Gas Transport in Halogen-Containing Aromatic Polycarbonates

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SYNOPSIS

The gas permeability and permselectivity of a series of halogen-containing polycarbonates are discussed in terms of the fundamental solubility and diffusivity factors. These materials have structural features that hinder interchain packing and intrachain rotational mobility. Both diffusion and solubility coefficients are higher in materials with higher fractional free volumes. Diffusivity selectivities tend to increase with increasing restriction of intrachain torsional mobility. The materials with four bromine atoms substituted on the phenyl rings ortho to the carbonate linkages display a significantly increased diffusivity selectivity relative to conventional polycarbonate. This improvement in the ability of the polymer matrix to discriminate between gas molecules of different sizes is due to a reduction in intrachain torsional mobility. The reduction in chain mobility is indicated by higher glass transition and higher sub-T_g transition temperatures in the bromine-substituted materials. The materials with hexafluoroisopropylidene moieties have high fractional free volumes and exhibit a very significant increase in permeability relative to conventional bisphenol-A polycarbonate. The material with both the hexafluoro and the tetrabromo substitutions displays significant *simultaneous* increases in permeability and permselectivity relative to conventional polycarbonate.

INTRODUCTION

In recent years, studies of the relationships between polymer structures and transport properties have led to significant improvements in the intrinsic separation performance of membrane materials and in the understanding of polymer barrier properties. Progress was made due to studies of the effects of varying the monomer structure within various classes of polymers.[1-3] Typically, a trade-off exists between gas permeability and permselectivity in common engineering resins. However, systematic variations of the monomer chemical structure have been used to achieve simultaneous increases in permeability and permselectivity in polyimides[4] and polycarbonates.[5,6] The present report examines the effects on the permeability and selectivity caused by substituting fluorine and bromine atoms in the repeat unit of bisphenol-A polycarbonate. The fundamental solubility and diffusivity terms that compose the permeability and permselectivity are identified.

The key index of the productivity of a membrane material is the permeability coefficient, P. The permeability of a gaseous penetrant can be written as a simple product of a concentration-averaged diffusivity coefficient, D, and an effective solubility coefficient, S, for the penetrant in the polymer matrix[7-9]:

$$P = DS \qquad (1)$$

For conditions of zero downstream pressure, as in this study, the solubility coefficient, S, is equivalent to the secant slope of the gas sorption isotherm evaluated at the upstream conditions. The average diffusivity, D, provides a measure of the effective

mobility of the penetrant in the polymer matrix between the conditions at the upstream and downstream sides of the film.

The second key index of the performance of a membrane material is the separation factor, or permselectivity, $\alpha_{A/B}$. When the downstream pressure is negligible, $\alpha_{A/B}$ is rigorously equal to the ideal separation factor, $\alpha_{A/B}^*$. In the absence of plasticizing responses due to strong gas–polymer interactions, $\alpha_{A/B}^*$ is approximately equal to the ratio of permeabilities for pure gases A and B[10]:

$$\alpha_{A/B}^* = \frac{P_A}{P_B} \qquad (2)$$

If eq. (1) is substituted into eq. (2), the ideal separation factor can be factored into two parts:

$$\alpha_{A/B}^* = \left[\frac{D_A}{D_B}\right] \left[\frac{S_A}{S_B}\right] \qquad (3)$$

where D_A/D_B is the diffusivity selectivity and S_A/S_B is the solubility selectivity. The solubility selectivity is determined by the differences in condensibility of the two penetrants and by their interactions with the membrane material. The diffusivity selectivity is based on the inherent ability of the polymer matrix to function as a size- and shape-selective medium through segmental mobility and intersegmental packing factors.

Free volume concepts, which describe the transport of gases in rubbery materials, can provide some qualitative insights into the transport of gases in glassy materials.[11-13] The basic idea behind free volume theories is that the mobilities of the polymer segments and the penetrant molecules in a polymer–penetrant mixture are primarily determined by the amount of so-called free volume in the system. As originally proposed by Fujita,[14]

$$\mathcal{M}_A = A_d \exp[-B_d/V_f] \qquad (4)$$

where $\mathcal{M}_A$ is the mobility of the penetrant, V_f is the average fractional free volume of the system, and A_d and B_d are empirical free volume parameters that are assumed independent of penetrant concentration and temperature. The parameter A_d depends on the size and kinetic velocity of the penetrant. The parameter B_d is equivalent to the critical hole free volume necessary for a penetrant to make a diffusive jump.[15] The free volume approach is simple and has evolved through the work of Stern et al.[16,17] and Duda and Vrentas[18] into several readily useful forms for

rubbery polymers. This theory predicts that the logarithm of the gas diffusion coefficients should decrease linearly as the inverse of the polymer's fractional free volume increases. Such correlations work well when comparing similar polymers such as the family of polycarbonates presented in this paper. Salame[19] used free volume concepts in developing a permachor technique for correlating the permeabilities of many common polymers with their chemical structure. The effectiveness of the theory is limited in predicting permeability characteristics of polymers with structures that differ significantly from those used in developing the correlation.[20]

Although the free volume concepts are often useful in correlating diffusion coefficients, it has long been known that polymer segmental mobility is also a crucial factor in gas diffusion.[21,22] In glassy polymers, the intramolecular backbone motions occurring over time scales of seconds or microseconds are believed to be primarily torsional oscillations.[23] The ability of polymer segments to move cooperatively to produce a decreased local density ("gap") allows the diffusive jump of a penetrant molecule to occur. If the available gap is larger than the critical dimension of a penetrant, a diffusional step can be taken. If the available gap is too small, a jump is precluded. It is intuitively reasonable to expect that factors which tend to reduce this chain mobility will result in lowering of a penetrant's diffusivity. Our studies have indicated that the degree of chain mobility of polymer segments is also important in determining the diffusivity selectivity of one penetrant relative to another. Materials that have substitutions hindering torsional motion seem to have a narrower distribution of transient gap sizes. Consequently, more rigid, less mobile polymer matrices appear to provide a more selective environment for separating molecules on the basis of their relative sizes.

EXPERIMENTAL

The structures of the polycarbonates studied here are shown in Figure 1. The tetrabromopolycarbonate (TBPC), tetrabromohexafluorobisphenol-A polycarbonate (TBHFPC), and the tetrabromo/tetrabromohexafluorobisphenol-A copolycarbonate (TB/TBHF) samples were synthesized by the authors. The data for conventional bisphenol-A polycarbonate (PC), tetramethylbisphenol-A polycarbonate (TMPC), hexafluorobisphenol-A polycarbonate (HFPC), and tetramethylhexafluorobisphenol-A polycarbonate (TMHFPC) are taken from our earlier paper[6] and are listed for comparison.
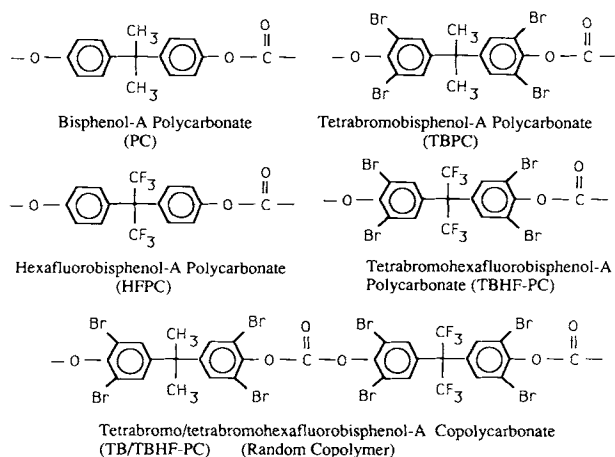
Polycarbonate Structures

Figure 1 Polycarbonate structures. The PC was supplied by GE and HFPC was supplied by Dow. The bromine-containing polycarbonates were synthesized by the authors.

Synthesis

Bisphenol-A and hexafluorobisphenol-A were allowed to react with bromine to produce the tetrabromobisphenol-A and tetrabromohexafluorobisphenol-A monomers according to literature procedures.[24,25] The bisphenols were purified by recrystallization from methanol/water. The melting points of the tetrabromobisphenol-A and the tetrabromohexafluorobisphenol-A were found to be 179–181°C and 257–259°C, respectively. The bisphenol monomers were allowed to condense with phosgene to produce the polycarbonates using an interfacial polymerization technique.[26] Interfacial synthesis methods have been reviewed by Millich and Carraher.[27] We used methylene chloride as the organic phase and triethylamine as the phase transfer catalyst. Triphosgene [32315-10-9] from Aldrich Chemical dissolved in methylene chloride was found to be a suitable substitute for phosgene in the TBHF phosgenation. The use of triphosgene has safety advantages in that it avoids the need to handle the

highly toxic gas. The TB/TBHF copolymer was synthesized using 50 mol % of each monomer. Elemental analysis of the resulting polymer (Table I) indicated that a 50/50 mol % copolymer was obtained.

Characterizations

Material characterizations relevant to studies of gas transport are listed in Table II. The data were taken on films cast from methylene chloride solutions. The films were slightly cloudy; however, no crystallinity was evident from differential scanning calorimetry (DSC) up to the degradation temperatures of the materials. Furthermore, the WAXD scans did not indicate crystallinity in the cloudy films either. The glass transition temperatures (T_g) were measured using a Perkin-Elmer DSC7 at 20°C per minute. The sub-T_g transition (T_γ) data were taken using a Rheovibron dynamic mechanical analyzer at 110 Hz. The densities of TBHFPC and TB/TBHF-co-PC were measured with a water pycnometer.

The permeabilities and solubilities of helium, nitrogen, oxygen, methane, and carbon dioxide were measured in the various polycarbonates. The data were taken using the standard permeation and sorption techniques employed in our labs.[28] The gases used in the study were Linde UHP and Big 3 Industries chromatographic grades with purities of 99.97% and higher. Only pure gas permeation results were measured; however, previous studies suggest that mixed gas results will be comparable for the O_2/N_2 gas pair and for the CO_2/CH_4 pair until plasticization occurs.[29] The downstream pressure was always 10 Torr or less. Pure gas sorption measurements were carried out with helium, oxygen, nitrogen, methane, and carbon dioxide. The measurements were made with a pressure decay sorption cell as described previously.[30,31]

As Sheu et al.[32] and Hellums et al.[6,29] have noted, the fractional free volume, V_f, is a useful method for estimating the extent of "openness" of a material for gas permeation. The fractional free volume is

Table I Elemental Analysis of Bromine-Containing Polycarbonates

Polymer	Wt % Bromine		Wt % Fluorine	
	Measured	Theoretical	Measured	Theoretical
TBHFPC	46.6	47.15	16.82	16.81
TB/TBHFPC (50/50 mol %)	50.39	49.64	9.23	8.85

Table II Polycarbonate Characterizations

Polymer	T_g (°C)	T_γ at 110 Hz (°C)	Density (g/cc)	Fractional Free Volume (V_f)
PC	150	−70	1.200	0.164
HFPC	176	−70	1.478	0.196
TMPC	193	111[a]	1.083	0.180
TMHFPC	208	107	1.286	0.216
TBPC	263	160	1.953	0.133
	(Ref. 5)		(Ref. 5)	
TBHFPC	255	165	1.987	0.200
TB/TBHF-co-PC (50/50)	252		1.973	0.166

[a] Extrapolated to 110 Hz from $T_\gamma = 50°C$ at 1 Hz using activation energy of 19 kcal/mol (Ref. 29).

the ratio of the estimated specific free volume and the polymer specific volume measured at 35°C:

$$V_f = \frac{V - V_0}{V} \qquad (5)$$

where V is the inverse of the measured polymer density and V_0 is the polymer occupied specific volume. The occupied specific volumes were estimated by the method of Lee[33] using the group contribution correlation of Van Krevelen and Hoftyzer[34] for calculation of van der Waals volumes. The fractional free volume, a purely volumetric quantity, is not distorted by the varying molecular masses of the substituent atoms as are the density and specific free volume. The fractional free volumes are, of course, dependent upon the occupied volumes assigned to the constituent moieties composing the polymer.

The tetramethyl, tetrabromo, and hexafluoro substitutions all cause the glass transition temperature to increase, indicating a stiffening of the substituted chains. The increases in the T_γ are even more dramatic. The T_γ measured at 110 Hz increases

by 180°C, comparing the tetramethyl-substituted materials (TMPC and TMHFPC) to the two materials with no substitution on the phenyl rings (PC and HFPC). Note that TMHFPC is like the TBHFPC in Figure 1 with the bromine atoms replaced by methyl groups. The T_γ increases by an additional 50°C in the tetrabromo-substituted materials relative to the tetramethyl-substituted materials. The increases in the T_γ are believed to be due to steric hindrance to chain torsional mobility caused by the large groups substituted on the phenyl rings ortho to the carbonate groups.

Spectroscopic studies of polycarbonates suggest that T_γ is the temperature at which small-scale rocking motions occur about the flexible carbonate linkages at the frequency of the test.[35–38] Therefore, the T_γ is a qualitative measure of the degree of chain torsional mobility in the polycarbonate family. The bulky methyl groups and bromine atoms sterically hinder this torsional mobility. The bromine atoms are larger than the methyl groups and appear to produce even more steric hindrance to torsional mobility. The phenyl ring substitutions tend to lock the polymer chains into fixed conformations, thereby

Table III Permeabilities, Solubilities, and Diffusivities of CO_2 and CH_4 at 35°C and 10 atm[a]

Polymer	P_{CO_2} (Barrers)	$\dfrac{P_{CO_2}}{P_{CH_4}}$	S_{CO_2} (cc STP/cc atm)	$\dfrac{S_{CO_2}}{S_{CH_4}}$	D_{CO_2} (10^{-8} cm²/s)	$\dfrac{D_{CO_2}}{D_{CH_4}}$
PC[b]	6.8	19	1.6	4.0	3.2	4.7
HFPC[b]	24	23	2.7	3.9	6.7	5.9
TBPC	4.2[c]	34[c]	2.6	2.8	1.2	12.2
TBHFPC	32	36	3.9	3.1	6.4	11.7
TB/TBHF-co-PC (50/50)	16	34	3.1	2.8	4.1	12.1

[a] P = permeability coefficient; S = solubility coefficient; D = diffusivity coefficient; Barrer = 10^{-10} cc STP cm/(cm² s cmHg); D = 0.76 × (P/S).

[b] PC and HFPC data of Ref. 4.

[c] Selected TBPC data from Ref. 5.

Table IV   Permeabilities, Solubilities, and Diffusivities of He and CH_4 at 35°C and 10 atm[a]

Polymer	P_{He} (Barrers)	$\dfrac{P_{He}}{P_{CH_4}}$	S_{He} (cc STP/cc atm)	$\dfrac{S_{He}}{S_{CH_4}}$	D_{He} (10^{-8} cm^2/ s)	$\dfrac{D_{He}}{D_{CH_4}}$
PC[b]	13	35	0.019	0.047	500	750
HFPC[b]	60	57	0.042	0.060	1100	940
TBPC	18[c]	140[c]	0.047	0.049	290	2800
TBHFPC	100	112	0.068	0.055	1100	2000
TB/TBHF-co PC (50/50)	49	110	0.049	0.044	770	2400

[a]-[c] See footnotes to Table III.

providing a more selective environment for separating gas molecules of different size and shape. This is indicated by the fact that the diffusivity selectivities are highest in the tetrabromo-substituted materials followed by the tetramethyl-substituted materials (see Tables III–V). Finally, the materials with no substitution on the phenyl rings have the lowest diffusivity selectivities.

RESULTS AND DISCUSSION

Overview of Permeability and Solubility Data

The permeability, solubility, and diffusivity coefficients measured for several gases in the polycarbonates are summarized in Tables III–V. The permeabilities are tabulated in Barrers $= 10^{-10}$ cm^3 (STP) cm/(cm^2 s cmHg). Conversion factors to many other permeability units have been tabulated in the literature.[39] The dominant effect of the tetrabromo substitution is to increase permselectivity, whereas the largest effect of the hexafluoro substitution is to increase permeability. Combining these substitutions in the TBHFPC produces a material with excellent combinations of permeability and permselectivity. For example, the TBHFPC has both the

highest permeability and the highest permselectivity for the CO_2/CH_4 pair in this homologous series of polymers.

The rigid substituted polycarbonates exhibit higher permeabilities relative to PC due to both diffusivity and solubility factors. The higher permeabilities of helium and CO_2 are largely due to higher diffusion coefficients. Interestingly, the higher permeabilities of oxygen are actually caused as much by increases in solubility as by increases in diffusivity. The changes in permselectivity from the fluorine or bromine substitutions are all strongly dominated by variations in the diffusivity selectivity. The variation in solubility selectivities is fairly small in this series of materials because the trifluoromethyl groups and the bromine atoms do not produce strong physical interactions with any of the gases studied. The higher sorption levels in the substituted polycarbonates relative to PC primarily reflect the increased free space in the materials, which makes it energetically easier to accommodate a sorbed penetrant. The sorption isotherms for several gases in the polycarbonates are shown in Figures 2–6. These data were used to calculate the solubility and diffusion coefficients in Tables III–V.

Figure 7 shows the data for some of the substituted polycarbonates compared to the O_2/N_2 per-

Table V   Permeabilities, Solubilities, and Diffusivities of O_2 and N_2 at 35°C and 2 atm[a]

Polymer	P_{O_2} (Barrers)	$\dfrac{P_{O_2}}{P_{N_2}}$	S_{O_2} (cc STP/cc atm)	$\dfrac{S_{O_2}}{S_{N_2}}$	D_{O_2} (10^{-8} cm^2/s)	$\dfrac{D_{O_2}}{D_{N_2}}$
PC[b]	1.6	4.8	0.21	1.5	5.8	3.2
HFPC[b]	6.9	4.1	0.47	1.3	11.0	3.2
TBPC	1.5[c]	7.4[c]	0.54	1.5	2.1	4.9
TBHFPC	9.7	5.4	0.80	1.3	9.2	4.2
TB/TBHF-co-PC (50/50)	4.9	6.2	0.78	1.5	4.8	4.2

[a]-[c] See footnotes to Table III.
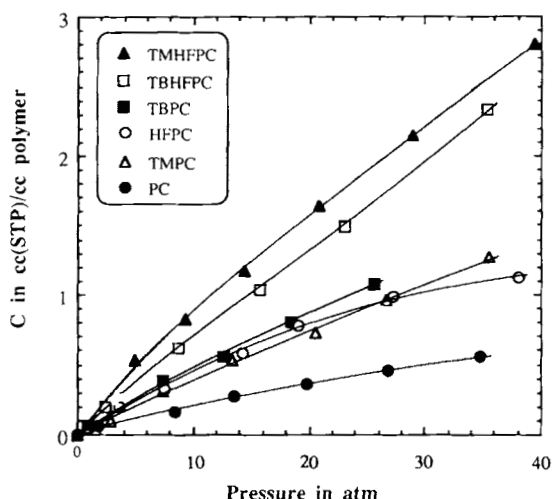
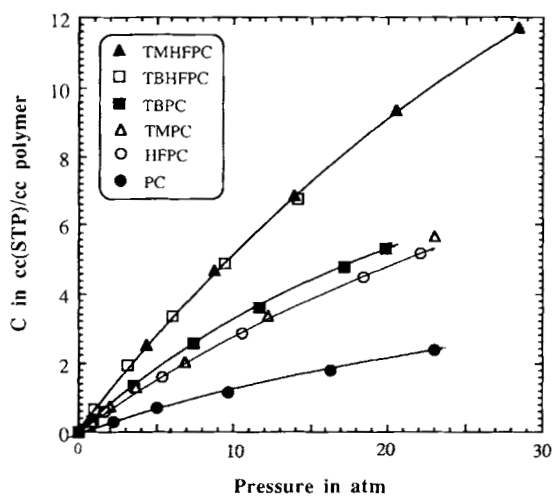**Figure 2** Sorption isotherms for helium in the polycarbonates of Figure 1.

Figure 4 Sorption isotherms for oxygen in the polycarbonates of Figure 1.
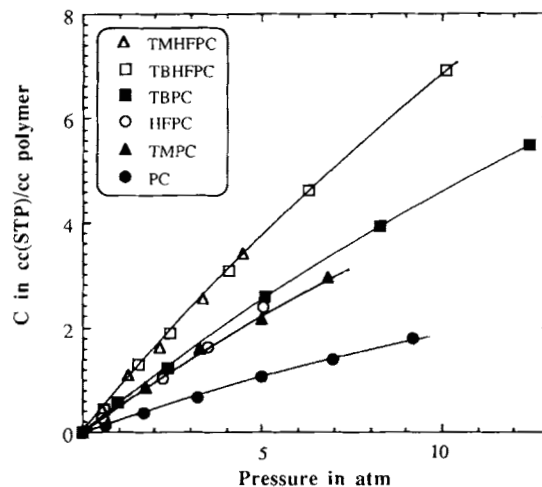
meability versus permselectivity data for several common glassy polymers taken from the literature.[40] Combining both the tetrabromo and the hexafluoro substitutions in one material (TBHFPC) produces a high flux (9.8 Barrers) and a good permselectivity ($\alpha_{O_2/N_2} = 5.4$) relative to these typical glassy polymers. The data for TBPC, TBHFPC, TB/TBHFPC, and TMHFPC lie in the high-flux, high-permeability portion of the graph.

Hexafluoro Substitution

The hexafluoro substitution produces significant increases in permeability in comparisons between

HFPC and PC or TBHFPC and TBPC. We reported previously a similar dramatic increase in permeability in comparing TMHFPC to TMPC.[6,26] These effects are due to the bulky fluorine atoms inhibiting the chain packing directly and, indirectly, by restricting the angular relationships permitted between the phenyl rings. The high permeabilities in the fluorine-containing polycarbonates occur due to their higher fractional free volume that causes both the gas solubilities and the gas diffusivities to increase.

The pure gas permselectivity is also higher in the hexafluoro-substituted materials for the CO_2/CH_4 gas pair in comparing HFPC to PC and TBHFPC

Figure 3 Sorption isotherms for nitrogen in the polycarbonates of Figure 1.
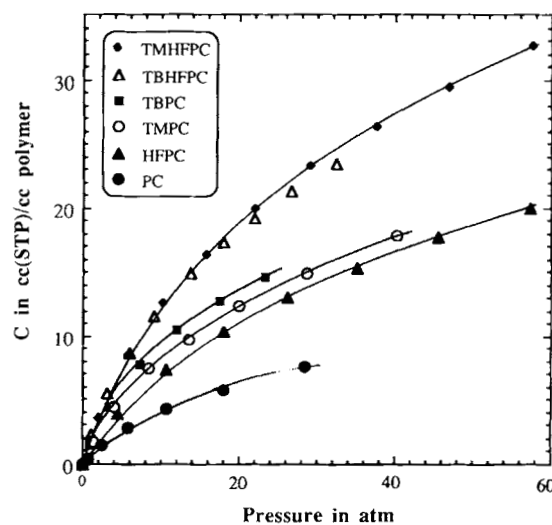
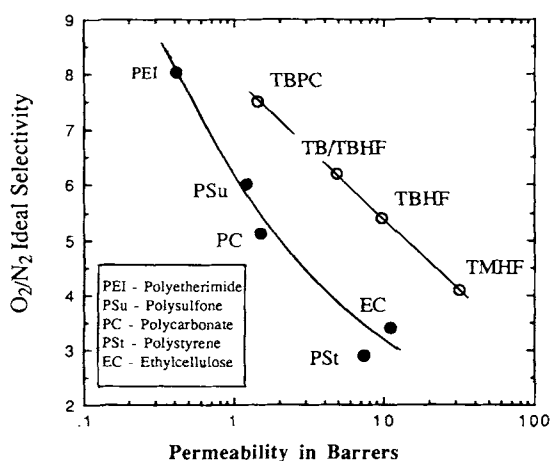**Figure 5** Sorption isotherms for methane in the polycarbonates of Figure 1.
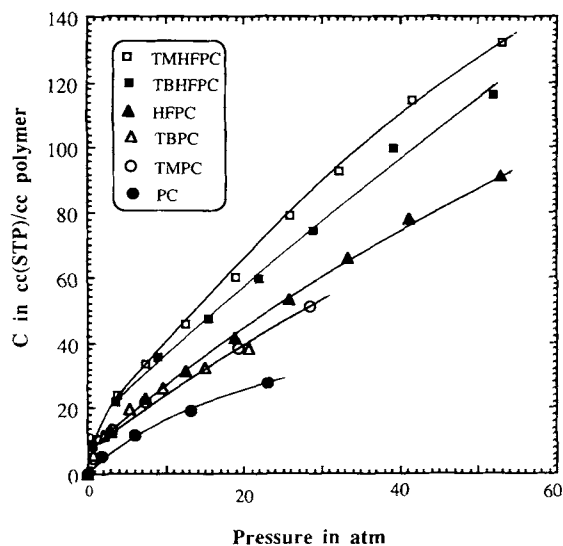
Figure 6 Sorption isotherms for carbon dioxide in the polycarbonates of Figure 1.

to TBPC. However, the large increase in permeability from the hexafluoro substitution comes with a noticeable decrease in permselectivity for the O_2/N_2 pair. This reflects the inherent difficulty in simultaneously increasing O_2 diffusivity and O_2/N_2 diffusivity selectivity because of the small difference in the molecular sizes of O_2 and N_2 (0.2 Å) as compared to CH_4 and CO_2 (0.5 Å).

The permeability isotherms for CO_2 and CH_4 are shown in Figures 8 and 9. The CO_2 solubility of the fluorine-containing polycarbonates was found to be

quite high. This leads to the plasticization behavior shown by the increase in the permeability at higher pressures in Figure 10. We previously described the plasticization behaviors that begin to occur in PC, TMPC, HFPC, and TMHFPC as the local concentration reaches 35 ± 2 cc (STP)/cc polymer.[41] Consequently, it is possible that the TBHF bisphenol-A-derived materials may be subject to plasticization by CO_2 at relatively low pressures (approx. 15 atm) as was shown to be the case for TMHF-PC.[26]

Tetrabromo Substitution

As reported by Muruganandam et al.[5] and by Dow Chemical researchers,[42] TBPC has a very high permselectivity for O_2/N_2 ($\alpha_{O_2/N_2} = 7.5$) relative to PC and relative to other glassy polymers. The tetrabromo substitution also produces a significant increase in permselectivity in comparing TBHFPC to HFPC. The major increase in the permselectivity is in the diffusivity selectivity term (see Tables III–V). It is believed that this is due to steric inhibition to rotation about the flexible carbonate linkages caused by the bromine atoms, thereby reducing the size and frequency of opening of transient gaps in the polymer matrix. This effect serves to improve the discrimination between gas molecules on the basis of size and shape. The diffusivity selectivities for the brominated materials are also significantly higher than those reported previously for the tetramethyl-substituted materials.[5,6]
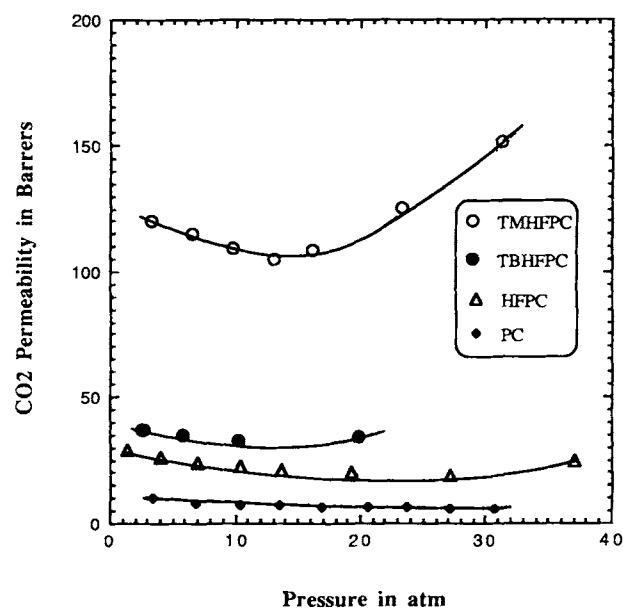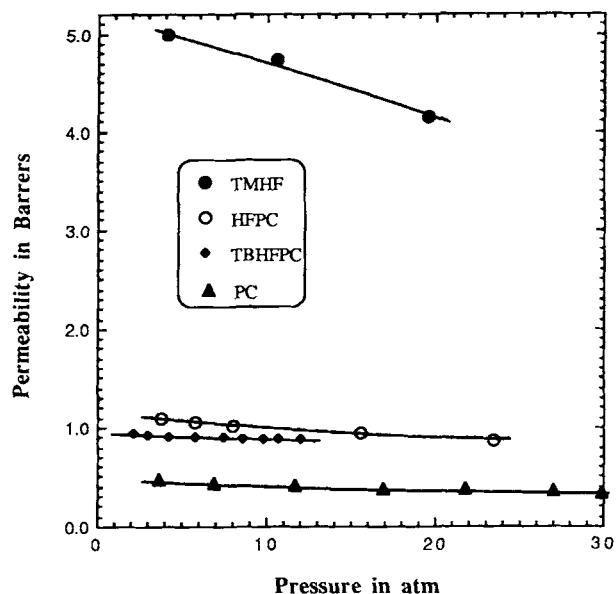

Figure 7 Permselectivity for oxygen over nitrogen vs. permeability for a variety of glassy polymers. Several of the halogen-containing polycarbonates offer an advantageous trade-off of the two properties relative to the typical glasses.

Figure 8 Permeability isotherms for carbon dioxide in the halogen-containing polycarbonates of Figure 1.

Figure 9 Permeability isotherms for methane in the halogen-containing polycarbonates of Figure 1.

It is interesting that the TBHFPC has a higher permeability for all gases than does HFPC. This was not the trend observed in Muruganandam et al.'s comparison of TBPC to PC. Their study showed that TBPC typically has lower permeabilities than does PC (helium is the lone exception). Muruganandam et al. proposed that polar attractions between bromine atoms of neighboring chains may tend to close down the matrix and reduce interchain spacings. Indeed, our calculations show that TBPC has a very low fractional free volume relative to the other polycarbonates. By contrast, the TBHFPC is very open according to the fractional free volume calculations. The bromine atoms in TBHFPC may be separated sufficiently to render the bromine–bromine attractive forces less significant.

Mixtures of the TBPC and TBHF–PC were found to be immiscible. The copolymer was synthesized, however, to demonstrate how membrane material properties can be adjusted between the properties of the two homopolymers. The copolymer transport properties generally lie between those of the homopolymers, as expected. The TB/TBHF copolycarbonate also has an attractive combination of permeability (4.9 Barrers for O_2) and permselectivity ($\alpha_{O_2/N_2} = 6.2$) for O_2/N_2.

Free Volume Comparisons

As shown in Figures 10 and 11, we have found that gas permeabilities and diffusivities tend to increase
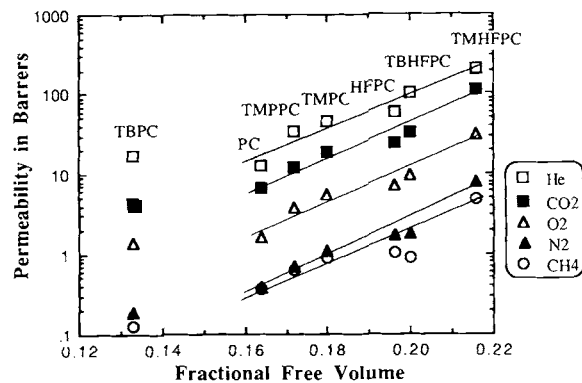
Figure 10 Permeability vs. fractional free volume in polycarbonates.

as the polymer fractional free volume increases. The diffusion coefficients are plotted vs. the inverse of the fractional free volume according to the free volume theory. The permeability coefficients are highest for helium followed by carbon dioxide, oxygen, nitrogen, and methane. The diffusion coefficients follow the same order with one exception. The diffusion coefficients of oxygen are higher than CO_2 in each of the materials. The very high solubility of CO_2 causes the permeabilities ($P = D \times S$) of CO_2 to be higher than those of oxygen.

Both the diffusivity and solubility coefficients are higher in the more "open" materials with higher fractional free volumes. The increases in solubility and diffusivity resulting from the hexafluoro substitution can be unambiguously explained using free volume arguments. Additional arguments are needed to explain the bromine-containing materials. The tetrabromo substitution reduced the fractional free volume in TBPC (compared to PC), but increased the fractional free volume in TBHFPC (compared
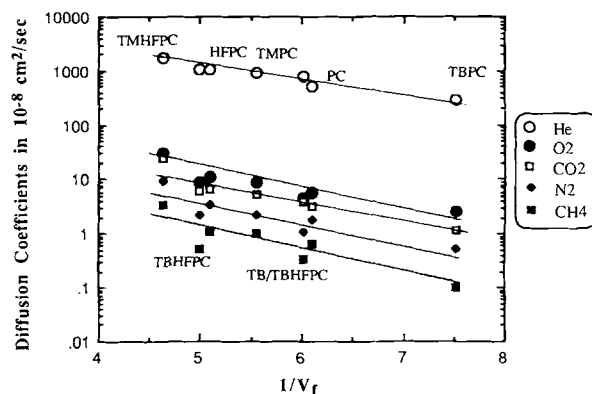
Figure 11 Gas diffusion coefficients vs. inverse fractional free volume.

to HFPC). In either case, the tetrabromo substitution causes gas diffusion coefficients to decrease, but gas solubility coefficients to increase. The decrease in diffusion coefficients is expected due to the polymer chain mobility effects discussed above. The decrease in diffusion coefficients is much greater in TBPC (compared to PC) than in TBHFPC (compared to HFPC) due to the low fractional free volume in TBPC.

The TBPC data fit the permeability vs. the fractional free volume correlation (Fig. 6) less well than do the other materials as the permeability of He, CO_2, and O_2 are higher than the correlation would predict. These relatively high permeabilities in TBPC result from surprisingly high gas solubilities. The solubilities in TBPC are nearly as high as in the much more open HFPC (see Figs. 2-6). Consequently, the gas diffusivity vs. the inverse fractional free volume plot (Fig. 7) according to the free volume theory produces a more consistent correlation.

Muruganandam[43] observed similar high gas solubilities in tetrachloropolycarbonate, which has approximately the same fractional free volume as does TBPC. However, the high gas solubilities in TBPC cannot be explained from free volume arguments. In fact, the solubility should be significantly lower in TBPC if free volume was the only factor contributing to the solubilities in the material. Physical interactions appear to be the most likely additional factor at play. It is possible that the large and polarizable bromine atoms increase the physical interactions between the polymer and the gas molecules, thereby leading to the relatively high gas solubilities in TBPC.

CONCLUSIONS

The data on the halogen-containing polycarbonates have added additional support to the hypothesis that simultaneous inhibition of chain packing and restriction of intrachain torsional mobility can lead to improved gas separation membrane performance. Substantial increases in permeability and permselectivity have been simultaneously achieved relative to unsubstituted PC. We have again observed[4,6] that substitutions that inhibit rotational mobility serve to improve membrane selectivity even when these substitutions substantially increase the permeability by increasing the average distance between polymer chains. The ability of the material to discriminate between gas molecules of different sizes can be improved *simultaneously* with significant increases in permeability.

We have noted that substitutions that increase the fractional free volume of the polymer tend to increase the gas permeability. We also have noted that polycarbonate materials with higher sub-T_g transition temperatures measured by dynamic mechanical spectroscopy tend to have higher diffusivity selectivity. Thus, relationships between dynamic mechanical properties and transport properties appear to be emerging within this group of materials with similar structures.

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