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Gas transport and dynamic mechanical behavior in modified polysulfones with trimethylsilyl groups: effect of degree of substitution

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Abstract

Trimethylsilyl (TMS) groups were introduced with controlled degree of substitution (DS) onto the phenylene rings of various polysulfones. The introduction of TMS groups resulted in a marked increase in oxygen permeabilities with small concurrent decreases in oxygen/nitrogen permselectivities. Although TMS groups are bulky, they are highly mobile and are expected to reduce chain packing as evidenced by larger specific volumes and *d*-spacings with increasing DS. The higher is DS, the greater the reduction in the chain packing that occurs. Dynamic mechanical analyses of sub-glass-transition relaxation, i.e., γ -relaxation behavior, showed that the TMS groups affected the local chain motion. In particular, the motion of unsubstituted phenylene rings increases with DS. Therefore, both the loosened chain packing and the increased local motion by substitution of TMS may result in the increase in the gas permeability.

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1. Introduction

Numerous studies on the permeation of gases through polymers have been carried out in an attempt to understand transport mechanism [1–7] and thereby to overcome the ‘trade-off’ trend in the relationship between gas permeability and permselectivity that is

frequently observed in common polymers [8,9]. The major physicochemical factors that determine the gas permeability and permselectivity of polymers are reported to be: (1) chain mobility, (2) polymer chain packing and (3) polymer–gas interactions. It is well known that there are hardly any specific interactions of polymers with permanent gases such as oxygen, nitrogen and methane at relatively low gas pressures such as below 10 bar, except carrier-mediated transport. Thus for a given permanent gas, permeation

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properties depend primarily on the packing density and the mobility of polymeric chains. The former has been frequently interpreted in terms of free volume, specific volume and *d*-spacing and the latter through dynamic mechanical analysis (DMA), nuclear magnetic resonance (NMR), and dielectric relaxation [10–13].

Modification of polymer structures has been performed to improve gas permeation properties and investigate the relationship between gas permeability and polymer structure. Experimental literature data for structural variants of bisphenol-A polysulfones can be summarized by: (a) symmetrical introduction of methyl groups into the phenylene rings of the bisphenol-A unit as in tetramethylpolysulfone, leads to increased glass-transition temperature, free volume and gas permeability but (b) in the case of asymmetrical substitution such as dimethylpolysulfone, vice versa occurs [1]. Furthermore, DMA studies suggested that the molecular motion of methyl-substituted phenyl rings was primarily responsible for changes in gas permeability in methyl-substituted polysulfones.

Trimethylsilyl (TMS) groups were reported to be an excellent substituent to increase permeability in silylated poly(1,4-dimethylphenylene oxide) (PPO) and poly(1-trimethylsilyl-1-propyne) (PTMSP) [14,15]. Such properties of TMS were reported to originate from steric bulkiness and high electrostatic interactions [16]. In a previous study [17], the size of the substituent group in polysulfones was systematically increased from TMS to bulkier dimethylphenylsilyl and methyldiphenylsilyl groups. It was found that TMS was the most effective in increasing permeability among the three silyl substituents. Therefore it is proposed that the shape and mobility of the substituent is a critical factor in determining transport properties rather than its size [17].

In the present work, TMS groups were introduced onto the phenylene rings of various polysulfones such as polysulfone (PSf), hexafluoropolysulfone (HF-PSf), tetramethylpolysulfone (TMPSf), and tetramethylpoly(phenylsulfone) (TMPPSf) with controlled degree of substitution (DS) in order to improve gas permeation properties. The effect of DS on gas permeation properties and its relationship with the sub-glass-transition behavior are investigated.

2. Experimental

2.1. Membrane and polymers

Chemical structures and notations of the polymers studied are shown in Table 1. TMS groups were introduced by chemical reaction onto phenylene rings of PSf, HFPSf, TMPSf and TMPPSf. Polymers were first lithiated using *n*-butyllithium, then quenched with a TMS electrophile such as chloro- or iodotrimethylsilane. Full details of modification procedures and structural characterization for all polymers except HFPSf are reported elsewhere [18,19].

HFPSf was also first activated by lithiation. However, the presence of the hexafluoroisopropylidene linkage necessitated the use of an additional 1 mol equivalent of *n*-butyllithium since 1 mol of reagent is believed to be inactivated though being complexed with the fluorine groups. Details of the initial lithiation procedure for HFPSf have been reported elsewhere [20]. The lithiated HFPSf was converted to TMS derivatives by quenching the intermediate with the appropriate TMS electrophile.

Dense membranes were prepared in the form of films, which were made from ~5 wt.% polymer solutions with tetrahydrofuran (THF). Polymer solutions were filtered through Whatman® 25 mm syringe filters of which pore size was 1 µm. The drying process was performed at 40 °C and residual solvent was removed in a vacuum oven for 3 days at 40 °C. Gas permeability coefficients were obtained by measuring downstream pressure change through the constant volume method. Steady-state pressure rate was chosen in the time region above 10 more than the time-lag and permeability was calculated using the following formula:

$$P (\text{cm}^3 (\text{STP})\text{cm}/\text{cm}^2 \text{ s cm Hg}) = \frac{\text{quantity of permeate} \times \text{film thickness}}{\text{area} \times \text{time} \times \text{pressure drop across film}}$$

2.2. Characterization

Glass-transition temperature (T_g) was obtained by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC7 with a scanning rate of 20 °C/min. X-ray diffraction was used to investigate *d*-spacing. Macscience model M18XHF22 was utilized with Cu Kα radiation of which wavelength (λ) was 1.54 Å

Table 1
Chemical structures of modified polysulfones

Code	DS ^a	Structure
PSf	0.0	
PSf10	1.0 (=a + b)	
PSf20	2.0 (=a + b)	
HFPSf	0.0	
HF20	2.0 (=a + b)	
HF35	3.5 (=a + b + c + d)	
TMPSf	0.0	
TM15	1.5 (=a + b + c + d)	

Table 1 (Continued)

Code	DS ^a	Structure
TM26	2.6 (=a + b + c + d)	
TMPPSf	0.0	
TMP15	1.5 (=a + b + c + d)	
TMP26	2.6 (=a + b + c + d)	

^a The number of TMS per polymer repeating unit.

and the scanning speed was 5°/min. The value of d -spacing was calculated by means of Bragg's law ($d = \lambda/2 \sin \theta$), using θ of broad peak maximum. The densities of the dried membranes were measured by the displacement method using a Mettler density kit with anhydrous ethanol at 23 °C.

Dynamic mechanical thermal analyzer MK III of Rheometrics Scientific was used. Samples were compression molded above T_g , and they had geometry of 30 mm × 8 mm × 2 mm. The temperature range from −150 °C to above T_g was studied, adopting a scanning rate of 2.5 °C/min and frequency of 10 Hz. Dual-cantilever bending mode was employed.

3. Results and discussion

3.1. Physical properties

d -Spacings, specific volumes (V_{sp}) and T_g of various polysulfones are listed in Table 2. All

TMS-substituted polysulfones showed an increase in specific volume compared with corresponding unmodified polysulfones. For example, V_{sp} of PSf increased with DS from 0.83 to 0.89 cm³/g at DS 2.0.

Table 2
Physical properties of modified-polysulfones with TMS groups

	T_g (°C)	V_{sp} (cm ³ /g)	d -Spacing (Å)
PSf	185	0.83	5.0
PSf10	167	0.86	5.2
PSf20	164	0.89	5.4
HFPSf	199	0.70	5.1
HF20	172	0.79	5.3
HF35	149	0.86	5.4
TMPSf	231	0.86	5.2
TM15	212	0.90	5.3
TM26	193	0.94	6.0
TMPPSf	280	0.82	5.2
TMP15	240	0.84	5.3
TMP26	234	0.93	6.1

This increase in V_{sp} indicates that the chain packing was reduced by the introduction of bulky but mobile TMS groups. Evidence for the reduction of chain packing by TMS was also found in wide-angle X-ray diffraction. Table 2 shows that the d -spacing values increased with the introduction of TMS groups. For example, the d -spacing value for PSf increased with DS from 5.0 to 5.4 Å at DS 2.0. The specific volume and d -spacing values suggest that the chain packing is suppressed by TMS groups and thereby loosened.

When TMS groups were introduced onto phenylene rings, T_g decreased with DS, possibly also suggesting a loosened chain packing. In the case of PSf, T_g decreased with DS from 185 to 167 °C at DS 1.0 and to 164 °C at DS 2.0. T_g of HFPSf also decreased from 199 to 172 °C at DS 2.0 and to 149 °C at DS 3.5. TMPSf and TMPPSf also showed a 40 °C decrease in T_g at DS 2.5. The decrease in T_g can be at least partly ascribed to a breakage in symmetry of the phenylene ring by the introduction of TMS. These results are consistent with the fact that polysulfones with asymmetrically methyl-substituted phenylene rings had a much lower T_g value than that with symmetrically methyl-substituted phenylene ring [1].

3.2. Gas permeation properties

Gas permeabilities and permselectivities of various polysulfones modified with TMS are listed in Table 3.

Table 3
Gas permeation properties of modified polysulfones with TMS groups

	$P(\text{CO}_2)$ (barrer) ^a	$P(\text{O}_2)$ (barrer)	$P(\text{N}_2)$ (barrer)	$P(\text{O}_2)/P(\text{N}_2)$
PSf	6.3	1.1	0.19	5.8
PSf10	10	2.2	0.38	5.8
PSf20	18	4.2	0.77	5.5
HFPSf	12	3.4	0.67	5.1
HF20	41	9.9	2.0	5.0
HF35	110	28	6.3	4.4
TMPSf	21	5.6	1.1	5.1
TM15	32	6.9	1.5	4.6
TM26	66	14	3.1	4.5
TMPPSf	32	5.8	1.2	4.8
TMP15	73	15	3.2	4.7
TMP26	126	29	6.3	4.6

^a Barrer = 10^{-10} cm³ (STP)/cm s cm Hg.

The gas permeabilities always increased markedly when TMS groups were introduced. In the case of PSf, oxygen permeability increased from 1.1 to 4.2 barrer at DS 2.0. Other TMS-substituted polysulfones also exhibited large increases in the gas permeabilities. When methyl groups were asymmetrically introduced onto phenylene rings, such as dimethylpolysulfone, gas permeabilities decreased due to greater chain packing [1]. However, TMS-substituted polysulfones showed that gas permeabilities increased in spite of the asymmetrical substitution. This may be associated with the effective loosening of the chain packing by the much more bulky but mobile TMS. As a result, it can be concluded that the TMS group is effective in increasing the gas permeabilities in various polysulfones and its effect becomes more significant with increasing DS.

Fig. 1 illustrates the increase in gas permeability with increasing DS. It shows that logarithmic gas permeabilities increase nearly linearly with DS. This semi-logarithmic relationship is identical with the mathematical model to estimate gas permeability by the group contribution method [21]. Robeson et al. [21] suggested that the logarithmic permeability of a copolymer is linearly proportional to its composition:

$$\ln P = \sum \phi_i \ln P_i$$

where P_i and ϕ_i are the permeability and volume fraction of specific group i , respectively. Therefore logarithmic permeability linearly increases with volume fraction of more permeable unit. Fig. 2 shows the effect of the volume fraction of the TMS-substituted phenylene unit on the gas permeabilities in PSf. The effect of the volume fraction of the TMS-substituted group on gas permeability is expected to be the same as that of DS because the volume fraction linearly increases with DS. These results suggest that gas permeabilities increase exponentially with DS.

Increases in permeability are generally known to be accompanied by decreases in permselectivity. Table 3 shows that the oxygen permeability increases with DS whereas the oxygen/nitrogen permselectivity decreased slightly. Fig. 3 shows a plot of oxygen/nitrogen permselectivity vs. logarithmic oxygen permeability, demonstrating the effects of TMS and DS clearly. Therefore, it can be concluded that gas permeation properties are improved by substitution of the TMS group on the polymer chains of various polysulfones

Fig. 1. The effect of DS on gas permeabilities of modified polysulfones: (a) PSf; (b) HFPSf; (c) TMPSf; (d) TMPPSf.

and its effect becomes more pronounced with increasing DS.

3.3. Dynamic mechanical analysis

The small-scale local molecular motion in polymers is an important parameter affecting diffusion behavior and consequently permeability. Some researchers have demonstrated that the correlation between gas permeability and T_g was rather poor [1,4,22]. This appears to be due primarily to the difference in the scale of motions necessary for gas diffusion and glass transition.

Small-scale local chain motions are sufficient for diffusion of small gas molecules whereas rather large-scale cooperative motions are involved in T_g . Thus the gas permeability is rather well correlated with small-scale local chain motions [23,24], which have been normally characterized by sub- T_g relaxation behavior (i.e., secondary relaxation or γ -relaxation). The γ -relaxation behavior has been investigated by DMA to understand the relationship between small-scale local chain motions and gas permeability [2,4,5,22,25,26].

The DMA results of the TMS-substituted HFPSfs and TMPSfs in comparison with unsubstituted

Fig. 2. The effect of volume fraction of TMS-substituted phenylene group on gas permeabilities in PSf.

polysulfones are presented in Figs. 4 and 5, respectively. As shown in Fig. 4, HFPSf showed the γ -relaxation near -100°C and β -relaxation near 40°C . It has been well known that the β -relaxation originates from thermal history and/or residual stress, as it could usually be removed or diminished by physical aging at that temperature. The TMS-substituted

Fig. 3. Logarithmic plot for oxygen/nitrogen permselectivity vs. oxygen permeability with varying DS.

HFPSfs showed only one γ -relaxation peak, contrary to methyl- or halogen-substituted PSfs. When substituents such as methyl or halogen were introduced onto phenylene rings, two γ -relaxation peaks appeared. The γ -relaxation peak at a higher temperature was called the γ_1 -peak and that at a lower temperature the γ_2 -peak, i.e., dimethylpolysulfone

Fig. 4. Dynamic mechanical spectra for HFPSf series.

Fig. 5. Dynamic mechanical spectra for TMPSf series.

showed the γ_1 -peak near 80°C and the γ_2 -peak near -80°C [5]. McHattie et al. proposed that the γ_1 -peak is related to the motion of the methyl-substituted phenylene and the γ_2 -peak to the motion of the unsubstituted phenylene. In the case of TMS-substituted HFPSfs, only the γ_2 -peak was observed but not the γ_1 -peak below the glass-transition temperature. This indicated that the motion of the TMS-substituted phenylene was hindered much more than that of the methyl-substituted phenylene and so the γ_1 -peak related to the TMS-substituted phenylene was not shown at temperatures below T_g , as also shown in silylated PSfs [20].

When TMS groups were introduced, the γ_2 -peak shifted to a lower temperature because the unsubstituted phenylene could become more mobile due to the loosening of the chain packing by the TMS groups as described previously. Furthermore, the γ_2 -peak shifted to a lower temperature with increasing DS. It is also found that the intensity of the γ_2 -peak decreased due to the decrease in the number of the unsubstituted phenylene with DS. Therefore the DMA results for the TMS-substituted HFPSf re-ascertain that the γ_2 -peak is related to the unsubstituted phenylene motion. In Fig. 5, TMPSf shows the γ_2 -peak near -100°C and the γ_1 -peak near -40°C . In the TMS-substituted TMPSfs, the γ_2 -peaks also shifted to a lower temperature with increasing DS and those

intensities decreased. In addition, the γ_1 -peak intensity decreased with DS and was not shown at DS 2.5. This was simply due to the decrease in the number of methyl-substituted phenylene with DS.

In the case of methyl-substituted polysulfones, it was proposed from DMA studies that the molecular motion of methyl-substituted phenyl rings was primarily responsible for changes in gas transport [1]. In the case of TMS-substituted polysulfones, the γ_1 -peak related to the motion of the TMS-substituted phenylene was not shown at temperatures below T_g . In a previous study of silyl-modified polysulfones, it was suggested that the mobility of a substituent was a critical factor in determining transport properties and the γ -peak related to molecular motion of TMS might be seen below -150°C [17]. Therefore, it may be concluded that the gas permeability increased due to the loosening of the chain packing by mobile TMS groups, as evidenced by a shift of the γ_2 -peak to a lower temperature and the chain packing reduction is more pronounced with increasing DS.

4. Conclusion

TMS groups were introduced onto phenylene rings of various polysulfones with controlled DS. Gas permeabilities increased markedly with the substitution

of TMS whereas the oxygen/nitrogen permselectivity decreased slightly. These improvements in transport properties are more pronounced with increasing DS. The enhanced gas permeability may be associated with both the loosened chain packing and the increased small-scale local motion by mobile TMS groups. Therefore it is concluded that TMS is very effective in improving gas separation properties and its effect is more pronounced at high DS. It is also seen that all TMS-substituted polysulfones showed decreases in T_g with DS primarily due to a disruption of the symmetry of the phenylene ring in polysulfones.

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References

- [1] C.L. Aitken, W.J. Koros, D.R. Paul, Effect of structural symmetry on gas transport properties of polysulfones, *Macromolecules* 25 (1992) 3424.
- [2] C.L. Aitken, W.J. Koros, D.R. Paul, Gas transport properties of bisphenol-A polysulfones, *Macromolecules* 25 (1992) 3651.
- [3] J.S. McHattie, W.J. Koros, D.R. Paul, Gas transport properties of polysulfones. 1. Role of symmetry of methyl group placement on bisphenol rings, *Polymer* 32 (1991) 840.
- [4] J.S. McHattie, W.J. Koros, D.R. Paul, Gas transport properties of polysulfones. 2. Effect of bisphenol connector groups, *Polymer* 32 (1991) 2618.
- [5] J.S. McHattie, W.J. Koros, D.R. Paul, Gas transport properties of polysulfones. 3. Comparison of tetramethyl-substituted bisphenols, *Polymer* 33 (1992) 1701.
- [6] Y. Hirayama, T. Yoshinaga, Y. Kusuki, K. Ninomiya, T. Sakakibara, T. Tamari, Relation of gas permeability with structure aromatic polyimides I, *J. Membr. Sci.* 111 (1996) 169.
- [7] Y. Hirayama, T. Yoshinaga, Y. Kusuki, K. Ninomiya, T. Sakakibara, T. Tamari, Relation of gas permeability with structure aromatic polyimides II, *J. Membr. Sci.* 111 (1996) 183.
- [8] L.M. Robeson, Correlation of separation factor versus permeability for polymeric membranes, *J. Membr. Sci.* 62 (1991) 165.
- [9] B.D. Freeman, Basis of permeability/selectivity tradeoff relationships in polymeric gas separation membranes, *Macromolecules* 32 (1999) 375.
- [10] J.Y. Park, D.R. Paul, Correlation and prediction of gas permeability in glassy polymer membrane materials via a modified free volume based group contribution method, *J. Membr. Sci.* 125 (1997) 23.
- [11] M.D. Sefcik, J. Schaefer, F.L. May, D. Raucher, S.M. Dub, Diffusivity of gases and main-chain cooperative motions in plasticized poly(vinyl chloride), *J. Polym. Sci. B* 21 (1983) 1041.
- [12] J. Schaefer, M.D. Sefcik, E.O. Stejskal, R.A. McKay, W.T. Dixon, R.E. Cais, Molecular motions in glassy polystyrenes, *Macromolecules* 17 (1984) 1107.
- [13] S.Y. Kwak, Relationship of relaxation property to reverse osmosis permeability in aromatic polyamide thin-film-composite membrane, *Polymer* 40 (1999) 6361.
- [14] J. Zhang, X. Hou, The gas permeation property in trimethylsilyl-substituted PPO and triphenylsilyl-substituted PPO, *J. Membr. Sci.* 97 (1994) 275.
- [15] R. Sisto, C. Bonfanti, C. Valenti, Structure and gas permeability of alkynylated poly(phenylene oxide), *J. Membr. Sci.* 95 (1994) 135.
- [16] M. Madkour, Development of the molecular design rules of ultra-permeable poly[1-(trimethylsilyl)-1-propyne] membranes, *Polymer* 41 (2000) 7489.
- [17] I.W. Kim, K.J. Lee, J.Y. Jho, H.C. Park, J. Won, Y.S. Kang, M.D. Guiver, G.P. Robertson, Y. Dai, Correlation between structure and gas transport properties of silyl-modified polysulfones and poly(phenyl sulfone)s, *Macromolecules* 34 (2001) 2908.
- [18] M.D. Guiver, G.P. Robertson, S. Rowe, S. Foley, Y.S. Kang, H.C. Park, J. Won, H.N. Le Thi, Modified polysulfones. 4. Synthesis and characterization of polymers with silicon substituents for a comparative study of gas transport properties, *J. Polym. Sci. A* 39 (2001) 2103.
- [19] Y. Dai, M.D. Guiver, G.P. Robertson, F. Bilodeau, Y.S. Kang, K.J. Lee, J.Y. Jho, J. Won, Modified polysulfones. 5. Synthesis and characterization of tetramethyl containing trimethylsilyl groups and their gas transport properties, *Polymer* 43 (2002) 5369.
- [20] M. Yoshikawa, A. Niimi, M.D. Guiver, G.P. Robertson, Modified polysulfone membranes. IV. Gas separation with aminated polysulfone membranes, *Sen'i Gakkaishi (J. Soc. Fiber Sci. Jpn.)* 56 (2000) 272.
- [21] L.M. Robeson, C.D. Smith, M. Langsam, A group contribution approach to predict permeability and permselectivity of aromatic polymers, *J. Membr. Sci.* 132 (1997) 33.
- [22] K. Ghosal, R.T. Chern, B.D. Freeman, W.H. Daly, I.I. Negulescu, *Macromolecules* 29 (1996) 4360.
- [23] S.Y. Kwak, J.C. Lee, Local molecular mobility as a crucial factor affecting gas permeability of poly(oxyethylene)s with

- (alkylsulfonyl)methyl side chains, *Macromolecules* 33 (2000) 8466.
- [24] T. Kanaya, M. Teraguchi, T. Masuda, K. Kaji, Local mobility of substituted polyacetylenes measured by quasielastic neutron scattering and its relationship with gas permeability, *Polymer* 40 (1999) 71.
- [25] M.R. Pixton, D.R. Paul, Gas transport properties of polyarylates. 1. Connector and pendant group effect, *J. Polym. Sci. B* 33 (1995) 1135.
- [26] C.L. Aitken, J.S. McHattie, D.R. Paul, Dynamic mechanical behavior of polysulfones, *Macromolecules* 25 (1992) 2910.