polymer

Modified polysulfones 5: synthesis and characterization of tetramethyl polysulfones containing trimethylsilyl groups and their gas transport properties[☆]

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Abstract

Polysulfones with rigid backbone structures and silyl-containing substituents were prepared as membrane materials with potentially enhanced gas transport properties. Tetramethylbisphenol-A polysulfone (TMPSf) and tetramethylbiphenol polysulfone (TMPPSf) were made by polycondensation then post-modified to introduce trimethylsilyl (TMS) groups by bromination and lithiation methodology. Substitution of high levels of TMS groups at the *ortho*-sulfone sites was achieved using direct lithiation followed by addition of a trimethylsilane electrophile. In an approach to increase the overall TMS substitution level as well as introduce these groups on the bisphenol segment, both TMPSf and TMPPSf were cleanly brominated to a degree of substitution (DS) of 2.0 for bromine. While the subsequent lithium−halogen exchange and reaction with TMS electrophile did not give high regioselectivity because of steric hindrance, the overall DS of TMS in the polymers was increased when excess *n*-butyllithium was used to activate both brominated and *ortho*-sulfone sites. The polymer structures were characterized by NMR spectroscopy. Their thermal properties as well as O_2, N_2, CO_2 and CH_4 gas transport properties were measured. Polymers with a high DS of TMS had very high CO_2 and O_2 permeabilities and good permselectivities from N_2. The permselectivities of CO_2/N_2 were at or close to the Robeson upper-bound performance line [J. Membr. Sci. 62 (1991) 165]. © 2002 Published by Elsevier Science Ltd.

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1. Introduction

Polysulfone (PSf) based on bisphenol A is a thermoplastic that is widely used as a membrane material or membrane support for liquid separation processes such as Ultrafiltration or Reverse Osmosis [2,3]. PSf was the material used for fabricating the first commercial gas separation membranes about two decades ago. It is utilized in the form of hollow fiber membranes commercially for gas separations because of its overall combination of relatively high permselectivities and adequate permeabilities to various gases as well as its good mechanical properties

and fiber spinning qualities [4]. Increased performance requirements provide incentives to develop new membrane materials. Many studies have shown that improvement in gas transport properties could be obtained by modifying or tailoring the polymer structure.

The most relevant and noteworthy previous work to the present study is by the groups of Koros and Paul. Parallel families of polysulfones in which systematic structural modifications were introduced were correlated with their gas transport properties [5–9]. The groups of Koros and Paul [5,7,10] and Pilato et al. [11] showed that symmetrical substitution of methyl group on the bisphenol or biphenol segment of PSf and polyphenylsulfone (PPSf) to give tetramethylbisphenol-A polysulfone (TMPSf) and tetramethylbiphenol polysulfone (TMPPSf) resulted in a large increase in permeability without too great a loss in

permselectivity because of increased chain stiffness and higher free volume.

We have been investigating the chemical modification of polysulfones in order to improve membrane separation properties. We reported the modification of polysulfone by direct lithiation [12] or by bromination–lithiation [13] to produce reactive intermediates that were converted by reaction with various electrophiles to yield carboxyl [14], hydroxyl [15], azide [16], amine [17], aldehyde [18], trimethylsilyl (TMS) [19] and a number of other derivatives [20,21].

In a previous study, we synthesized PSfs and PPSfs with different sequentially sized silicon side groups [19] and correlated the effect on gas transport properties [22]. TMS side groups gave the most favorable result with permeability coefficients for oxygen increasing with DS and with minimal loss in O_2/N_2 ideal permselectivity. 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 arise primarily from the increase in free volume and the 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 and that the mobility characteristics rather than the size of the pendant substituents provide extra free volume for gas transport resulting in improved gas permeability [22]. Another study by Bickson et al. investigated gas transport properties of polysulfones containing both TMS and sulfonic acid groups [23].

In the present work, we combine the good gas transport properties of TMPSf and TMPPSf with permeability-enhancing TMS groups. 11-substituted TMS derivatives were obtained by lithiating TMPSf and TMPPSf directly. Both 5 and 11-substituted TMS derivatives with higher overall DS were obtained by lithiating dibrominated TMPSf and TMPPSf. Lithium–halogen exchange on the bisphenol ring combined with direct lithiation on the sulfone ring when using excess *n*-butyllithium, follow by reaction with a TMS halide electrophile, yielded the substituted polymers. In this investigation, similar procedures were employed as previous studies [19] to introduce TMS groups to TMPSfs.

2. Experimental

2.1. Materials

Bisphenol monomers 3,3′,5,5′-tetramethylbisphenol-A (Aldrich) and 3,3′,5,5′-tetramethylbiphenol (kindly donated by Mitsubishi Chemical Corporation, Japan) were further purified by sublimation at 180 °C under vacuum. Sulfone monomers 4,4′-dichlorodiphenylsulfone (Pfaltz & Bauer, Inc.) and 4,4′-difluorodiphenylsulfone (Aldrich) were further purified by crystallization from ethanol 95%. Before

polymerization, all monomers were dried in a vacuum oven at 55 °C for 24 h. Anhydrous potassium carbonate (BDH, K_2CO_3, analytical reagent from) was dried in an oven at 110 °C for 24 h. *N*-methylpyrrolidinone (NMP) was distilled over barium oxide under vacuum and analytical reagent toluene from BDH was used as received. Analytical reagent tetrahydrofuran (THF) freshly distilled over lithium aluminum hydride ($LiAlH_4$), *n*-butyllithium (Aldrich, 10 M in hexane) and anhydrous chlorotrimethylsilane (Aldrich, TMSCl) or iodotrimethylsilane (Gelest Chemicals, TMSI) were used as received for modification reactions. All reactions were conducted under a constant argon purge. A dry ice/ethanol bath was used for reactions requiring cooling. Polymers were normally recovered by precipitation in ethanol using a blender, washed thoroughly sequentially in ethanol and water, then dried in a vacuum oven at 55 °C.

2.2. Preparation of tetramethyl polymers

2.2.1. TMPSf (*1a*)

The polymerization was conducted according to a procedure developed by Mohanty et al. [24,25] and modified by McHattie [26] and Aitken [27]. In a 1 l glass resin kettle equipped with heating mantle, a stainless steel mechanical stirrer, argon inlet, thermocouple and Dean-Stark trap were placed 3,3′,5,5′-tetramethylbisphenol-A (63.36 g, 222.8 mmol), 4,4′-difluorodiphenylsulfone (56.65 g, 222.8 mmol), K_2CO_3 (41.56 g, 300.7 mmol), NMP (400 ml) and toluene (200 ml) and the mixture stirred until the monomers had dissolved. The temperature of the mixture was raised slowly, in the range of 143–152 °C over a period of 6.5 h, accompanied by the gradual removal of water by azeotropic distillation. After removing the remaining toluene, the reaction temperature was increased to 180 °C and maintained between 180 and 188 °C for about 4 h. The progress of polymerization was monitored by a marked viscosity increase and continued until the maximum mechanical stirring torque available was reached. The highly viscous mixture was diluted with NMP (700 ml) and cooled to about 50 °C before glacial acetic acid (20 ml) was added to quench the polymer end-groups. The polymer was recovered and 102.5 g (92% yield) pale yellow polymer with 0.84 inherent viscosity in NMP was obtained after drying in a vacuum oven at 55 °C for a 24 h.

2.2.2. TMPPSf (*1b*)

The procedure similar to the previous one was followed using 3,3′,5,5′-tetramethylbiphenol (60.58 g, 250.0 mmol), 4,4′-dichlorodiphenylsulfone (71.78 g, 250.0 mmol), K_2CO_3 (44.91 g, 325.0 mmol), NMP (500 ml) and toluene (250 ml) and the mixture was polymerized at ∼185 °C for 4 h. to give 110.0 g (92% yield) of pale yellow polymer with 0.66 inherent viscosity in NMP.

2.2.3. Dibromo-tetramethyl polysulfone (TMPSf-5-Br₂) (*2a*)

Excess bromine (45 ml, 139.5 g, 0.872 mol) was added

to a magnetically stirred solution of TMPSf (15.00 g, 30.0 mmol) in chloroform (150 ml) at room temperature and under argon atmosphere. The dark red mixture was left stirring at room temperature for 1 h and then precipitated into methanol. The recovered polymer was left standing in methanol to leach out residual free bromine, then filtered and washed again until bromine had been completely removed. 18.56 g (96% yield) white polymer TMPSf-5-Br$_2$ which had two bromine atoms per repeat unit at the *ortho*-isopropylidene linkage was obtained after drying it in a vacuum oven at 55 °C for 24 h. Elemental Analysis, calcd C$_{31}$H$_{28}$Br$_2$O$_4$S 24.34% Br, found 24.94% Br.

2.2.4. Dibromo-tetramethyl polyphenylsulfone (TMPPSf-5-Br$_2$) (2b)

In a similar procedure, bromine (20 ml, 61.94 g, 0.3876 mol) was added to a magnetically stirred solution of TMPPSf (20 g, 42.2 mmol) in chloroform (170 ml) and stirred at room temperature for 4 h before precipitation into methanol. 25.0 g (96% yield) white polymer TMPPSf-5-Br$_2$ which had two bromine atoms per repeat unit at the 5-site was obtained after drying in a vacuum oven at 55 °C for 24 h. Elemental Analysis, calcd C$_{28}$H$_{22}$Br$_2$O$_4$S 26.01% Br, found 25.02% Br.

2.2.5. TMPSf-5,11-TMS (DS 1.5) (3a) and TMPPSf-5,11-TMS (DS 1.5) (3b)

Colorless TMPSf-5-Br$_2$ (~6%) and TMPPSf-5-Br$_2$ (~1%) solutions in THF were lithiated at −77 °C. 2 mol equiv. of *n*-butyllithium were injected dropwise over a period of 15 min using a syringe pump. After stirring for an additional 15 min, 5 mol equiv. TMSI were injected promptly into the reaction, then the solution was stirred with gradual warming to −5 °C and kept stirring for 2 h at −5 °C before being recovered. The resulting polymers had a DS of 1.51 and 1.50 TMS groups per repeat unit, respectively. When TMSCl was used as the electrophile instead of TMSI, a lower DS of 1.33 was obtained. NMR analysis showed that the substitution was not regioselective and that TMS groups had been added at both 5 and 11-sites. Elemental analysis confirmed the presence of 7.72 and 10.87% residual bromine, respectively, indicating that both polymers had not undergone complete metal–halogen exchange.

2.2.6. TMPSf-11-TMS (4a)

A colorless TMPSf (10.00 g, 20 mmol) solution in THF (1000 ml) and under argon atmosphere was cooled to −40 °C. *n*-Butyllithium (4.41 ml, 44.1 mmol) was injected dropwise using a syringe pump over a period of 15 min. After stirring for an additional 15 min. TMSI (24.07 g, 120.3 mmol) was injected promptly into the polymer solution, then the solution was stirred with gradual warming to −5 °C and kept stirring for 2 h at −5 °C before being recovered. 12.60 g (91.0% yield) white product with a DS of 1.7 was obtained.

2.2.7. TMPPSf-11-TMS (4b)

n-Butyllithium (0.35 ml, 3.5 mmol) was added to THF (50 ml) cooled at −40 °C. The partially THF-soluble TMPPSf (0.50 g, 1.1 mmol) was divided into five 0.10 g fractions that were added into the magnetically stirred lithiation solution at intervals of 10 min. The yellow lithiated polymer solution was stirred for 30 min. while the temperature was raised to −20 °C. TMSCl (0.60 g, 5.5 mmol) was syringed quickly into the flask and the resulting yellow liquid was stirred for 2 h at −5 °C before being recovered from 95% ethanol. The white product (0.61 g, 93.0% yield) had a DS of 1.70.

### 2.2.8. TMPSf-5,11-TMS (DS 2.6) (5a) and TMPPSf-5,11-TMS (DS 2.6) (5b)

Using TMPSf-Br$_2$ and TMPPSf-Br$_2$ as before, the polymers were lithiated with excess *n*-butyllithium (5 mol equiv.) using similar conditions. The resulting polymers had DSs of 2.60 and 2.64 TMS groups per repeat unit, respectively. It was determined by NMR analysis that substitution was not regioselective and that TMS groups had been added at both the 5 and 11 sites in approximately equal amounts. Elemental analysis confirmed the presence of only residual bromine (both <0.5%) indicating that although metal–halogen exchange was almost complete, TMS could not fully substitute on the bromine sites due to steric hindrance.

2.3. Characterization methods

Nuclear magnetic resonance spectra were recorded on a Varian Unity Inova spectrometer at a resonance frequency of 399.961 MHz for ^{1}H and 100.579 MHz for ^{13}C. For each analysis, ~10 wt% solution was prepared in CDCl$_3$. TMS was used as the internal standard except for polymers with trimethylsilyl groups where the CHCl$_3$ peak at 7.25 ppm in CDCl$_3$ solvent was used as the chemical shift reference. The inherent viscosity of polymers were determined using an Ubbelohde viscometer at a polymer concentration of 0.4 g/dl in NMP at 35 °C. The DS of modified polymers was readily determined using ^{1}H NMR by comparison of the integration of the distinct upfield trimethylsilyl signal with that of the two isopropylidene methyl groups or with the four aromatic methyl groups.

A DuPont 951-thermogravimetric analyzer was used for measuring degradation temperatures by TGA and for measuring glass transition temperature (T_g) by differential scanning calorimetry (DSC). Polymer samples for TGA were ramped to 60 °C at 1 °C/min, held isothermally for 120 min, then heated to 600 °C at 10 °C/min for degradation temperature measurement. 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 were made from 5 wt% polymer chloroform solutions. Polymer solutions were filtered
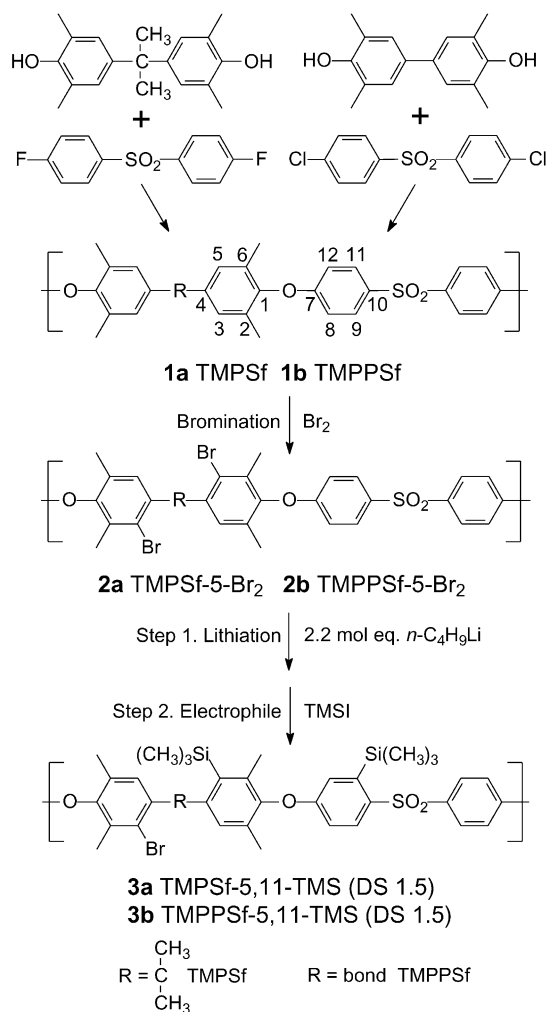
Scheme 1. Preparation of TMS derivatives of TMPSf and TMPPSf by bromination–lithiation.

through Whatman® 25 mm polytetrafluoroethylene syringe filters having a pore size of 1 μm, then poured into flat-glass dishes and dried at 30 °C. The detached films were further dried for 3 days in a vacuum oven at 40 °C to remove the residual solvent. Optically clear films were obtained with thickness of about 100 μm. The absence of residual solvent in the films was confirmed by observing T_g using DSC. Gas permeability coefficients were obtained by measuring downstream pressure change using the constant volume method at 35 °C with an upstream pressure of 1 atm. Steady-state pressure rate was chosen in time region above ten more than the time-lag and permeability was calculated using the following formula

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

X-ray diffraction was used to investigate d-spacing. A Macscience Model M18XHF22 was utilized with Cu K_α radiation of which wavelength (λ) was 1.54 Å. 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 the 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.

## 3. Results and discussion

3.1. Synthesis

The polycondensation method using the potassium carbonate/dimethylacetamide process developed by the McGrath group for preparing TMPSf and TMPPSf has been reported previously [24–28]. It is considered the most convenient polymerization method for laboratory preparation and produces polymers of high molecular weights. A comprehensive review of synthetic methods for preparing polyarylethers has been published by Cotter [29]. In our laboratory, the monomers purified by sublimation gave much higher molecular weight polymers than those we produced from as-supplied monomers.

Bromination reactions were performed simply with elemental bromine in solvent at room temperature and resulted in polymers fully dibrominated on the bisphenol or biphenol rings as shown in Scheme 1. TMPSf was dibrominated within 1 h, whereas TMPPSf required 4 h for full reaction.

TMPSf-5-Br₂ (**2a**) and TMPPSf-5-Br₂ (**2b**) were lithiated with either 2.2 mol equiv. of *n*-butyllithium for metal–halogen exchange then quenched with TMSCl or TMSI electrophiles according to Scheme 1. Both dibrominated polymers were also lithiated with an excess of *n*-butyllithium (5 mol equiv.) 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. The brominated polymers were highly soluble in THF, and were readily lithiated under the conditions described. However, the lithiation reaction for **2b** required more dilute solutions (~1% vs. ~6%) than those of **2a** since the reaction solution developed a much higher viscosity. For the simple metal–halogen exchange reaction using 2.2 mol *n*-butyllithium, it was somewhat unexpected that the resulting DS of TMS was the same (~1.5) for both polymers considering the differences in electron density and steric hindrance around the substituted position. Bromine analyses of these products indicated incomplete metal–halogen exchange, and NMR analysis 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). Similarly, in both cases where excess butyllithium (5 mol equiv.) was used, the DS of TMS was the same (~2.6). Bromine analyses of these products showed only trace amounts of bromine indicating almost complete metal–halogen exchange. NMR analysis showed that the increase in DS for TMS groups occurred predominantly at
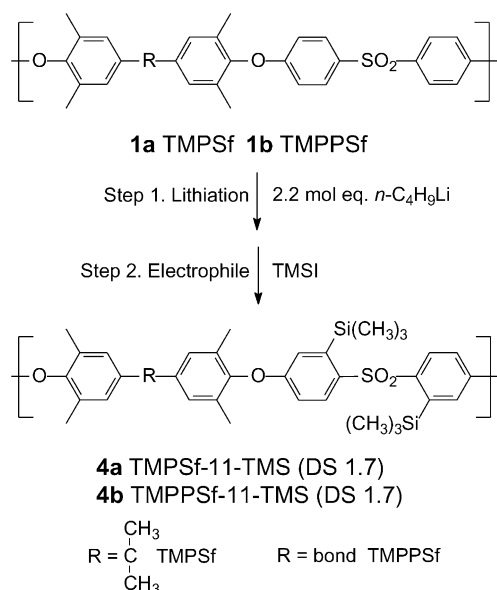
Scheme 2. Preparation of TMS derivatives of TMPSf and TMPPSf by direct lithiation.
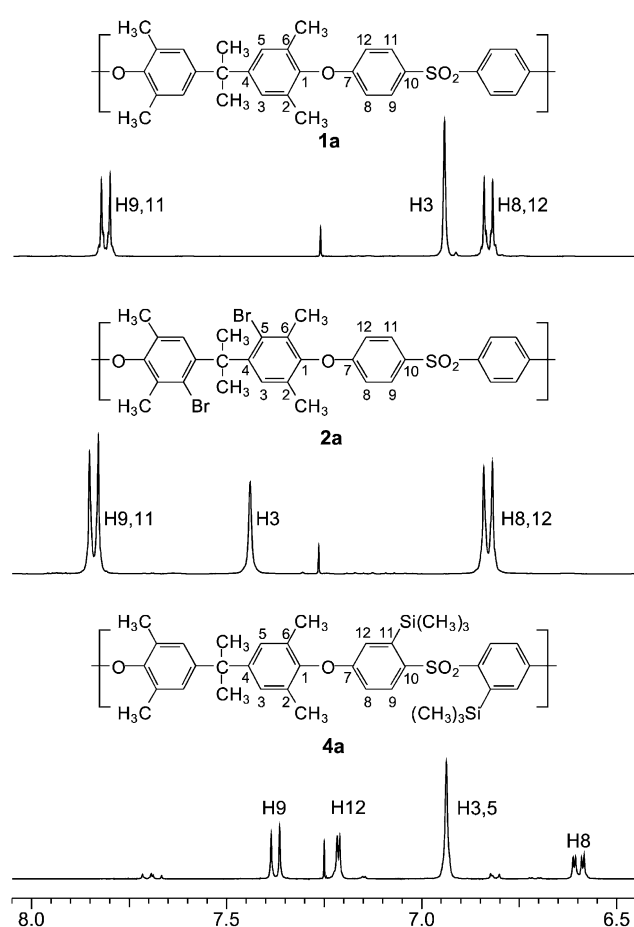
Fig. 1. Comparative ^{1}H NMR spectra (aromatic region) of TMPSf **1a**, TMPSf-Br$_2$ **2a** and TMPSf–TMS **4a**.
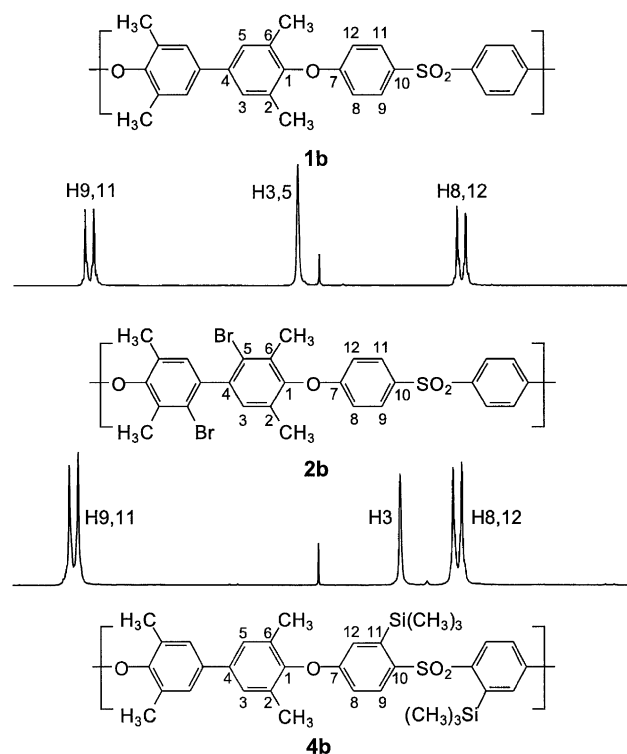
Fig. 2. Comparative ^{1}H NMR spectra (aromatic region) of TMPPSf **1b**, TMPPSf-Br$_2$ **2b** and TMPPSf–TMS **4b**.

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. Additional brominated sites that underwent lithium–halogen exchange were protonated during work-up since the steric hindrance was too high to allow greater substitution of TMS groups.

Direct lithiation of TMSPF and TMPPSf resulted in 11-substituted TMS products **4a** and **4b** having high regioselectivity and each with DS of 1.7 (Scheme 2). The TMPSf polymer was readily soluble in THF while the TMPPSf was only partially soluble, necessitating a modified lithiation procedure as outlined in Section 2.

For all reactions, TMSI resulted in a higher DS of TMS (e.g. ∼ 1.5 vs. 1.3 for polymers **3a** and **3b**) than when TMSCl was used as the electrophile, since iodine is a better leaving group for this type of reaction. Bromotrimethylsilane gave similar results (DS ∼ 1.44) to those of TMSI.

3.2. Structural characterization

Figs. 1 and 2, and Tables 1 and 2 show the chemical shifts (ppm), multiplicity (s: singlet, d: doublet) and

Table 1
^{1}H NMR data TMPSf and selected derivatives

Proton number	TMPSf **1a**	TMPSf-5-Br$_2$ **2a**	TMPSf-11-TMS **4a**
H3	6.94 (s)	7.44 (s)	6.94 (s)
H5	6.94 (s)	–	6.94 (s)
H8	6.83 (d, J 8.8)	6.83 (d, J 9.2)	6.59 (dd, J 8.4, 2.4)
H9	7.81 (d, J 8.8)	7.84 (d, J 8.8)	7.38 (d, J 8.4)
H11	7.81 (d, J 8.8)	7.84 (d, J 8.8)	–
H12	6.83 (d, J 8.8)	6.83 (d, J 9.2)	7.21 (d, J 2.4)
SiCH_3	–	–	0.30 (s)
ArCH_3	2.03 (s)	C2–CH_3 2.09 (s)	2.04 (s)
		C6–CH_3 2.11 (s)	
CH_3	1.66 (s)	1.89 (s)	1.64 (s)

Table 2
^{1}H NMR data TMPPSf and selected derivatives

Proton number	TMPPSf **1b**	TMPPSf-5-Br$_2$ **2b**	TMPPSf-11-TMS **4b**
H3	7.32 (s)	7.05 (s)	7.30 (s)
H5	7.32 (s)	–	7.30 (s)
H8	6.90 (d, J 8.8)	6.91 (d, J 8.8)	6.58 (d, J 8.8, 2.4)
H9	7.86 (d, J 8.8)	7.89 (d, J 9.2)	7.40 (d, J 9.2)
H11	7.86 (d, J 8.8)	7.89 (d, J 9.2)	–
H12	6.90 (d, J 8.8)	6.91 (d, J 8.8)	7.37 (d, J 3.2)
SiCH_3	–	–	0.35 (s)
ArCH_3	2.15 (s)	C2–CH_3 2.08 (s)	2.15 (s)
		C6–CH_3 2.25 (s)	

coupling constants (Hz) of proton signals for the synthetic polymers and their brominated and TMS derivatives *ortho*-sulfone.

3.2.1. TMPSf and TMPPSf

The spectra of **1a** and **1b** shown in Figs. 1 and 2, respectively, are simple and are both composed of three aromatic signals. On the phenol segments, H$_{3-5}$ are singlets and the phenylsulfone H$_{8-12}$ and H$_{9-11}$ are coupled ($^3J = 8.8$ Hz). Downfield *ortho*-sulfone protons (H$_{9-11}$) are strongly deshielding by the sulfone group. The H$_{3-5}$ singlets of **1b** are shifted downfield by 0.4 ppm compared with **1a** because of the anisotropic effect of the aryl groups on H$_{3-5}$.

3.2.2. TMPSf-5-Br$_2$ and TMPPSf-5-Br$_2$

The spectra of the phenylsulfone segment of bromine modified polymers are closely similar with those of the starting polymers indicating that no bromination occurs on this ring. On the phenol segments, H$_3$ are singlets with 2H integration compared with 4H for the starting polymer. H$_3$ of **2a** show a downfield shift of 0.5 ppm because of the more electronegative effect of the bromine atom on the aryl ring. In contrast, H$_3$ of **2b** shows an upfield shift of 0.3 ppm due to electron shielding from the abundant electron cloud of the nearby bromine atoms on the opposing phenyl rings.

3.2.3. TMPSf–TMS and TMPPSf–TMS derivatives

The polymers obtained from **2a** and **2b** by lithium–halogen exchange using 2.2 mol equiv. of *n*-butyllithium contained significant amounts of residual bromine at the 5-site: 7.72 and 10.87%, respectively, compared with ∼25% in the starting materials. Apart from incomplete lithium–halogen exchange, lithiation also occurred at the *ortho*-sulfone site. This suggests that the brominated position was difficult to access because of steric hindrance, and once lithiated, did not fully convert to TMS groups on exposure to TMSI electrophile. The approximate distribution of TMS groups in each of the polymers TMPSf-5,11-TMS (**3a**) and TMPPSf-5,11-TMS (**3b**) was approximately DS ∼ 0.75 at the 5-site and DS ∼ 0.75 at the 11-site. The NMR spectra (not shown) are complex due to the presence of several

different repeat units. When the same brominated polymers were lithiated with excess *n*-butyllithium (5 mol equiv.), an increase in TMS substitution occurred at the *ortho*-sulfone site but not at the 5-site. Interestingly, elemental analysis revealed only trace amounts of bromine suggesting that the brominated sites were almost completely lithiated, but could not be substituted by TMS groups beyond DS ∼ 0.75 as determined by NMR. NMR analysis showed that the DS of TMS groups at the 11-site was ∼1.85, giving a total DS ∼ 2.6 TMS groups per repeat unit for each of the polymers **5a** and **5b**.

The NMR spectra of the polymers obtained from **1a** and **1b** by direct lithiation were much less complex because substitution occurred only at the 11-site, and the DS of TMS was 1.7 giving polymers with mainly one type of repeat unit. Both TMPSf-11-TMS (**4a**) and TMPPSf-11-TMS (**4b**) had identical spin systems as shown in Figs. 1 and 2, respectively: a H$_8$ doublet of doublets three-bond coupled (8.8 Hz) to H$_9$ and also long-range (four-bond, 2.4 Hz) coupled to H$_{12}$. The aromatic signals of the two polymers are different only in chemical shift displacement. H$_{12}$ is shifted downfield by the effect of the silyl substituent on the aromatic ring whereas H$_8$ and H$_9$ are shifted upfield because of shielding from the nearby trimethylsilyl groups on the opposing aryl rings.

On the phenol rings, H$_{3,5}$ are unaffected by the substitution and the singlets have the same chemical shift as the unmodified polymers. Disubstituted repeat units give rise to the predominant peaks with any remaining minor signals representing residual monosubstituted repeat units as a result of incomplete disubstitution.

3.2.4. ^{13}C NMR

The ^{13}C NMR chemical shift values for brominated and 11-TMS polymers are listed in Tables 3 and 4. Fig. 3 shows the aromatic carbon spectra of **4a** and of **4b**. The signals were assigned unambiguously by a combination of one-bond and three-bond long-range ($^3J_{C-H}$ set to 7.5 Hz) carbon–hydrogen heteronuclear correlation.

3.3. Solubility and molecular weight

The polymers synthesized in the present study were fully

Table 3
^{13}C NMR chemical shifts of TMPSf and selected derivatives (ppm)

Carbon number	TMPSf **1a**	TMPSf-5-Br$_2$ **2a**	TMPSf-11-TMS **4a**
C1	148.19	148.50	148.18
C2	130.11	129.63	130.14
C3	127.57	128.94	127.47
C4	147.89	145.25	147.83
C5	127.57	122.98	127.47
C6	130.11	132.52	130.14
C7	161.57	161.24	159.94
C8	115.23	115.26	113.82
C9	129.82	129.98	131.52
C10	134.59	134.92	139.53
C11	129.82	129.98	142.85
C12	115.23	115.26	123.19
SiCH$_3$	–	–	0.97
ArCH$_3$	16.48	C2–CH$_3$ 16.63 (s)	16.53
		C6–CH$_3$ 17.66 (s)	
CH$_3$–C–CH$_3$	31.00	29.80	31.01
CH$_3$–C–CH$_3$	42.15	46.61	42.13

soluble in CHCl$_3$ and THF except **1b**, which was only partially soluble in THF. Clear films for gas permeability measurements could be prepared from all the polymers. We demonstrated in previous studies that the direct lithiation and the bromination–lithiation derivatization process applied to polysulfones did not result in any significant loss of molecular weight [13,16,17,19].

3.4. Thermal measurements

The glass transition temperatures (T_gs) were determined from DSC measurements and are listed in Table 5. When compared with their non-tetramethylated counterparts, it is evident that the TM-polysulfones had significantly higher glass transition temperatures due to the increased chain rigidity induced by the methyl groups. Compared with a T_g of 231 °C for **1a** and 280 °C for **1b**, both dibrominated polymers had increased T_gs suggesting chain stiffening

Table 4
^{13}C NMR chemical shifts of TMPPSf and selected derivatives (ppm)

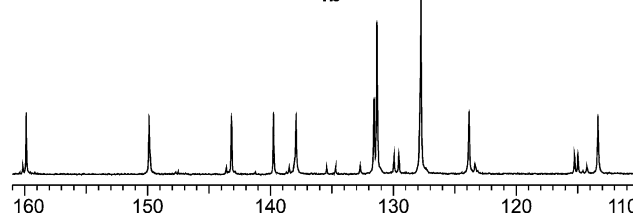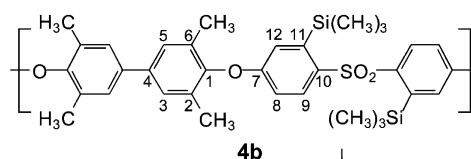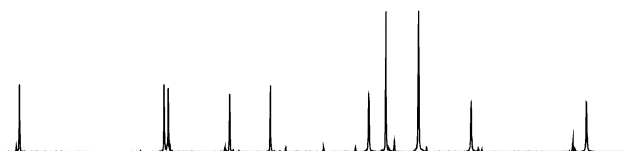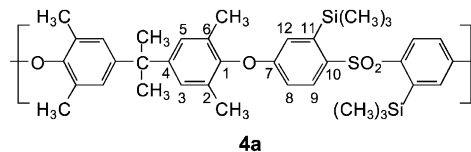| Carbon number	TMPPSf **1b**	TMPPSf-5-Br$_2$ **2b**	TMPPSf-11-TMS **4b**
C1	149.76	149.78	149.87
C2	131.28	130.06	131.33
C3	127.87	130.53	127.76
C4	137.99	124.39	137.91
C5	127.87	140.50	127.76
C6	131.28	131.93	131.33
C7	161.44	161.01	159.86
C8	115.25	115.31	113.35
C9	129.93	130.06	131.57
C10	134.65	135.03	139.74
C11	129.93	130.06	143.17
C12	115.25	115.31	123.84
SiCH$_3$	–	–	1.00
ArCH$_3$	16.44	C2–CH$_3$ 16.29 (s)	16.49
		C6–CH$_3$ 17.24 (s)	

Fig. 3. ^{13}C NMR spectra (aromatic region) of TMPSf–TMS **4a** and TMPPSf–TMS **4b**.

arising from the bulky bromine atoms. The T_gs of silylated polymers were substantially reduced from those of unmodified polymers as found in our previous results of silicon-containing polymers [19], which suggests that the mobile TMS groups had the effect of reducing chain stiffening on the polymer backbone. 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 substituted polymers.

Table 5 also lists both the actual onset of degradation temperatures as well as the extrapolated onsets of degradation, at a heating rate of 10 °C/min in nitrogen. All polymers showed good stability with degradation temperatures above 277 °C with no early-step transitions. All

Table 5
Glass transition temperatures (T_gs) and thermal degradation tests of polymers

Polymer	T_g (°C)	Actual onset (°C)	Extrapolated onset (°C)
PSf	188.1	455.0	521.1
1a	231.3	396.0	432.1
2a	275.4	310.0	425.2
3a	212.4	310.1	413.6
5a	193.0	334.8	438.7
4a	189.1	364.0	434.2
PPSf	225.6	461.4	518.9
1b	280.2	400.0	443.5
2b	298.2	310.0	432.2
3b	240.2	335.5	407.2
5b	234.3	306.2	417.5
4b	226.4	277.0	420.1

Table 6
Gas permeabilities, *d*-spacing and specific volume of modified TMPSf and TMPPSf

Polymer	$P(CO_2)$[a]	$P(O_2)$	$P(N_2)$	$P(CH_4)$	$\alpha\ O_2/N_2$[b]	$\alpha\ CO_2/N_2$	$\alpha\ CO_2/CH_4$	d (Å)	V_{sp} (cm^3/g)
1a[c]	21.0	5.6	1.06	0.95	5.28	19.8	22.1	5.2	0.86
3a	32.1	6.9	1.51	2.54	4.6	21.3	12.6	5.3	0.90
5a	66.3	14.4	3.07	4.55	4.69	21.6	14.6	6.0	0.94
1b[c]	31.8	5.8	1.21	1.27	4.79	26.3	25.0	5.2	0.82
3b	73.0	14.8	3.23	5.13	4.58	22.6	14.2	5.3	0.84
5b	126	28.9	6.28	9.69	4.60	20.1	13.0	6.1	0.93

[a] Permeability coefficients measured at 35 °C and 1 atm pressure. 1 Barrer = 10^{-10} (cm^3 (STP) cm]/(cm^2 s cm Hg).

[b] Ideal selectivity $\alpha = (P_a)/(P_b)$.

[c] Literature values [30].

extrapolated onset points were in the range of ~410–440 °C. However, brominated polymers showed lower actual onsets than the unmodified polymers.

3.5. Gas transport properties

A summary of permeability coefficients and permselectivities for O_2, N_2, CO_2 and CH_4 gases is shown in Table 6. For both series of TMPSf and TMPPSf polymers, gas permeability coefficients for all gases increased with the introduction of TMS groups. The increase in permeability by the introduction of TMS was shown in our previous study [22] and those of others.

The gas transport properties for the O_2/N_2 pair showed an overall performance increase that was greatest for **5b**. For the TMPSf-5,11-TMS series, the DS 2.6 polymer had more than double the $P(O_2)$ than the DS 1.5 polymer. The lower DS polymer **3a** showed only a slight increase in $P(O_2)$ above the starting material but at the cost of a considerable drop in permselectivity. The higher DS polymer **5a** had a moderate improvement in the overall gas transport properties since the drop in permselectivity was more than offset by the $P(O_2)$ increase. This suggests that a threshold amount of TMS groups is required to increase interchain distance and increase chain stiffening, at least for this polymer backbone. This differs from the results for the TMPPSf-5,11-TMS series **3b** and **5b**, which show that there is a continuous and quasi-linear significant increase in $P(O_2)$ with increasing DS, but with only a concomitant moderate loss in selectivity. Aitken et al. [30] published a comprehensive explanation of the gas transport property differences between polymers **1a** and **1b** in terms of the effects of structure on solubility and diffusivity coefficients. The O_2/N_2 separation factor is smaller for **1b** than for **1a**. Thus for O_2/N_2, **1a** starts with a higher α that decreases to a greater extent with the introduction of TMS than for the case of **1b**, which has a lower initial permselectivity. This situation is reversed in the case of CO_2/N_2 or CO_2/CH_4, where the permselectivity of the starting polymer **1b** is greater than **1a**. This is explained by Aitken et al. [30] who reported that the diffusion and solubility coefficients for CO_2 are about 20–25% higher for **1b** than for **1a**. It was also reported that the solubility coefficient for CH_4 follows the same trend, but for

N_2 it is reversed. Pilato et al. [11] investigated the correlation between CO_2 permeability and structures of polysulfones. It was suggested that the sulfone group could facilitate or enhance CO_2 solubility via a strong dipole–dipole interaction.

The data for CO_2/N_2 showed a different trend than those for O_2/N_2. When compared with either **1a** or **1b**, the TMS derivatives showed a lesser drop in permselectivity while having significantly large gains in permeability. In all cases, the TMS polymers had improved performance over the tetramethyl polymer starting materials. Polymer **5b** (DS 2.6) was at the Robeson 'upper-bound' limit [1,31] for the $P(CO_2)$ vs. $P(CO_2)/P(N_2)$ plot. Polymer **5a** (DS 2.6) had a three-fold increase in $P(CO_2)$ and even exhibited a higher CO_2/N_2 permselectivity compared with **1a**. Polymer **5b** (DS 2.6) had the best overall performance and was approximately at the upper-bound limit with a four-fold permeability increase and with a moderate drop in permselectivity compared with TMPPSf.

The silylated polymers had higher $P(CH_4)$ than $P(N_2)$, resulting in lower $\alpha(CO_2/CH_4)$. The high permeability coefficients for both CO_2 and CH_4 in these polymers suggest that TMS leads to an enhancement in solubility coefficient for these condensable gases.

The general increases in gas permeability coefficients can be explained in terms of interchain packing. It can be assumed that the TMS group, which is sterically bulky and spherical in nature, may hinder the interchain packing and therefore give rise to increases in the *d*-spacing values. At a DS of 1.5 TMS groups, polymers **3a** and **3b** showed only a small increase in the *d*-spacing values. The DS 1.5 polymers have a distribution of TMS groups of ~0.75 as well as some residual unreacted bromine on the already hindered tetramethyl units, and ~0.75 on the less hindered phenylsulfone units. The higher substitution polymers **5a** and **5b** maintain the same distribution of TMS groups of ~0.75 on the tetramethyl units, but the substitution on the phenylsulfone units is greatly increased to ~1.85. Clearly, the additional level as well as the distribution of TMS groups in both **5a** and **5b** appear to have a strong impact on the packing ability of the polymers' chains. The *d*-spacing results derived from XRD and summarized in Table 6 supported the above assumption since there was a dramatic

increase in *d*-spacing to 6.0 Å and above. Table 6 also shows that specific volume (V_{sp}) increased by the introduction of TMS groups further supporting the assumption of reduced interchain packing. It is possible that a detailed computed conformational analysis of the polymers would demonstrate that the additional level and distribution of TMS reduces chain mobility through steric interactions and simultaneously reduces interchain packing through conformational change. It is interesting to note that both **3a** and **3b** have the same DS and distribution of TMS and *d*-spacing values, yet the gas permeability increase for **3b** is much greater than for **3a**. Perhaps this is because the TMS group has a larger effect on the polymer **3b** conformation by a greater change in the torsional angle on the biphenyl rings vs. the bisphenol rings.

In terms of significant conformational change occurring around the phenylsulfone with the introduction of TMS, some evidence for this can be found in the NMR spectral data for **4a** (Table 1) and **4b** (Table 2). The conformation of diphenylsulfone in the solid state is known to have a periplanar spatial arrangement allowing a strong interaction between the π-electrons of both benzene rings and the 3d sulfur orbitals [32]. This conjugative interaction is expected to raise the energy barrier to rotation about the Phenyl–Sulfur bond causing the rotation to become thermodynamically restricted. NMR studies have shown that even disubstitution of methyl or chloro groups at the *ortho*-site (H_{11} sites) around the phenylsulfone does not result in significant conformational change in relative phenyl angles about the sulfone, indicating a strong preference for a conjugative conformation [32]. Evidence for this was the lack of diamagnetic shielding of H_9 that would result if one phenyl ring was rotated out of plane to better accommodate the substituents. In the present study, TMS groups are sterically much larger than methyl or chloro substituents. The NMR data for **4a** and **4b** suggests that this Phenyl–Sulfone–Phenyl rotation does occur since H_9 exhibits diamagnetic shielding to a significant extent as shown by upfield shifts of > 0.4 ppm. This shift would not be expected to arise from the substituent effect of TMS on position H_9, which is approximately zero. Thus, NMR data suggests a significant conformational change at the diphenylsulfone site occurs from the introduction of TMS.

4. Conclusions

Polysulfones with rigid backbone structures and pendant trimethylsilyl groups were prepared as potential membrane materials for gas separation. It has already been shown in previous separate studies that the introduction of tetramethyl as well as trimethylsilyl groups onto aromatic polysulfones improve gas transport properties by increasing permeability with only minor decreases in permselectivity. Aromatic polysulfones combining both these structural features were prepared in order to correlate structure with anticipated further improvements in gas transport properties. Tetramethyl polysulfones and tetramethyl polyphenylsulfones were synthesized then modified by bromination and/or lithiation to introduce trimethylsilyl groups. An average DS of 1.7 trimethylsilyl groups per repeat unit could be introduced exclusively to the *ortho*-sulfone sites using the methodology of direct lithiation followed by addition of a trimethylsilane electrophile. Attempts to convert the cleanly dibrominated tetramethyl polymers to trimethylsilyl derivatives by metal–halogen exchange resulted in non-regiospecific substitution (DS $\sim$ 1.5) at both the bromine sites (C5) and at the *ortho*-sulfone sites (C11) due to steric hindrance of tetramethyl sites adjacent to bromine. When excess lithiating agent was used, higher DSs of 2.6 trimethylsilyl groups were obtained for both tetramethyl polymers, with substitutions distributed approximately equally at each site as before. The new polymer structures were characterized in detail by NMR spectroscopy, and their thermal properties were investigated. Both dibrominated polymers had increased T_gs due to chain stiffening from hindered rotation from the bromine atoms. However, T_gs of silylated polymers were somewhat reduced from those of unmodified polymers, suggesting additional mobility associated with the trimethylsilyl groups. Gas transport properties of films made from these polymers were measured for four gases: O_2, N_2 CO_2 and CH_4. Polymers with the highest DS of TMS exhibited the largest increases in CO_2 and O_2 permeabilities and good permselectivities from N_2. Of the gases tested, the O_2/N_2 and especially CO_2/N_2 pairs showed the greatest improvements in gas transport properties as evidenced by performance close to the upper-bound line. **5a** exhibited a $\sim$ three-fold increase in $P(O_2)$ compared with the starting polymer with some drop in $\alpha(O_2/N_2)$. The $P(CO_2)$ was also increased $\sim$ three-fold but with a concomitant increase in $\alpha(CO_2/N_2)$. **5b** had the best overall gas transport properties. The polymer exhibited a five-fold increase in $P(O_2)$ with a minor decrease in $\alpha(O_2/N_2)$. The $P(CO_2)$ increased $\sim$ four-fold increase with some increase decrease in $\alpha(CO_2/N_2)$.

References

[1] Robeson LM. J Membr Sci 1991;62:165.

[2] Petersen RJ. J Membr Sci 1993;83:81.

[3] Lundy KA, Cabasso I. Ind Engng Chem Res 1989;28:742.

[4] Henis JMS, Tripodi MK. Sep Sci Technol 1980;15:1059.

[5] Aitken CL, Koros WJ, Paul DR. Macromolecules 1992;25:3424.

[6] Aitken CL, Mchattie JS, Paul DR. Macromolecules 1992;25:2910.

[7] McHattie JS, Koros WJ, Paul DR. Polymer 1992;33:1701.

[8] McHattie JS, Koros WJ, Paul DR. Polymer 1991;32:2618.

[9] McHattie JS, Koros WJ, Paul DR. Polymer 1991;32:840.

[10] Moe MB, Koros WJ, Paul DR. J Polym Sci, Polym Phys Ed 1988; 26:1.

[11] Pilato LA, Litz LM, Hargitay B, Osborne RC, Farnham AG, Kawakami JH, Fritze PE, McGrath JE. Polym Prepr (Am Chem Soc, Div Polym Chem) 1975;16:41.

[12] Guiver MD, ApSimon JW, Kutowy O. J Polym Sci, Polym Lett Ed 1988;26:123.

[13] Guiver MD, Kutowy O, ApSimon JW. Polymer 1989;30:1137.

[14] Guiver MD, Croteau S, Hazlett JD, Kutowy O. Br Polym J 1990;23: 29.

[15] Brownstein SK, Guiver MD. Macromolecules 1992;25:5181.

[16] Guiver MD, Robertson GP. Macromolecules 1995;28:294.

[17] Guiver MD, Robertson GP, Foley S. Macromolecules 1995;28:7612.

[18] Guiver MD, Zhang H, Robertson GP, Dai Y. J Polym Sci, Part A: Polym Chem 2001;39:675.

[19] Guiver MD, Robertson GP, Rowe S, Foley S, Kang YS, Park HC, Won J, Le Thi HN. J Polym Sci, Part A: Polym Chem 2001;39:2103.

[20] Guiver MD, ApSimon JW, Kutowy O. US Patent 4,797,457 and US Patent 4,833,219; 1989.

[21] Guiver MD, Robertson GP, Yoshikawa M, Tam CM. In: Pinnau I, Freeman B, editors. Membranes formation and modification. ACS symp ser 744, Washington, DC: American Chemical Society; 1999. p. 137. ISBN: 0-8412-3604-6, chapter 10.

[22] Kim I-W, Lee KJ, Jho JY, Park HC, Won J, Kang YS, Guiver MD, Robertson GP, Dai Y. Macromolecules 2001;34:2908.

[23] Bickson B, Nelson JK, Götz G, Ozcayir Y. US Patent 5,071,448; 1991.

[24] Mohanty DK, Sachdeva Y, Hedrick JL, Wolfe JF, McGrath JE. Polym Prepr (Am Chem Soc, Div Polym Chem) 1984;25:19.

[25] Mohanty DK. PhD Dissertation. Virgina Polytechnic Institute and State University; 1983.

[26] McHattie JS. PhD Dissertation. University of Texas at Austin; 1990.

[27] Aitken CL. PhD Dissertation. University of Texas at Austin; 1992.

[28] Viswanathan R, Johnson BC, McGrath JE. Polymer 1984;25:1827.

[29] Cotter RJ. Engineering plastics: handbook of polyarylethers. New York: Gordon & Breach; 1995.

[30] Aitken CL, Koros WJ, Paul DR. Macromolecules 1992;25:3651.

[31] Park JY, Paul DR. J Membr Sci 1997;125:23.

[32] Montaudo G, Finocciaro P, Trivellone E, Bottino F, Maravigna P. J Mol Struct 1973;16:299.