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Effect of Basic Substituents on Gas Sorption and Permeation in Polysulfone

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ABSTRACT: The gas permeability, diffusivity, and solubility of a series of polysulfones bearing basic aryl substituents were determined at 35 °C and pressures up to 20 atm. Gas permeability and diffusivity values of the aryl-substituted polysulfones were markedly lower than those of unmodified polysulfone. These effects were ascribed to decreased fractional free volume and increased restriction to sub-T_g torsional motion in the substituted polymers. Polysulfone bearing benzylic amine substituents exhibited higher CO_2 solubility and CO_2/CH_4 solubility selectivity than polysulfone, presumably due to favorable interactions between acidic CO_2 molecules and basic $-CH_2\text{-}NH_2$ groups. CO_2 diffusivity in polysulfone bearing benzylic amine substituents is lower than expected based on free volume considerations, suggesting that interactions between CO_2 and benzylic amine moieties may be strong enough to impede CO_2 mobility in the modified polymer. These results are consistent with infrared spectroscopy data which suggest that the benzylic amino groups undergo reversible reaction with CO_2 to form carbamate moieties.

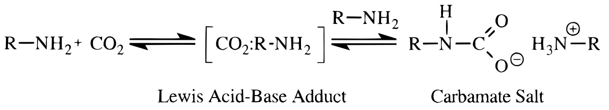
Introduction

Membrane gas separation is becoming increasingly important in the separation of industrial gas streams.[1,2] Commercial applications include CO_2 stripping from natural gas streams, production of high-purity nitrogen from air, and separation of hydrogen from refinery process streams. Recent advances in membrane formation and module design have made membrane-based gas separation more competitive relative to traditional gas separation technologies such as cryogenic distillation, pressure swing adsorption, and amine absorption.[1,2]

The development of highly permeable and selective materials assists further advances in the utilization of membranes in gas separation applications. Typically, polymers which are highly permeable to gases have low permselectivity and *vice versa*.[1] However, polymer backbone chemical structure modifications which simultaneously frustrate chain packing and inhibit torsional mobility have been found to increase both permeability and permselectivity.[1−4] Permselectivity increases obtained by this strategy are largely due to substantial increases in diffusivity selectivity which more than offset losses in solubility selectivity. Little work has focused on tailoring polymer backbone structure to increase solubility selectivity for gas separation applications. The present work is directed toward exploring the influence of gas−polymer interaction on gas transport properties in an effort to identify substituents which could increase solubility selectivity. A previous paper examined the effect of polar aryl NO_2 substituents on gas transport properties of polysulfone.[5] The present study explores the influence of basic substituents such as amines and phthalimides on gas transport properties.

Gases such as CO_2 and H_2S, which are acidic in nature, are expected to be more soluble in polymers containing basic moieties than in polymers without such groups. This notion is not limited to polymers; aqueous solutions of alkanolamines, such as monoethanolamine and diethanolamine, have been used industrially as absorbents for acidic gases such as CO_2 and H_2S since the 1930s.[6] These amines absorb CO_2 from gas streams at low temperatures (typically 30−60 °C) and high pressures, and the CO_2-rich solution is regenerated by desorption of CO_2 at high temperatures (typically 110−130 °C) and low pressures.[7]

There is some disagreement in the literature over the kinetics and precise sequence of reactions between alkanolamines and CO_2.[8,9] Using a molecular orbital approach, the donor properties and amine−CO_2 interaction for a series of primary amines were modeled, and the following reaction pathway was proposed[10]



$$R{-}NH_2 + CO_2 \rightleftharpoons \left[CO_2{:}R\text{-}NH_2\right] \xrightleftharpoons{R-NH_2} R{-}\overset{H}{\overset{|}{N}}{-}C\overset{\displaystyle O}{\underset{\displaystyle O^{\ominus}}{\lessgtr}}\ H_3\overset{\oplus}{N}{-}R \qquad (1)$$

If the N−C bond in the adduct is sufficiently strong, a proton can be transferred to a second amine functionality and a carbamate salt, a zwitterion, will be formed. Alternatively, in the presence of water or hydroxide ion, the Lewis acid−base adduct may react via a base displacement to form a bicarbonate species as follows:

$$CO_2{:}R{-}NH_2 + H_2O \rightleftharpoons HCO_3^{\ominus} + H_3\overset{\oplus}{N}{-}R \qquad (2)$$

Reaction 1 is predominant for primary amines that form relatively stable carbamates. The reaction of water with the amine adduct is slow but will occur, particularly with tertiary amines that cannot form stable carbamates. For most gas separation operations, primary amines with α-methyl substituents are favored due to the relative instability of the carbamates, which allows for reversible carbon dioxide complexation.

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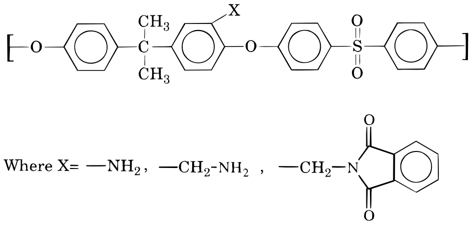
Table 1. Physical Properties of Modified and Unmodified Polysulfones[a]



polymer	density (g/cm^3)	PD[b]	FFV[c]	T_g (°C)	$T\gamma_1$ (°C)	$T\gamma_2$ (°C)	$[\eta]$[d] (cc/g)
PSF	1.235	2.90	0.147	185		−82	0.24
PSF-NH_2 (16%)	1.253	3.00	0.134	179	42	−77	0.10
PSF-NH_2 (38%)	1.273	3.11	0.118	183	46	−78	0.27
PSF-CH_2-NH_2 (51%)	1.253	3.06	0.125	185	40	−80	0.24
PSF-CH_2-imide (51%)	1.279	3.08	0.122	164	45	−80	0.23

[a] WAXD *d*-spacing for all polymers in this study was 5.0 Å. [b] $PD = V/(V - V_w)$. [c] $FFV = (V - 1.3V_w)/V$. [d] In DMF at 25 °C.

These results suggest that basic substituent groups such as amines could interact favorably with acidic gases such as CO_2 and H_2S and be used to enhance CO_2/CH_4 solubility selectivity. Such membranes could be useful for the stripping of CO_2 from natural gas and the selective separation of H_2S from petrochemical gas streams.

Polysulfone (PSF) was chosen as the base polymer for this study since it is used commercially as a gas separation membrane material, and its gas transport properties have been extensively studied.[11,12] Moreover, it has a stable backbone which is amenable to chemical modification. The polymers prepared and characterized in this study are PSF-NH_2 (16%), PSF-NH_2 (38%), PSF-CH_2-imide (51%), and PSF-CH_2-NH_2 (51%). The number in parentheses reflects the degree of substitution (DS) of the polymer, expressed on a percentage basis. The DS is the average number of substituent groups per 100 repeat units.

Experimental Section

Materials, Synthesis, and Structural Characterization. Polysulfone, similar to the commercial product Udel, was kindly supplied by Amoco Chemical Co., Alpharetta, GA. The primary structures of polysulfone and the substituents used in this study are presented in Table 1. All other reagents were purchased commercially and used as received without further purification. CO_2, N_2, and O_2 were acquired from Linde, and CH_4 was obtained from Air Products. All gases had a purity of >99.5%.

Amine substituents were added to the PSF backbone by first introducing nitro (NO_2) substituents and then reducing the NO_2 groups to amine (NH_2) groups. Nitro substituents were added to PSF via the electrophilic substitution route described by Crivello[13] and modified by Daly.[14] Ammonium nitrate and trifluoroacetic anhydride were used as the nitrating agents. The ether linkage in polysulfone is ortho directing, and therefore, the nitro groups were introduced in the bisphenol A entity ortho to the ether linkage. NMR studies[14,15] confirm this substituent location. PSF-NH_2 was prepared by reducing PSF-NO_2 (dissolved in THF) at 70 °C for 48 h in the presence of tetrabutylammonium chloride.[14,16] The reducing agents were $SnCl_2$ and HCl.

PSF-CH_2-imide was prepared by contacting PSF with *N*-(hydroxymethyl)phthalimide in a mixture of trifluoromethanesulfonic acid and trifluoroacetic acid, as described by Daly.[14,17] PSF-CH_2-NH_2 was prepared by the hydrozinolysis of PSF-CH_2-imide by hydrazine hydrate.[14,17]

The chemical structure of the modified polymers was characterized by proton NMR (Bruker ACF 300) and infrared spectroscopy (Perkin Elmer 1760X FTIR). The infrared spectrum of PSF-NO_2 exhibited a peak at 1533 cm^{-1}, corresponding to an NO_2 stretch,[18] which disappeared after reduction to PSF-NH_2, suggesting essentially complete reduction of PSF-NO_2 to PSF-NH_2. The infrared spectrum of PSF-NH_2 exhibited absorption bands at 3375 cm^{-1}, corresponding to the NH stretch, and at 1625 cm^{-1}, corresponding to the NH_2 deformation.[18] Relative to PSF-NO_2, the NMR spectrum of PSF-NH_2 exhibited a new peak at $\delta = 3.5$ ppm, which was ascribed to protons on the amine group.

The infrared spectrum of PSF-CH_2-imide exhibited a peak at 1718 cm^{-1}, corresponding to a carbonyl stretching motion. The infrared spectrum of PSF-CH_2-NH_2 exhibited absorption bands at 3383 cm^{-1}, corresponding to NH stretching motions, and did not exhibit bands between 1650 and 1870 cm^{-1}, suggesting complete conversion of PSF-CH_2-imide to PSF-CH_2-NH_2. The NMR spectrum of PSF-CH_2-imide and PSF-CH_2-NH_2 exhibited peaks at $\delta = 4.7$ and 3.7 ppm, respectively, which are ascribed to protons on the methylene spacer connecting the phthalimide and amine groups to the polymer backbone. Elemental analysis performed by Atlantic Microlabs Inc., Norcross, GA, was used to determine nitrogen content of the polymers, and this value was used to calculate the degree of substitution.

Film Preparation. All films were prepared by dissolving the polymers in chloroform (10−15%, w/v) and then casting on a clean, flat glass plate. The solution was filtered through a Gelman 1 μm glass fiber filter. After drying, the film was lifted from the glass plate by flotation in water and air-dried overnight. Finally, the films were dried for 24 h at 100 °C in vacuum. All films were between 1 and 2 mils (25−50-μm) thick. No trace of solvent or crystallinity could be detected from differential scanning calorimeter scans.

Thermal and Mechanical Characterization. Glass transition temperatures were determined using a Perkin-Elmer DSC-7 instrument at a heating rate of 20 °C/min. The samples were scanned twice, and the midpoint of the endothermal displacement of the second scan was taken to be the T_g. The glass transition was the only thermal event observed in the temperature window from 50 to 250 °C. Dynamic mechanical relaxation spectra were recorded using a Perkin Elmer DMA-7 instrument operating in the extension mode, at a frequency of 10 Hz and a heating rate of 1 °C/min.

Gas Permeability and Sorption Determinations. A barometric permeation system was used to determine steady state pure gas permeability at 35 °C over a range of pressures up to 20 atm.[19] The downstream pressure was kept below 10 mmHg, while the upstream pressure was maintained at superatmospheric pressures. All permeability determinations were made using films that had been “vector conditioned” with CO_2 at 20 atm.[20] Permeation determinations were made first for CO_2 and then for other gases. Mixed gas permeation determinations were made using an on-line Varian 3700 gas chromatograph and a Hewlett Packard 3396 Series II integrator. The stage cut (*i.e.*, the fraction of gas fed which permeates through the film) was maintained below 0.05% to minimize concentration polarization.

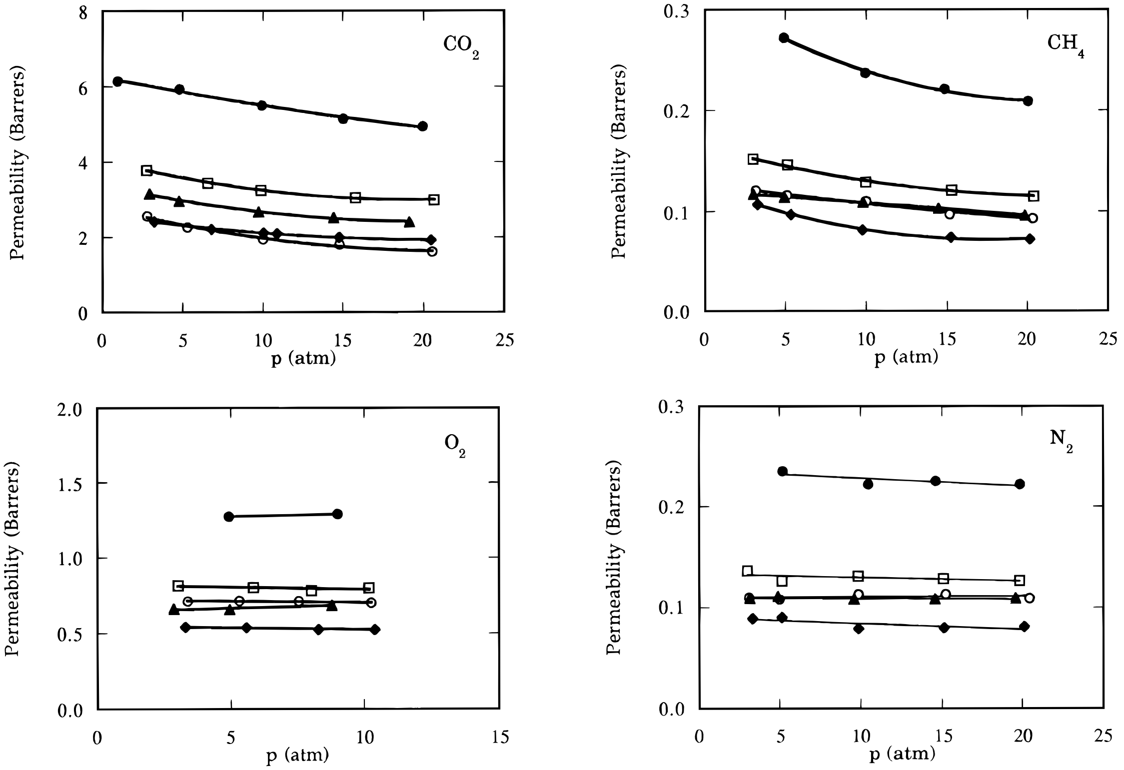


Figure 1. Effect of upstream pressure on gas permeability at 35 °C: (●) PSF, (▲) PSF-NH_2 (16%), (□) PSF-NH_2 (38%), (○) PSF-CH_2NH_2 (51%), and (◆) PSF-CH_2-imide (51%).

Pure gas sorption isotherms were determined at pressures up to 20 atm at 35 °C using a dual transducer barometric device.[21] All sorption isotherms were determined after the polymer was conditioned with CO_2 at 20 atm. Sorption determinations were made first for CO_2 and then for the other gases. For safety reasons, permeability and solubility of O_2 were not determined at pressures beyond 10 atm.

Physical Characterization. Polymer density was determined by flotation of small samples of as-cast films in a density gradient column, maintained at 23.0 ± 0.1 °C. Aqueous solutions of zinc chloride or sodium bromide in the column provided the gradient. Glass beads, whose densities are known to ±0.0001 g/cm^3, were used to calibrate the column.

Wide angle X-ray diffraction (WAXD) spectra were obtained with a Siemens WAXD spectrometer, using Cu Kα radiation having a wavelength of 1.54 Å. An amorphous halo was the only feature observed in the WAXD spectrum of as-cast films of these polymers. The *d*-spacing was calculated from Bragg's equation, $d = \lambda/2 \sin \theta$,[22] where λ is the wavelength of the radiation and 2θ is the angle of maximum intensity of the amorphous halo exhibited by these polymers.

The intrinsic viscosity of all polymer samples was determined in dimethylformamide at 25 °C using a Ubbelohde viscometer.

Chain-Packing Analysis. The fractional free volume of each polymer (FFV) was estimated from the relation:[23]

$$\mathrm{FFV} = \frac{V - V_o}{V} = \frac{V - 1.3V_w}{V} \qquad (3)$$

where V_o, the specific occupied volume, is taken as 1.3 V_w, the specific van der Waals volume,[24] and V is the polymer specific volume. The van der Waals volume was calculated via the group contribution method of Bondi.[24] A related measure of chain packing, the polymer chain-packing density of each polymer (PD), was calculated using the following relation:[3]

$$\mathrm{PD} = \frac{V}{V - V_w} \qquad (4)$$

Results

The physical, thermal, and mechanical properties of polysulfone and the substituted variants of polysulfone are presented in Table 1. Figure 1 presents the pressure dependence of permeabilities of the polymers to pure CO_2, CH_4, N_2, and O_2 at 35 °C. All of the permeability values were determined twice, and the difference between these duplicate measurements was smaller than the symbols used in the figure. CO_2 and CH_4 permeabilities decrease with pressure, whereas O_2 and N_2 permeabilities are practically independent of pressure. In the absence of strong plasticization effects which lead to increasing permeability with increasing pressure, the dependence of permeability on pressure presented in Figure 1 is typical of that observed for glassy polymers.[25] Table 2 provides a summary of gas permeability and permselectivity data of unmodified and modified polysulfone at 35 °C and 10 atm.

Table 2. Permeability and Permselectivity of the Modified and Unmodified Polysulfones at 35 °C and 10 atm[a]

	P_{O_2}	P_{N_2}	P_{CO_2}	P_{CH_4}	P_{CO_2}/P_{CH_4}	P_{O_2}/P_{N_2}
PSF	1.29	0.22	5.5	0.24	23	5.7
PSF-NH_2 (16%)	0.69	0.11	2.7	0.11	24	6.3
PSF-NH_2 (38%)	0.80	0.13	3.2	0.13	25	6.2
PSF-CH_2-NH_2 (51%)	0.70	0.11	1.95	0.11	18	6.4
PSF-CH_2-imide (51%)	0.54	0.08	2.12	0.08	26	6.7

[a] Permeability values are expressed in barrers, where 1 barrer = 10^{-10} cm^3 (STP)cm/cm^2·s·cmHg.

Pure component sorption isotherms are presented in Figure 2. Each isotherm was measured twice in two separate experiments. The scatter in the data points from the two experiments was less than the symbol size used in Figure 2. The "concentration averaged" diffusivity has been calculated from permeability and solubility data using the relation: $D = P/S$.[2,26,27] Figure 3 presents the concentration dependence of the diffusion coefficient for unmodified and modified polysulfones. Gas diffusivity and solubility values at 35 °C and 10 atm are tabulated in Table 3.

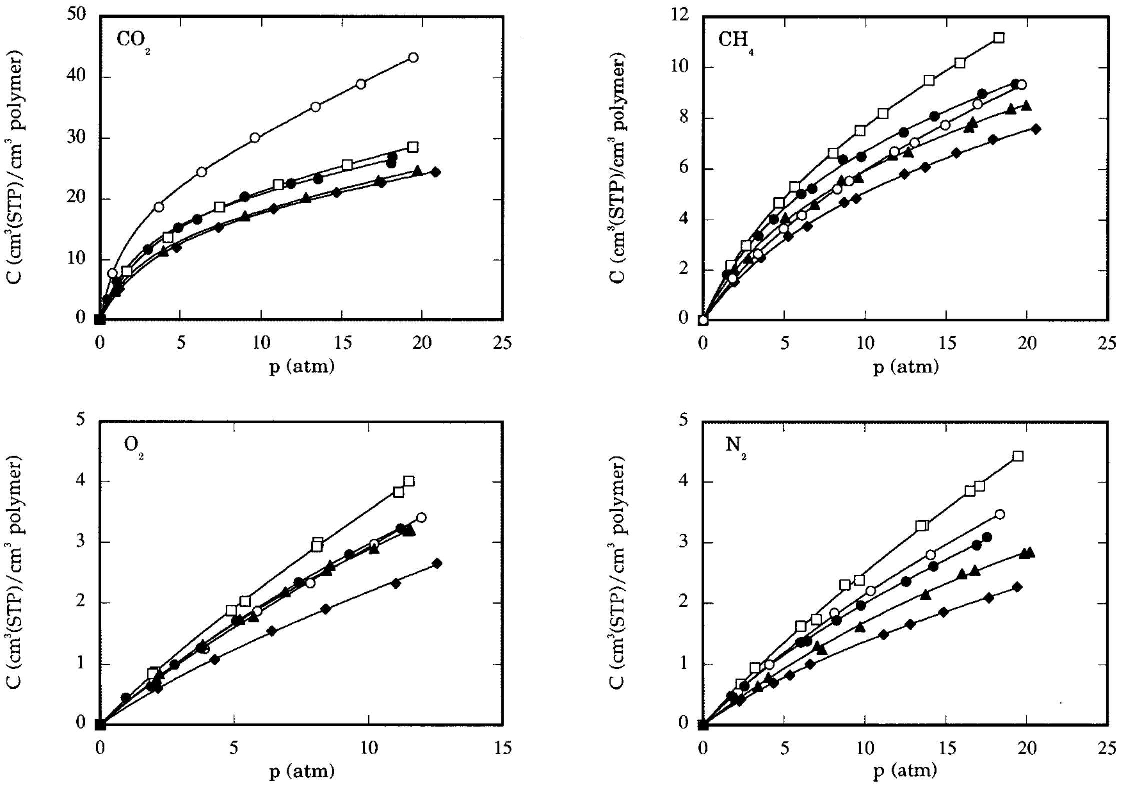


Figure 2. Sorption isotherms at 35 °C: (●) PSF, (▲) PSF-NH$_2$ (16%), (□) PSF-NH$_2$ (38%), (○) PSF-CH$_2$NH$_2$ (51%), and (◆) PSF-CH$_2$-imide (51%).

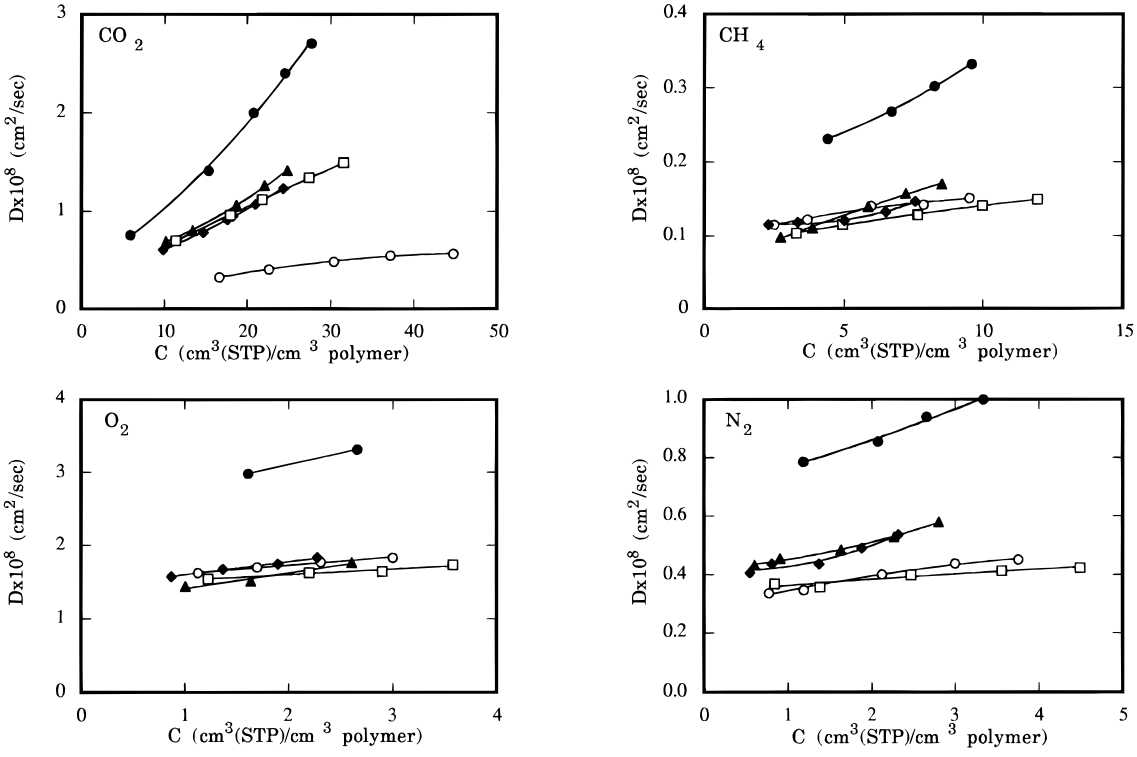


Figure 3. Effect of penetrant concentration on diffusivity at 35 °C: (●) PSF, (▲) PSF-NH$_2$ (16%), (□) PSF-NH$_2$ (38%), (○) PSF-CH$_2$NH$_2$ (51%), and (◆) PSF-CH$_2$-imide (51%).

Discussion

Free Volume. As presented in Table 1, the fractional free volume of the modified polysulfones is significantly lower than that of unmodified polysulfone. This observation is consistent with other studies, which found that low levels of both polar and nonpolar aryl substituents decrease free volume.[5,28] In contrast, high levels of nonpolar aryl substituents increase free volume. For example, McHattie *et al.*[28] found that two aryl methyl substituents per repeat unit of polysulfone decreased FFV by 4.5% but four methyl groups per repeat unit increased FFV by 9.6% relative to unsubstituted polysulfone. In a separate study,[5] FFV of polysulfone was found to decrease by 23% upon substitution of two aryl nitro groups per repeat unit of polysulfone. In the present study, the maximum degree of substitution was

Table 3. Solubility and Diffusivity Contributions of Modified and Unmodified Polysulfone[a]

	S_{O_2}	S_{CO_2}	S_{O_2}/S_{N_2}	S_{CO_2}/S_{CH_4}	D_{O_2}	D_{CO_2}	D_{O_2}/D_{N_2}	D_{CO_2}/D_{CH_4}
PSF	0.29	2.08	1.5	3.1	3.4	2.0	4.0	7.4
PSF-NH_2 (16%)	0.29	1.90	1.7	3.2	1.8	1.1	3.6	7.9
PSF-NH_2 (38%)	0.35	2.20	1.4	2.8	1.7	1.1	4.3	8.5
PSF-CH_2-NH_2 (51%)	0.29	3.04	1.4	4.7	1.8	0.5	4.6	3.5
PSF-CH_2-imide (51%)	0.22	1.76	1.6	3.4	1.8	0.9	4.1	7.6

[a] Solubility and diffusivity at 35 °C and 10 atm. Solubility in cm^3(STP)/cm^3(polymer)·atm and diffusivity in 10^{-8} cm^2/s.

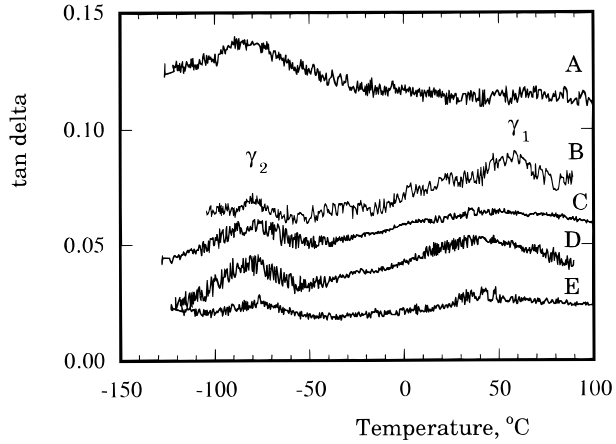


Figure 4. Sub-T_g mechanical relaxation spectra for polysulfone and modified polysulfones: A = PSF, B = PSF-CH_2-imide (51%), C = PSF-NH_2 (38%), D = PSF-CH_2-NH_2 (51%), and E = PSF-NH_2 (16%). The spectrum of PSF-NH_2 (16%) has been shifted by −0.01 units for clarity. Frequency = 1 Hz.

51%, *i.e.*, *ca.* one substituent for every two repeat units, or one substituent for every eight phenyl rings. At these low levels of substitution, the observed decrease in free volume is, therefore, consistent with other studies.

X-ray diffraction has often been used to characterize short range order in amorphous polymers.[28−31] In the polymers prepared for this study, *d*-spacing was not observed to change markedly with packing density or chemical structure. This observation is consistent with results obtained by Jacobson,[32] who suggested that WAXD spectra reflect both intrachain as well as interchain diffraction effects and may not, therefore, always be sensitive to polymer chain packing.

Thermal and Mechanical Analysis. Sub-T_g mechanical relaxations can be sensitive to local chain dynamics.[2] Such segmental motions can, in turn, depend on local scale chain packing and chain stiffness factors which are important in gas transport in polymer matrices.[2] Figure 4 presents sub-T_g dynamic mechanical relaxation spectra in the temperature window from −130 to *ca.* 100 °C for the polymers in this study. The dynamic mechanical transitions are reported in Table 1. PSF exhibits a sub-T_g transition (γ_2) with a peak at *ca.* −82 °C, consistent with previous reports concerning the dynamic mechanical behavior of polysulfone.[28,33] In aromatic polymers such as polysulfones and polycarbonates, the γ_2 transition is believed to be associated with local scale segmental dynamics, such as phenyl ring flips.[33−35]

In contrast, the aryl-substituted polysulfones considered in this study exhibit two transitions, γ_1 and γ_2, which are indicated in Figure 4 and Table 1. The γ_2 transition in these polymers, occurring at about −80 °C, is, presumably, related to molecular motions associated with the unsubstituted phenyl rings. The γ_1 transition, which occurs at 40−46 °C for the modified polysulfones prepared for this study, is ascribed to molecular motions associated with substituted phenyl rings. Similar results were found by McHattie in polysulfones bearing aryl methyl substituents.[28] The motions of substituted rings leading to the γ_1 peak in the mechanical relaxation spectrum are, presumably, more hindered than motions of unsubstituted rings. Hence, the γ_1 transition occurs at a higher temperature than the γ_2 transition. All of the aryl-modified polysulfones in this study exhibit a γ_1 transition at about the same temperature.

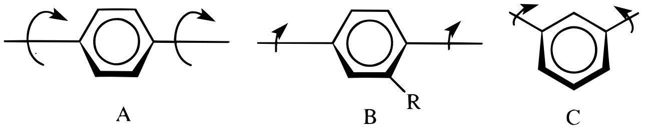


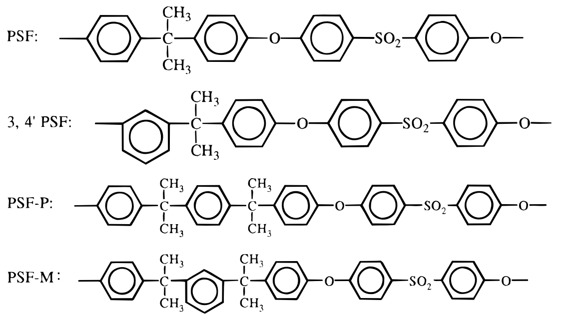
Figure 5. Schematic diagram of phenyl ring motions.

In polysulfone, dynamic mechanical[28,33] and solid state NMR studies[36] confirm that para-connected backbone aromatic rings are activated for rotation (π flips) about the 1,4 axis at temperatures far below ambient (*ca.* −80 °C). Thus, near room temperature where density determination and gas permeation measurement are often performed, these aromatic rings are highly activated for π flip motion about the main chain axis as indicated in Figure 5A. These local segmental motions effectively sequester sufficient free volume in the polymer matrix to permit highly activated rotational motion about the 1,4 axis of the aromatic rings. The volume required for this motion is, of course, more than the occupied volume of the aromatic ring and contributes to the overall free volume of the polymer.

On the basis of the dynamic mechanical relaxation results reported in this study and elsewhere,[28,33] the addition of an aryl substituent, as shown in part B of Figure 5, greatly increases the temperature at which molecular motion about the aromatic ring chain axis is activated. This, in turn, suggests that the mobility of these substituted rings at temperatures where gas permeation and density determinations are performed may be strongly reduced, as indicated by the small arrows of rotation in part B of Figure 5. The attenuation in substituted aromatic ring mobility is probably due to both intramolecular effects (increased rotational energy barriers) and intermolecular effects (more extensive interchain cooperative motion needed to open a transient gap in the matrix sufficient to permit rotation of the bulky substituted ring). If the main chain aromatic ring rotational motion of these substituted rings is greatly inhibited, then these rings will be less efficient than unsubstituted rings at sequestering the volume swept out by the π flipping motion and other local segmental motions, permitting more efficient packing of the polymer chains in the amorphous matrix. In this way, overall free volume may be reduced as chain backbone aromatic ring segmental mobility is reduced by addition of bulky substituents to the chain backbone.

Based on calculations by Bondi, the van der Waals volume of a para-connected benzene ring is 43.3 cm^3/mol (or 72.0 Å^3/ring). Based on a CPK space-filling

Table 4. Effect of Meta/Para Connector Groups on Gas Transport Properties[a]



polymer	FFV	T_g (°C)	$T_{\gamma1}$ (°C)	$T_{\gamma2}$ (°C)	P_{CO_2}	P_{O_2}	P_{O_2}/P_{N_2}	S_{CO_2}	D_{CO_2}
PSF	0.156	186	−80		5.6	1.4	5.6	2.1	2.0
3,4′-PSF	0.149	156	−40	>100	1.5	0.39	5.9	1.3	0.9
PSF-P	0.168	191	−85		6.8	1.8	5.6	2.1	3.2
PSF-M	0.158	140	−75	40	2.8	0.69	6.3	1.1	2.7

[a] Permeability in barrers, where 1 barrer = 10^{-10} $cm^3(STP)cm/cm^2 \cdot s \cdot cmHg$. Solubility in $cm^3(STP)/cm^3(polymer) \cdot atm$ and diffusivity in 10^{-8} cm^2/s at 35 °C, CO_2 at 10 atm, and O_2/N_2 at 2 atm. Data from Aitken *et al.*[37]

molecular model of a para-connected benzene ring, a model ring is *ca.* 3.3 Å thick and has a mean diameter of *ca.* 5.3 Å, which corresponds to a volume of 72.8 $Å^3$/ring, if the ring is modeled as a disk. This hypothetical ring would sweep out *ca.* 78.0 $Å^3$ (46.9 cm^3/mol) in executing a 180° flip. Thus, even within the bounds of this crude model, highly mobile rings may effectively sequester *ca.* 8% more free volume in the polymer matrix than equally sized but immobile rings.

Similarly, the free volume of para-connected, amorphous polymers is typically lower than the free volume of meta-connected, amorphous analogs. Several examples of this phenomenon are presented in Table 4. The para-connected polysulfones in Table 4 have greater FFV than the meta-connected polysulfones. As presented in part C of Figure 5, the meta-connected rings cannot undergo extensive ring flipping about the main chain axis without cooperative motion involving atoms connected to the meta ring.[37] This inhibition to motion results in lower free volume and, in turn, lower gas permeability in meta-connected analogs.[37,38]

The foregoing discussion has focused on the geometric or steric effects which could lead to the observed changes in dynamic mechanical properties and polymer chain packing. Additional effects related to changes in the electron distribution along the backbone as a result of aryl substitution are not described, and their effect on chain packing is not well understood. The characterization data which were obtained during the course of this study do not permit a detailed discussion of these effects.

Pure Gas Permeation. As indicated in Figure 1 and Table 1, the permeability of all gases studied is lower in the substituted polysulfones than in unmodified polysulfone. O_2/N_2 permselectivity in all of the substituted PSFs is higher than in unsubstituted PSF. The permeability decrease is accompanied by an increase in CO_2/CH_4 permselectivity, with the exception of PSF-CH_2-NH_2 (51%). All gas permeabilities except CO_2 are in the order: PSF > PSF-NH_2 (38%) > PSF-NH_2 (16%) ≈ PSF-CH_2-NH_2 (51%) > PSF-CH_2-imide (51%).

The permeability of PSF-CH_2-NH_2 (51%) to CO_2 is lower than that of PSF-CH_2-imide (51%). The permeability of PSF-CH_2-NH_2 (51%) to CO_2 does not follow the trend of the other polymer−gas pairs since both permeability and CO_2/CH_4 permselectivity are reduced relative to PSF. This phenomenon is ascribed to an acid−base interaction between acidic CO_2 and the basic CH_2-NH_2 groups in PSF-CH_2-NH_2 (51%). The net result of this interaction is to impede the permeation of CO_2 through the polymer, reducing both CO_2 permeability and CO_2/CH_4 permselectivity.

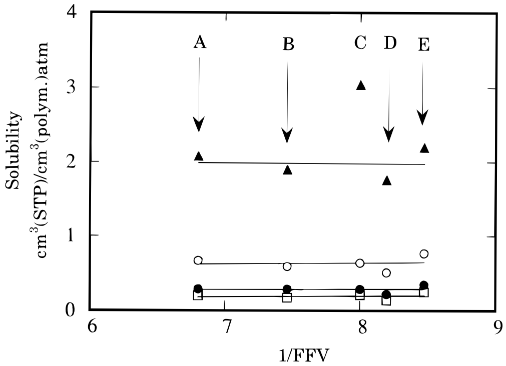


Figure 6. Dependence of gas solubility at 10 atm and 35 °C on fractional free volume: (▲) CO_2, (○) CH_4, (●) O_2, and (□) N_2; A = PSF, B = PSF-NH_2 (16%), C = PSF-CH_2-NH_2 (51%), D = PSF-CH_2-imide (51%), and E = PSF-NH_2 (38%).

Gas Solubility. Typically, in the absence of strong polymer−gas interactions, solubility is a weak function of FFV and increases with increasing FFV.[2] As shown in Figure 6, gas solubility for the polymers in this study is almost independent of FFV, with the exception of CO_2 in PSF-CH_2-NH_2 (51%). At 10 atm, CO_2 is about 50% more soluble in PSF-CH_2-NH_2 (51%) than in the other polymers. Moreover, the CO_2/CH_4 solubility selectivity is about 50% greater in PSF-CH_2-NH_2 (51%) than in PSF. This enhancement in CO_2 solubility is ascribed to interactions between CO_2 and the pendent benzylic amine moieties. Such behavior is consistent with the notion that gases are more soluble in materials with which they have specific interactions.[39] For example, polyamides exhibit a strong affinity for water. Water forms hydrogen bonds with amide linkages, and water solubility increases with increasing concentration of amide groups.[40]

Sorption isotherms for gases in glassy polymers have been successfully modeled by the dual mode model.[2] In this model, penetrant molecules are partitioned between the dense equilibrium structure of the polymer (dissolved mode) and the nonequilibrium excess volume of the glassy polymer (Langmuir mode). The model can be expressed analytically as:

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

where C is the total concentration of the penetrant in the polymer, k_D is the Henry's law constant, C'_H is the hole saturation constant or Langmuir sorption capacity, b is the Langmuir affinity parameter, and p is the pressure. The dual mode parameters for CO_2 and CH_4 are presented in Table 5. The parameters were estimated using a least-squares fit to the sorption data. For CO_2, the Henry's law parameter, k_D, and the affinity parameter, b, are larger in PSF-CH_2-NH_2 (51%) than in the other polymers, consistent with the notion that CO_2 solubility-enhancing interactions are strongest in this polymer. The Langmuir capacity parameters for carbon dioxide and methane in PSF-CH_2-NH_2 (51%) are not significantly different from C'_H values in the other polymers.

A correlation between $k_D(CO_2)/k_D(CH_4)$ and the concentration of polar groups in the matrix in which the gases were dissolved has been reported.[41] As the concentration of polar moieties in the polymer increases, solubility selectivity of CO_2 increases. This relation is presented in Figure 7, along with solubility selectivity data for the polymers in this study. The substituted polysulfone bearing benzylamine moieties lies on the line with other materials which presumably do not interact with CO_2 by covalent chemical bonding. The introduction of amine and phthalimide functions to polysulfone actually reduces solubility selectivity. The aminated polysulfones have solubility selectivity similar to nonpolar materials, whereas PSF-CH_2-imide (51%) has solubility selectivity similar to that of polysulfone. The reason for the reduction in CO_2/CH_4 matrix solubility selectivity in the amine- and imide-bearing polysulfones is not clear.

Gas Diffusivity. Gas diffusivity, D, is often observed to depend on free volume as follows:[42]

$$D = A e^{-B/FFV} \qquad (6)$$

where A and B are constants characteristic of the polymer-penetrant system. This relation often provides a good description of gas diffusivity within a given family of polymers.[23,43] Figure 8 presents the relationship of gas diffusion coefficients and 1/FFV for all gases. The diffusion coefficients for this family of aminated polysulfones are in the order $O_2 > CO_2 > N_2 > CH_4$, typical of what is observed in other studies of gas transport in glassy polymers.[28,29,31,43,44] A notable exception to this trend is the CO_2 diffusivity of PSF-CH_2-NH_2 (51%), which is considerably lower than that predicted by eq 6. This result is consistent with the notion that diffusion of CO_2 through PSF-CH_2-NH_2 (51%) may be retarded by specific chemical interactions between CO_2 and the CH_2-NH_2 moiety.

The diffusion coefficient depends, in part, on a complex interplay between FFV and torsional mobility. A decrease in FFV or torsional mobility tends to decrease gas diffusivity.[2] On the basis of mechanical relaxation spectra of the polymers under study, bulky side groups may hinder the mobility of the phenyl ring to which it is attached. The observed decrease in gas diffusivity in the substituted polymers would be consistent, therefore, with the observed decrease in FFV and the decrease in torsional mobility accompanying addition of aryl substituents.

Mixed Gas Permeation. Figure 9 presents mixed gas permeabilities and permselectivities of PSF-CH_2-NH_2 (51%) to a mixture of CO_2 and CH_4 which contains 29.5 mol % CO_2. The mixed gas CO_2 permeability is lower than the pure gas CO_2 permeability. Likewise, the CH_4 permeability is also lower in the mixture. For example, the CH_4 mixed gas permeability is 0.03 barrer at 10 atm, and the pure gas permeability is 0.11 barrer. Such a depression in gas permeability in the presence of a second component is commonly observed in glassy polymers.[15,45−47] For example, at 35 °C and 10 atm of CO_2 pressure, the permeability of PMMA to pure CO_2 is 0.58 barrer but decreases to 0.38 barrer for an equimolar mixture of CO_2 and CH_4.[48] The reduction in CO_2 permeability in the presence of CH_4 has been attributed to competition from CH_4 molecules for the limited number of Langmuir sites and to a reduction in CO_2 mobility due to the presence of the larger CH_4 molecules. The mixed gas permselectivity is higher than the pure gas value, which has also been observed for other nonplasticizing binary gas pairs.[49,50]

Since water plays a role in the reaction between primary amines and CO_2 (eq 2), a mixed gas permeation experiment was performed using a humidified CO_2/CH_4 mixture. Water was introduced to the system by bubbling the CO_2/CH_4 mixture through a tank of water. The mole fraction of water in the feed gas stream was 0.022 (42% relative humidity (RH) at 35 °C), as estimated by moisture uptake on a column of magnesium perchlorate. As shown in Figure 9b, water in the feed enhances CO_2/CH_4 permselectivity beyond the values obtained using anhydrous mixtures. It was not possible to determine individual permeabilities of the three components because the gas chromatographic peak for water, which was broad and ill defined, could not be integrated accurately.

The increase in CO_2/CH_4 permselectivity in the presence of water could be due to the reaction between the benzylamine groups and CO_2. This reaction should be facilitated by water as suggested by the discussion relating to eq 2. Since the formation of carbamate salts introduces polar functions into a nonpolar matrix, the water reduces the energy required to generate and destroy the carbamates by providing a solvation shell for the salts. The conversion of amines to carbamates and *vice versa* occurs more readily in a polar environment. These factors may make the reaction more reversible, leading to enhanced CO_2 selectivity coupled with enhanced CO_2 permeability.

Polymer−Gas Interaction. The high CO_2 solubility of PSF-CH_2-NH_2 (51%) is attributed to acid−base interactions between CO_2, an acidic gas, and $-CH_2$-NH_2, a basic moiety. These interactions have been investigated using infrared (IR) spectroscopy. Previous infrared spectroscopic studies[51,52] have shown that −OH, −C═O, and −NH stretching peaks shift to lower wave numbers when these groups are hydrogen bonded, and the shift increases as the extent of hydrogen-bonding increases.[51] Hydrogen bonding in a series of vinyl alcohol/vinyl butyral copolymers has been examined by IR spectrometry.[51] The hydroxyl groups in vinyl alcohol hydrogen bond with neighboring hydroxyl groups. The IR peak characterizing the hydroxyl stretch shifted to lower wavenumbers as the concentration of vinyl alcohol in the polymer increased. The peak shift was ascribed to an increase in hydrogen bonding as the vinyl alcohol concentration increased.

Table 5. Dual Mode Parameters for CO_2 and CH_4

	CO_2			CH_4		
	k_D (cm^3(STP)/cm^{3}polymer·atm)	b (atm^{-1})	C'_H (cm^3(STP)/cm^{3}polymer)	k_D (cm^3(STP)/cm^{3}polymer·atm)	b (atm^{-1})	C'_H (cm^3(STP)/cm^{3}polymer)
PSF	0.52 ± 0.07	0.40 ± 0.06	20 ± 2	0.16 ± 0.04	0.15 ± 0.03	9 ± 1
PSF-NH_2 (16%)	0.40 ± 0.04	0.26 ± 0.02	21 ± 1	0.16 ± 0.04	0.15 ± 0.03	7 ± 1
PSF-NH_2 (38%)	0.73 ± 0.003	0.37 ± 0.003	18.6 ± 0.1	0.30 ± 0.002	0.15 ± 0.01	7.7 ± 0.6
PSF-CH_2-NH_2 (51%)	1.22 ± 0.03	0.60 ± 0.05	21.2 ± 0.8	0.23 ± 0.02	0.10 ± 0.01	7 ± 1
PSF-CH_2-imide (51%)	0.43 ± 0.05	0.26 ± 0.03	18 ± 1	0.11 ± 0.03	0.10 ± 0.02	8 ± 1

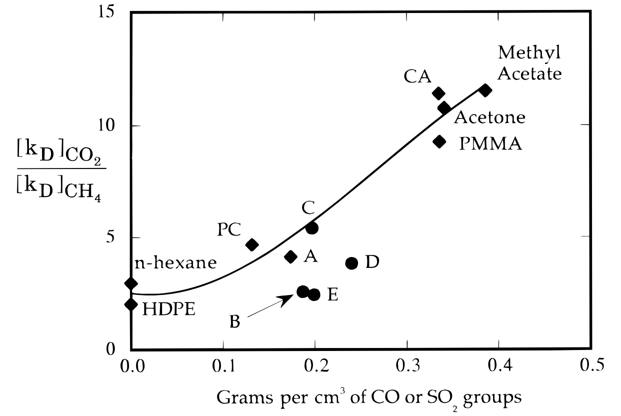


Figure 7. Effect of polar group concentration on solubility selectivity:[41] HDPE = high-density polyethylene, PC = polycarbonate, PMMA = poly(methyl methacrylate), and CA = cellulose acetate; A = PSF, B = PSF-NH_2 (16%), C = PSF-CH_2-NH_2 (51%), D = PSF-CH_2-imide (51%), and E = PSF-NH_2 (38%).

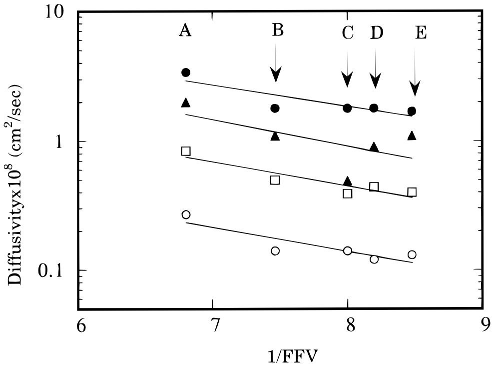


Figure 8. Dependence of gas diffusivity at 10 atm and 35 °C on fractional free volume: (▲) CO_2, (○) CH_4, (●) O_2, and (□) N_2; A = PSF, B = PSF-NH_2 (16%), C = PSF-CH_2-NH_2 (51%), D = PSF-CH_2-imide (51%), and E = PSF-NH_2 (38%).

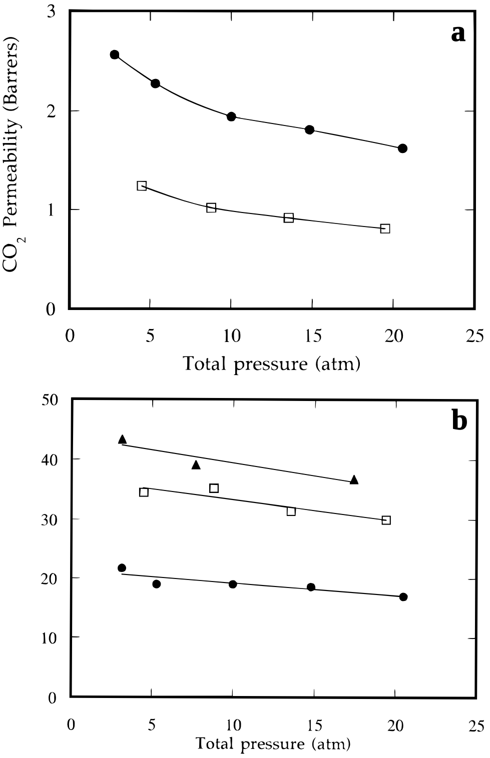


Figure 9. (a) CO_2 permeability of PSF-CH_2NH_2 (51%) as a function of total pressure at 35 °C: (●) pure CO_2 and (□) 29.5/70.5% (molar) CO_2/CH_4 mixture. (b) CO_2/CH_4 permselectivity of PSF-CH_2NH_2 (51%) as a function of total pressure at 35 °C: (●) pure gas, (□) 29.5/70.5% (molar) CO_2/CH_4 mixture, and (▲) 29.5/70.5 CO_2/CH_4 mixture with 42% RH water vapor.

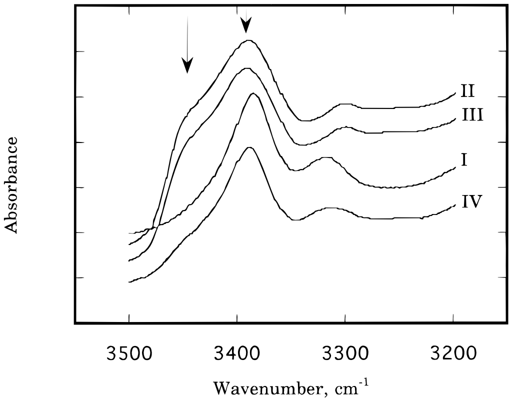


Figure 10. Infrared spectra of the N−H stretch in PSF-CH_2-NH_2 (51%): I = unexposed to CO_2, II = collected immediately after exposure to CO_2, III = collected after 30 min, and IV = collected after 21 h.

Prior to CO_2 exposure, PSF-CH_2-NH_2 (51%) exhibits a peak at 3383 cm^{-1} attributed to the N−H stretch. This sample was equilibrated with 20 atm of CO_2; it was removed from the cell and inserted into the FTIR spectrometer. IR spectra were collected as a function of time and are presented in Figure 10. The spectra collected immediately after the polymer was removed from the cell, II, and after 30 min exposure to air, III, developed a shoulder at *ca.* 3450 cm^{-1}. In addition, both spectra exhibited a band at 3389 cm^{-1}. The spectrum collected after 21 h, IV, was almost identical with the original spectrum of the unexposed sample, I, and only a small shoulder at 3450 cm^{-1} can be perceived.

In the absence of CO_2, amine moieties in PSF-CH_2-NH_2 (51%) are presumably hydrogen bonded to other amine or adjacent aryl ether groups in the polymer chain as shown in Figure 11. The band at 3383 cm^{-1} can be assigned to a hydrogen-bonded N−H stretch. When the amine groups are exposed to high concentrations of CO_2, the carbamate function forms; the shoulder at 3450 cm^{-1} can be attributed to the N-H in the carbamate linkage. This absorption is consistent with similar bands for N-H in benzamide and acetamide.[53]

Since the formation of the carbamate is reversible, after 21 h most of the CO_2 is released and diffuses out of the sample film as evidenced by the marked decrease

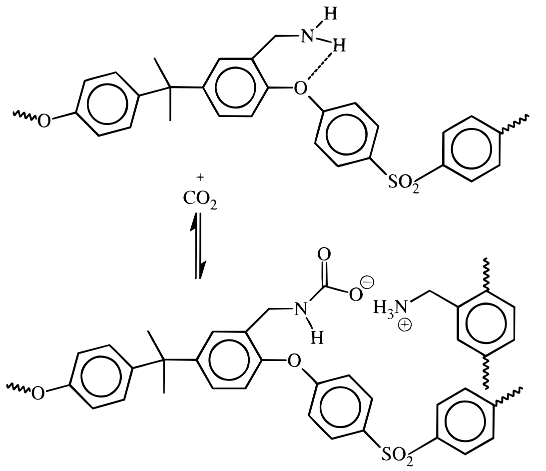


Figure 11. Proposed interaction of carbon dioxide with benzylic amine subtituents in PSF-CH_2-NH_2 (51%).

of the shoulder at 3450 cm^{-1}. The infrared study confirms the interaction between CO_2 and PSF-CH_2-NH_2 (51%); the slow release of CO_2 from the polymer film suggests that the complex is too stable for gas separation processes.

The influence of the benzylamine function on CO_2 sorption and transport properties is much greater than the effect of the aromatic amine function on these properties. Aromatic amines (Ph-NH_2) are much less basic than benzylamines (Ph-CH_2-NH_2).[10,51] In aromatic amines, the nitrogen's lone pair of electrons are delocalized in the aromatic ring; this resonance stabilization is not present in the conjugate ammonium ion. Thus, the energy of conjugation favors the free amine over the conjugate ammonium species, and the basicity of the amine is significantly reduced. Complexation of aromatic amines with CO_2 would require similar disruption of conjugation and would not be expected to occur to a significant extent. In contrast, the methylene “spacer” in the benzylamine impedes delocalization of the nitrogen lone pair, and the benzylamines exhibit a basicity comparable to aliphatic amines which complex readily with CO_2.[10]

Summary and Conclusions

The objective of this work was to identify basic substituents which can interact with CO_2 to enhance CO_2 solubility and CO_2/CH_4 solubility selectivity. Of the three substituents used in this study (arylamine, benzylamine, and phthalimide), only benzylamine exhibited favorable interactions with CO_2. Benzylamine ($pK_a = 9.33$) is a much stronger base than aniline ($pK_a = 4.63$)[10,51] and does form a stable carbamate with CO_2. The low basicity of aromatic amine functions precludes the formation of stable complexes; thus the solubility of CO_2 in the PSF-NH_2 polymers is not markedly enhanced relative to the solubility of other gases. Since the phthalimide function is effectively neutral, no specific interaction between CO_2 and the phthalimido polymers was detected.

Due to synthetic difficulties, the highest level of substitution achieved in this study was approximately one substituent per two repeat units of polysulfone (one substituent per eight phenyl rings). The enhancement in CO_2 solubility and CO_2/CH_4 solubility selectivity upon introduction of benzylamine groups is all the more dramatic considering the low degree of substitution which was achieved.

To make effective gas separation membranes, polymers with high diffusivity, solubility, diffusivity selectivity, and solubility selectivity are desired. Benzylamine substituents enhance CO_2 solubility and CO_2/CH_4 solubility selectivity. However, this moiety reduces the diffusion coefficient of CO_2 through the membrane. Polymer−gas interactions which enhance solubility and solubility selectivity without reducing diffusivity selectivity are desirable, but it is not clear that such “tuning” of these interactions (or bonds) is practical for separation of permanent gas mixtures such as carbon dioxide and methane.

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