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Publisher's version / Version de l'éditeur:
https://doi.org/10.1021/bk-2004-0876.ch010
Advanced Materials for Membrane Separations, ACS Symposium Series, pp. 154-166, 2004-04-20

ACS SYMPOSIUM SERIES **876**

Advanced Materials for Membrane Separations

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American Chemical Society, Washington, DC

Chapter 10

Gas Transport Properties of Tetramethyl Polysulfones Containing Trimethylsilyl Group Side Substituents

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Polysulfones with rigid chain structures and trimethylsilyl (TMS) substituents were prepared as potential membrane materials having enhanced gas transport properties. Tetramethyl polysulfones were modified by bromination and lithiation methodology to introduce high levels of TMS groups. Direct lithiation resulted exclusively in ortho-sulfone TMS. Bromination followed by excess lithiation resulted in a high degree of substitution (DS) of TMS on both the bisphenol and phenylsulfone rings. Polymers with a high DS of TMS had high CO_2 and O_2 permeabilities and good permselectivities from N_2. Permeabilities were correlated with *d*-spacing and specific volume.

[1] NRCC No. 44385

Introduction

Bisphenol A Polysulfone (PSf) is a commercial thermoplastic widely used as a membrane material or support for liquid separation processes (*1,2*). It was used for fabricating the first commercial gas separation hollow fiber membranes about two decades ago because of its relatively high permselectivities and adequate permeabilities to various gases as well as its combination of good mechanical properties and fiber spinning qualities (*3*). Increased performance requirements provide incentives to develop new membrane materials since many studies have shown that an improvement in gas transport properties could be obtained by modifying or tailoring the polymer structure.

The groups of Koros and Paul studied parallel families of polysulfones in which systematic structural modifications were correlated with their gas transport properties (*4-8*). The groups of Koros and Paul (*4,6,9*) and Pilato et al. (*10*) showed that symmetrical substitution of methyl groups onto the bisphenol or biphenol segment of PSf and polyphenylsulfone (PPSf) to give tetramethylbisphenol-A polysulfone (TMPSf) and tetramethylbiphenol polysulfone (TMPPSf) respectively, resulted in a large increase in permeability without too great a loss in permselectivity because of increased chain stiffness and higher free volume. The objective of the present work was to modify these materials with TMS and other bulky substituents and correlate the structural effect on gas transport properties.

We reported the modification of polysulfones by direct lithiation (*11*) or by bromination-lithiation (*12*) to produce reactive intermediates that were converted by reaction with various electrophiles to yield TMS (*13*) and a number of other derivatives (*14,15*). Using this chemistry, we previously synthesized PSfs and PPSfs with sequentially increasing sizes of silicon substituents containing methyl and phenyl groups (*13*) and correlated their structural effect on gas transport properties (*16*). TMS substituents gave the most favorable properties with permeability coefficients for O_2 increasing with DS and with minimal loss in O_2/N_2 permselectivity. In the present work, we combine the good gas transport properties of TMPSf and TMPPSf with permeability-enhancing TMS groups.

Experimental

Polymer syntheses and characterization methods

Complete details of polymer syntheses and corresponding detailed structural characterization data are reported elsewhere (*17*). A DuPont 951

thermogravimetric analyzer was used for measuring glass transition temperature (T_g) by differential scanning calorimetry (DSC). Samples for DSC were heated initially to at least 30°C above T_g at 10°C/min, quenched with liquid nitrogen, held isothermally for 10 min and re-heated at 10°C/min for the T_g measurement. Dense polymer films (~100 μm thickness) were made from chloroform solutions as detailed in (*17*). The absence of residual solvent in the films was confirmed by observing T_g. Gas permeability coefficients were obtained by measuring downstream pressure change using the constant volume method at 35°C with an upstream pressure of 1 atmosphere. Steady-state pressure rate was chosen in time region above ten more than the time-lag and permeability was calculated using the following formula:

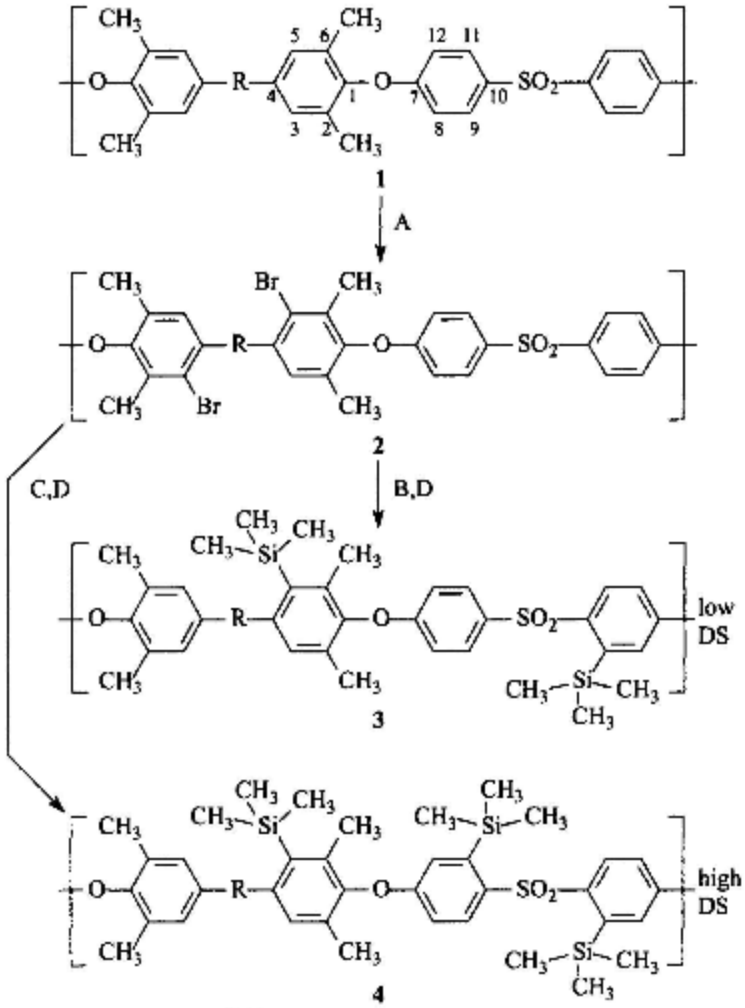
$$P = \frac{(\text{quantity of permeate})(\text{film thickness})}{(\text{film area})(\text{time})(\text{pressure drop across film})} \left[\frac{\text{cm}^3(\text{STP})\,\text{cm}}{\text{cm}^2\,\text{s}\,\text{cmHg}}\right]$$

X-ray diffraction was used to determine *d*-spacing. A Macscience Model M18XHF22 was utilized with Cu K_α radiation of which wavelength (λ) was 1.54 Å and a scanning speed of 5°/min. The value of *d*-spacing was calculated by means of Bragg's law ($d = \lambda / 2\sin\theta$), using θ of the broad peak maximum. Densities of the films were measured by the displacement method using a Mettler density kit with anhydrous ethanol at 23°C.

Results and Discussion

Syntheses

The starting polymers TMPSf (**1a**) and TMPPSf (**1b**) were prepared by the potassium carbonate / dimethylacetamide McGrath polycondensation conditions (*18-22*) and gave polymers with inherent viscosities in NMP solvent of 0.84 and 0.66 respectively (*17*). Bromination reactions were performed with bromine at room temperature and resulted in fully dibrominated polymers as shown in Scheme 1. It was anticipated that when TMPSf-5-Br_2 (**2a**) and TMPPSf-5-Br_2 (**2b**) were lithiated with 2.2 mol equivalents of *n*-butyllithium, then quenched with TMSCl or TMSI electrophiles according to Scheme 1, simple metal-halogen exchange would occur giving TMS groups substituting only at the 5-bromine site. However, for both resulting "low DS" silylated polymers **3a** and **3b**, a DS of ~1.5 was obtained. Bromine analyses showed incomplete metal-halogen exchange, and NMR spectroscopy indicated that TMS groups were approximately equally distributed at both the bromine site (DS~0.75 at the 5-position) and *ortho* to the sulfone group (DS~0.75 at the 11-site) (*2*).



1a TMPSf, R is -C(CH$_3$)$_2$- **1b** TMPPSf, R is sigma bond

2a TMPSf-5-Br$_2$ **2b** TMPPSf-5-Br$_2$

3a TMPSf-5,11-(SiMe$_3$) DS~1.5 **3b** TMPPSf-5,11,(SiMe$_3$) DS~1.5

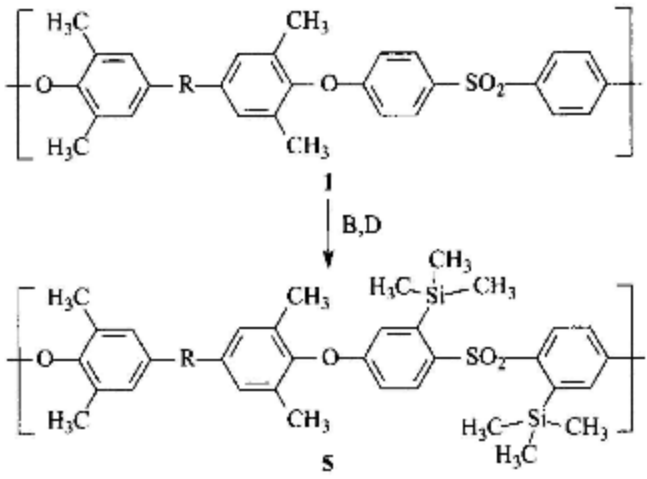
4a TMPSf-5,11-(SiMe$_3$) DS~2.6 **4b** TMPPSf-5,11-(SiMe$_3$) DS~2.6

A: Br$_2$/CHCl$_3$; B: 2.2 mol eq. *n*-C$_4$H$_9$Li; C: 5 mol eq. *n*-C$_4$H$_9$Li

D: iodotrimethylsilane or chlorotrimethylsilane

Scheme 1 Preparation of TMS derivatives by bromination – lithiation

Both dibrominated polymers **2a** and **2b** were also lithiated with an excess of *n*-butyllithium (5 mol equivalents) for lithium-halogen exchange in addition to direct lithiation at the sulfone site in order to achieve the maximum amount of TMS groups on the polymer chain. For both resulting "high DS" silylated polymers **4a** and **4b**, a DS of ~2.6 was obtained and in a second synthesis, a DS 2.8 was obtained for **4b**. Bromine analyses of these products showed only trace residual amounts of bromine indicating almost complete metal-halogen exchange. NMR analysis (*17*) showed that the increase in DS for TMS groups occurred predominately at the 11-site, resulting in a polymer having the composition of TMS DS~0.75 at the 5-position and TMS DS~1.85 at the 11-position. Although almost all brominated sites underwent lithium-halogen exchange, the majority of sites were protonated during work-up since the steric hindrance was too high to allow any greater than DS~0.75 of TMS groups at the 5-site. As anticipated, direct lithiation of **1a** and **1b** resulted exclusively in 11-substituted TMS polymers **5a** and **5b**, each with a DS of 1.7 as shown in Scheme 2 (*17*).



1a TMPSf, R is $-\overset{CH_3}{\underset{CH_3}{C}}-$ **1b** TMPPSf, R is sigma bond

5a TMPSf-11-($SiMe_3$) DS~1.7 **5b** TMPSf-11-($SiMe_3$) DS~1.7

B: 2.2 mol eq. *n*-C_4H_9Li;

D: iodotrimethylsilane or chlorotrimethylsilane

Scheme 2 Preparation of TMS derivatives by direct lithiation

Glass transition temperature

When compared with their non-tetramethylated counterparts (T_g (PSf) 188.1°C, T_g (PPSf) 225.6°C (*17*)) it is evident from Table I that the respective TM-polysulfones **1a** and **1b** have significantly higher T_gs due to the increased chain rigidity induced by the methyl groups. The T_gs of the TMS polymers were substantially reduced with increasing DS from those of **1a** and **1b** as found in our previous study of related polymers (*13*). This is possibly due to a disruption in symmetry of the phenylene rings (*4*). For the 5,11-TMS substituted polymers, increasing DS led to reduced T_g. The relative reduction in T_g was greater for the directly-lithiated 11-TMS polymer **5a** than for the 5,11-TMS polymer **4a**.

Table I Physical property data for polymers

Polymer	T_g °C	V_{sp} cm³/g	*d*-space Å	[a]$P(CO_2)$	$P(O_2)$	$P(N_2)$	$P(CH_4)$
1a	231.3	0.86	5.2	[b]21	[b]5.6	[b]1.06	[b]0.95
[c]**3a**	212.4	0.90	5.3	32	6.9	1.5	2.5
[d]**4a**	193.0	0.94	6.0	66	14	3.1	4.5
[e]**5a**	189.1	–	–	51	12	2.6	–
1b	280.2	0.82	5.2	[b]32	[b]5.8	[b]1.2	[b]1.3
[c]**3b**	240.2	0.84	5.3	73	15	3.2	5.1
[d]**4b**	234.3	0.93	6.1	126	29	6.3	9.7
[e]**5b**	226.4	–	–	–	–	–	–

a Permeability coefficients measured at 35°C and at 1 atm upstream pressure. 1 Barrer = 10^{-10} [cm³ (STP) · cm] / (cm² · sec · cm Hg).

b Literature values (*23*); c DS~1.5; d DS~2.6; e DS~1.7

Gas transport

The permeability coefficients (P_{gas}) for four gases are also summarized in Table I, showing that they increase for all gases with the introduction of TMS. Permselectivity *versus* permeability data are plotted relative to the Robeson 'upper bound' line (*24*) for two representative gas pairs: O_2/N_2 in Figure 1 and CO_2/N_2 in Figure 2. Figure 1 shows there are considerable losses in permselectivity for the TMPSf derivatives **3a-5a**. Only the high DS polymer **4a** had a moderate overall improvement in gas transport properties since the drop in permselectivity was offset by a $P(O_2)$ increase more than double that of the low DS **3a** polymer. In contrast, the TMPPSf derivatives **3b** and **4b** show a greater increase in $P(O_2)$ with increasing DS, with only a moderate loss in selectivity.

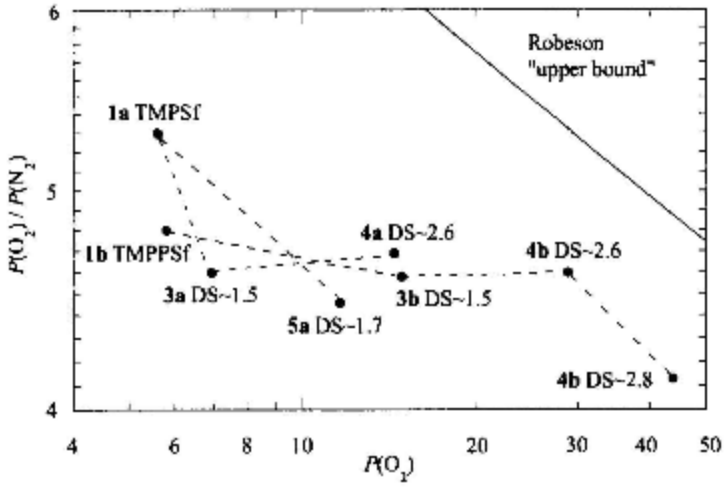


Figure 1. Permselectivity versus permeability for the O_2 / N_2 gas pair

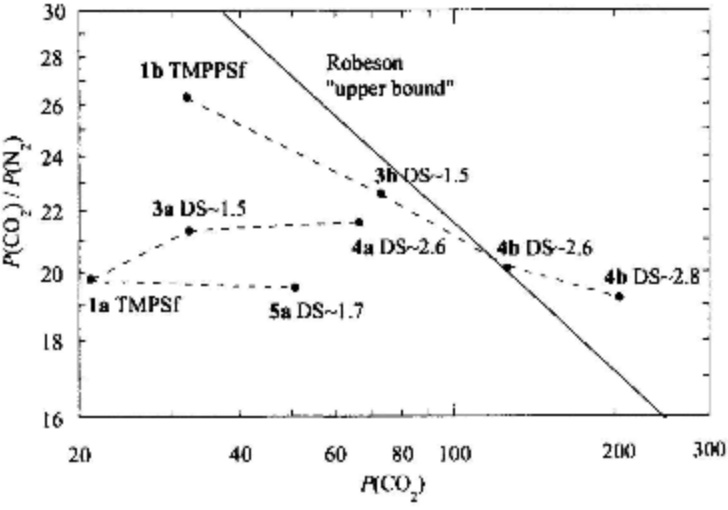


Figure 2. Permselectivity versus permeability for the CO_2 / N_2 gas pair

Here it is worth noting that the O_2/N_2 permselectivity of starting polymer **1b** is rather less than **1a**. Polymer **4b** with DS~2.6 maintained reasonable permselectivity with a five-fold increase in $P(O_2)$, but permselectivity unexpectedly dropped for the same polymer with DS~2.8.

The CO_2/N_2 gas pair data plotted in Figure 2 show different behavior; here the permselectivity for starting polymer **1b** is considerably higher than **1a** (*23*). The TMPSf series **3a-5a** show significant increases in $P(CO_2)$ as well as a surprising increase in CO_2/N_2 permselectivity. Both **3a** and **5a** have a similar DS, but **3a** having TMS substituents on both the 5-site and on the 11-site has higher permselectivity than **5a**, which is exclusively substituted on the 11-site. This supports our previous finding that the substitution site is an important parameter for gas transport properties (*16*). In this case, the higher permselectivity of **3a** over **5a** could be due to increased relative chain rigidity as shown by T_g. TMS substitution at the 11-site tends to give higher gas permeability while at the 5-site, higher permselectivity. Polymer **4b** (DS 2.6 and 2.8) was at or above the Robeson upper-bound limit, with a 4 to 6-fold permeability increase and with a moderate drop in permselectivity compared with TMPPSf. For the TMS polymers, the CO_2/CH_4 permselectivity was lower because $P(CH_4) > P(N_2)$. The relatively high permeability coefficients for both CO_2 and CH_4 condensable gases suggest that TMS increases the solubility coefficients.

Polymer chain packing

The bulky and spherical TMS group hinders interchain packing giving rise to increases in the *d*-spacing values as shown in Table I. Low DS~1.5 polymers **3a** and **3b**, where the TMS groups are distributed ~0.75 on the 5 and 11-sites, have only a small increase in the *d*-spacing values (see Table I) compared with starting polymers. The high DS~2.6 polymers **4a** and **4b** also have DS~0.75 on the 5-site, but the TMS on the *ortho*-sulfone 11-site is increased to ~1.85. The high DS combined with the distribution of TMS groups have a large effect on decreasing the packing ability of the polymers' chains. Figure 3 shows the extent of this effect of the increase in *d*-spacing with increasing DS for TMPSf derivatives. Comparative data (*17*) for PSfs TMS-substituted at the *ortho*-ether 6-site and *ortho*-sulfone 11-site are also included in the graph. Similar trends can be observed for the TMPPSf series (not shown). A single 11-TMS substituent per repeat unit on PSf gives a roughly equivalent *d*-spacing value compared with the tetramethyl substituted polymer **1a**, although the $P(CO_2)$ for the polymers are 10 and 21 Barrers respectively. Even polymer **3a**, where the TMS DS~1.5, there is only a small increase in the *d*-spacing value. As the TMS DS increases towards 2, the *d*-spacing values for the PSf derivatives substituted

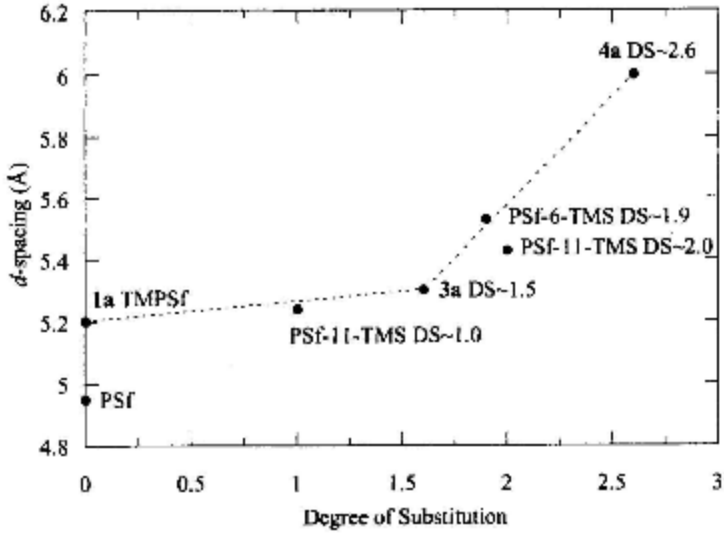


Figure 3. Effect of TMS substitution level on d-spacing.

ortho-sulfone (11-site) and *ortho*-ether (6-site) exhibit significant increases. It is noteworthy that TMS substituted at the more 'open' ether linkage site 6-TMS has a larger effect in reducing interchain packing and has higher permeability than the 11-TMS polymer. Although the PSf-11-TMS polymer has a larger *d*-spacing value than **3a**, it has lower gas permeability ($P(CO_2)$ 18). Both **3a** and **3b** have the same distribution and DS of TMS and *d*-spacing values, yet the gas permeability increase for **3b** is much greater than for **3a** as shown for CO_2 in Figure 4. This is possibly because TMS may induce a larger change in chain conformation of **3b** compared with **3a** through increasing the torsional angle on the biphenyl ring. At DS~2.6, much larger increases in *d*-spacing to 6.0 Å and above were observed for the tetramethylated polymers **4a** and **4b**

The specific volume (V_{sp}) increased with the introduction of TMS groups as shown in Table I, further supporting the assumption of reduced interchain packing. The effect of chain packing on gas permeability is often evaluated by correlating P with fractional free volume (FFV) (*25,26*). The FFV values calculated by group contribution date did not correlate well with P for the trimethylsilyl tetramethyl polysulfones or for modified PSfs investigated previously (*16*). The FFV calculation is very sensitive to small errors in density measurements, in this case measured by the displacement method.

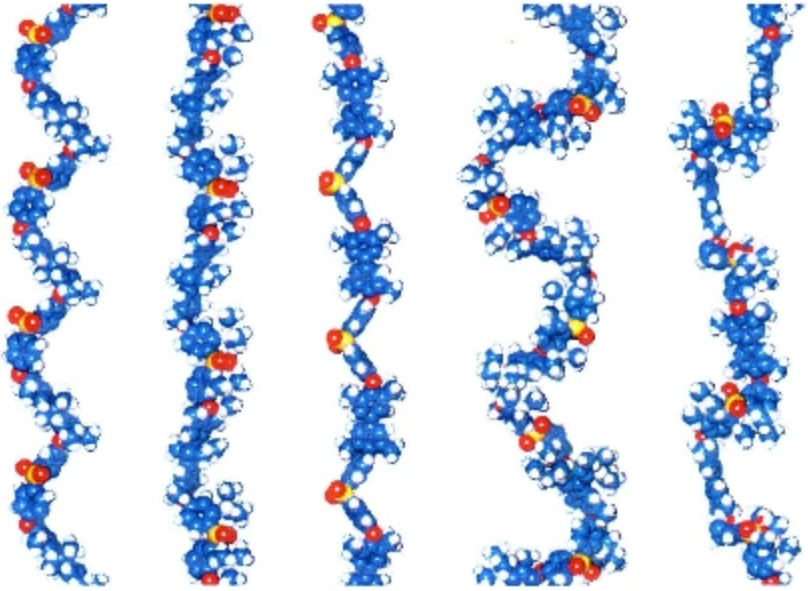


Figure 5. Chain conformation of various unmodified and TMS substituted tetramethylpolysulfones.

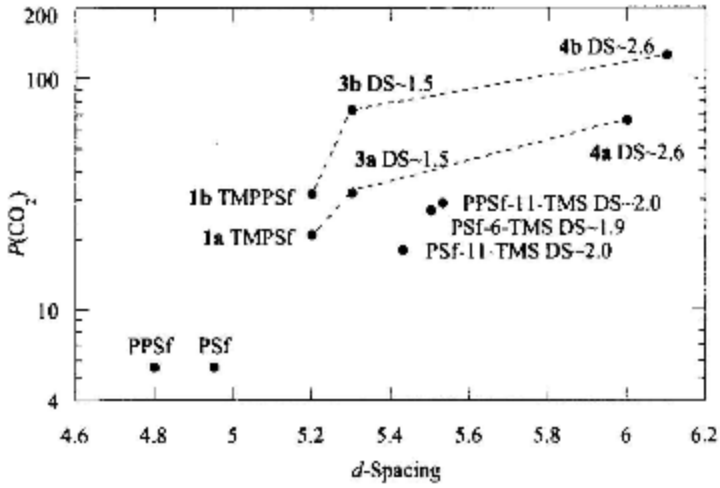


Figure 4. Correlation between $P(CO_2)$ and d-spacing for various polysulfones.

Molecular modeling

Diphenylsulfone has a periplanar conformation allowing conjugative interaction between the phenyl π-electrons and the 3*d* sulfur orbitals (*27*). The high energy barrier to rotation about the Phenyl–Sulfur bond necessary to overcome the strong preference for this conjugative conformation is evident since disubstitution of methyl or chloro groups at the *ortho*-sulfone (H_{11} sites) did not result in significant conformational change in relative phenyl angles about the sulfone as shown by NMR studies (*27*). Our previous NMR data (*17*) for **4a** and **4b** suggest that conformational change by Phenyl–Sulfone–Phenyl rotation occurs to better accommodate the more bulky TMS substituents.

Conformational analysis of the polymers using HyperChem™ (Hypercube Inc. software, Florida) was performed on eight repeat unit chain lengths of the polymer structures 'as drawn' to study the effect of TMS substitution and distribution of TMS on chain geometry and steric interactions. Molecular modeling software gives a visual indication of major conformational changes in the polymers containing TMS groups. Figure 5 shows partial central views of eight repeat unit model lengths that were optimized for minimum energy. TMPSf **1a** is compared with **5a**, the 11-substituted TMS at the ortho-sulfone linkage. Surprisingly, although **5a** changes conformation compared with **1a**,

both chains are relatively linear. However, in the case of the TMS-substituted polymers **4b** and **5b**, both polymers exhibit considerable visible conformational change compared with the linear TMPPSf **1b**. In particular, the chain of **4b** is non-linear and kinked with a somewhat corkscrew conformation. It was difficult to ascertain the relative pseudo-torsional angles between aromatic rings connected by linkages such as sulfone or ether (i.e. across five bonds), since both the linkage angle relative to the phenyl plane and the phenyl planar angle are combined. Polymer **1b** and **4b** were compared first by true torsional angles between the biphenyl rings. The unmodified polymer had torsional angles typically ~18°, whereas the TMS modified one had a range of angles from 45-56°, relieving the steric restriction of the bulky TMS group and supporting our previous NMR studies. The central repeat units of the eight repeat unit lengths were examined for pseudo-torsional angles between the planes of the diphenyl ether and the diphenylsulfone. Unexpectedly, a range of values was obtained, even for the unmodified **1b**. For **1b**, diphenylether was 56-63° and diphenylsulfone had several distinct angles of ~0, ~8, ~15, ~30 along the polymer chain repeat units. There are two types of diphenylether linkages in **4b**, those with and without TMS in the biphenol ring. The diphenyls around the ether linkage were typically twisted out of plane for the rings containing TMS and those around the sulfone linkage had increased relative angles between 58-83° for three repeat units calculated.

Conclusions

Tetramethyl polysulfone and polyphenylsulfone were modified with TMS substituents to investigate their potential as membrane materials for gas separation. The TMS substituents were introduced on the bisphenol and on the phenylsulfone segments of the polymer chains. The T_gs of the polymers were reduced by the addition of pendant TMS, possibly due to a disruption of symmetry in the phenylene rings. TMS Polymers with high DS had the largest increases in CO_2 and O_2 permeabilities and good permselectivities from N_2. The O_2/N_2 and CO_2/N_2 pairs showed considerable improvements in gas transport properties since performance was close to the Robeson upper-bound line. Polymer **4b** had the best overall gas transport properties, exhibited a 5-fold increase in $P(O_2)$ with a minor decrease in α (O_2/N_2). The $P(CO_2)$ increased ~4-fold with some decrease in α (CO_2/N_2). An investigation of d-spacing for TMS polymers showed that it increased sharply for DS>2, indicating increases in free volume. Molecular modeling of the polymer chains suggests that TMS groups introduced onto PPSf **1b** result in chain kinking and considerable conformational changes.

Acknowledgements

Partial financial support was provided from an international collaborative project between the National Research Council of Canada and the Korea Institute of Science and Technology. We are most grateful to Dr. Takashi Kowada of the Fine Chemicals Department, Mitsubishi Chemical Corporation, Tokyo, Japan, for kindly donating the monomer 3,3',5,5'-tetramethylbiphenol. We thank Fatima Haggar for assistance in molecular modeling.

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Advanced Materials for Membrane Separations
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