Gas Transport Properties of Biphenol Polysulfones

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ABSTRACT: Gas sorption and transport properties at 35 °C are reported for the polysulfone based on 4,4′-biphenol (BIPSF) and corresponding polysulfones with methyl ring substitutions, tetramethylbiphenol polysulfone (TMBIPSF) and hexamethylbiphenol polysulfone (HMBIPSF). Comparisons are made to bisphenol A polysulfone (PSF) and tetramethylbisphenol A polysulfone (TMPSF). BIPSF and PSF have very similar transport characteristics. This is attributed to the similar packing behavior of these polymers. Tetramethyl substitution on the biphenyl rings increases permeability, while hexamethyl substitution does not lead to a comparable further increase but does enhance selectivity characteristics for certain gas pairs. Permeability values are discussed in terms of chain packing, fractional free volume, and sub-T_g relaxation behavior.

Introduction

For more than a decade, the polysulfone based on bisphenol A has been widely used to form commercial hollow-fiber membranes for gas separations. Increased performance requirements and harsher operating environments provide incentives to develop new membrane materials. This has prompted our detailed investigation of the relationships between structure and the gas transport properties of polysulfones and polycarbonates.[1-7] In general, there is a trade-off between the permeability and permselectivity of candidate membrane materials, but several examples of polymers with desirable deviations from this trade-off have been identified.[1-10] The polysulfones or polycarbonates that have these advantageous combinations of productivity and selectivity typically have either methyl- or halogen-substituted backbone phenyl rings (e.g., tetramethylbisphenol A polysulfone (TMPSF) and tetrabromobisphenol A polycarbonate (TBPC)), bulky groups connecting the phenyl rings (e.g., hexafluorobisphenol A polysulfone (HFPSF) and hexafluorobisphenol A polycarbonate (HFPC)), or both modifications. These studies show that increasing chain rigidity and decreasing chain packing is a useful strategy for designing membrane materials with improved transport characteristics.

Recent reports have described the attractive thermal and mechanical properties of the polysulfone (PSF) derived from 4,4′-biphenol.[11,12] The purpose of this work is to evaluate biphenol polysulfone (BIPSF) as a potential membrane material for gas separations. In addition, we examine the effect of adding methyl groups to the phenyl rings of the biphenol moiety on gas permeability by characterizing tetramethylbiphenol polysulfone (TMBIPSF) and hexamethylbiphenol polysulfone (HMBIPSF). The effects of interchain packing and chain mobility on transport properties are explored using a variety of experimental techniques including X-ray diffraction, differential scanning calorimetry, thermogravimetric analysis, and dynamic mechanical analysis in addition to gas permeation and sorption measurements.

Experimental Section

All of the polysulfones described here were synthesized in our laboratories via nucleophilic condensation reactions. In addition, permeation studies were made on the commercially available biphenol polysulfone, Radel R, obtained from Amoco Performance Products. Biphenol monomers from Kennedy and Klim, Inc. were reacted with bis(4-fluorophenyl) sulfone to form polysulfones by the synthesis procedure developed by Mohanty[13,14] and modified by McHattie.[4,15] Monomers were purified by sublimation and reacted with anhydrous K_2CO_3 in *N*-methylpyrrolidinone (NMP) and toluene. The reaction temperature was increased to 165 °C over 6 h as water was removed from the mixture. After 3 h, the polymerization was carried out at 175 °C for approximately 4 h. For these more reactive biphenol monomers, polymerization times were shorter than the bisphenol reaction times reported by McHattie.[1] After the polymer synthesis, special attention was given to solvent removal. The polymers were precipitated in ethanol several times and then washed by Soxhlet extraction in water and then ethanol for 3 days each. In addition, the polymers were dried at 60 °C under vacuum for 1 week. Intrinsic viscosity measurements at 25 °C are used as a relative indication of molecular weight.

Due to solubility differences among these polysulfones, slightly different solution casting procedures were employed to prepare membranes from each polymer. Of the three biphenol polymers used in this study, HMBIPSF is the most soluble; e.g., it readily dissolves in methylene chloride. TMBIPSF is soluble in chloroform. Dense films of 1–3 mils were prepared by solution casting from the appropriate solvent on glass plates. The films were dried at 60 °C for 1 week to remove the solvent. Since BIPSF is not soluble in chlorinated hydrocarbons, amorphous films were cast from NMP onto Petri dishes in an argon environment. Over the 2-week drying time, the oven temperature was slowly ramped to 240 °C to remove solvent without film damage. All polymer solutions were passed through 5-μm Teflon filters prior to casting in order to remove particulate contamination.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to ensure solvent-free films. Residual solvent can be detected using TGA by observing any weight loss at temperatures below the degradation temperature. The TGA was operated at a heating rate of 20 °C/min up to the polymer degradation temperature (T_d). A Perkin-Elmer differential scanning calorimeter, with a heating rate of 20 °C/min, was used to measure the glass transition temperature of the polymers. The T_g was calculated from the second trace using the midpoint method. Solvent contamination also can be detected by observing any difference in the measured T_g from the first and second heats. All of the polymers were found to be amorphous with no crystalline melting point.

An Imass Autovibron dynamic mechanical viscoelastomer or Rheovibron was used to measure the mechanical spectra of the polymer films at an operating frequency of 110 Hz. The temperature range was −150 to 200 °C with a heating rate of 1 °C/min. Besides the Rheovibron, a dynamic mechanical thermal analyzer (DMTA) from Polymer Laboratories was used to characterize PSF and HMBIPSF at 1 Hz with a temperature range from −150 to 300 °C.

Wide-angle X-ray diffraction measurements (WAXD) were taken at a wavelength of 1.54 Å on a Philips APD 3520 X-ray diffractometer. For these amorphous materials, there is no long-range order; thus, a broad peak characteristic of the most probable

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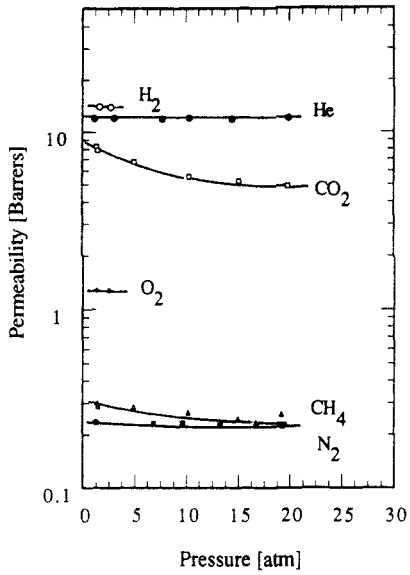


Figure 1. Pressure dependence of He, H_2, O_2, N_2, CH_4, and CO_2 permeability coefficients for BIPSF at 35 °C.

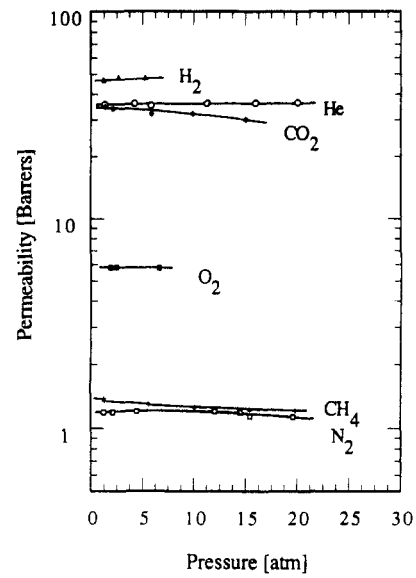


Figure 2. Pressure dependence of He, H_2, O_2, N_2, CH_4, and CO_2 permeability coefficients for TMBIPSF at 35 °C.

distances between chains was observed. The d-spacing calculated with Bragg's equation $n\lambda = 2d \sin \theta$ is an approximate, average distance between the axes of neighboring chains in the polymer matrix.

The densities of the polymers were determined by a density gradient column based on aqueous solutions of calcium nitrate at 30 °C. The measured densities were then used to calculate fractional free volumes (FFV) as described elsewhere.[1,16,17]

Pure gas permeability coefficients were measured for BIPSF, TMBIPSF, and HMBIPSF. The data for PSF and TMPSF are from McHattie[1] and are included for comparison. Permeability coefficients for six chromatographic grade gases were determined at 35 °C for pressures from 1 to 20 atm using permeation cells previously described.[18] The gases were tested in the following order: He, H_2, O_2, N_2, CH_4, and CO_2. Conditioning effects were noted by observing any change in the permeability of a gas at 1 atm after exposure to 20 atm of the same gas. Pure gas sorption isotherms were measured with pressure decay cells that have been described extensively in previous papers.[18] The sorption levels were measured from 1 to 20 atm with nitrogen, methane, and carbon dioxide.

Results

The pure gas permeability coefficients for BIPSF, TMBIPSF, and HMBIPSF are shown as a function of pressure in Figures 1–3. The permeability coefficients remain constant or decrease with pressure for all gases and polymers; no plasticization was observed at these pressures. In addition, minimal conditioning effects were noted.

The permeability and selectivity coefficients as well as polymer structures are shown in Table I. Interestingly, replacing the isopropylidene group of PSF with a single bond to give BIPSF does not significantly affect transport characteristics. In fact, the permeability and selectivity coefficients for BIPSF and PSF are virtually identical. The permeability coefficients for TMBIPSF are approximately 5 times higher than those for PSF or BIPSF, and in some cases, the permeability coefficients for TMBIPSF are even higher than those for TMPSF. As noted in previous reports,[1,5,6,9] symmetric methyl additions to the phenyl rings of polymers like polysulfones or polycarbonates increase permeability. Yet, the addition of two more methyl groups to give HMBIPSF does not lead to a comparable further increase in the permeability coefficients but does slightly enhance the selectivity characteristics for some gas pairs.

To better understand the transport through these materials, it is useful to separate the permeability coefficient into its kinetic and thermodynamic components.[6,19,20] The N_2, CH_4, and CO_2 sorption isotherms for the five polymers are shown in Figures 4–6. A comparison of these three isotherms shows that the solubility for each gas increases with methyl substitution of the polymer. The solubility coefficients listed in Tables II and III were calculated from the secant slope of these isotherms at 10 atm. The diffusion coefficients can be calculated from

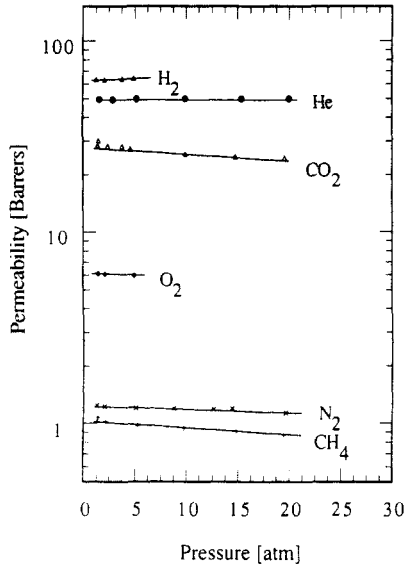
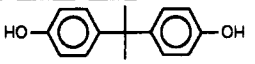
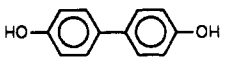
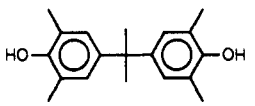
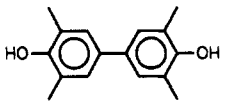
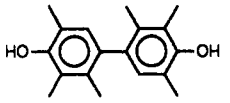


Figure 3. Pressure dependence of He, H_2, O_2, N_2, CH_4, and CO_2 permeability coefficients for HMBIPSF at 35 °C.

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

The oxygen diffusion coefficients listed in Table III were computed from transient permeation time lag data, allowing the O_2 solubility coefficients to be calculated from eq 1. The solubility and diffusion coefficients for oxygen are not listed for TMBIPSF because the film was too thin to obtain accurate time lag data. The solubility coefficients for each gas are about the same in BIPSF as in PSF. Likewise, the solubility coefficients for each gas are similar among methyl-substituted polymers but higher than for PSF and BIPSF. When there are no methyl groups on the phenyl rings, elimination of the isopropylidene group has little effect on the solubility coefficients, and consequently, the diffusion coefficients for BIPSF are about the same as that for PSF. However, both the diffusion

Table I
Permeability and Selectivity Coefficients for Methyl-Substituted Bisphenol A and Biphenol Polysulfones[a]

polymer	bisphenol monomer	P_{CO_2}[b]	$\alpha^*_{CO_2/CH_4}$[b]	P_{O_2}[c]	$\alpha^*_{O_2/N_2}$[c]	P_{He}[b]	α^*_{He/CH_4}[b]	α^*_{He/He_2}[c]
PSF[d]		5.6	22	1.4	5.6	13	49	0.93
BIPSF		5.6	22	1.3	5.5	12	47	0.86
TMPSF[d]		21	22	5.6	5.3	41	45	1.3
TMBIPSF		31.8	25	5.8	4.8	36	28	1.3
HMBIPSF		25.5	27	6.0	5.0	53	58	0.84

[a] P in barrers. Barrer = 10^{-10}[cm·cm³(STP)/cm²·s·cmHg]. [b] Data at 10 atm. [c] Data at 2 atm. [d] Data from McHattie et al.[1]

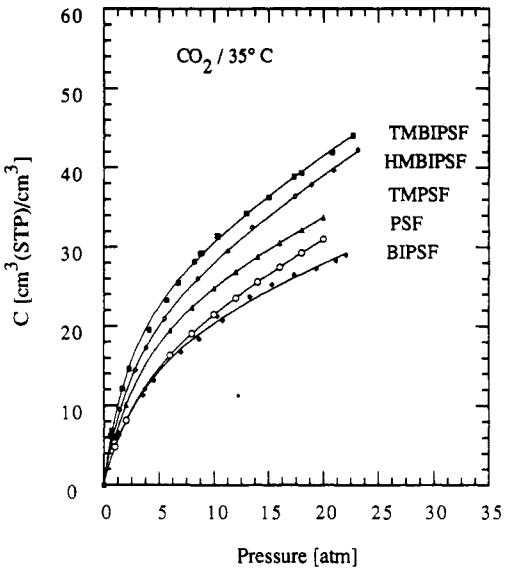


Figure 4. Sorption isotherms for CO_2 at 35 °C.

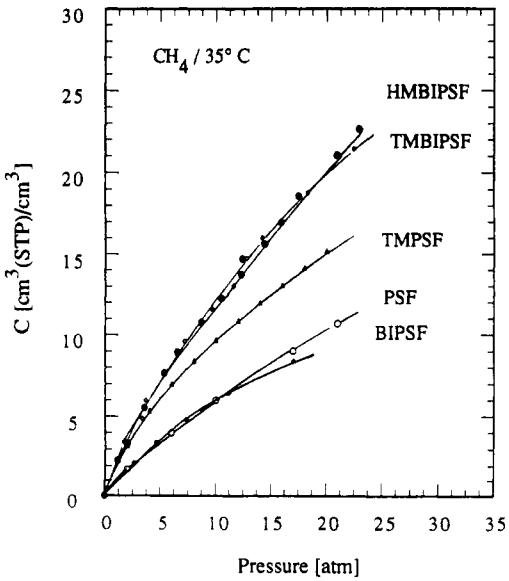


Figure 5. Sorption isotherms for CH_4 at 35 °C.

and solubility coefficients for CO_2 are about 20–25% higher for TMBIPSF than for TMPSF, which leads to substantially higher permeability coefficients when the isopropylidene unit is removed from the methyl-substituted polysulfone. The solubility and diffusivity coefficients for methane also increase with the elimination of the isopropylidene group from TMPSF; however, these increases are somewhat smaller than those for carbon dioxide, as indicated by the increase in selectivity for the CO_2/CH_4 separation. Although the permeation coefficients for carbon dioxide and methane are substantially larger in TMBIPSF than TMPSF, the oxygen permeability is only slightly larger for TMBIPSF than for TMPSF while the helium permeability is actually smaller in TMBIPSF than in TMPSF. This is probably a result of the relative solubility of these gases in the tetramethyl polysulfones. The O_2/N_2 separation factor is also smaller for TMBIPSF

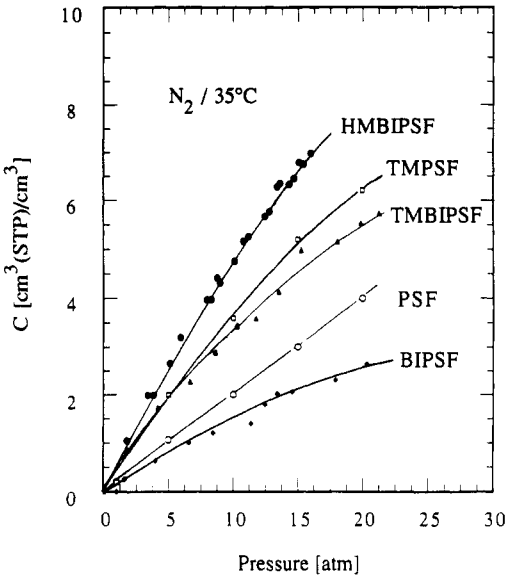


Figure 6. Sorption isotherms for N_2 at 35 °C.

Table II
Solubility and Mobility Components of CO_2/CH_4 Separation Factors[a]

polymer	P_{CO_2}	$\alpha^*_{CO_2/CH_4}$	$\bar{S}_{CO_2}$	$\bar{S}_{CO_2}/\bar{S}_{CH_4}$	$\bar{D}_{CO_2}$	$\bar{D}_{CO_2}/\bar{D}_{CH_4}$
PSF[b]	5.6	22	2.1	3.7	2.0	5.9
BIPSF	5.6	22	1.9	3.3	2.2	5.8
TMPSF[b]	21	22	2.5	2.7	6.4	8.1
TMBIPSF	31.8	25	3.0	2.6	8.1	9.1
HMBIPSF	25.5	27	2.7	2.2	7.2	12.0

[a] P, 10^{-10}[cm·cm³(STP)/cm²·s·cmHg]. S, cm³(STP)/cm³·atm. D, 10^{-8} cm²/s. Data at 10 atm and 35 °C. [b] Data from McHattie et al.[1]

Table III
Solubility and Mobility Components of O_2/N_2 Separation Factors[a]

polymer	P_{O_2}	$\alpha^*_{O_2/N_2}$	$\tilde{S}_{O_2}$	$\tilde{S}_{O_2}/\tilde{S}_{N_2}$	$\tilde{D}_{O_2}$	$\tilde{D}_{O_2}/\tilde{D}_{N_2}$
PSF[b]	1.4	5.6	0.24	1.6	4.4	3.6
BIPSF	1.3	5.5	0.25	2.0	4.0	2.7
TMPSF[b]	5.6	5.3	0.53	1.4	8.0	3.8
TMBIPSF	5.8	4.8				
HMBIPSF	6.0	5.0	0.68	1.1	7.0	3.7

[a] P, 10^{-10}[cm·cm³(STP)/cm²·s·cmHg]. S, cm³(STP)/cm³·atm. D, 10^{-8} cm²/s. Data at 2 atm and 35 °C. [b] Data from McHattie et al.[1]

Table IV
Dual-Mode Sorption and Diffusion Coefficients

polymer	gas	k_d[a]	C_H'[b]	b[c]	D_D[d]	D_H[d]
PSF[e]	N_2	0.166	0.957	0.104	1.06	0.15
	CH_4	0.257	6.58	0.0901	0.60	0.13
	CO_2	0.728	19.6	0.260	4.64	0.58
BIPSF	CH_4	0.201	7.82	0.103	1.06	0.12
	CO_2	0.475	22.4	0.228	8.35	1.07
TMPSF[e]	N_2	0.225	3.74	0.0461	2.54	1.57
	CH_4	0.460	7.26	0.233	1.22	0.16
	CO_2	0.597	26.0	0.261	22.00	1.57
TMBIPSF	N_2	0.179	4.40	0.0660	2.80	1.72
	CH_4	0.730	5.86	0.329	1.64	0.131
	CO_2	0.822	28.4	0.365	25.5	1.73
HMBIPSF	CH_4	0.735	7.43	0.267	1.17	0.171
	CO_2	0.98	23.8	0.348	23.3	1.39

[a] k_d, cm³(STP)/cm³·atm. [b] C_H', cm³(STP)/cm³. [c] b, atm⁻¹. [d] D, 10^{-8} cm²/s. [e] Data from McHattie et al.[1]

than for TMPSF, which is in contrast to the CO_2/CH_4 case. The permselectivity is factored into diffusivity and solubility selectivity terms in Tables II and III. These data show in every case that methyl substitutions increase the diffusive component while the solubility selectivity decreases. The result is that the overall permselectivity is not dramatically changed. The overall O_2/N_2 and CO_2/CH_4 separation factors are slightly higher for HMBIPSF than for TMBIPSF. This increase in permselectivity apparently stems from the high diffusivity selectivity.

The sorption and transport characteristics of these polymers are well described by the dual-mode transport model[20-22]

$$C = k_D p + [C_H' bp/(1 + bp)] \quad (2)$$

$$P = k_D D_D + [D_H C_H' b/(1 + bp_2)] \quad (3)$$

The sorption and transport parameters, obtained by fitting of the data to eq 2, are listed in Table IV. The Langmuir capacity term C_H' and the affinity parameter b are similar for PSF and BIPSF while the Henry's constant k_D is somewhat lower for BIPSF. In general, the Langmuir capacity term tends to increase with fractional free volume and T_g, thus, with increasing methyl substitutions. The Henry's law coefficient k_D increases when the number of pendant methyls is increased from four to six. However, k_D is actually lower for TMPSF than for PSF although the solubility coefficients are higher. To obtain the Henry's law and Langmuir mode diffusion coefficients D_D and D_H, the permeability data were plotted vs $1/(1 + bp_2)$, as suggested by eq 3, where p_2 is the upstream gas pressure. The results calculated from the slopes and intercepts are listed in Table IV. Figure 7 shows a plot of D_H vs D_D for CO_2 in a variety of polymers studied to date in this laboratory. The diffusion coefficients for the Langmuir population seem to be a fixed fraction (~0.078) of the coefficient for Henry's law population. As a previous study of a smaller number of polymers suggested,[23] the

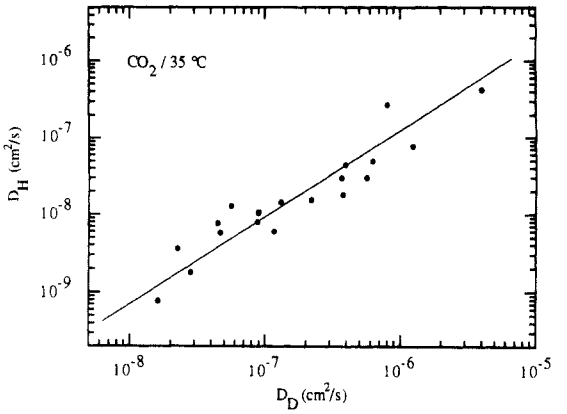


Figure 7. Plot of Langmuir mode diffusivity, D_H, vs the Henry's law mode diffusivity, D_D, for CO_2 in a wide range of glassy polymers studied in our laboratory including polysulfones, polycarbonates, and poly(phenylene oxide).

Table V
Properties of Bisphenol A and Biphenol Based Polysulfones

polymer	T_g (°C)	ρ (g/cm³)	FFV $[(V - V_o)/V]$	d-spacing (Å)	$[\eta]$[a] (dL/g)
PSF	186	1.240	0.156	4.9	0.40
BIPSF	231	1.291	0.154	4.8	0.58,[b,c] 1.8[b]
TMPSF	230	1.151	0.171	5.3	1.06
TMBIPSF	288	1.195	0.164	5.3	0.68
HMBIPSF	295	1.144	0.178	5.3	0.81

[a] In chloroform. [b] In NMP. [c] Radel R.

mobilities of the penetrant in the two sorption modes are, in general, about equally influenced by changes in polymer molecular structure. Further analysis of the sorption parameters for polysulfones is presented elsewhere.[24]

Both the X-ray d-spacing and the fractional free volume have been used to characterize the openness of the polymer structure. The fractional free volume used here was calculated from

$$\mathrm{FFV} = (V - V_o)/V \quad (4)$$

where V is the specific volume computed from the measured density and V_o is the occupied chain volume obtained using the Bondi group contribution method described elsewhere.[1,16,17,25] Several authors have obtained good correlations between these parameters and the gas permeability for various polymer structures.[1,5,25,26] Table V shows that the d-spacing of BIPSF is just slightly lower than that for PSF. The X-ray diffraction patterns for BIPSF and PSF in Figure 8 are similar; however, the peak for BIPSF is somewhat broader. While the d-spacing values indicate that the methyl-substituted polymers are more open than PSF or BIPSF, there is not enough resolution with this technique to distinguish among these three materials. Fractional free volume calculations likewise show that TMPSF, TMBIPSF, and HMBIPSF are more open than the unsubstituted polymers and that the fractional free volumes of PSF and BIPSF are almost identical. Figure 9 shows a correlation of oxygen permeability for a number of polysulfones with the reciprocal of their fractional free volume. The current materials are shown by open symbols identified by their acronyms. The points not identified are for other polysulfones described elsewhere.[2-4,24] In general, the correlation is quite good; however, finer features that lead to the subtle differences among the various methyl-substituted materials discussed here are not fully accounted for by such approaches.

The glass transition temperatures, listed in Table V, are much higher for the biphenol polymers than for their

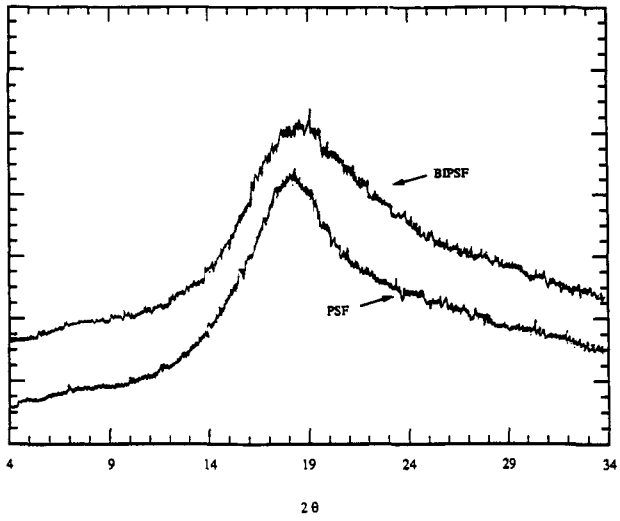


Figure 8. Wide-angle X-ray diffraction patterns for PSF and BIPSF at a wavelength of 1.54 Å.

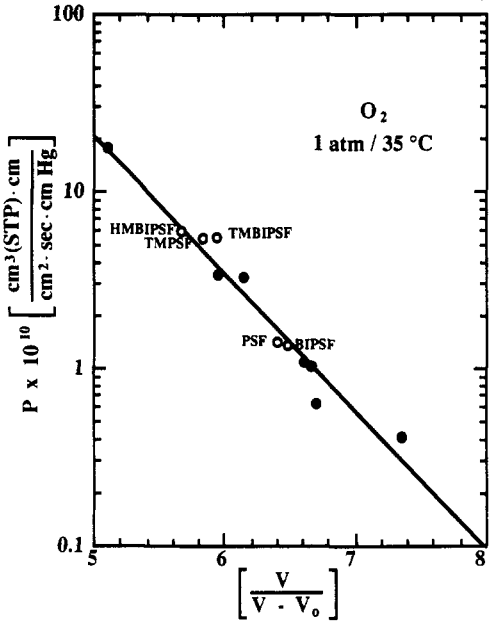


Figure 9. Correlation of the O_2 permeability coefficient with inverse fractional free volume calculated using the Bondi method. Open dots represent polysulfones in this study.

bisphenol A counterparts. The T_g for BIPSF is 35 °C higher than that for PSF, while the T_g of TMBIPSF is almost 60 °C higher than that for TMPSF. Substitutions onto the biphenol unit leads to very rigid chains. The tetramethyl and hexamethyl substitutions increase the glass transition temperature relative to PSF by more than 100 °C.

The sub-T_g relaxations of these polymers have been discussed in a previous paper.[27] For convenience, the tan δ curves of the five polysulfones of interest here are compared in Figure 10. In spite of the rigidity of the connecting bond and the proximity of the two phenyls, the γ peak for BIPSF is nearly the same as that for PSF. For BIPSF this peak is somewhat broader, and there is a small peak at a higher temperature that we have tentatively labeled γ_1, as discussed previously.[27] The similarity between the two spectra suggests that the biphenyl bond and the isopropylidene unit have about equal influence on the mobility of the groups contributing to the sub-T_g relaxation.

There is a clear splitting of the tan δ curve into two γ peaks for the tetramethylbiphenol polysulfone. We have

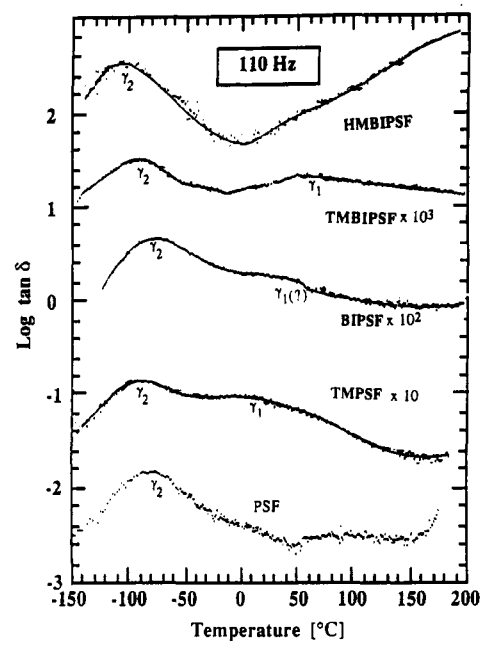


Figure 10. Tangent δ at 110 Hz as a function of temperature showing the sub-T_g γ peaks. Assignments are described in text.

proposed previously that the γ_1 peak has its origin in motions of the bisphenol unit, while the γ_2 peak reflects motions characteristic of the diphenyl sulfone unit. These two γ peaks are more distinct for TMBIPSF than for TMPSF. While the elimination of the isopropylidene group in the tetramethyl polysulfone does not dramatically affect the γ_2 relaxation temperature, the motions associated with the γ_1 peak are more hindered. The γ_1 relaxation for HMBIPSF is almost 300 °C higher than the γ_2 temperature for the unsubstituted BIPSF and is 150 °C higher than the γ_1 relaxation temperature for TMBIPSF. It is apparent from space-filling molecular models that the ortho CH_3 groups in HMBIPSF eliminate rotation of the phenyl rings about the biphenyl bond. While there is rotation around the biphenyl bond[28] for BIPSF and probably for TMBIPSF, it does not occur for HMBIPSF.

As discussed previously,[27] there is some intermolecular influence on the temperature at which the sub-T_g relaxations occur. As proposed above, the γ_2 relaxation stems from the diphenyl sulfone unit, which is the same for all of the polysulfones; hence, this peak should be a good indicator of intermolecular effects. For a broad range of polysulfones, Figure 11 shows how the temperature at which this peak is maximum depends on intermolecular chain packing or free volume. Polymers with high free volumes such as HMBIPSF have low T_{γ_2}. This indicates that as FFV increases, intermolecular barriers to small-scale motions are reduced and the relaxation occurs at a lower temperature. In addition, Figure 12 shows there is also a relationship between the O_2 permeation coefficient and the T_{γ_2} for this series of polysulfones. It is quite likely that the motions associated with the γ_2 peak do not regulate permeability as the results in Figure 12 might suggest, but rather that both T_{γ_2} and permeability are influenced by free volume. Although there does seem to be a relationship between permeability and T_{γ_2}, no relationship was found between gas permeability and T_{γ_1} or T_g for these polysulfones.

Discussion

Previous studies have noted that replacing the isopropylidene group in the bisphenol A based polysulfones and polycarbonates with the more bulky CF_3CCF_3 connecting

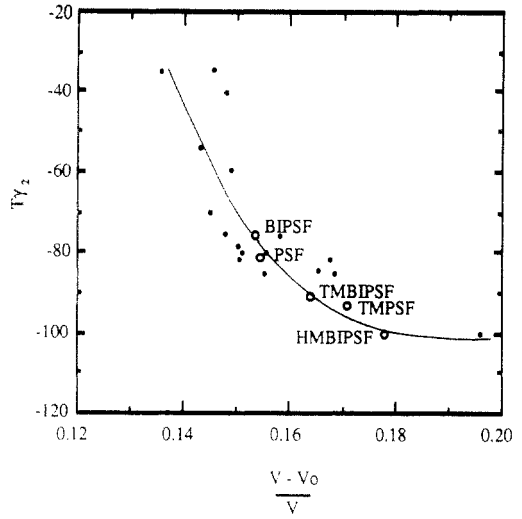


Figure 11. Relationship between the sub-T_g relaxation temperature T_{γ_2} and fractional free volume for various polysulfones. Open dots represent polysulfones described in this study.

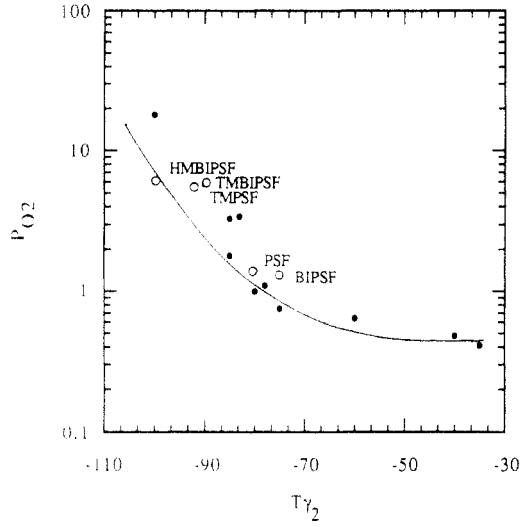


Figure 12. Relationship between the O_2 permeability coefficient and the sub-T_g relaxation temperature T_{γ_2}. Open dots represent polysulfones described in this study.

unit leads to more open polymers with higher permeabilities.[1,5,29] Thus, it might be expected that the elimination of the isopropylidene unit altogether would allow the polymer chains to pack more efficiently and that BIPSF would have lower gas permeability coefficients than PSF. However, as noted above, the transport and fractional free volume characteristics of BIPSF are almost identical with those of PSF. The *d*-spacings are similar; however, the broader X-ray peak for biphenol polysulfone suggests that the distribution of free volume may be somewhat different for BIPSF than PSF.

There are important differences between the bisphenol A and the biphenol monomer structures. In the liquid state, the phenyl rings of biphenyl are believed to be rotated at 45° with respect to each other, while in the crystalline state they are in the same plane.[28] Thus, the preferred conformation in the glassy state should be somewhere between these two extremes. There has been considerable discussion in the literature about the structure of the bisphenol A unit in polymers, especially for polycarbonate. Schaefer et al.[30] found that the phenyl rings in crystalline bisphenol A are orthogonal and used this fact in a representation of packing in glassy polycarbonate (PC).[31] However, the orientation of phenyls in the crystalline state may be quite different from the amorphous or liquid state. Using quantum mechanical and force field methods, several authors have mapped the minimum conformational energy for diphenylpropane and the phenyl conformations of PC.[31-36] It appears that there are several arrangements of the phenyl rings with respect to each other that minimize the conformational energy. There is a consensus among recent authors,[32-35] however, that the phenyl rings are twisted out of the plane of the isopropylidene unit by approximately 50° each at the global energy minimum. In the glassy matrix, all phenyl rings are obviously not at the energy minima calculated for isolated molecules; however, these calculations indicate the more probable conformations. The connecting group does appear to affect the orientation of the phenyls at the energy minima. This orientation could influence the interchain packing in these polymers. The biphenyl units are no doubt more planar than phenyls connected by an isopropylidene group, and in principle, this could lead to a more efficient chain packing. However, the permeability data and the FFV calculations indicate that this is not so.

We propose the following packing model as a way to understand why BIPSF is not more densely packed than PSF in spite of the tendency described above. The top half of Figure 13 is a schematic of PSF and BIPSF chains in their most packed and ordered positions while the lower half shows the two chains out of axial registry by one monomer group. The isopropylidene central carbon in the bisphenol and the sulfur atom in the sulfone unit[37] are both tetrahedral, while the biphenyl unit is linear. If the monomer groups were in registry, the phenyl rings of BIPSF could stack and create a very packed matrix that might lead to lower FFV and gas permeability. However, Figure 13 also shows that when two chains are offset by one monomer unit, alteration of the linear biphenyl unit and tetrahedral bisphenol A unit can disrupt the packing. In contrast, for the polysulfone based on bisphenol A, where the bisphenol and the sulfone units both have similar geometries, such disruption does not occur. Thus, we propose that the tendency for efficient chain packing resulting from the planarity of the linear biphenol is offset in a randomly packed matrix by stacking disruptions caused by the alternation of collinear biphenyl units and tetrahedral sulfone monomers. As a result, BIPSF and PSF have about the same average free volume. Other possible evidence to support this argument includes some preliminary futile attempts in this laboratory to synthesize biphenol polycarbonate by interfacial polymerization. This material appears to be extremely crystalline with a melting point at 405 °C, and because of its insolubility, only low molecular weight polymers could be made by interfacial polymerization.[38] Since the polycarbonate, of course, does not have a tetrahedral sulfone unit to disrupt phenyl stacking, this could lead to a regular, packed structure and low solubility.

While BIPSF and PSF have similar permeability and selectivity coefficients, BIPSF has some added advantages that may be important for a membrane material. Due to its higher T_g, biphenol polysulfone has higher resistance to heat than bisphenol A polysulfone.[39] Analysis of the sub-T_g spectra shows that although the T_g is significantly higher for BIPSF than for PSF, the T_γ is not affected much by the elimination of the isopropylidene group. The toughness of BIPSF is nearly comparable to that of polycarbonate. For example, the notched Izod impact strength for BIPSF is 640 J/m while that for PC is 800 J/m. The Izod value for PSF is much lower at 70 J/m. BIPSF may also have greater chemical resistance than PSF. The solubility of commercially available polysulfones in com-

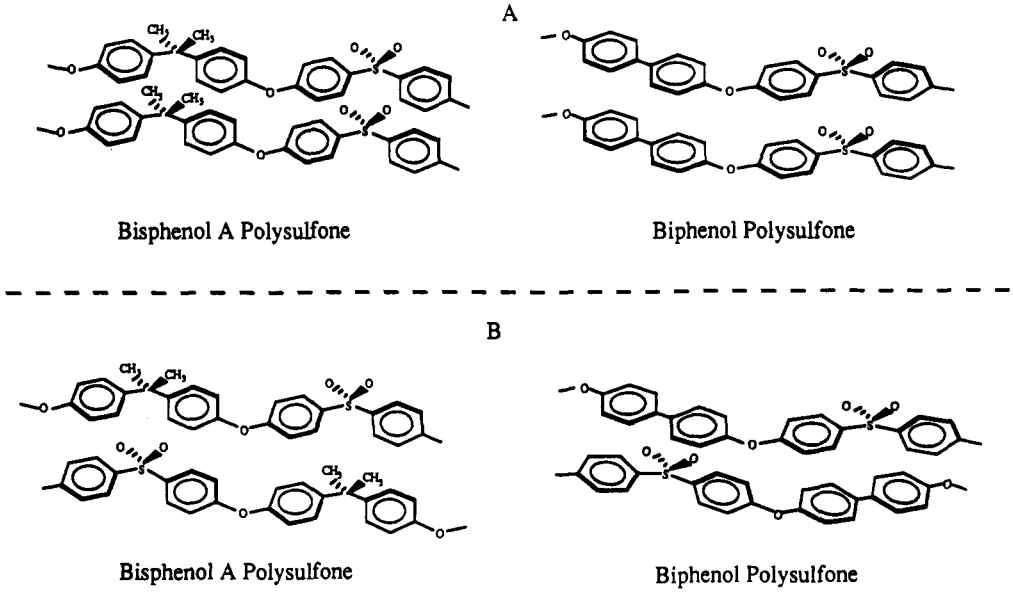


Figure 13. Schematic comparison of chain packing for PSF and BIPSF. In the top section (A), the chains are shown in their most packed and ordered positions, while the lower section (B) shows the two chains out of axial registry by one monomer group.

mon solvents can be ranked in the following order:[39]

Udel PSF > Radel A PSF > Vitrex PES > Radel R PSF

In this study, biphenol polysulfone was found to be insoluble in chlorinated hydrocarbons such as methylene chloride and chloroform and only slightly soluble in aprotic dipolar solvents such as tetrahydrofuran (THF), dimethylacetamide (DMAC), dimethylformamide (DMF), and dimethyl sulfoxide (DMSO). Although Radel R has been described as partially soluble in THF,[11] we found that only NMP was adequate for membrane casting purposes.

In Table V, viscosity values are listed for the commercial BIPSF and the polymer synthesized in our laboratories. The intrinsic viscosity obtained here for Radal R of 0.58 dL/g at 30 °C agrees well with the recent data of Roovers[11] of 0.55 dL/g at 35 °C. By use of the Mark–Houwink equation developed for Radel R at 35 °C,[11] the viscosity of the material synthesized by us corresponds to a very high molecular weight of 180 000. Because of this, cleaning the polymer and casting thin membranes proved difficult.

The tetramethyl- and hexamethyl-substituted biphenol polysulfones tend to have higher permeability and sometimes higher selectivity coefficients than their bisphenol A counterparts. However, it appears that there is no general increase in transport properties for these biphenol-based polymers. In some cases the permeability and selectivity both increase relative to TMPSF (see for example the CH_4/CO_2 separation), while in other cases the exact opposite is true (viz., He/CH_4). In addition, they have glass transition temperatures that are among the highest reported for polysulfones.[1,2,12,13,40-43] Dynamic mechanical data show that the γ_1 relaxation is significantly affected by the methyl additions while the γ_2 relaxation is less so. The γ_1 relaxation, which has been associated with motions of the bisphenol segment,[27] is very restricted for HMBIPSF. Yet, the permeability coefficients for HMBIPSF are not much less than for TMBIPSF. This suggests that free rotation about the biphenyl bond is not a requirement for diffusive jumps to occur.

It was noted above that increases in permeability correlate well with increases in FFV for these polysulfones. Of the polymers described here, HMBIPSF has the highest FFV, yet its CO_2 and CH_4 permeability coefficients are not the highest. This is reflected in a relatively minor deviation from the correlation with FFV shown in Figure 9. It is not yet clear whether deviations like this reflect inaccuracies in the estimation of V_0 or subtle factors not accounted for by free volume. The typical rank of penetrant diffusion coefficients in glassy polymers is He, H_2, O_2, CO_2, N_2, and CH_4. This order is related to the average size of the gas molecule as it permeates through the membrane. The diffusion coefficients for the smaller gases are higher for HMBIPSF than for TMBIPSF, while the opposite is true for the larger gases. One possibility is that the ortho methyl groups on the biphenol unit cause a more narrow distribution of transient gap sizes for diffusion in HMBIPSF than TMBIPSF which effectively retards the transport of larger gases while the larger FFV for HMBIPSF allows the smaller gases to diffuse faster. That is, the distribution of free volume, in addition to the total free volume, may be important in the transport process. The limited mobility of HMBIPSF, as reflected by the high relaxation temperatures T_{γ_1} and T_g, could contribute to a narrow size distribution of diffusive gaps and, thus, increased membrane selectivity. The structure of this polymer also has an unsymmetric component since there are three methyl groups on each phenyl ring. There is a tendency for unsymmetrically substituted polymers to exhibit lower permeability and higher selectivity coefficients.[1,10] The unsymmetric nature of HMBIPSF may be a contributing factor to its higher selectivity.

Conclusions

This study of polysulfones based on 4,4′-biphenols has shown that these rigid polymers have equivalent or, for some separations, better transport properties than the polysulfones based on bisphenol A. The gas permeability coefficients for BIPSF are almost identical with those for bisphenol A polysulfone. Like tetramethylbisphenol A polysulfone, permeability coefficients for all gases are increased by methyl additions to the biphenyl rings; however, permselectivity may increase or decrease depending on the gas pair to be separated. For the separation of carbon dioxide from methane, TMBIPSF and HMBIPSF have higher permeability and selectivity coefficients than TMPSF. Likewise, HMBIPSF simultaneously exhibits the highest helium permeability and He/CH_4 separation factors of the five polysulfones in this study.

In contrast, for the oxygen/nitrogen separation, TMBI-PSF is not exceptional since the increased permeability is accompanied by lower selectivity coefficients (lower than for TMPSF) typical of the trade-off often observed.

The permeability coefficients were analyzed in terms of diffusion and sorption components, fractional free volume, and sub-T_g relaxation behavior. Methyl substitution increases solubility coefficients. The permeability coefficients for these polymers correlate well with the level of fractional free volume. In addition, the sub-T_g relaxation temperature T_{γ_2} is affected by the efficiency of packing in the polymer matrix. Because of the influence of FFV on both permeability and T_{γ_2}, these two quantities are also related.

The biphenol-based polysulfone chains are extremely rigid for this class of engineering thermoplastics, as evidenced by their high glass transition temperatures. The methyl-substituted biphenol polysulfones each have a T_g of almost 300 °C. Even though BIPSF and PSF have similar transport characteristics, the enhanced thermal, mechanical, and chemical-resistant properties of BIPSF could make this a desirable material for gas separation membranes for use in harsh environments. The similar free volume and, thus, permeability characteristics of these two polymers may be a result of the ability of the alternating biphenyl and tetrahedral sulfone units to disrupt interchain packing.

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