gas permeation; gas sorption; fluorine)

## INTRODUCTION

Recently Tullos *et al.*<sup>1</sup> reported the synthesis of a series of poly(aryl ether ketones) (PEK). PEK polymers, and in particular Victrex<sup>®</sup> poly(ether ether ketone) (PEEK), have been commercially successful owing to their excellent thermal stability and solvent resistance. Conversely, these polymers are difficult to synthesize and to process owing to poor solubility. Addition to the polymer backbone of functional groups that increase solubility is often accompanied by an undesirable loss of thermal stability. The objective of Tullos *et al.* was to enhance solubility without decreasing thermal stability by incorporating hexafluoroisopropylidene groups ( $-\text{C}(\text{CF}_3)_2-$ ) into the polymer backbone. The four polymers synthesized in that study are shown in *Table 1* and are named according to the number of hydrogen and fluorine atoms on the isopropylidene groups of the repeat unit. Naming begins with the isopropylidene group between the ketone functions. The authors report that addition of the  $-\text{C}(\text{CF}_3)_2-$  group into the backbone of PEK improves solubility, electrical properties, optical transparency and thermal stability.

The objective of this research was to study the gas transport properties of this PEK polymer series. Previous studies on polycarbonate<sup>2</sup>, polysulphone<sup>3</sup> and silicone polymers<sup>4</sup> have shown that incorporation of trifluoromethyl groups results in favourable gains in both permeability and permselectivity. In the PEK series, the systematic substitution of  $-\text{C}(\text{CF}_3)_2-$  into the polymer backbone provides another way to study the effect this group has on gas transport. The 6H6F and 6F6H PEK

polymers each have one  $-\text{C}(\text{CF}_3)_2-$  group, but the position of the group in the repeat unit is different. Differences in physical properties or gas transport due to molecular interactions caused by this substitution, if any, can be investigated. Free-volume calculations, differential scanning calorimetry and dynamic mechanical testing were used to judge the chain packing and mobility. These results are then related to the gas sorption and transport properties of these materials.

## MATERIALS AND PROCEDURES

### Materials

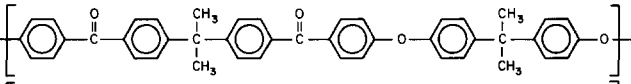
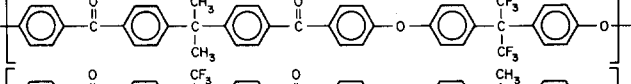
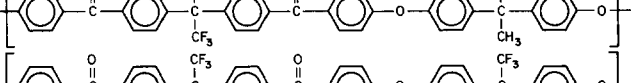
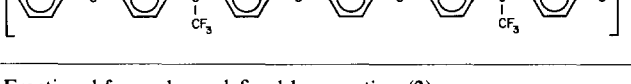
The PEK polymers were synthesized by Tullos by procedures described previously<sup>1</sup>. Films 2–4 mil (50–100  $\mu\text{m}$ ) in thickness were prepared from each polymer by casting a 5 wt% solution in chloroform onto a glass plate. The films were air dried for 24 h and then placed into a vacuum oven. The oven temperature was increased in steps over several days to 10°C above the polymer's  $T_g$ , where it was held for 12 h. Thermogravimetric analysis confirmed that no solvent remained in the films after this drying procedure.

### Gas sorption and transport

Gas permeability coefficients for six pure gases were measured at 35°C. Permeability coefficients of hydrogen, helium and oxygen were measured at 5 atm upstream driving pressure. Data for nitrogen and methane were taken as a function of pressure up to 20 atm. Carbon dioxide permeability measurements were made after completing those for the other five gases. The time-dependent hysteretic effects often associated with

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**Table 1** Structure and physical properties of the series of poly(ether ketone) polymers

Polymer structure	Designation	Density (g cm <sup>-3</sup> )	FFV <sup>a</sup>	T <sub>g</sub> (°C)	T <sub>v</sub> (°C)
	12H	1.166	0.151	171	-78
	6H6F	1.287	0.166	179	-77
	6F6H	1.284	0.168	181	-77
	12F	1.401	0.175	185	-70

<sup>a</sup> Fractional free volume defined by equation (2)

carbon dioxide were observed by conducting a pressurization/depressurization cycle. Permeability measurements were made as the pressure was stepped up to 20 atm. The pressure was held at 20 atm for 24 h and then permeability measurements were taken as the pressure was stepped back down to 1 atm. The pressure was held at each level for ample time to reach a diffusional steady state. Permeation measurements were made using the previously described techniques of this laboratory<sup>5,6</sup>, where essentially zero pressure was maintained downstream and the increase in pressure with time was measured by a sensitive pressure transducer and recorded.

Sorption measurements for methane and carbon dioxide were made at 35°C with a pressure decay method<sup>6,7</sup>. Measurements were made from 1 to 20 atm and methane was tested first to avoid the conditioning effects that can result at high pressures of carbon dioxide<sup>8</sup>. A non-linear regression analysis was used to fit the data to the dual-mode sorption model.

#### Characterization

The density of each polymer was measured at 30°C in a density gradient column based on calcium nitrate solutions.

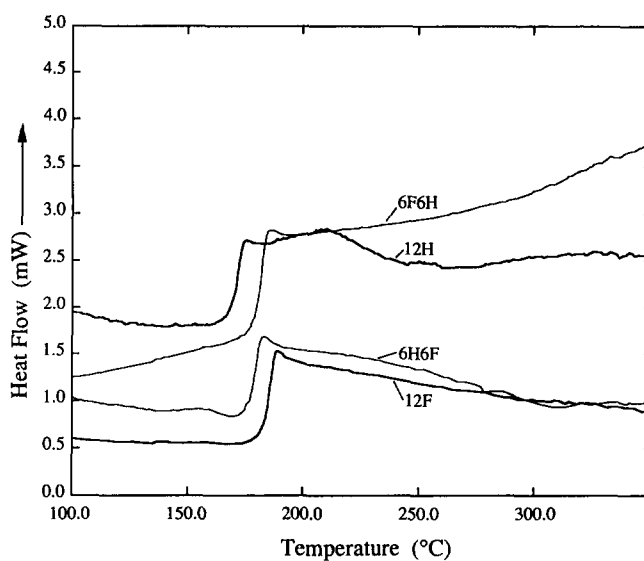
Differential scanning calorimetry (d.s.c.) scans were made with a Perkin-Elmer DSC-7 at a heating rate of 20°C min<sup>-1</sup>. The samples were scanned twice consecutively and the glass transition temperatures reported are taken as the mid-point of the transition from the second scan. Comparison of first and second scans confirmed that the drying protocol did indeed remove all solvent and did not result in any sub-T<sub>g</sub> annealing effects in the final film.

Dynamic mechanical thermal analysis (d.m.t.a.) was carried out to examine the secondary relaxation processes. The instrument used was an IMASS Autovibron Dynamic Mechanical Viscoelastometer. Measurements were made at 110 Hz while heating at 1°C min<sup>-1</sup>.

## RESULTS AND DISCUSSION

#### Polymer characterization

**Thermal analysis.** The second of two consecutive d.s.c. scans for each polymer is shown in Figure 1. The glass



**Figure 1** D.s.c. thermograms for the poly(ether ketone) polymer series

transition temperatures T<sub>g</sub> are in the order:

$$12\text{H} < 6\text{H}6\text{F} \approx 6\text{F}6\text{H} < 12\text{F}$$

The large fluorine atoms in the -C(CF<sub>3</sub>)<sub>2</sub>- group, relative to the smaller hydrogen atoms in the -C(CH<sub>3</sub>)<sub>2</sub>- group, hinder molecular rotations within the backbone. The -C(CF<sub>3</sub>)<sub>2</sub>- group interferes with other segments during conformational rearrangements, thus decreasing the chain mobility such that the glass transition occurs at a higher temperature. As shown in Table 1, 12H PEK has the lowest T<sub>g</sub> because of the relative ease of mobility about the -C(CH<sub>3</sub>)<sub>2</sub>- groups. On the other hand, 12F PEK has the highest T<sub>g</sub> because of the greater barriers to rotations caused by the larger trifluoromethyl units. The T<sub>g</sub> values of 6H6F and 6F6H are intermediate between these extremes and differ from each other by only about 2°C. The d.s.c. thermograms show no evidence of crystalline melting for any of these polymers; hence, these materials appear to be completely amorphous as prepared here.

Dynamic mechanical analysis was used to probe the more subtle secondary transitions of the polymers, and in particular to discern any differences between the 6H6F and 6F6H. The loss factor tan δ is shown in Figure 2 as

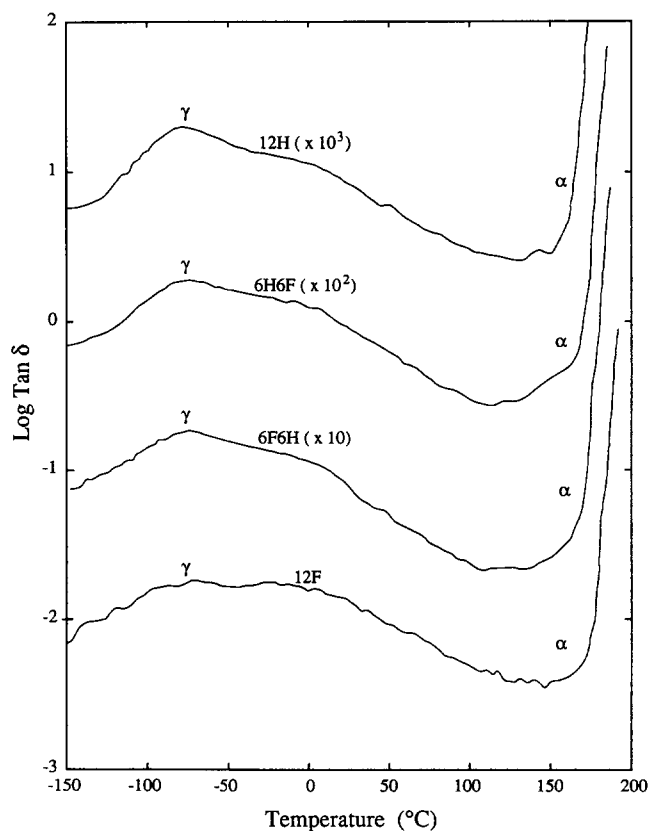


Figure 2 Loss tangent versus temperature for the poly(ether ketones). Curves are offset vertically by factors of 10 for clarity

a function of temperature for each of the PEK polymers. The curves are offset vertically by a shift of one order of magnitude between each. The transitions are labelled from high to low temperature with the symbols  $\alpha$ ,  $\beta$  and  $\gamma$ . The  $\alpha$  transition corresponds to the  $T_g$ . The  $\beta$  transition in related polymers has been attributed to packing defects or orientational stresses created during processing that can be reduced or eliminated by annealing<sup>9,10</sup>. Since the PEK polymers were annealed above the glass transition after casting, no such  $\beta$  transition is expected or observed. The low-temperature transition is then believed to be similar to the  $\gamma$  peaks observed in many other polymers of related structure, so we use the  $\gamma$  notation here. Such  $\gamma$  transitions are believed to be the result of small-scale molecular motions about flexible linkages in the polymer chain<sup>11,12</sup>. Previous studies on polymers with aromatic backbones have shown that phenylene ring motions tend to be the most significant contributors to the  $\gamma$  transition<sup>11-13</sup>. However, the transition is broad and is believed to be a composite of several superimposed peaks associated with the different parts of the repeat unit<sup>10</sup>.

The broad  $\gamma$  transition of 12H PEK shows a main peak at  $-78^\circ\text{C}$  with a shoulder at higher temperature. The  $\gamma$  transition of polycarbonate and polysulphone, also determined at 110 Hz, occur at  $-75$  and  $-80^\circ\text{C}$ , respectively<sup>3</sup>. The main peaks between  $-75$  and  $-80^\circ\text{C}$  for the latter two polymers are attributed to phenylene ring motion and it seems reasonable to assume that the corresponding peak for 12H PEK has a similar origin. In 6H6F and 6F6H PEK the main peak of the  $\gamma$  transition occurs at  $-77^\circ\text{C}$ . The transition is broader than that for the 12H transition, but a main peak with a shoulder is still evident. The  $\gamma$  transition of 12F PEK is flat and broad, and the previous structural feature of a main peak

with a shoulder is gone. This flattening and broadening of the  $\gamma$  region upon addition of the  $-\text{C}(\text{CF}_3)_2-$  group has also been observed for polysulphone and hexafluoropolysulphone<sup>3</sup>. The disappearance of the main peak and the broadening of the spectra suggests that addition of the  $-\text{C}(\text{CF}_3)_2-$  group hinders the small-scale motions of the repeat unit. Motions in the 12F PEK are more difficult than in the 6H6F or 6F6H. Since the spectra of the 6H6F and 6F6H are identical, the difference in location of the  $-\text{C}(\text{CF}_3)_2-$  group makes no detectable difference to the small-scale molecular motions.

**Free volume.** The specific free volume  $SFV$  of a polymer can be determined by subtraction of a calculated occupied volume  $V_0$  from the measured specific volume  $V$ :

$$SFV = V - V_0 \quad (1)$$

Group contribution methods of Bondi<sup>14</sup> and of Sugden<sup>15</sup> can be used to estimate  $V_0$ . Previous work in this laboratory<sup>3</sup> has shown that gas permeation gives a better statistical correlation with the Bondi method. Also, the fractional free volume ( $FFV$ ):

$$FFV = \frac{(V - V_0)}{V} \quad (2)$$

gives a better correlation when dealing with polymers containing elements heavier than carbon, oxygen and hydrogen<sup>3</sup>.

The density of each of the PEK polymers was measured to determine the specific volume. Table 1 shows the density of each and the resulting calculated fractional free volume. 12H PEK has the smallest free volume, approximately 15.1%, while 12F PEK has the highest at 17.5%. The  $FFV$  of 6F6H and 6H6F are nearly identical at 16.8% and 16.6%, respectively. Since  $V_0$  is calculated to be the same for these isomers, this small effect is directly a result of the fact that 6H6F has a slightly higher density than 6F6H. This difference may be due to inter- and intramolecular interactions between the  $-\text{C}(\text{CH}_3)_2-$  group and the ketone function in the 6H6F, which allow better chain packing.

#### Gas sorption and transport

**Permeation.** The gas permeability coefficients measured for the PEK polymer series are summarized in Table 2. Substituting the  $-\text{C}(\text{CF}_3)_2-$  group for the  $-\text{C}(\text{CH}_3)_2-$  units opens up the polymer structure as the free-volume calculations shown in Table 1 indicate. The opening of the polymer structure allows for higher diffusion rates and increased sorption levels and, therefore, an increase in the permeability coefficient. Hence, 12H PEK is the most tightly packed of the four polymers and it has the lowest permeability to all gases. Addition of one  $-\text{C}(\text{CF}_3)_2-$  group to the repeat unit, as in 6H6F and 6F6H, opens up the structure, giving an increase in permeability. Adding a second  $-\text{C}(\text{CF}_3)_2-$  group to form 12F PEK opens the structure more and further increases the permeability. The difference between the 6H6F and 6F6H PEK permeability values is not statistically significant. Thus, it is not possible to comment on the effects of the position of the  $-\text{C}(\text{CF}_3)_2-$  units in these materials.

Ideal separation factors for several gas pairs, calculated from the pure gas permeability coefficients, are shown in Table 2. The  $\text{O}_2/\text{N}_2$  selectivity follows the typical trend of decreasing selectivity with increasing permeability.

**Table 2** Permeability coefficients and ideal selectivities for the poly(ether ketone) polymers at 35°C and 5 atm

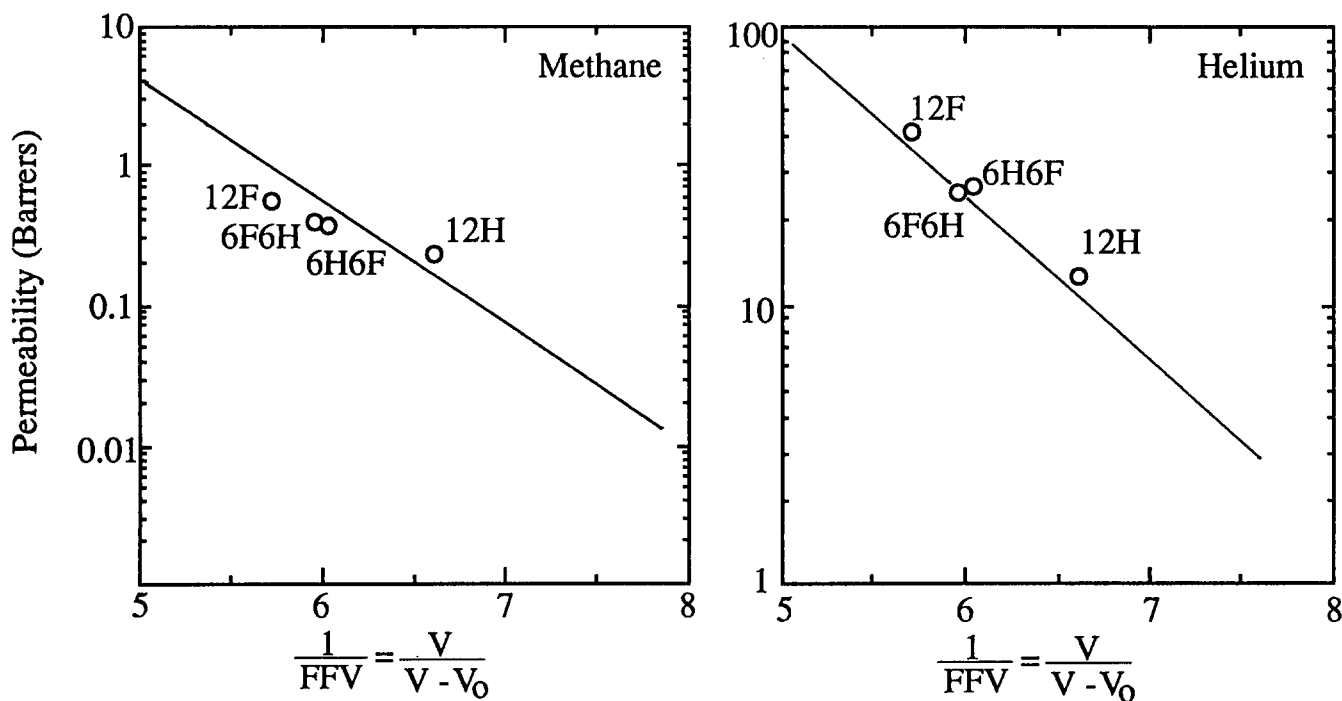
Polymer	Permeability <sup>a</sup>						Selectivity			
	N <sub>2</sub>	O <sub>2</sub>	CH <sub>4</sub>	H <sub>2</sub>	He	CO <sub>2</sub>	O <sub>2</sub> /N <sub>2</sub>	H <sub>2</sub> /CH <sub>4</sub>	He/CH <sub>4</sub>	CO <sub>2</sub> /CH <sub>4</sub>
12H	0.21	1.1	0.23	12.4	11.8	4.6	5.7	56.1	53.9	20.0
6H6F	0.44	2.4	0.37	22.8	26.4	8.6	5.4	61.6	71.4	23.2
6F6H	0.42	2.3	0.38	22.2	24.8	8.9	5.5	58.4	65.3	23.4
12F	0.76	3.7	0.54	31.4	42.0	12.9	4.8	58.5	78.2	24.1

<sup>a</sup> Units: 10<sup>-10</sup> cm<sup>3</sup>(STP) cm cm<sup>-2</sup> s<sup>-1</sup> cmHg<sup>-1</sup>

**Table 3** Comparison of hexafluoro substitution on three polymer types

Structure	Polymer	Permeability <sup>a</sup>			Selectivity	
		He	CO <sub>2</sub>	CH <sub>4</sub>	He/CH <sub>4</sub>	CO <sub>2</sub> /CH <sub>4</sub>
	Polycarbonate (PC)	13	6.8	0.36	35	19
	Hexafluoro-PC	60	24	1.0	57	23
	Polysulphone (PSF)	13	5.6	0.26	49	22
	Hexafluoro-PSF	33	12	1.9	63	22
	12H PEK	12	4.6	0.22	54	20
	12F PEK	42	13	0.54	78	24

<sup>a</sup> Units: 10<sup>-10</sup> cm<sup>3</sup>(STP) cm cm<sup>-2</sup> s<sup>-1</sup> cmHg<sup>-1</sup>



**Figure 3** Methane and helium permeability coefficients at 35°C versus reciprocal fractional free volume for the poly(ether ketone) polymers. The full lines represent the general band formed by a number of commercial polymers

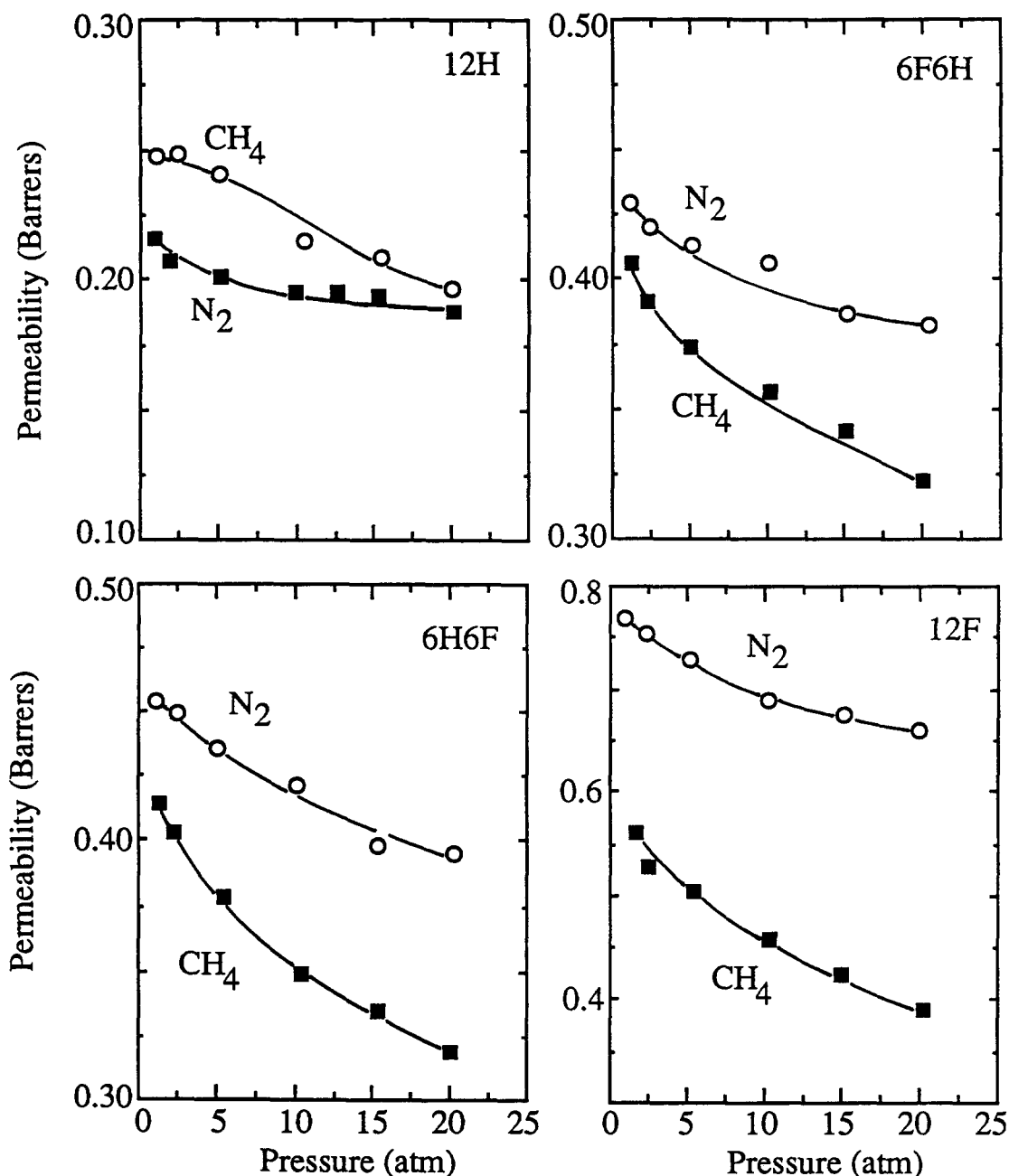


Figure 4 Nitrogen and methane permeability coefficients versus upstream driving pressure at 35°C

However, the selectivities of H<sub>2</sub> and He relative to CH<sub>4</sub> increase with increasing permeability. This has been observed when  $-\text{C}(\text{CF}_3)_2-$  groups are incorporated into polycarbonate<sup>2</sup> and polysulphone<sup>3</sup>. Table 3 compares the helium, carbon dioxide and methane permeability coefficients of polycarbonate, polysulphone and 12H PEK and their fluorinated analogues. In each polymer, substitution of the  $-\text{C}(\text{CF}_3)_2-$  group for the  $-\text{C}(\text{CH}_3)_2-$  unit results in an increase in permeability along with an increase in He/CH<sub>4</sub> selectivity. The CO<sub>2</sub>/CH<sub>4</sub> selectivity increases in two of the three cases and stays the same in the third.

Free volume has been successfully used to correlate gas permeability coefficients<sup>16,17</sup>. The full lines in Figure 3 indicate the general relation between permeability and reciprocal *FFV* for several commercial polymers, using methane and helium as examples. The circles represent the PEK polymers, which fall along the general band formed by the commercial polymers.

The nitrogen and methane permeability coefficients of the PEK polymers are shown in Figure 4 as a function of upstream driving pressure. The permeability coefficients decrease with increasing pressure as expected for glassy polymers. The amount of permeability decrease is influenced by the  $-\text{C}(\text{CF}_3)_2-$  group, with the 12F permeability decreasing the most over the 20 atm pressure interval. The hysteretic effects of carbon dioxide are shown in Figure 5. The carbon dioxide permeability decreases with increasing pressure in the pressurizing leg of the cycle. The pressure was held for 24 h to condition the polymer, and then permeability measurements were made as the pressure was stepped down from 20 atm. The carbon dioxide permeability of 12H was not changed by the 24 h conditioning period, as the depressurization and pressurization readings are the same. The permeability of the PEK polymers with a  $-\text{C}(\text{CF}_3)_2-$  group are affected by the conditioning period. The carbon dioxide permeability is higher during the depressurization

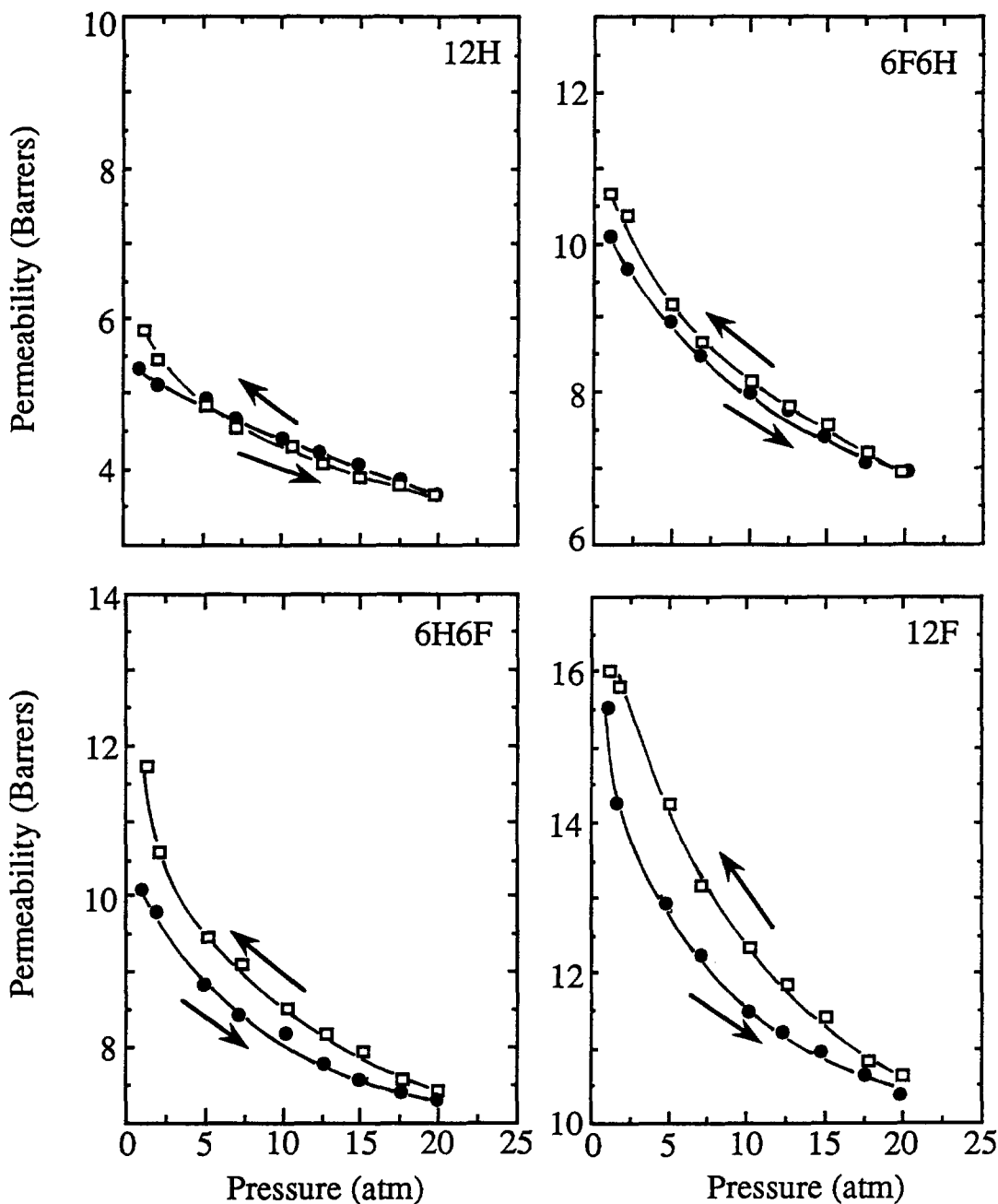


Figure 5 Pressurization and depressurization cycles showing the hysteretic response of carbon dioxide permeability in the poly(ether ketone) polymers. Full points denote data obtained while increasing the pressure; open points denote results obtained during depressurization

portion of the cycle, with the effect being the greatest in the 12F PEK.

**Sorption.** Sorption isotherms for methane and carbon dioxide at 35°C are shown in Figure 6. The solubility for each gas ranks in the order 12F > 6F6H ≈ 6H6F > 12H. The solubility levels of the 6F6H and 6H6F are identical for carbon dioxide, but the methane solubility for 6F6H is slightly higher than that for 6H6F.

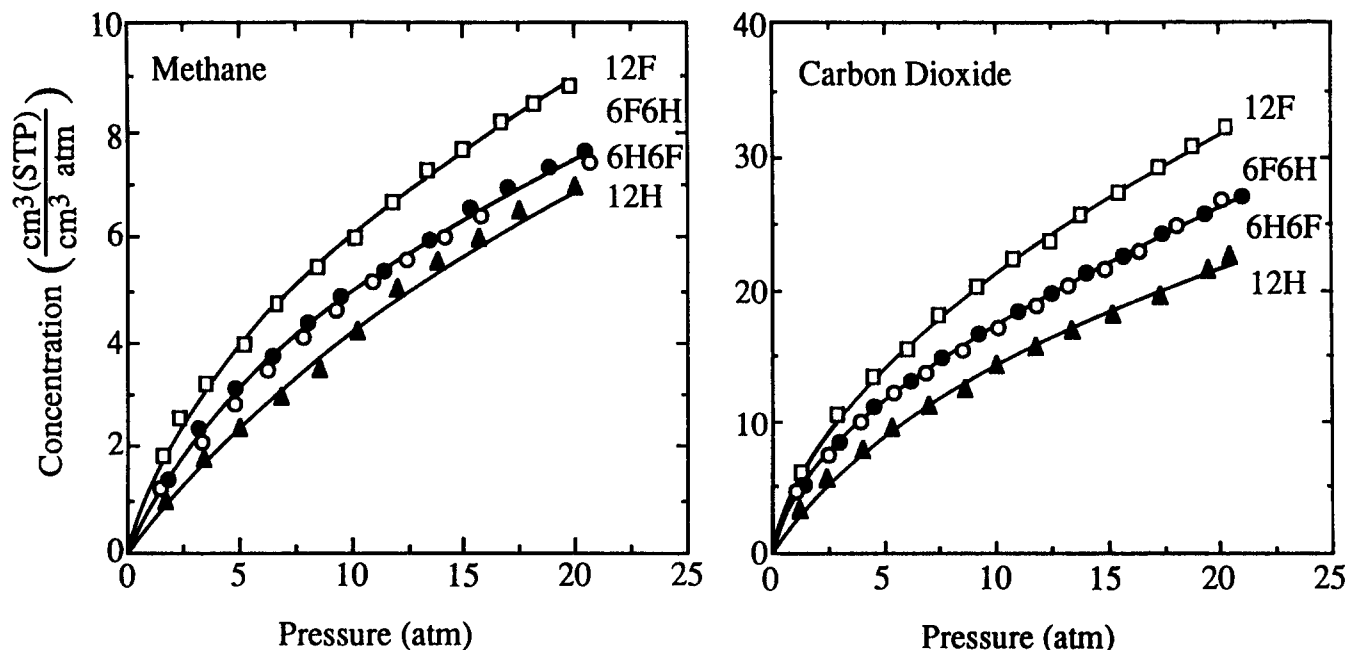
The solubility and diffusivity contributions to the permeability are given by the relation:

$$P = \bar{D} \bar{S} \quad (3)$$

where  $\bar{D}$  is a diffusion coefficient averaged across the membrane thickness, and  $\bar{S}$  is a solubility coefficient obtained from:

$$\bar{S} = C/p \quad (4)$$

where  $C$  is the concentration of gas sorbed at pressure  $p$ . The diffusion coefficient can then be calculated from independent permeation and solubility experiments. Table 4 shows the permeability, solubility and diffusion coefficients of carbon dioxide in the PEK polymers. The solubilities of both carbon dioxide and methane increase as  $-\text{C}(\text{CH}_3)_2-$  units are replaced by  $-\text{C}(\text{CF}_3)_2-$  units. The increases for the two gases are quite similar in value, so the solubility selectivity,  $S_{\text{CO}_2}/S_{\text{CH}_4}$ , does not change very much. In general, the dominant factor in the increased permselectivity noted is the improved mobility selectivity. In addition to this, the absolute diffusion coefficient for carbon dioxide increases by nearly a factor of 2 in going from 12H to 12F. The solubility and diffusivity selectivities for carbon dioxide to methane show that this increase in diffusivity accounts for the permeability selectivity increase.



**Figure 6** Carbon dioxide and methane sorption isotherms at 35°C for the poly(ether ketone) polymers. The middle curve is for both 6F6H PEK (●) and 6H6F PEK (○)

**Table 4** Transport coefficients, solubility coefficients and ideal selectivities for CO<sub>2</sub> and CH<sub>4</sub> in poly(ether ketone) polymers at 35°C and 10 atm

Polymer	$P_{\text{CO}_2}$ (barrers)	$\frac{P_{\text{CO}_2}}{P_{\text{CH}_4}}$	$S_{\text{CO}_2}$ (cm <sup>3</sup> cm <sup>-3</sup> atm <sup>-1</sup> )	$\frac{S_{\text{CO}_2}}{S_{\text{CH}_4}}$	$D_{\text{CO}_2}$ (× 10 <sup>8</sup> cm <sup>2</sup> s <sup>-1</sup> )	$\frac{D_{\text{CO}_2}}{D_{\text{CH}_4}}$
12H	4.4	20.0	1.56	3.78	2.29	5.52
6H6F	8.0	23.2	1.70	3.52	3.58	6.55
6F6H	8.0	23.4	1.73	3.48	3.53	6.52
12F	11.5	24.1	2.12	3.60	4.11	6.70

**Table 5** Dual-mode sorption parameters for carbon dioxide in the poly(ether ketone) polymers at 35°C

Polymer	$k_D$ (cm <sup>3</sup> (STP) cm <sup>-3</sup> (polymer) atm <sup>-1</sup> )	$C'_H$ (cm <sup>3</sup> (STP) cm <sup>-3</sup> (polymer))	$b$ (atm <sup>-1</sup> )
12H	0.700	9.22	0.305
6H6F	0.840	10.90	0.373
6F6H	0.756	12.70	0.331
12F	0.970	14.32	0.381

The dual-mode sorption model<sup>18,19</sup> assumes that there are two distinct mechanisms by which glassy polymers sorb gas molecules, a Henry's law mode and a Langmuir mode. The resulting model is of the form:

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

where  $k_D$  is the Henry's law coefficient, and  $C'_H$  and  $b$  are the saturation capacity and the hole affinity constant for the Langmuir mode, respectively. The carbon dioxide sorption isotherms in Figure 6 were fitted to the dual-mode model using a Marquardt least-squares statistical analysis program. The resulting parameters are listed in Table 5.

## CONCLUSIONS

The gas transport and sorption properties for a series of poly(ether ketones), where the two  $-\text{C}(\text{CH}_3)_2-$  groups in the repeat unit of the base polymer were systematically replaced with  $-\text{C}(\text{CF}_3)_2-$  units, have been described. The substitution of  $-\text{C}(\text{CF}_3)_2-$  for  $-\text{C}(\text{CH}_3)_2-$  units results in a stiffer polymer chain, as evidenced by the increase in glass transition temperature, and also opens up the polymer structure, resulting in a higher free volume. The latter leads to higher diffusion and permeability coefficients for gases. This substitution also increases the level of gas solubility, which may reflect simply the higher free volume but may also reflect a more attractive interaction of the gas molecules with  $-\text{C}(\text{CF}_3)_2-$  units relative to  $-\text{C}(\text{CH}_3)_2-$  units. Any interaction effect that exists must be relatively non-specific since the solubility coefficients change by nearly the same amount for all gases. The free-volume effect does, however, enhance the rate of diffusion of some gas molecules more than others, which results in greater permselectivity. The simultaneous increase in permselectivity and permeability is especially attractive for membrane separation processes. Similar trends were recently found when  $-\text{C}(\text{CH}_3)_2-$  groups in polycarbonates and polysulphones were replaced with  $-\text{C}(\text{CF}_3)_2-$  units. Thus, this trend seems general for a number of polymer types. The magnitude of the change in transport properties seems to be related

to the relative fraction that the  $-\text{C}(\text{CH}_3)_2-$  unit contributes to the repeat unit of the polymer.

#### ACKNOWLEDGEMENTS

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