Correlation between Structure and Gas Transport Properties of Silyl-Modified Polysulfones and Poly(phenyl sulfone)s

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ABSTRACT: An improvement in gas permeation properties has been obtained by introducing bulky silyl side groups at sites *ortho* to either the ether or sulfone linkage of polysulfone and poly(phenyl sulfone) chains. The sizes of the substituents were systematically increased from trimethylsilyl, to dimethylphenylsilyl, and to diphenylmethylsilyl, and the degree of substitution was also controlled. The sterically smallest trimethylsilyl group substituted at the *ortho* ether site markedly increased the oxygen permeability from 1.1 to 7.1 barrers compared with that of unmodified polysulfone at a small tradeoff in oxygen/nitrogen selectivity. Unexpectedly, the oxygen permeability remained almost unchanged from polysulfone with the introduction of more bulky dimethylphenylsilyl and diphenylmethylsilyl substituents. It was also found that substitution at the sites *ortho* to ether linkage was more effective than the sulfone linkage in improving transport properties. The improved gas separation properties appear to be associated with increased free volume, evidenced from the increased *d*-spacing and specific volume. Further, the mobility of pendant substituents, characterized by dynamic mechanical analysis, correlated strongly with the *d*-spacing and specific volume. This leads us to the conclusion that it is substituent mobility rather than the size of the pendant side group that is the critical factor in determining free volume and transport properties.

Introduction

Numerous studies on the relationship between the molecular structure of polymers and gas transport properties have been reported in an attempt to gain a better understanding of transport mechanism.[1] The motivation is to improve transport properties by overcoming the “tradeoff” behavior between permeability and permselectivity of polymers, i.e., to increase gas permeability and selectivity simultaneously. Pixton and Paul reviewed studies concerned with the effect of bulky side groups in glassy polymers on their gas transport properties.[1] When the methyl groups were introduced at the phenyl rings of polysulfones and polycarbonates, their gas permeability was in general increased with relatively small decrease in the permselectivity. Conversely, bromine and chlorine atoms resulted in increased permselectivities.[2] Symmetry of substitution was also found to have a strong effect on the gas transport properties of the modified polymers.[3] Analogous modification studies have also been conducted for other glassy polymers like polyarylates[3−6] and poly(2,6-dimethyl-1,4-phenylene oxide).[7,8]

It has been reported that the major physicochemical factors influencing control over the gas permeability and permselectivity of polymers are (1) the mobility of polymer chains, as reflected in many cases by glass or sub-glass transition temperature of the polymer, (2) the intersegmental spacing, which is taken as a measure of the mean free volume of polymer, and (3) the penetrant−polymer interactions, as reflected by the solubility of the penetrant gases in polymers.[1,9,10] For permanent gases, the penetrant solubility depends insignificantly on material properties of polymers mainly because permanent gases do not undergo specific interactions with polymers. Thus, the penetrant solubility typically scales with convenient measures of penetrant condensability, such as boiling point, critical temperature, or Lennard-Jones temperature.[10]

Therefore, from a material viewpoint, it has been suggested that polymer chain mobility or stiffness and intersegmental distance are the two critical factors in determining transport properties, at least in glassy polymers. Typically, chain rigidity results in increased permselectivity but lower permeability, whereas greater intersegmental distance gives the higher permeability but lower selectivity. To achieve simultaneously higher permeability and selectivity, chain stiffness should be coupled with an increase in interchain separation. The approach taken here is to introduce bulky side groups onto rigid glassy polymer chains to improve gas transport properties.

The presence of bulky silyl groups on the polymer chain is of special interest to gas separation technology because of their potential to inhibit chain mobility and to give more open chain packing, thus improving both

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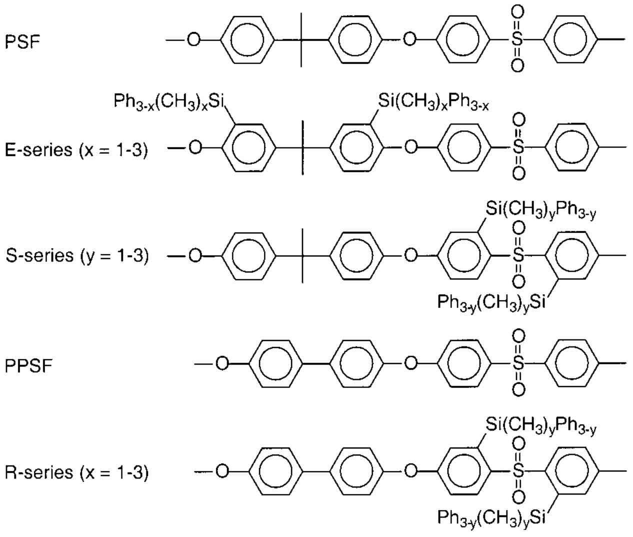

Figure 1. Structure of the polymers used in the present study.

Table 1. Structures of the Polymers Used in the Present Study

code	substitution site	substituent	deg of substitution
PSF			
EM3	*o*-ether	$Si(CH_3)_3$	1.9
EM2	*o*-ether	$Si(CH_3)_2Ph$	1.9
EM1	*o*-ether	$Si(CH_3)Ph_2$	1.7
SM3(2)	*o*-sulfone	$Si(CH_3)_3$	2.0
SM3(1)	*o*-sulfone	$Si(CH_3)_3$	1.0
SM1	*o*-sulfone	$Si(CH_3)Ph_2$	0.5
PPSF			
RM3	*o*-sulfone	$Si(CH_3)_3$	2.0
RM2	*o*-sulfone	$Si(CH_3)_2Ph$	2.0
RM1	*o*-sulfone	$Si(CH_3)Ph_2$	1.8

the selectivity and permeability of a polymer membrane. Gas transport properties have been shown to be significantly improved by silylation of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) as well as polysulfone.[7,8,11] Likewise, trialkylsilyl groups introduced on phenyl rings of polystyrene[12] and on main chains of polypropyne[13] showed improved characteristics. Many efforts have been made to improve the permeation properties of polysulfones by modifying the chemical structure[1,14−17] because aromatic polysulfones such as bisphenol A polysulfone and poly(phenyl sulfone) have been widely used for gas separation membranes. This involves synthesis of new polysulfones containing side groups and as well as the chemical modification of commercial polysulfones.

In this study, silyl groups with different steric size were introduced on the phenylenes of both bisphenol A polysulfone and poly(phenyl sulfone) at sites *ortho* to ether and to sulfone linkages. The effects of silyl group substitution on the gas transport properties were studied in relation to the physical properties of the polymers in terms of the sub-glass transition, in particular γ-transition, as well as the intersegmental distance and specific volume.

Experimental Section

Materials. Chemical structures and notations of polymers studied are shown in Figure 1 and Table 1. Silyl side groups of trimethylsilyl, dimethylphenylsilyl, and diphenylmethylsilyl were introduced by chemical reaction into phenyl rings of bisphenol A polysulfone (PSF; Udel P3500, Amoco) and poly(phenyl sulfone) (PPSF; Radel R5000, Amoco). The silylated polysulfones were prepared by reaction of the appropriate chlorosilanes with lithiated polysulfones. Details of polymer modification and structural characterization are reported elsewhere.[18] Modified PSFs were largely divided into two groups on the basis of substitution sites: *ortho* to the sulfone and *ortho* to the ether. PPSFs were substituted only at the *ortho* sulfone sites due to solubility limitations in the modification chemistry.

Table 2. Permeability Coefficients and Ideal Separation Factors Measured at 35 °C and 1 atm[a]

code	P(He)	$P(CO_2)$	$P(O_2)$	$P(N_2)$	$P(CO_2)/P(N_2)$	$P(O_2)/P(N_2)$
PSF	11	6.3	1.1	0.19	33	5.8
EM3	46	29	7.1	1.3	22	5.5
EM2	15	6.2	1.4	0.24	26	5.8
EM1	12	4.8	1.0	0.16	30	6.3
SM3(2)	34	18	4.2	0.77	23	5.5
SM3(1)	20	10	2.2	0.38	26	5.8
SM1	12	5.1	1.1	0.17	30	6.5
PPSF[b]	6.0	3.2	0.49	0.10	32	4.9
RM3	40	27	6.2	1.9	14	3.3
RM2	16	6.7	1.7	0.60	11	2.8
RM1	14	6.9	1.6	0.61	11	2.6

[a] Permeability values are given in a unit of barrers, where 1 barrer = 10^{-10} cm^3 (STP) cm/(cm^2 s cmHg). [b] PPSF film was prepared from NMP solution.

Gas Permeation Measurement. Dense polymer films were made from 5 wt % polymer solutions in anhydrous tetrahydrofuran (THF) with the exception of unmodified PPSF. Polymer solutions were filtered through 1 μm poly(tetrafluoroethylene) filters, then poured into Petri dishes, and dried under a nitrogen atmosphere at room temperature. After films were detached from the Petri dishes, they were further dried for 3 days in a vacuum oven at 40 °C to remove the residual solvent. Films of PPSF were prepared from 1-methyl-2-pyrrolidinone (NMP) due to its poor solubility in THF. In this case, casting and drying processes were performed at 80 °C, and then the films were dried for 5 days in a vacuum oven at 40 °C. Optically clear films were obtained with thickness of about 20 μm in all cases. The absence of residual solvent in the films was confirmed by observing T_g by using differential scanning calorimetry (DSC). Permeability coefficients of helium, carbon dioxide, oxygen, and nitrogen were measured by the constant volume method at 35 °C with an upstream pressure of 1 atm.

Characterization. Wide-angle X-ray diffractometry (WAXD) analysis was performed with Macscience M18XHF, using Cu Kα radiation having 1.54 Å wavelength (λ). The d-spacing was calculated by means of Bragg's law, $d = \lambda/(2 \sin \theta)$, with θ of broad peak maximum. Polymer films, whose permeability coefficients were measured, were directly employed for this measurement. Densities of the dried membranes were measured by the displacement method using a Mettler density kit with distilled water at 21 °C. Samples for density measurement were prepared in a sheet of 25 × 8 × 2 mm by compression molding at 35 °C above their glass transition temperatures and then quenched with cooling water. Glass transition temperature (T_g) was measured using a Perkin-Elmer DSC-4 with a heating rate of 20 °C/min. A Rheometrics Scientific MK III analyzer was used for dynamic mechanical analysis (DMA) in the dual-cantilever bending mode. Samples were prepared in the same manner as for the density measurement samples. The DMA was carried out in the temperature range from −150 °C to T_g of each polymer sample with a scanning rate of 2.5 °C/min and a frequency of 10 Hz.

Results and Discussion

Gas Permeation. The permeability coefficients of four gases and ideal separation factors between oxygen and nitrogen are given in Table 2. The gas permeability decreased in the order of $P(\mathrm{He}) > P(CO_2) > P(O_2) > P(N_2)$ for all modified PSFs and PPSFs. This trend has been generally observed in the case of single gas

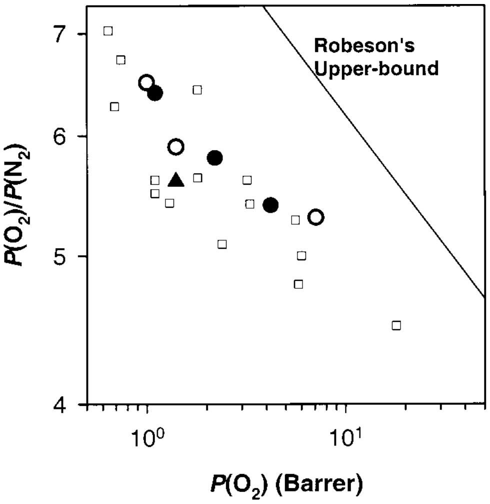

Figure 2. Relationship between oxygen permeability coefficients ($P(O_2)$) and ideal separation factors ($P(O_2)/P(N_2)$): (▲) PSF, (●) E-series, (○) S-series, other modified polysulfones [Robeson, L. M. *J. Membr. Sci.* **1991**, *62*, 165].

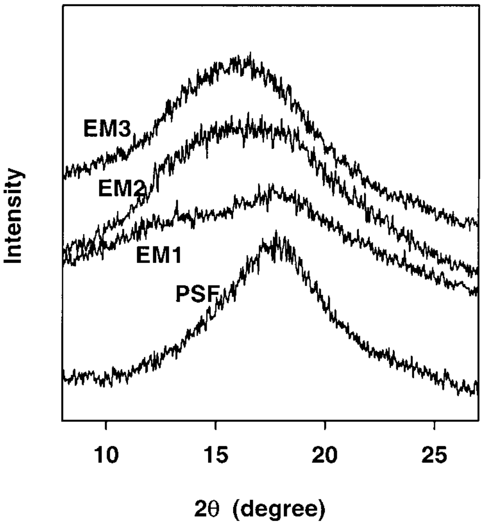

Figure 3. Wide-angle X-ray diffraction patterns of PSFs.

permeation through polymeric materials and is attributed to the increasing kinetic diameters of the gases above.[1,7,19]

The effect of various silyl substitutions on the gas transport properties was readily observed in the modified PSF series. The gas permeability coefficients were increased significantly by introducing trimethylsilyl substituents into PSF at positions *ortho* to ether- or sulfone-linkage as shown in Figure 2. An improvement in transport properties could be expected from previous studies. It has been pointed out by other researchers that bulky side group substitutions on the polymer main chain would restrict main-chain motions and increase interchain distance, thereby enhancing both the membrane gas permeability and the permselectivity.[1] Paradoxically, it was observed that the permeabilities for all four gases increased in the order of EM1 < EM2 < EM3 while the sizes of substituents increased in the reverse order. For instance, EM3 having the smallest substituent ($SiMe_3$) at the ortho position to the ether linkage (E-series) unexpectedly showed the most significant increase in the gas permeability. Oxygen permeability of EM3 increased up to 7.1 barrers, nearly 7 times compared with that of unmodified PSF, while its O_2/N_2 selectivity only decreased by less than 10%. EM2 showed slightly higher oxygen permeability than unmodified PSF with a similar or slightly higher selectivity, while EM1 gave the highest selectivity with almost unchanged oxygen permeability. A possible explanation for this observation is that the planarity of the phenyl rings on the silyl side groups are capable of allowing more interchain packing, thereby reducing permeability and increasing permselectivity through rigidifying the system. A significant difference in electron density and electron distribution between methyl and phenyl groups may also contribute to the difference in permeability to some extent[20] although the role of these electronic effects on permeability is not yet well understood.

The substitution of silyl groups at the site *ortho* to the sulfone-linkage (S-series), SM3(2), SM3(1), and SM1, also resulted in increased gas permeability, but to a lesser extent compared with that of the E-series. SM3(2) having $SiMe_3$ with the degree of substitution of 2 had an oxygen permeability of 4.2 barrers, almost 4 times that of PSF, and with a marginal tradeoff in O_2/N_2 selectivity. A similar effect of substitution position on the gas permeability was observed for the modified poly(2,6-dimethyl-1,4-phenylene oxide).[7] This indicates that substitution at the *ortho* ether sites is more effective in increasing permeability than at the *ortho* sulfone sites. This is due to the fact that the ether-linkage is rather more flexible and is hindered more readily by bulky substituents than the already hindered sulfone-linkage.

In the case of modified PPSFs, the substitution of all three silyl groups on PPSF chains resulted in enhanced gas permeabilities, but with a generally greater tradeoff in permselectivity than silylated PSFs. In particular, RM3 showed a ~12-fold increase in oxygen permeability with a substantial decrease in the O_2/N_2 selectivity compared with PPSF. The analogous SM3 permeability increase was only ~4-fold with a marginal decrease in the selectivity compared with PSF. However, the trends of the effects of each type of substituent in relation to gas permeation properties are somewhat similar between PSF and PPSF.

The effect of degree of substitution was demonstrated by comparison between SM3(1) and SM3(2). SM3(2) having two $SiMe_3$ groups per repeat unit showed almost twice the permeability of SM3(1) having only one $SiMe_3$ group, indicating a rather linear effect. A similar behavior has been observed in PPO.[7,8]

Chain Packing. The X-ray diffraction patterns of modified PSFs and PPSFs are shown in Figures 3 and 4, respectively, and the calculated *d*-spacings using the Bragg equation are listed in Table 3. The values of 2θ showing the maximum intensity decreased and *d*-spacing increased by the substitution. The incremental increase in *d*-spacing was higher in EM3 (or RM3) than in EM2 and EM1 (or RM2 and RM1), despite its smaller substituent size. The higher permeabilities of EM3 and RM3 over the polymers with larger pendant groups correlate well with their observed increased *d*-spacing. The effect of chain packing on the gas permeability of polymers has been normally evaluated by correlating the gas permeability with the fractional free volume.[21,22] The free volume values of modified PSFs and PPSFs of this work, calculated by the group contribution data,[22] did not correlate well with gas permeability. Instead, the specific volumes obtained from density measurements were used in an attempt to correlate with

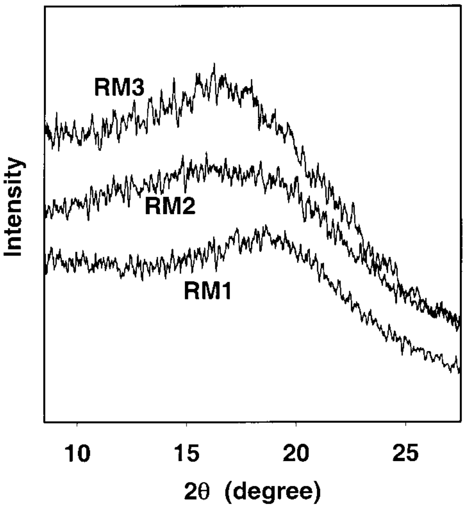

Figure 4. Wide-angle X-ray diffraction patterns of PPSFs.

Table 3. Properties of the Polymers Used in the Present Study

code	T_g (°C)	d (Å)	ρ (g/cm^3)
PSF	185	4.95	1.205
EM3	155	5.53	1.136
EM2	117	5.33	1.157
EM1	136	4.95	1.191
SM3(2)	165	5.43	1.125
SM3(1)	163	5.24	1.166
SM1	165	4.95	1.193
PPSF	225[a]	4.80[a]	1.286
RM3	170	5.50	1.141
RM2	140	5.20	1.191
RM1	145	4.80	1.200

[a] Reference 21.

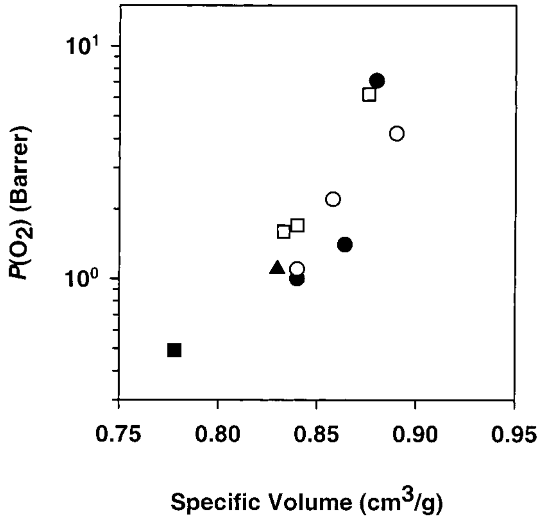

Figure 5. Relationship between specific volume and permeability coefficients ($P(O_2)$): (▲) PSF, (●) E-series, (○) S-series, (■) PPSF, and (□) R-series.

permeabilities. The O_2 permeability is plotted in Figure 5 as a function of specific volume for PSFs and PPSFs. A fairly linear relationship is observed, suggesting a correlation between increasing permeability and polymer free volume. In summary, the packing density, evidenced from specific volume and d-spacing, was increased by replacing methyl with phenyl groups in the substituent, and this coincided with a decrease in the oxygen permeability. The high packing density was thought to be due to the partial stacking of phenyl groups themselves or with phenylene groups of main chains. A discussion of this is elaborated in the following section.

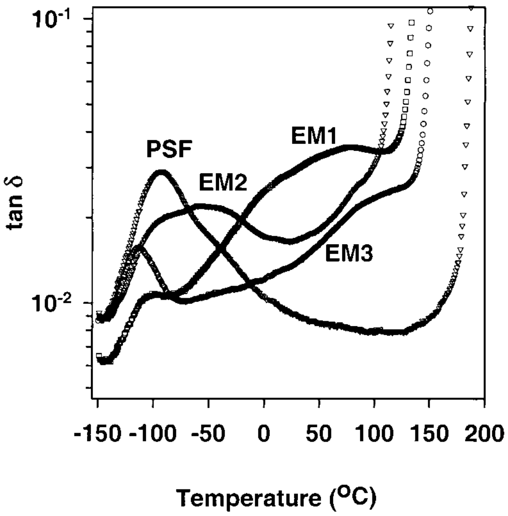

Figure 6. Dynamic mechanical spectra of PSFs.

Dynamic Mechanical Analysis. The chain flexibility of polymers is a result of the molecular motions available at a given temperature and is a most important parameter in determining diffusion behavior. Although glass transition temperature can be an indication of chain flexibility, some researchers have demonstrated that the correlation between glass transition and gas permeability is rather poor.[3,14,16] Such poor correlation appears to be due primarily to the difference in the scale of motions between gas diffusion and glass transition. This may be supported by the fact that small scale molecular motion is sufficient for the diffusion of small gas molecules while a rather large-scale cooperative motion is involved in glass transition. We also found here that the glass transition temperatures of the polymers, listed in Table 3, were poorly related to the permeabilities.

Instead, the sub-T_g relaxation behavior below room temperature was investigated to determine whether it is related to the permeability, as demonstrated previously by others.[5,6,14–16,23] The DMA results of modified PSFs and PPSFs in comparison with unmodified polymers are presented in Figures 6 and 7, respectively. For all the polymers the highest-temperature relaxation observed at above 100 °C is the glass transition, which is also designated as α relaxation. The peaks around 80 °C are β relaxation, which are often observed in aromatic polymers like polycarbonate and PSF. The β relaxation is considered to be related to the residual stress, as it could usually be removed or diminished by physical aging at that temperature. The peaks observed at temperatures between −110 and 40 °C, designated as γ peaks, are real secondary relaxation peaks representing local molecular motions.

One γ peak was observed in the samples of pure PSF, PPSF, EM3, and RM3 whereas two γ peaks were observed for EM1, EM2, RM1, and RM2 as summarized in Table 4. It is obvious, from the present result and those of previous studies,[2,6,14–16,23] that the emergence of two γ peaks is due to the substitution on the phenylene ring. In a relaxation and simulation study with PSF and tetramethyl PSF, Paul and co-workers assigned the higher temperature (γ_1) peak at −10 °C to the motion of (tetramethyl)-substituted diphenyl sulfone

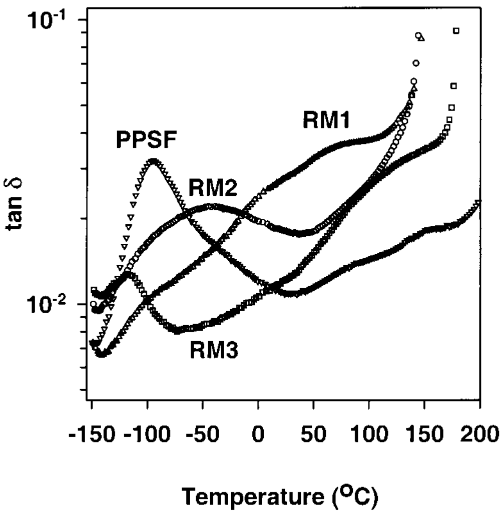

Figure 7. Dynamic mechanical spectra of PPSFs.

Table 4. Secondary Relaxation Temperatures and Activation Energies for the Motions of the Polymers

code	$T_{\gamma 2}$ (°C)	$T_{\gamma s}$ (°C)	$E_{a,\gamma s}$ (kcal/mol)
PSF	−90		
EM3	−110	NO[a]	
EM2	−100	−30	12
EM1	−100	20	16
PPSF	−100		
RM3	−110	NO[a]	
RM2	−100	−40	13
RM1	−100	10	16

[a] Not observed.

(DPS) units and the lower temperature peak (γ_2) at −92 °C to the motion of (unsubstituted) bisphenol A (BPA) units.[23] In a recent study with amino-substituted polysulfone, the γ_1 peak between 40 and 60 °C was related to the flip motion of substituted phenylene rings and the γ_2 peak at −80 °C to that of unsubstituted phenylenes.[16]

Since elucidating the origin of secondary relaxation motion is neither a simple task nor the goal of this study, we interpreted our results on the basis of the previous studies. For the assignment of γ_2 peak, the above two studies in common suggested that the motion involved unsubstituted phenylenes, since the motion of BPA units comprises that of phenylenes. The lower temperature (γ_2) peaks observed at around −100 °C in the spectra of EM1, EM2, RM1, and RM2 of the present study could also be assigned to the motion involving unsubstituted phenylene rings.

The higher temperature (γ_1) peak has been assigned to the motion of substituted phenylene rings[12] or substituted diphenyl sulfone.[23] A cooperative motion along the substituted main chain appears to be of the same sort as suggested for the peak at around 50 °C in studies with polycarbonates containing substituted BPA units.[24,25] As is done for the γ_2 peak above, the γ_1 peak could appear to be assigned to the motion involving substituted phenylene rings, since all the proposed motions comprise that of substituted phenylenes.

The above interpretation, however, was not directly applicable to the higher temperature γ peak of the present study. If the γ_1 peak is assigned to the peak observed at −30 °C for EM2 and the peak at 20 °C for EM1, the γ_1 peak of EM3 should appear between −30 and −100 °C. However, no peak was observed in this temperature range, implying the need of alternative assignment. We propose here that the γ_1 peak arising from motions involving substituted phenylenes may appear at temperatures above 100 °C and is not observable because of its superimposition with the α peak. The rationale for this argument is that the introduction of even a small group on PSF main chain enhances the peak position toward a higher temperature to a large extent. For instance, the substitution with amine groups on only 16% of BPA phenylenes of PSF increased the peak position markedly from −82 to 42 °C.[16] In the case of modified PSF and PPSFs of this study, the substituent is much bulkier than amine, and the degree of substitution is 2.0 instead of 0.16. Therefore, it is not unreasonable to believe that the γ_1 peak will appear at temperatures above 100 °C, which is experimentally not observable due to the superimposition of peaks.

It becomes necessary to reassign the peaks observed at −30 °C for EM2 and that at 20 °C for EM1. We propose here that the peaks, designated as γ_s, are due to the motions of substituent themselves: $SiMe_2Ph$ of EM2 and $SiMePh_2$ of EM1. The γ_s peak position was decreased markedly from 20 to −30 °C by substituting one phenyl group with methyl. When both phenyl groups are replaced with methyl groups as in EM3 or RM3, the peak position may possibly be decreased to a temperature below −150 °C, which is the experimental limit of this study. We believe this may be the reason why only one γ peak is observed in the spectrum of EM3 or RM3. The $SiMe_3$ group is considered to be so mobile as to relax at a very low temperature. This high mobility of $SiMe_3$ is thought to be the reason for the high permeability of EM3 and RM3. In summary of the characterization of the motions for the observed γ peaks, the γ_2 peak is assigned to the motions involving unsubstituted phenylenes and the γ_s peak to the motions of substituent themselves.

The lower mobility of $SiMePh_2$ and $SiMe_2Ph$ groups, compared with that of $SiMe_3$, could arise from inter- or intrachain association with the side-chain phenyl groups resulting in lower specific volume. The inter- or intrachain association can be deduced from the intensity of the γ_2 peaks. The intensity of the γ_2 peak for EM3 is higher than that for EM1. This implies that the number concentration of unhindered phenylene groups is higher in EM3 than in EM1. In other words, some unsubstituted phenylene groups may associate with the phenyl groups of the substituents in EM1. Only some of the unsubstituted phenylene rings participate in the secondary relaxation, resulting in lower peak intensity. An analogous interaction between adjacent motional units has been demonstrated for polymethacrylates, where the secondary relaxation originates from the motion of oxycarbonyl side chains.[26] The intensity decreased with increasing size of alkyl side groups because the alkyl group acted as a potential barrier to the motion of oxycarbonyl groups.

To confirm our assignment of the γ_s peaks, the activation energies were calculated. The activation energy was estimated from the following equation: $\ln \nu = \ln \nu_0 - E_a/RT_m$, where T_m is the temperature of peak maximum and E_a is the activation energy of motions. ν is the experimental frequency (10 Hz), and ν_0 can be assumed as 10^{13} Hz in the case of side-chain motions.[26] It is shown in Table 4 that the γ_s motions of EM1 and RM1 have higher activation energy than EM2 and RM2. It is indicated by this calculation that the motion of larger substituent is more hindered, which agrees with the current assignment of the motion. The activation energy for the γ_s motion of EM3 and RM3 is expected to be much lower, although the result is not available. In summary, both peak intensity and the activation energy value for the γ_s peak demonstrate that the mobility of the substituents decreases in the order of $SiMe_3 > SiMe_2Ph > SiMePh_2$. The decreased mobility of the substituents leads to the smaller *d*-spacing, lower specific volume, and consequently lower gas permeability.

The importance of the local mobility of substituent rather than its size has been also demonstrated by the difference in meta/para substituent effects.[1,4] For example, both meta and para substituents in polysulfones have the same size, but para-substituted analogues always have higher permeability than meta-substituted analogues due to their higher local mobility.[4]

Conclusions

The effect of the substituent size and the degree and site of substitution on gas transport properties has been investigated for chemically modified polysulfones and poly(phenyl sulfone)s, where bulky silyl groups were substituted on their phenylene units. The substitution of bulky pendant groups was observed to enhance the gas permeability of the polymers in the order of $SiMePh_2 < SiMe_2Ph < SiMe_3$. In particular, when the smallest $SiMe_3$ group was introduced at the *ortho* sites to ether linkage, the oxygen permeability increased almost 7-fold with only a marginal decrease in selectivity compared with that of the unmodified polysulfone. The improved gas separation properties appear to arise primarily from the increase in free volume and the high mobility of pendant substituents, as investigated by a dynamic mechanical analysis study. We found that the substituent mobility is well correlated with the *d*-spacing as well as the gas permeability. It was concluded that the mobility characteristics rather than the size of the pendant substituents provide extra free volume for gas transport resulting in improved gas permeability.

References and Notes

(1) Pixton, M. R.; Paul, D. R. In *Polymeric Gas Separation Membranes*; Paul, D. R., Yampolskii, Y. P., Eds.; CRC Press: Boca Raton, FL, 1994; Chapter 3, pp 83−153.

(2) McCaig, M. S.; Seo, E. D.; Paul, D. R. *Polymer* **1999**, *40*, 3367.

(3) Aitken, C. L.; Koros, W. J.; Paul, D. R. *Macromolecules* **1992**, *25*, 3424.

(4) Pixton, M. R.; Paul, D. R. *Macromolecules* **1995**, *28*, 8277.

(5) Pixton, M. R.; Paul, D. R. *J. Polym. Sci., Part B: Polym. Phys.* **1995**, *33*, 1135.

(6) Aitken, C. L.; Koros, W. J.; Paul, D. R. *Macromolecules* **1992**, *25*, 3651.

(7) Zhang, J.; Hou, X. *J. Membr. Sci.* **1994**, *97*, 275.

(8) Perego, G.; Roggero, A.; Sisto, R.; Valentini, C. *J. Membr. Sci.* **1991**, *55*, 325.

(9) Yamamoto, H.; Mi, Y.; Stern, S. A. *J. Polym. Sci., Part B: Polym. Phys.* **1990**, *28*, 2291.

(10) Freeman, B. D. *Macromolecules* **1999**, *32*, 375.

(11) Nagase, Y.; Udea, T.; Matsui, K.; Uchikura, M. *Polym. J.* **1986**, *43*, 733.

(12) Kawakami, Y.; Karasawa, H.; Aoki, T.; Yamamura, Y.; Yamashita, Y. *Polym. J.* **1985**, *17*, 1159.

(13) Nagase, Y.; Takamura, Y.; Matsui, K. *J. Appl. Polym. Sci.* **1991**, *42*, 185.

(14) McHattie, J. S.; Koros, W. J.; Paul, D. R. *Polymer* **1991**, *32*, 840, 2618.

(15) McHattie, J. S.; Koros, W. J.; Paul, D. R. *Polymer* **1992**, *33*, 1701.

(16) Ghosal, K.; Chern, R. T.; Freeman, B. D.; Daly, W. H.; Negulescu, I. I. *Macromolecules* **1996**, *29*, 4360.

(17) Bonfanti, C.; Lanzini, L.; Sisto, R.; Valentini, C. *J. Appl. Polym. Sci.* **1997**, *64*, 1987.

(18) Guiver, M. D.; Robertson, G. P.; Yoshikawa, M.; Tam, C. M. In *Membranes Formation and Modification*; Pinnau, I., Freeman, B., Eds.; ACS Symp. Ser. 744; American Chemical Society: Washington, DC, 1999; pp 137−161.

(19) Xu, Z.-K.; Bohning, M.; Schultze, J. D.; Li, G.-T.; Springer, J.; Glatz, F. P.; Mulhaupt, R. *Polymer* **1997**, *38*, 1573.

(20) Madkour, T. M. *Polymer* **2000**, *41*, 7489.

(21) Park, J. Y.; Paul, D. R. *J. Membr. Sci.* **1997**, *125*, 23.

(22) van Krevelen, Q. W. In *Properties of Polymers*; Elsevier: Amsterdam, 1990; pp 455−623.

(23) Aitken, C. L.; McHattie, J. S.; Paul, D. R. *Macromolecules* **1992**, *25*, 2910.

(24) Jho, J. Y.; Yee, A. F. *Macromolecules* **1991**, *24*, 1905.

(25) Xiao, C.; Yee, A. F. *Macromolecules* **1992**, *25*, 6800.

(26) Heijboer, J. In *Molecular Basis of Transitions and Relaxations*; Meier, D. J., Ed.; Gordon and Breach: New York, 1978; pp 75−102.

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