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Gas transport in modified polysulfones with trimethylsilyl groups: effect of substitution site

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Abstract

Trimethylsilyl (TMS) groups were chemically introduced on to the phenylene group of bisphenol-A polysulfone (PSf) at sites ortho to ether (EM3) or to sulfone (SM3) linkages. Gas permeabilities increased by substitution of TMS and especially oxygen permeability increased from 1.1 barrer for PSf to 4.2 barrer for SM3 and to 7.1 barrer for EM3. Perm-selectivity of oxygen to nitrogen decreased from 5.8 to 5.5 and therefore substitution of TMS on polysulfone resulted in improved gas transport properties. In addition, it was found that EM3 is more effective in enhancing the gas transport properties than SM3.

In order to interpret the effect substitution site on gas transport, d-spacing was investigated in terms of interchain packing. Furthermore, the effect of substitution site on chain motion was investigated through dynamic mechanical analyzer (DMA), dielectric analyzer (DEA), and solid-state NMR. DMA and DEA experiments showed that motions of unsubstituted phenylene and sulfonyl linkage are much more hindered in SM3 than in EM3. NMR experiments showed that motion of TMS is more mobile in EM3 than in SM3. These results revealed that chain motions of SM3 are more hindered than those of EM3 and substitution site affects chain motions. Therefore, we can conclude that these changes in chain motion also gas transport in modified polysulfones with silyl side group.

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1. Introduction

Over the last several decades, numerous experimental data on the permeation of gases through many glassy aromatic polymers have been reported [1–7]. Most of these studies were done in an attempt to understand transport mechanism and thereby to overcome the ‘trade-off’ trend in the relation between gas permeability and selectivity of polymers [8,9]. A qualitative principle that appears useful to guide the search for significantly improved materials based on almost any family of polymer is stated that a “suppression
of interchain packing by addition of bulky groups
and/or kinks in the backbone which also cause si-
multaneous inhibition of intrachain motion around
flexible hinge points tends to increase permeabil-
ity without unacceptable losses in perm-selectivity”
[10]. The bulky pendant groups must disrupt the in-
terchain packing of the polymer by hindering the
mobility of mobile linkages and also provide enough
steric space for diffusion, i.e. the intersegmental
distance.
It has also been reported that major physicochem-
ical factors to control the gas permeability and se-
lectivity of polymers are (1) chain mobility and (2)
chain packing of polymer and (3) gas–polymer inter-
action. However, it has been well known that there are
hardly any specific interactions of permanent gases
with polymer at a relatively low gas pressure such as
below 10 bar, except carrier-mediated transport. Thus,
gas permeation properties depend significantly on the
chain mobility and the chain packing. The latter has
been interpreted in terms of free volume and d-spacing
and accepted by most authors [11]. The former has
been investigated through dynamic mechanical anal-
ysis (DMA), NMR, and dielectric relaxation [12–14].
Pace and Datyner proposed that gas molecules can
move through a polymer matrix in two distinct ways:
(a) sliding longitudinally along interchain channels
or (b) jumping from one interchain channel to other
channel whenever adjacent polymer chains are suffi-
ciently separated, as shown in Fig. 1 [15–17]. The sec-
don process is the rate-determining step in diffusion
and is related to low-frequency, cooperative motions
($10^{-4}$–$10^{-8}$ Hz) of the polymer chains.
Modification of polymer structure had been per-
formed in order to improve gas permeation properties
and investigate the relationship between gas perme-
ation and polymer structure. Experimental literature
data for structural variants of bisphenol-A polysul-
fones can be summarized by: (a) symmetrical intro-
duction of methyl groups into the phenylene rings
of the bisphenol-A unit as in tetramethylbisphenol-A
polysulfone (TMBPA-PSf), leads to increased glass
transition temperature ($T_g$), free volume and gas per-
meability increase but (b) in the case of unsymmetri-
cal substitution, vice versa occurs [1]. Furthermore,
dynamic mechanical analysis (DMA) studies led to
the suggestion that the molecular motion of methyl
substituted phenyl rings was primarily responsible
for changes in gas transport. Moreover, trimethylsilyl
(TMS) was reported to be excellent substituent to
increase permeability in poly(1,4-dimethylphenylene
oxide) (PPO), poly(1-trimethylsilyl-1-propyne)
(PTMSP) and polystyrene [18–20]. The excellent
properties of TMS originate from steric bulkiness and
high electrostatic interactions [21].
In this paper, TMS groups were introduced by
chemical reaction into phenyl rings of bisphenol-A
polysulfone with different substitution site (o-ether
or o-sulfone site). We attempt to explain differences
in gas permeabilities of PSFs with TMS at o-ether
or o-sulfone sites in terms of the mobilities of both
the main chain and pendant groups because the ef-
flect of the substitution site on permeation properties
cannot be explained well by the group contribution
method.

2. Experimental
2.1. Membrane and polymers

Chemical structures and notations of polymers stud-
ied are shown in Fig. 2. TMS groups were introduced
by chemical reaction into phenyl rings of PSf (Udel
P3500, BP Amoco). As shown in Fig. 2, EM3 and
SM3 are the structures of PSf silylated at the pheny-
lene ring in bisphenol-A (BPA) and at diphenyl sul-
fone (DPS) units, respectively. Details of modification
and structural characterization are reported elsewhere [22,23]. Dense membranes were prepared in the form of film, which were made from ca. 5 wt.% polymer solutions with tetrahydrofuran (THF). Polymer solutions were filtered through Whatmann® 25 mm syringe filters of which pore size was 1 μm. Drying process was performed at 40 °C and residual solvent was removed in a vacuum oven for 3 days at 40 °C. The resulting thickness of the films was about 40 μm. Gas permeability coefficients were obtained by measuring downstream pressure change through the constant volume method. Steady-state pressure rate was chosen in time region above 10 more than time-lag and permeability was calculated using the following formula:

\[
P = \frac{(\text{quantity of permeate}) \times (\text{film thickness})}{(\text{area}) \times (\text{time}) \times (\text{pressure drop across film})} \times \frac{1}{(\text{cm}^3 \text{(STP)} \times \text{cm})} \times \frac{1}{(\text{cm}^2 \times \text{s} \times \text{cmHg})}.
\]

2.2. Characterization

Glass-transition temperature \((T_g)\) was obtained through Perkin-Elmer DSC7 with scanning rate of 20 °C/min. X-ray diffraction was used to investigate \(d\)-spacing. Model M18XHF22 of Macscience was utilized with Cu Kα radiation of which wavelength \((\lambda)\) was 1.54 Å. Scanning speed was 5°/min. The value of \(d\)-spacing was calculated by means of the Bragg’s law \((d = \lambda/2 \sin \theta)\), using \(\theta\) of broad peak maximum.

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. 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.

Dielectric analyzer, DEA 2970 (TA Instruments) was used to obtain change of dielectric constant with temperature. Samples were made through solution-casting and resulting thickness was ca. 100 μm. From −150 °C to above \(T_g\) was studied, adopting a scanning rate of 2 °C/min and frequency range from 10 to 10,000 Hz.

Solid-state NMR experiments were performed with a Bruker 400 DSX spectrometer. Cross-polarization, magic angle spinning (CP/MAS) \(^{13}\text{C}\) and \(^{29}\text{Si}\) NMR experiments were performed at Larmor frequencies of 100.6 and 79.5 MHz, respectively. Samples in a
powder state were placed in the CP-MAS probe. The spinning rates were set at about 11 kHz for $^{13}$C and 5 kHz for $^{29}$Si to minimize the spinning sideband overlap. Pulse sequences for spin-lattice relaxation time in a rotating frame, $T_1\rho$, of $^{13}$C (or $^{29}$Si) are drawn schematically in Fig. 3. The $\pi/2$ pulse time was 5.25 $\mu$s for $^{13}$C and 5.6 $\mu$s for $^{29}$Si, corresponding to a spin-locking field strength of 47.6 and 44.64 kHz, respectively. The spin-lattice relaxation times in a rotating frame, $\langle T_1\rho \rangle$, were measured at 308 K by analyzing the magnetization decay.

3. Results and discussion

3.1. Gas permeation properties

Gas permeabilities and ideal perm-selectivity for oxygen and nitrogen are listed in Table 1. All gas permeabilities increased irrespective of substitution site although TMS was asymmetrically substituted onto phenylene ring of PSf. Oxygen permeability increased by 3.8 times for SM3 and by 6.5 times for EM3. Therefore, TMS was very effective in increasing permeability. Substitution site also affected gas permeabilities although the same TMS was introduced into the identical PSf. TMS itself or the TMS-substituted phenylene of SM3 is assumed to be more sterically hindered than those of EM3 in terms of molecular structure, as shown in Fig. 4. In other words, the substitution at the more mobile ether linkage is more effective in hindering the interchain packing than at the sulfone linkage. This molecular origin affected glass transition

![Fig. 3. Pulse sequence for spin-lattice relaxation time in a rotating frame, $T_1\rho$, of $^{13}$C (or $^{29}$Si) where CP and SL are cross-polarization and spin-locking, respectively.](image)

![Fig. 4. Molecular structure of TMS-substituted phenylene unit: (a) BPA unit of EM3 and (b) DPS unit of SM3.](image)

| Table 1: Gas permeation properties of polysulfone and silylated polysulfones |
|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
|                             | $P(O_2)$ (barrer)$^a$       | $P(N_2)$ (barrer)$^a$       | $P(O_2)/P(N_2)$             | $E_p(O_2)$ (kJ/mol)        | $E_p(N_2)$ (kJ/mol)        |
| PSf                         | 1.1                         | 0.19                        | 5.8                         | 3.7                        | 5.5                        |
| SM3                         | 4.2                         | 0.77                        | 5.5                         | 3.6                        | 5.1                        |
| EM3                         | 7.1                         | 1.3                         | 5.5                         | 2.7                        | 3.9                        |

$^a$ (barrer) $= 10^{-10}$ cm$^3$ (STP) cm$^{-2}$ s$^{-1}$ cmHg.
Temperature and *d*-spacing, as listed in Table 2, *T*<sub*>g</sub> decreased when TMS was asymmetrically substituted onto phenylene ring. EM3 showed a lower glass transition temperature than SM3. The *d*-spacing results indicated that interchain packing was disturbed by TMS and EM3 was more permeable to gas than SM3. The *d*-spacing results correlated well with gas permeation results.

Increases in permeability are generally known to be accompanied by decreases in selectivity and this relationship was also shown in modified polysulfones with silyl side group. The perm-selectivity of oxygen and nitrogen decreased from 5.8 for PSf to 5.5 for EM3 although oxygen permeability increased by 6.5 times. Fig. 5 shows that TMS groups improve the gas permeation properties although EM3 did not approach the upper-bound.

### 3.2 Chain mobility and its effect on gas permeation

DMA spectra are presented in Fig. 6. PSf showed more intensive \( \gamma_2 \)-peak near \(-100^\circ \text{C}\) than SM3 or EM3 because the \( \gamma_2 \)-peak is related to motion of unsubstituted phenylene and cooperative motion. In case of SM3 or EM3, there was fewer numbers of unsubstituted phenylene rings than PSf and cooperative motion is hindered by the bulky TMS side group. Therefore, SM3 or EM3 showed less intense \( \gamma_2 \)-peaks than PSf. Contrary to methyl-substituted polysulfones, SM3 or EM3 did not show \( \gamma_1 \)-peaks related to substituted phenylene motion. This is because motion of substituted phenylene was much more hindered by bulkier TMS than by methyl and thereby was not shown in the DMA spectrum, as suggested by Kim et al. [24]. In addition, there exists a difference between SM3 and EM3. The \( \gamma_2 \)-peak of SM3 is less intense at higher temperature than that of EM3. This suggests that sub-*T*<sub*>g</sub> motions of SM3 are more hindered than those of EM3.

Fig. 7 shows DEA spectra for EM3 and SM3. The DEA spectrum of EM3 is similar to the one of DMA.
spectrum, i.e. the γ-peaks at 10 Hz exist near −100°C and the γ-peak shifted to higher temperature with frequency. These γ-peaks are related to sulfonyle linkage in the main chain because DEA can only measure dipole moment. Activation energy for the γ-peak for EM3 was calculated as 16 kJ/mol using an Arrhenius plot. This value is similar to that for PSf (16 kJ/mol). However, SM3 showed no well-defined γ-peak contrary to EM3. This is attributed to more hindered motion in SM3. From DMA and DEA, we know that chain motions of SM3 are more hindered than those of EM3 and therefore difference in chain motion between SM3 and EM3 affects the interchain packing and gas permeation.

Solid-state NMR was used in order to study more specific chain motion. The 13C CP/MAS NMR spectra of PSf, EM3 and SM3 are shown in Fig. 8. Peaks for methyl and quaternary carbons in the isopropylidene linkage appeared at chemical shifts of δ = 29.8 and 41.9 ppm, respectively. Peaks of protonated phenylene carbons in BPA and DPS units were superimposed and appeared as two big peaks at δ = 130.0 and 121.5 ppm, respectively. Peaks of non-protonated phenylene carbon occurred above 130 ppm. The spectra of EM3 and SM3 were similar to that of PSf. The TMS methyl carbon signal was near 0 ppm. The 29Si spectra shown in Fig. 8b exhibited one rather sharp Si peak for both EM3 and SM3.

The ⟨T1ρ⟩ values for each carbon and silicon were taken with variable spin-locks on the carbon and silicon channel following cross-polarization. ⟨T1ρ⟩ measurements generally can be used as measure of molecular motion in glassy polymers at ambient temperature and is most sensitive to thermal motions in the mid-kilohertz regime [25,26]. Fig. 9 shows the
Fig. 9. Semi-logarithmic plot of magnetization decay for (a) protonated phenylene carbon in main-chain and (b) silicon in substituent.

Fig. 9 may show that the relationship is not linear, indicating at least two apparent relaxation modes (i.e. the different initial and final slopes). The non-linearity feature (or $T_1$ dispersion) was often shown in other glassy polymers and is a prominent feature of $\langle T_1^\rho \rangle$ plots for glassy polymers [27]. The final slope represents the real molecular motion of the polymeric chains more accurately than the initial slope because the initial slope is mainly affected by thermal history. Therefore, we calculated $\langle T_1^\rho \rangle$ values from the final slopes instead of the initial slopes, whose calculation method was shown in elsewhere [13]. For the rigid glassy polymers, their molecular motion near room temperature is usually in a so-called “slow motion region” and thus the solid molecules with longer $\langle T_1^\rho \rangle$ are in slower molecular motion.

The $\langle T_1^\rho \rangle$ values and permeation properties are summarized in Table 3. $\langle T_1^\rho \rangle$ of protonated phenylene carbon was smaller in PSf than in EM3 and SM3, which might indicate that the motion of phenylene rings in EM3 and SM3 was hindered by the silyl substituent. The $\langle T_1^\rho \rangle$ values of 34.2 and 31.3 ms for EM3 and SM3, respectively, differ only 3 ms and so could be considered within an experimental error range. However, the $\langle T_1^\rho \rangle$ value of PSf is one-order of magnitude smaller than that of EM3 or SM3. This must indicate that main-chain phenylene motion of EM3 and SM3 is much more restricted compared with that of unmodified polysulfone. A comparison of gas permeabilities for EM3 and SM3 in Table 1 shows that the oxygen permeability of EM3 is about double that of SM3. However, for both silylated PSfs, the $\langle T_1^\rho \rangle$ values of protonated phenylene carbons are not different significantly. This supports the argument that the mobility of phenylene rings in silylated PSfs has little effect on the gas permeability. However, the $\langle T_1^\rho \rangle$ values for silicon atom obtained from the solid-state $^{29}$Si NMR experiments show a big difference, i.e. 59.0 ms for EM3 versus 130.5 ms for SM3. This strongly suggests that the mobility of the trimethylsilyl group of EM3 is much higher than that of SM3.

The high mobility of pendant TMS provides extra interstitial space or free volume for gas diffusion, as supported by the evidence of higher $d$-spacing, resulting in a higher permeability. Another important fact is that the TMS group in EM3 is less hindered geometrically and more mobile than that in SM3 due to the more flexible ether linkage. The higher $\langle T_1^\rho \rangle$ of Si suggests an enhanced mobility of the TMS group in EM3 and results in an almost two-fold increase in oxygen permeability compared with SM3. Conclusively, the difference in TMS mobility appears to correlate well with the gas permeability difference between EM3 and SM3, which also coincides with our previous DMA study.

4. Conclusion

In order to investigate the effect of substitution site on gas permeation, TMS groups were chemically introduced into phenylene rings. TMS was an effective
side group in increasing gas permeability and was more effective at the o-ether site than at the o-sulfone site. This effect of substitution site on gas permeation was related to chain motions which was investigated by DMA, DEA, and solid-state CP/MAS NMR. From DMA and DEA, we deduced that motions of main-chain phenylene and sulfonyl linkage are more hindered in SM3 than EM3. From NMR, the motion of main-chain phenylene of EM3 and SM3 is much more restricted compared with that of PSf and the mobility of TMS in EM3 is much higher than that in SM3.

Comparing the above DMA, DEA and NMR results with gas permeability, it can be argued that the substitution site affects motion of main-chain as well as side group and thereby also affects gas transport.

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