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Modified Polysulfones. IV. Synthesis and Characterization of Polymers with Silicon Substituents for a Comparative Study of Gas-Transport Properties

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ABSTRACT: We previously conducted a detailed study of gas-transport and other properties of a series of silicon derivatives of Udel polysulfone (PSf) and Radel polyphenylsulfone; we now report the details of their preparation by the reaction of lithiated polymer intermediates with chlorosilylalkylaryl electrophiles. Ortho-sulfone-substituted polymers with pendant trimethylsilyl, dimethylphenylsilyl, and diphenylmethylsilyl and other groups were obtained by direct metalation followed by the reaction of the dilithiated intermediate with the appropriate silyl electrophile. In addition, the structural regularity and geometry of the dilithiated site was also exploited to introduce silicon into the main chain by the reaction of dichlorosilyl electrophiles, leading to the formation of a new tricyclic heteroatom ring. Ortho-ether PSf derivatives were obtained from a dibrominated polymer via the lithiation of brominated polymer and reaction with a silyl electrophile. The degree of substitution of the silyl groups was 2.0 or less from dilithiated polymers and was dependent on the electrophile reactivity and reaction conditions. A detailed structural characterization of the polymers by NMR and IR spectroscopy is reported in addition to glass-transition temperatures and thermal stabilities.
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INTRODUCTION

Polysulfone (PSf) is a membrane material widely used for processes such as ultrafiltration, reverse osmosis, and gas separation. We have been investigating the modification of PSf for tailoring membrane properties. In previous studies, we used a direct lithiation[1] or bromination–lithiation[2] procedure for producing reactive PSf intermediates that were converted by reaction with various electrophiles to give carboxyl,[3] hydroxyl,[4] azide,[5] amine,[6] aldehyde,[7] and a number of other derivatives.[8,9]

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Polymeric materials with bulky silicon side groups result in significant changes in polymer properties such as gas permeability and permselectivity; mechanical, thermal and surface properties; and photochemical reactivity.[10] Polymers containing silicon substituents either in the main chain or attached as side groups are of particular interest for gas-separation membranes because of their potential ability to hinder chain motions and to disrupt chain packing, thereby improving gas permeability with minimal loss in selectivity.

Polytrimethylsilylpropyne (PTMSP) is a glassy polymer noted for having the highest gas permeation of all known polymers.[11–14] The unusually high gas permeabilities are the result of the very high fractional free volume of this low-density polymer. This property arises from the structural architecture of the stiff polymer backbone, consisting of alternating double bonds, combined with alternating bulky trimethylsilyl groups that severely hinder chain mobility and rotation and may also disrupt chain packing. The introduction of other sterically more bulky silyl side groups led to a large decrease in oxygen permeability, but with an increase in oxygen/nitrogen permselectivity.[13] A similar trend was observed in polydiphenylacetylenes with very bulky triphenylsilyl groups, where the decrease in permeability from trimethylsilyl was more than 2 orders of magnitude.[15] Polydimethylsiloxane is a rubbery polymer with a silicon backbone that also has very high gas permeabilities, although of an order of magnitude less than PTMSP.[16,17] Both polymers have low gas permselectivities.

In contrast, conventional glassy polymers such as PSf and poly(phenylene oxide) (PPO) generally exhibit low gas permeabilities and high permselectivities.[16,17] One approach to increase their gas permeability is modification to introduce trimethylsilyl side-group substituents. Trimethylsilylated PPO, prepared by lithiation followed by a reaction with chlorotrimethylsilane, had a fourfold increase in oxygen permeability, with a minimal loss of oxygen/nitrogen selectivity with respect to PPO.[18,19] Modification conditions on PPO can be manipulated to moderately favor lithiation either on the aromatic ring or on the methyl group. Ring-substituted silyl groups had more favorable gas permeation performance than methyl-substituted side groups.[18] The introduction of a more bulky triphenylsilyl group onto PPO resulted in decreased permeability and permselectivity.[20] PPO substituted with trimethylsilyl groups separated from the aromatic ring with a linear ethynyl spacer increased oxygen permeability by an order of magnitude, but at the expense of permselectivity.[21]

In comparison with PPO, there are very few gas-transport studies on silyl-modified PSf, and they have been limited to only trimethylsilyl, even though the parent polymer was used in the first generation of commercial gas-separation membranes. In a study similar to the study of PPO, the oxygen permeation of trimethylsilylethynyl-substituted PSf increased and the oxygen/nitrogen permselectivity decreased to the same extent as with PPO.[22] Someone else reported that CO_2 permeability increased for one silicon derivative.[23] Gas permeation data for some PSf substituted with trimethylsilyl and sulfonated groups are reported in a patent.[24]

In this article, we report details of the synthesis and characterization of PSf and polyphenylsulfone (PPSf) containing a number of different silyl substituents for our reported study[25] on the correlation of structural side-chain size variations and other physical data such as chain mobility with pure gas permeation coefficients. PSf is well suited to silyl modification by the reaction of lithiated polymer intermediates with various chlorosilanes. The introduction of pendant groups with incrementally increasingly steric size is described for trimethylsilyl, dimethylphenylsilyl, methyldiphenylsilyl, triisobutylsilyl, and triphenylsilyl. Under carefully selected experimental conditions, the more reactive chlorosilane electrophiles yield substituted polymers with a high degree of structural regularity, whereas less reactive or sterically bulky electrophiles give products containing less than two groups per repeat unit from dilithiated intermediates. A detailed NMR structural characterization of the derivatives with a high degree of substitution (DS) is also reported.

EXPERIMENTAL

Materials and Methods

Udel P3500 PSf and Radel R5000 PPSf (BP Amoco Polymers Inc.) and all glassware were dried at 120 °C before use. *n*-Butyllithium (10 M in hexane) solution, chlorosilane electrophiles, and other reagent-grade chemicals were obtained

from Aldrich Chemical Co. and were used as received. Tetrahydrofuran (THF) was freshly distilled under argon from lithium aluminum hydride. Reactions were performed under a dry argon atmosphere in three-necked flasks equipped with a high-torque mechanical paddle stirrer, a gas inlet, and a septum. For all lithiation reactions, *n*-butyllithium was injected dropwise through a flexible line inlet into cooled polymer solutions via a syringe pump. Polymers were recovered by precipitation from ethanol, then washed sequentially in ethanol and hot water, and finally dried in a vacuum oven.

Polymer Analyses and Measurements

Proton and carbon spectra were obtained on a Varian Unity Inova 400 NMR spectrometer operating at a proton frequency of 400.13 MHz and a carbon frequency of 100.61 MHz. Spectra were acquired at 25 °C with deuterated chloroform as the polymer solvent. Short-range and long-range proton–carbon connectivities were determined by heteronuclear correlation (HETCOR) and long-range heteronuclear correlation (LRHETCOR) with J ^{13}C–^{1}H values of 140 and 7.5 Hz, respectively. Chemical shifts, referenced to δ 7.25 for $CHCl_3$ present in $CDCl_3$, are expressed in parts per million (ppm), and the spectral resonances are designated singlet (s), doublet (d), doublet of doublets (dd), and multiplet (m). Coupling constants (J) are in hertz. Unmodified, monosubstituted, and disubstituted repeat units are designated U, M, and D, respectively. Chemical modifications targeting a DS of 2.0 but that actually give less than a DS of 2.0 contain monosubstituted repeat units associated with the modification site. These contain segments with one substituted (Ms) and one unsubstituted (Mu) aromatic ring, thereby giving rise to several additional minor signals for polymers not fully disubstituted.

IR spectra were measured on a Nicolet 520 Fourier transform infrared spectrometer. We mounted polymer samples by evaporating a THF solution on a NaCl window. Gel permeation chromatography (GPC) profiles for THF polymer solutions were generated with a Waters 510 pump, a Waters 996 UV detector, and a selection of μ-Styragel columns. The reported molecular weights (MWs) were estimated by direct comparison against a set of calibrated polystyrene standards. Thermal decompositions of silicon polymers were determined with a DuPont 951 thermogravimetric analyzer. Samples were heated under a nitrogen flow at 50 mL/min, from room temperature to 900 °C at a rate of 10 °C/min, after a 30-min isothermal period at room temperature. Glass-transition temperatures (T_g's) were obtained with a DuPont 910 differential scanning calorimeter by the heating of samples at a rate of 10 °C/min to a temperature below the polymer degradation point, quenching in liquid nitrogen, and then reheating at the same rate.

Lithiated PSf (2a)

A PSf solution in dry THF was reacted with an approximately 5% excess (of desired DS) of *n*-butyllithium at reduced temperature (−50 °C). *n*-Butyllithium (10 M) was injected dropwise at a typical rate of 30 mL/h via a syringe pump. During the first few drops of butyllithium addition, a color change occurred. **2a** formed a homogeneous red-brown solution and became increasingly viscous as the DS reached 2.0. The mixture was stirred for an additional 15 min after the addition, and then the temperature was adjusted before addition of the electrophile, which was also adjusted to the reaction temperature.

Lithiated PPSf (2b)

PPSf was dissolved in cooled THF (−5 °C) because the polymer is more soluble at a reduced temperature than at room temperature. The gray solution was cooled to −45 °C, and *n*-butyllithium (10 M) was injected dropwise. A bright lemon-yellow color developed that changed to a more viscous, orange solution as the addition progressed. The mixture was stirred for an additional 25 min and then adjusted as previously.

Lithiated Dibrominated PSf (11a)

A solution of dibrominated PSf (**10a**) in THF was cooled to −78 °C with a dry-ice/alcohol bath. The polymer was lithiated by the dropwise addition of *n*-butyllithium (10 M) and then stirred for 30 min to give a soluble dilithiated intermediate.

Poly[sulfone (ortho-sulfone) trimethylsilane] (3a; DS = 2.0)

A solution of PSf (50.0 g, 113 mmol) in THF (750 mL) was dilithiated with *n*-butyllithium (23.76

mL, 237 mmol), and then the solution was warmed to −30 °C. Chlorotrimethylsilane (43 mL, 340 mmol) cooled to the same temperature was introduced promptly into the reaction solution, which immediately became less viscous. Over a 1-h period, the solution was stirred with gradual warming to −10 °C, and color changes from clear red to clear yellow were observed. A colorless solution resulted during the time stirring was continued at −10 °C for an additional 0.5 h. The polymer was recovered by precipitation from 90% ethanol, washed, and dried in a vacuum oven at 25 °C. The white product had a DS of 2.00.

ELEM. ANAL. Calcd. for PSf—$(SiMe_3)_2$: C, 67.54%; H, 6.53%; S, 5.46%. Found: C, 68.54%; H, 6.82%; S, 5.64%.

3a (DS = 1.0)

PSf was monolithiated with a 1.1 mol equiv of *n*-butyllithium and silylated as before. A more complex NMR spectrum was due to the presence of U, M, and D repeat units.

DS: 1.03. ^{1}H NMR (δ): 7.84 (d, H9, J9.0, U), 7.74 (d, H9, J9.0, Mu), 7.70 (d, H9 J8.8, Ms), 7.39 (d, H9, J8.8, D), 7.35 (d, H12, J2.6, D), 7.29 (d, H12, J2.6, Ms), 7.26–7.21 (m, H3, U, M, D), 7.00–6.88 (m, H2, U, M, D, H8, U, M), 6.82 (dd, H8, J2.6, J8.8, D), 1.68 (s, 6H, CMe_2), 0.36 (s, M, $SiMe_3$), 0.33 (s, D, $SiMe_3$). ELEM. ANAL. Calcd. for PSf—$(SiMe_3)_1$: C, 70.01%; H, 5.87%; S, 6.23%. Found: C, 70.17%; H, 6.02%; S, 6.78%.

Poly[phenylsulfone (ortho-sulfone) trimethylsilane] (3b)

A solution of PPSf (42.6 g, 106 mmol) in THF (1200 mL) was lithiated with *n*-butyllithium (23.43 mL, 230 mmol) and then reacted at −25 °C with chlorotrimethylsilane (43 mL, 340 mmol) as before. A less viscous, dark red solution resulted that became clear yellow after stirring for 1.5 h. After stirring for an additional 0.7 h, the polymer was recovered from 80% aqueous ethanol.

DS: 1.97. ELEM. ANAL. Calcd. for PPSf—$(SiMe_3)_2$: C, 66.14%; H, 5.92%; S, 5.88%. Found: C, 65.82%; H, 5.86%; S, 5.65%.

Poly[sulfone (ortho-sulfone) dimethylphenylsilane] (4a)

A solution of **2a** (from PSf; 20.0 g, 45 mmol) was reacted with chlorodimethylphenylsilane (25 g, 146 mmol), as summarized in Table I. The resulting dark brown solution was gradually warmed to −10 °C over a 0.75-h period and changed to a clear pale yellow color. The polymer was precipitated from 90% ethanol.

DS: 1.93. ELEM. ANAL. Calcd. for PSf—$(SiMe_2Ph)_2$: C, 72.64%; H, 5.95%; S, 4.51%. Found: C, 76.90%; H, 6.26%; S, 4.04%.

Poly[phenylsulfone (ortho-sulfone) dimethylphenylsilane] (4b)

A solution of **2b** (from PPSf; 15 g, 37.5 mmol) was reacted with chlorodimethylphenylsilane (25 mL, 150 mmol), as summarized in Table I. The resulting dark mixture was warmed gradually and lightened, finally forming a clear colorless solution at −5 °C. The solution was stirred for an additional 0.75 h at −5 °C, and then the polymer was recovered from 95% ethanol. The product (22.31 g, 89% yield) had a DS of about 1.80.

Poly[sulfone (ortho-sulfone) diphenylmethylsilane] (5a)

A solution of **2a** (from PSf; 3 g, 6.8 mmol) was reacted with chlorodiphenylmethylsilane (14.3 mL, 68 mmol), as summarized in Table I. The recovered product (4.7 g) had a DS of 1.20.

^{1}H NMR (δ): 7.87–7.83 (m, H9s, U, M, D), 7.44–6.76 (m, H2s, H3s, H8s, H12s, U, M, D), 1.72–1.64 (m, CMe_2), 1.07 (s, SiMe), 0.86 (s, SiMe), 0.69 (s, SiMe).

Poly[phenylsulfone (ortho-sulfone) diphenylmethylsilane] (5b)

A solution of **2b** (from PPSf; 20 g, 50 mmol) was reacted with chlorodiphenylmethylsilane (100 g, 430 mmol), as summarized in Table I. The recovered polymer (95% ethanol) had a DS of about 1.30.

^{1}H NMR (δ): 7.93 (d, H9), 7.63–6.82 (m, remaining ArH), 1.11 (s, SiMe), 0.94 (s, SiMe), 0.76 (s, SiMe).

Poly[sulfone (ortho-sulfone) triphenylsilane] (6a)

A solution of **2a** (from PSf 1.55 g, 3.5 mmol) was reacted with a solution of chlorotriphenylsilane (4.60 g, 16 mmol) in THF (15 mL), as summarized in Table I. The resulting pale yellow solution con-

Table I. Experimental Conditions for the Preparation of Silicon Derivatives

Polymer	Quantity (mmol)	THF Concentration (%)	BuLi (mmol)	E+ (mmol/°C)	Conditions after Electrophile Addition	DS
3a	113	6.6	237	340/−30	−30 to −10 °C (1 h, yellow), −10 °C (0.5 h, colorless)	2.0
3b	106	3.5	230	340/−25	−25 (2.2 h, clear yellow)	1.97
4a	45	2.0	95	146/−30	−30 to −10 °C (0.75 h, clear yellow)	1.93
4b	37.5	2.0	78.8	150/−30	−30 to −5 °C (until colorless), −5 °C (0.75 h)	~ 1.80
5a	6.8	2.5	14.3	68/−28	−28 to −5 °C (0.75 h, black), −5 °C (1.45 h, clear yellow)	1.20
5b	50	2.5	105	430/−30	−30 to −5 °C (0.75 h), −5 °C (2.75 h, clear yellow)	~ 1.30
6a	3.5	1.7	7.5	16-THF/−10	−5 °C (5 h), 0 °C (10 h, pale yellow)	0.40
7a	23	1.5	47.5	106/−10	−10 °C (0.35 h), −5 °C (0.75 h, dark orange), −5 °C (9 h), 0 °C (4 h)	~ 0.50
8a	53	1.6	118	88/−20	Slow dichlorodimethylsilane addition (5 mL/h, 2 h), −20 °C (1.5 h, clear yellow)	95% cyclic
8b	50	1.2	110	83/−33	Slow dichlorodimethylsilane addition (3.3 mL/h, 3 h), −30 °C (0.75 h, colorless)	88% cyclic
9a	45	1.5	94.5	74/−21	Slow dichloromethylphenylsilane addition (4 mL/h, 3 h), −21 °C (0.75 h, clear yellow)	~ 85% cyclic
9b	50	1.2	110	82.5/−32	Slow dichloromethylphenylsilane addition (3 mL/h, 4.5 h), −32 °C (1.75 h, clear yellow)	~ 81% cyclic
12a	40	4.0	88	120/−40	−40 °C (0.5 h, yellow), −40 to −20 °C (1.5 h)	~ 1.80
13a	41.7	2.0	90	146/−40	−40 to −10 °C (1.5 h), −10 °C (3.5 h, clear yellow)	~ 1.90
14a	6.7	2.6	14	20/−37	Brown, −37 to −5 °C (3 h, light brown), −5 °C (1 h)	1.45
15a	2.5	2.0	5.25	25/−12	Dark orange, −10 °C (0.5 h), −5 °C (5 h)	0.33

tained some insoluble material that was removed before the polymer was recovered (90% ethanol).

DS: 0.40. ^{1}H NMR (δ): 7.84–6.50 (m), 1.69 (s, CMe_2, U), 1.66 (s, CMe_2, M).

Poly[sulfone (ortho-sulfone) triisobutylsilane] (7a)

A solution of **2a** (from PSf; 10.0 g, 23 mol) was reacted with chlorotriisobutylsilane (25.0 g, 106 mmol), as summarized in Table I. The recovered pale yellow product (90% ethanol) had a DS of about 0.5.

^{1}H NMR (δ): 7.85 (d, H9, J8.6, U), 7.79 (d, H9, Mu), 7.63 (d, H9, Ms), 7.34–7.33 (m), 7.24 (broadened d, H3, U, M), 7.18–7.04 (m, minor), 7.00 (d, H8, J8.6, U), 6.94 (broadened d, H2, U, M), 1.81–1.74 [m, —CH_2—C*H*—$(CH_3)_2$], 1.69 (broadened s, CMe_2), 1.10–0.78 [m, —CH_2—CH—(CH_3)$_2$]. IR (ν): 2872–2956 cm^{-1} (s, aliphatic; see also Table VII, shown later). ELEM. ANAL. Calcd. for PSf—(Si-isobutyl$_3$)$_2$: C, 72.98%; H, 8.89%; S, 3.82%. Found: C, 74.00%; H, 7.38%; S, 3.55%.

Poly(sulfone cyclic-dimethylsilane) (8a)

An approximately 1.6 w/v % solution of PSf (23.6 g, 53.3 mmol) in THF (1.5 L) was lithiated with *n*-butyllithium (11.75 mL, 118 mmol). The solu-

tion was warmed to −20 °C, which was determined to be the optimum temperature for the reactivity of chlorodimethylsilane electrophile with the lithiated polymer. Chlorodimethylsilane (10.69 mL, 88 mmol) was added very slowly via a syringe pump at a rate of 5 mL/h. Efficient mixing was essential to minimize interchain side reactions. During addition, the solution darkened to a deep red and then lightened after 1.5 h. After complete addition, stirring of the clear yellow solution was continued for 1.5 h, and then the polymer was precipitated from 80% aqueous ethanol. The white product (21.77 g, 82% yield) contained approximately 95% cyclic dimethylsilane repeat units.

ELEM. ANAL. Calcd. for PSf—(cyclic-$SiMe_2$): C, 69.85%; H, 5.26%; S, 6.43%. Found: C, 69.88%; H, 5.15%; S, 6.15%.

Poly(phenylsulfone cyclic dimethylsilane) (8b)

Under conditions similar to those for **8a**, an approximately 1.25 w/v % solution of **2b** (from PPSf; 20.0 g, 50 mmol) was reacted with dichlorodimethylsilane (10.0 mL, 83 mmol), as summarized in Table I. Initially, the solution viscosity increased, and the solution darkened to a red-orange color. A colorless solution resulted 0.75 h after the addition. The recovered polymer (90% ethanol) contained approximately 88% cyclic dimethylsilane repeat units.

ELEM. ANAL. Calcd. for PPSf—(cyclic-$SiMe_2$): C, 68.40%; H, 4.42%; S, 7.02%. Found: C, 68.28%; H, 4.44%; S, 6.91%.

Poly(sulfone cyclic methylphenylsilane) (9a)

Under conditions similar to those for **8a**, a 1.5 w/v % solution of **2a** (from PSf; 19.9 g, 45 mmol) was reacted with dichloromethylphenylsilane (12.1 mL, 74 mmol), as summarized in Table I. After 0.75 h following complete electrophile addition, a pale, clear yellow solution resulted, and stirring was continued for an additional 0.75 h at −21 °C. The recovered polymer (90% ethanol) contained approximately 85% cyclic methylphenylsilane repeat units.

ELEM. ANAL. Calcd. for PSf—(cyclic-SiMePh): C, 72.83%; H, 5.03%; S, 5.72%. Found: C, 71.29%; H, 4.97%; S, 5.52%.

Poly(phenylsulfone cyclic methylphenylsilane) (9b)

Under conditions similar to those for **8a**, a 1.25 w/v % solution of **2b** (from PPSf; 20.0 g, 50 mmol) was reacted with dichloromethylphenylsilane (13.4 mL, 82.5 mmol), as summarized in Table I. Ten minutes after addition, the dark red solution began to lighten, and it became pale yellow 1 h later. The solution was stirred for another 0.75 h at −32 °C, and then the polymer was recovered from ethanol. The product contained approximately 81% cyclic methylphenylsilane repeat units.

ELEM. ANAL. Calcd. for Radel PSf—(cyclic-SiMePh): C, 71.79%; H, 4.28%; S, 6.18%. Found: C, 72.76%; H, 4.45%; S, 5.72%.

Poly[sulfone (ortho-ether) trimethylsilane] (12a)

10a (24.0 g, 40 mmol) in THF (600 mL) was lithiated with *n*-butyllithium (8.8 mL, 88 mmol) and then reacted at −40 °C with chlorotrimethylsilane (15.23 mL, 120 mmol) by its rapid introduction into the solution. The resulting green solution immediately became less viscous and changed to a cloudy, yellow solution after 0.5 h of stirring. The temperature was raised gradually to −20 °C over a 1-h period, and then the polymer was recovered from 95% ethanol.

DS: ~1.80. ELEM. ANAL. Calcd. for PSf—($SiMe_3$)$_2$: C, 67.54%; H, 6.53%; S, 5.46%. Found: C, 67.49%; H, 6.66%; S, 5.13%.

Poly[sulfone (ortho-ether) dimethylphenylsilane] (13a)

10a (25.0 g, 41.7 mmol) in THF (1.25 L) was reacted with *n*-butyllithium (9.0 mL, 90 mmol) and then reacted at −40 °C with chlorodimethylphenylsilane (25 g, 146 mmol). A green solution immediately resulted; it became clear pale yellow as it was warmed slowly to −10 °C over 1.5 h. The solution was stirred for an additional 3.5 h at −10 °C and then precipitated from 90% ethanol. The product (28 g, 84% yield) had a DS of about 1.90.

Poly[sulfone (ortho-ether) diphenylmethylsilane] (14a)

A solution of **11a** (from **10a**; 4.0 g, 6.7 mmol) was reacted with a cooled solution of chlorodiphenylmethylsilane (4.20 mL, 20 mmol) in THF (5 mL), as summarized in Table I. The polymer (5 g) was recovered from 95% ethanol and had a DS of 1.45.

^{1}H NMR (δ): 7.84–7.81 (m, minor), 7.60 (d, H9, J8.8), 7.38–7.35 (m, H14), 7.21–7.12 (m), 7.03–6.91 (m, minor), 6.76 (d, H2, J9.1), 6.66 (d, H8,

J9.0), 1.69 (s, minor, CMe_2 U), 1.61 (s, CMe_2), 1.52 (s, CMe_2), 0.75 (s, minor, SiMe), 0.74 (s, minor, SiMe), 0.72 (s, SiMe).

Poly[sulfone (ortho-ether) triphenylsilane] (15a)

A solution of **11a** (from **10a**; 1.5 g, 2.5 mmol) was reacted with a solution of chlorotriphenylsilane (7.33 mL, 25 mmol) in THF (15 mL), as summarized in Table I. The polymer was precipitated from 70% ethanol and had a DS of 0.33.

^{1}H NMR (δ): 7.86–6.50 (m), 1.69 (s, CMe_2, U), 1.57 (s, CMe_2, M).

Dibrominated Radel (10b)

This procedure was adapted from our previously reported bromination reaction.[2] To a magnetically stirred solution of PPSf (100 g, 0.25 mol) in chloroform (830 mL) contained in a 3-L flask was poured bromine (96.60 mL, 1.875 mol). Stirring ceased after 1.5 h. The following day, chloroform was decanted, and methanol was added to the mixture to solidify the polymer. The polymer was redissolved in *N*-methylpyrrolidinone and recovered from methanol.

DS: 2.00. ^{1}H NMR (δ): 7.02 (d, 2H, H8), 7.14 (d, 1H, H2), 7.51 (dd, 1H, H3), 7.84 (d, 1H, H5), 7.90 (d, 2H, H9). ELEM. ANAL. Calcd. for PPSf—Br_2: C, 51.64%; H, 2.53%; S, 5.74%. Found: C, 50.85%; H, 2.41%; S, 5.05%.

Poly[phenylsulfone (ortho-ether) trimethylsilane] (12b), Attempted

n-Butyllithium (1 mL, 1 mmol) was added to a solution of dibrominated PPSf (2.5 g, 4.5 mmol) in THF (250 mL) cooled to −15 °C, immediately resulting in a cloudy, dark brown coloration. The solution was warmed to −10 °C, and then chlorotrimethylsilane (2.8 mL, 22 mmol) at −10 °C was added into the flask. After 2 h, the polymer was precipitated from 95% ethanol. The recovered polymer was insoluble. Several lithiation conditions for **10b** did not achieve the desired products. With THF as the solvent, polymer concentration ranges between 1.5 and 4 w/v % and temperature ranges between −60 and −30 °C resulted in insoluble polymers. THF/diglyme solvent mixtures (1/1–3/1) and a 2 w/v % polymer concentration at −40 °C were also ineffective.

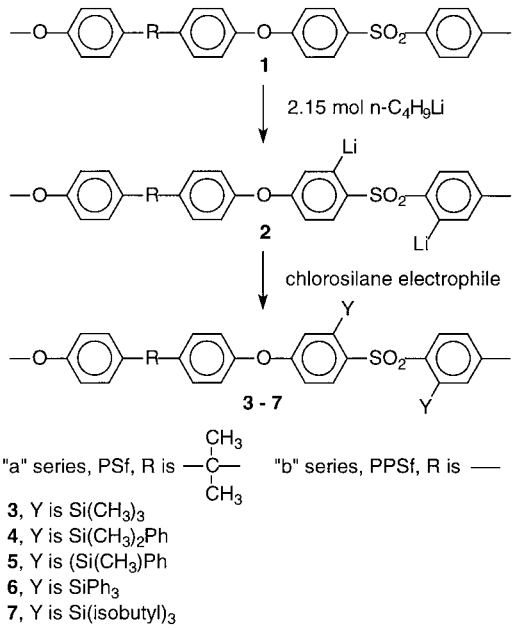

Figure 1. Modification pathway for the introduction of silyl side groups at the ortho-sulfone site by direct lithiation.

RESULTS AND DISCUSSION

Synthesis

A series of pendant silicon substituents were introduced onto commercial Udel P3500 PSf (**1a**) or Radel R5000 PPSf (**1b**) by direct lithiation. Figure 1 shows the chemical modification pathway in which **1a** or **1b** was lithiated directly by *n*-butyllithium to afford a THF-soluble intermediate **2a** or **2b**. For polymers having substituents with DS < 2.0, Y represents the side group and hydrogen. The sulfone group has a powerful activating and directing ability such that direct lithiation results in almost quantitative lithiation ortho to the sulfone group and the DS is controlled by the molar ratio of *n*-butyllithium to polymer. In general, dilithiated intermediates were prepared for conversion to silyl derivatives to give the highest DS. Chlorosilane electrophiles were subsequently reacted with the dilithiated intermediates to give the resulting silyl-modified polymer containing trimethylsilyl (**3a**, **3b**), dimethylphenylsilyl (**4a**, **4b**), and methyldiphenylsilyl (**5a**, **5b**) derivatives. Chlorotrimethylsilane and chlorodimethylphenylsilane electrophiles were sufficiently reactive under the right temperature conditions to yield highly substituted silyl polymers with DS values

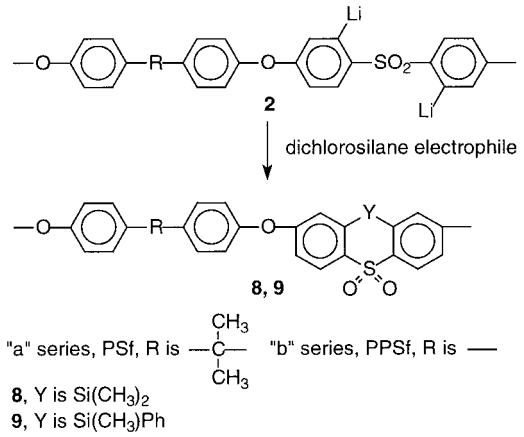

Figure 2. Modification pathway for the introduction of cyclic silyl groups into the main chain by direct lithiation.

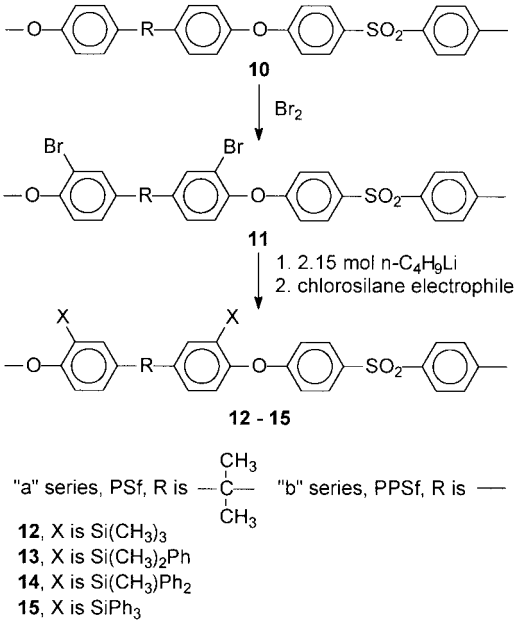

Figure 3. Modification pathway for the introduction of silyl side groups at the ortho-ether site by bromination–lithiation.

of 2.0 or slightly less. Chloromethyldiphenylsilane was less reactive, giving products with DS values of 1.20–1.30. Apart from the less electrophilic nature of Si—Cl with increasing phenyl substitution, it is likely that the steric hindrance of the resulting polymer around the sulfone site is a strong contributing factor in the lower reactivity of the electrophile. For the reaction with chlorotriphenylsilane, the least reactive electrophile, and containing sterically the most bulky substituent, only a low DS of 0.40 was observed for the derivative **6a**. Triisobutylchlorosilane gave the corresponding sterically bulky triisobutylsilyl derivative **7a**, also with a low DS.

Polymers containing silicon-containing heterocyclic structures were prepared by a ring-closure reaction, exploiting the lithiation geometry around the ortho-sulfone site. The unusually high level of structural modification control enables the preparation of polymer intermediates containing two lithium atoms per repeat unit throughout the polymer chain. Ring closure around the sulfone linkage to form the new tricyclic units in the main chain was achieved with dichlorosilane electrophiles under carefully controlled reaction conditions with the dilithiated intermediate. This ring-forming reaction with dichlorosilanes was previously explored with small molecules such as diphenylsulfone,[26–28] but in macromolecular systems there are obvious complicating factors. Exacting reaction conditions are required, whereby the reaction with difunctional electrophiles must strongly favor intrachain reactions while minimizing interchain (crosslinking) reactions. In practical terms, this requires the use of well-mixed and very dilute polymer solutions and a slow addition of the dichlorosilane electrophile under conditions where the reaction occurs rapidly. If the electrophile addition is not at the optimally reactive temperature, a surplus accumulates until an appropriate temperature is

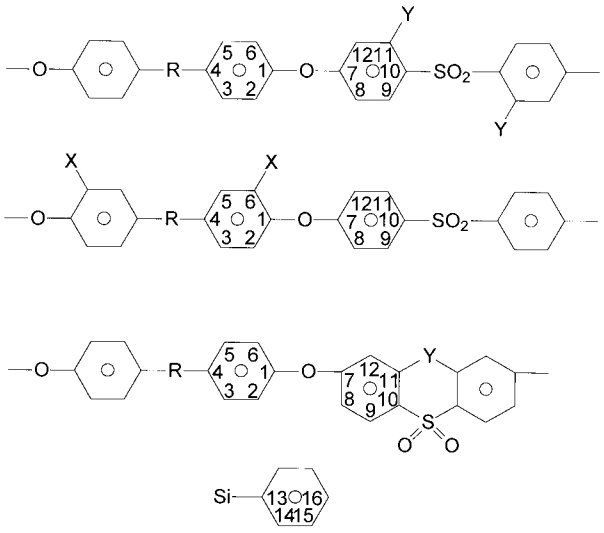

Figure 4. Numbering system for the assignment of protons and carbons in the NMR spectra.

Table II. Proton Shift Assignments for Ortho-Sulfone Disubstituted Polysulfones and Polyphenylsulfones

Proton	PSf **1a** R: Isopropylidene, Y: H	**3a** R: Isopropylidene, Y: $SiMe_3$	**4a** R: Isopropylidene, Y: $SiMe_2Ph$	PPSf **1b** R: Bond, Y: H	**3b** R: Bond, Y: $SiMe_3$	**4b** R: Bond, Y: $SiMe_2Ph$
H2, H6	6.94	6.95 J8.8	6.86 J8.7	7.11 J8.4	7.12 J8.6	7.03 J8.4
H3, H5	7.24	7.23 J8.8	7.16 J8.7	7.58 J8.4	7.58 J8.6	7.52–7.50
H8	7.00	6.83 J2.6, J8.7	6.77 J2.6, J8.7	7.07 J9.2	6.89 J2.6, J8.8	6.88 J2.4, J8.4
H9	7.85	7.40 J8.8	7.23 J8.7	7.90 J8.8	7.46 J8.8	7.29 J8.8
H12	7.00	7.35 J2.6	7.13 J2.6	7.07 J9.2	7.47 J2.7	7.14 J2.4
H14	—	—	7.51–7.49	—	—	7.52–7.50
H15	—	—	7.29–7.27	—	—	7.27–7.26
H16	—	—	7.29–7.27	—	—	7.27–7.26
—C—CH_3	1.69	1.68	1.69	—	—	—
—Si—CH_3	—	0.33	0.62	—	0.37	0.66

reached, and then the reaction occurs in an uncontrolled manner. Although this ring-closure method may not be practical for large scale preparations, it offers convenient access to novel polymers for our studies. The general reaction is shown in Figure 2. Cyclic dimethylsilane derivatives of **8a**, and **8b** were prepared by the careful addition of dichlorodimethylsilane to dilithiated polymers. The soluble PSf derivative **8a** contained approximately 95% cyclized repeat units. Similarly, cyclic dimethylphenylsilane derivatives of **9a**, and **9b** were prepared with dichlorodimethylphenylsilane.

A bromination–lithiation reaction[2] was used to difunctionalize PSf ortho to the ether linkage, as described previously. The reaction for producing silyl derivatives is outlined in Figure 3. Although we could dibrominate PPSf, anomalous solubility

Table III. Carbon Shift Assignments for Ortho-Sulfone Disubstituted Polysulfones and Polyphenylsulfones

Carbon Atom	PSf **1a** R: Isopropylidene, Y: H	**3a** R: Isopropylidene, Y: $SiMe_3$	**4a** R: Isopropylidene, Y: $SiMe_2Ph$	PPSf **1b** R: Bond, Y: H	**3b** R: Bond, Y: $SiMe_3$	**4b** R: Bond, Y: $SiMe_2Ph$
C1	152.9	152.8	152.7	154.7	154.9	154.3
C2	119.7	119.7	119.6	120.6	120.4	120.5
C3	128.4	128.3	128.2	128.7	128.5	128.4
C4	147.1	146.9	146.8	137.1	136.8	136.7
C5	128.4	128.3	128.2	128.7	128.5	128.4
C6	119.7	119.7	119.6	120.6	120.4	120.5
C7	161.9	160.3	160.1	161.8	160.1	160.1
C8	117.7	116.3	117.0	118.0	116.8	117.1
C9	129.6	131.3	131.5	129.9	131.5	131.6
C10	135.5	140.4	140.7	135.9	140.9	140.8
C11	129.6	142.9	141.4	129.9	143.4	141.6
C12	117.7	125.6	126.7	118.0	126.1	126.8
C13	—	—	138.9	—	—	138.7
C14	—	—	134.4	—	—	134.4
C15	—	—	127.6	—	—	127.6
C16	—	—	128.8	—	—	128.8
—*C*—CH_3	42.4	42.5	42.3	—	—	—
—C—*C*H_3	30.9	31.0	31.0	—	—	—
—Si—*C*H_3	—	1.1	−0.4	—	1.1	−0.55

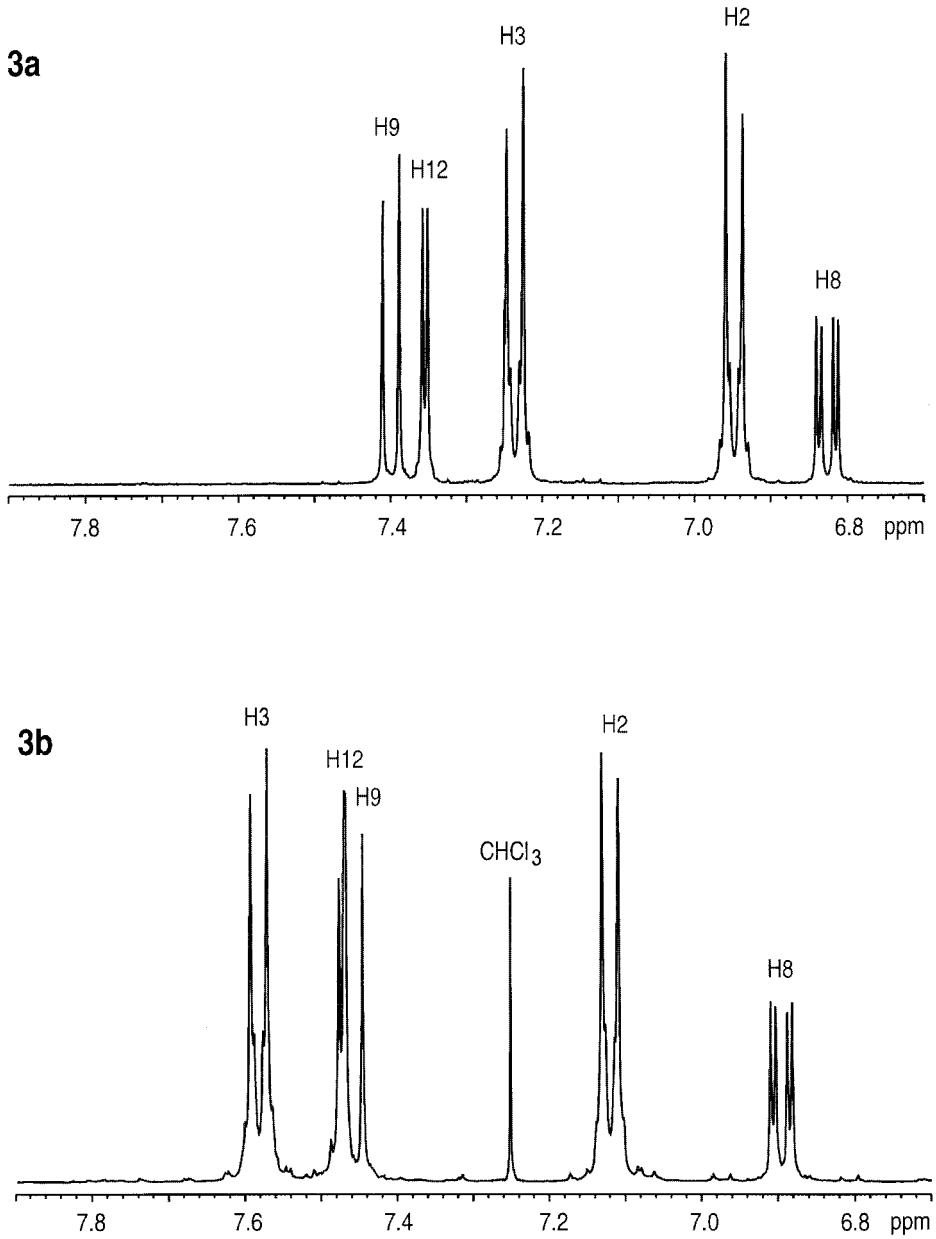

Figure 5. Aromatic-region ^{1}H NMR for PSf—$SiMe_3$ (**3a**) and PPSf—$SiMe_3$ (**3b**).

behavior, possibly a result of crystallinity, prevented us from obtaining ortho-ether derivatives for this polymer. Lithium–bromine exchange is by far the most predominant reaction over direct lithiation at the ortho-sulfone site. Minimal amounts of lithium substitution occurred at the ortho-sulfone site because the bromine on the bisphenol portion of the polymer chain assisted in deactivating the ortho-sulfone site, so that a lithium–bromine exchange was the predominant reaction.[29] The regiospecificity of this reaction is increased with reduced temperature. For this reason, lithiation was conducted at −78 °C, and then the temperature of the formed dilithiated intermediate **11a** was increased to achieve optimum reaction conditions for the addition of the chlorosilane electrophile. Polymers containing trimethylsilyl (**12**) and dimethylphenylsilyl (**13**) groups had high DS values, although NMR spectroscopic analysis indicated the presence of small amounts of ortho-sulfone-substituted silyl. The presence of a small amount of ortho-sulfone silyl

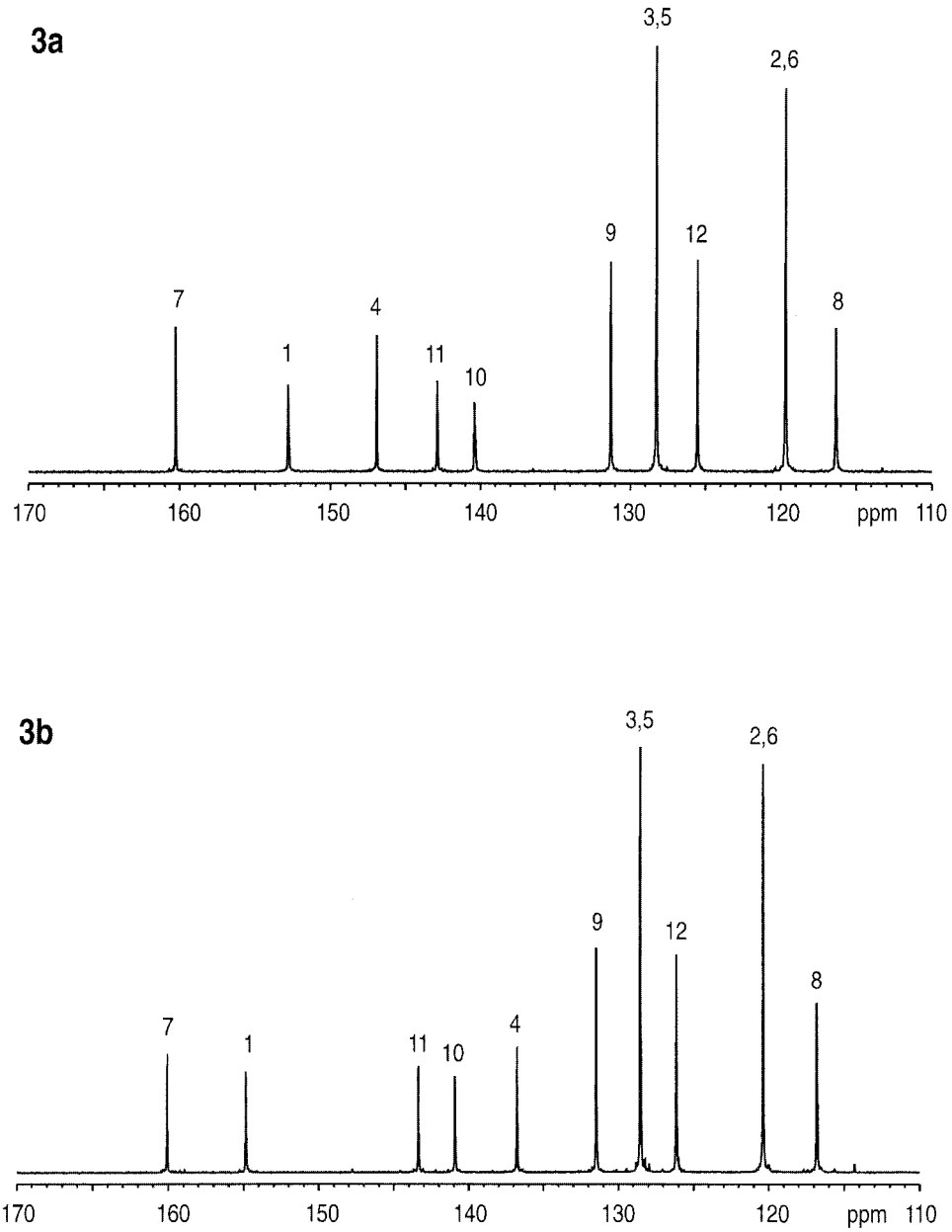

Figure 6. Aromatic-region ^{13}C NMR for PSf—$SiMe_3$ (**3a**) and PPSf—$SiMe_3$ (**3b**).

arises because of a small amount of competitive lithiation at that site and because when a slight excess of *n*-butyllithium is used, the excess readily lithiates the ortho-sulfone site once all the bromine atoms have been exchanged. The DS of the diphenylmethylsilyl polymer (**14**) was 1.45, indicating the site is somewhat more accessible to the bulky electrophile than the ortho-sulfone site. As before, the triphenyl derivative **15** had a low DS value.

Structural Characterization by NMR

The ^1H NMR spectra of PSf and PPSf are the aromatic AA′XX′ type composed of four doublets, and changes in protons in either the bisphenol or phenylsulfone proton doublets indicate the site of modification. For polymers with substituents at a DS of 2.0 or slightly less, ^1H and ^{13}C NMR spectra were relatively simple because of the presence of only one type of repeat unit. Spectra of polymers

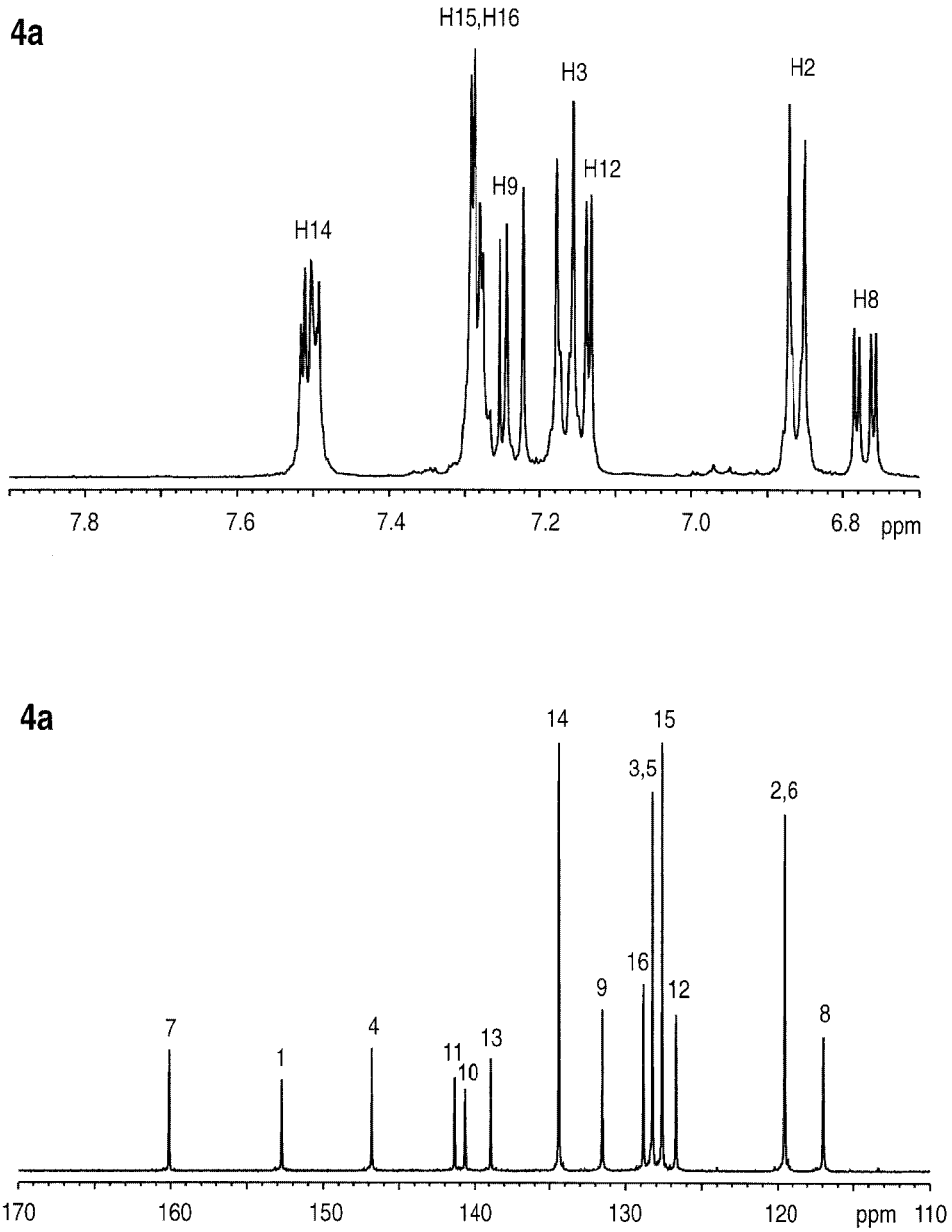

Figure 7. Aromatic-region ^{1}H and ^{13}C NMR for PSf—$SiMe_2Ph$ (**4a**).

with DS values considerably less than 2 were complex because of the presence of monosubstituted, disubstituted, and unsubstituted repeat units. The DS for PSf derivatives was calculated by comparative integration of the 6H isopropylidene methyl signal on the polymer chain with the silyl methyl substituent. In some instances, this method was not entirely accurate because of the close signal proximity of isopropylidene methyl and trace water present in the sample. For PPSf derivatives, the DS measurement is less convenient because of the absence of the isopropylidene methyl signal. Instead, DS was determined by the plotting of the expected ratio of total aromatic to aliphatic protons against the theoretical DS. The experimental DS was calculated by interpolation of the experimental ratio onto the plot.

The numbering system adopted for the protons and carbons in the polymer derivatives is shown in Figure 4. Ortho-sulfone silyl side-group derivatives were initially analyzed by ^{1}H NMR. In the perturbed phenylsulfone portion of the repeat

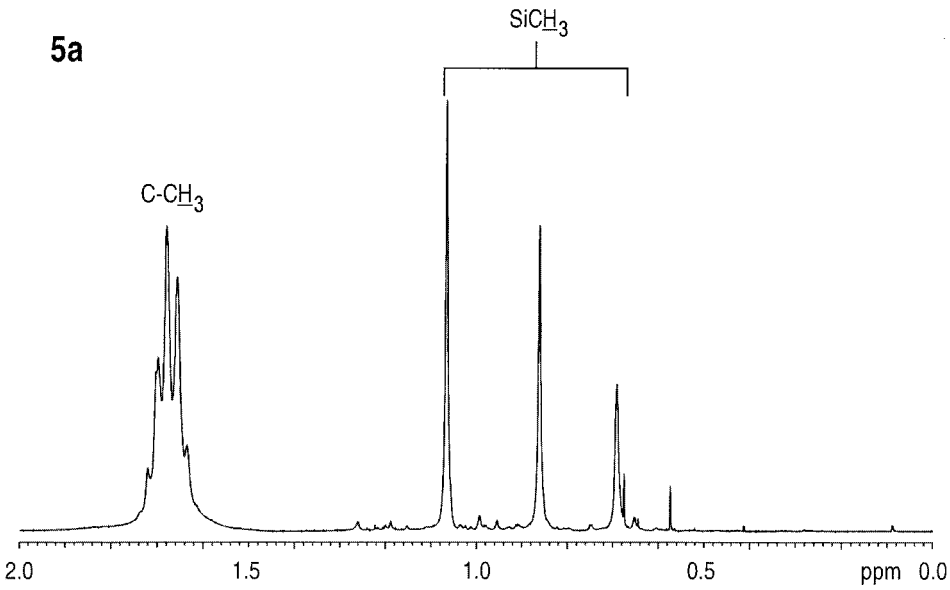

Figure 8. Aliphatic-region ^{1}H NMR for PSf—$SiMePh_2$ (**5a**).

unit, the disubstitution of a silyl substituent resulted in a downfield 2H doublet corresponding to H9. The H9 signal is downfield because of the deshielding effect of sulfone, and it is coupled to H8. The 2H H8 signal is upfield, being an ortho-ether proton, and is a characteristic doublet of doublets due to coupling to H9 and long-range coupling to H12. The 2H H12 signal appears as a long-range-coupled doublet of about J = 2.5 Hz and is shifted downfield by proximity to the silyl substituent. All ^{1}H–^{1}H couplings were confirmed by homonuclear decoupling experiments, including correlation spectroscopy. Sharp upfield signals correspond to methylsilyl protons. Short-range carbon–proton connectivities for C2, C3, C8, C9, and C12 were determined by HETCOR. Long-range (three bond) carbon–proton connectivities for the remaining carbon nuclei were determined unambiguously by LRHETCOR. For PSf, C4 was determined from the isopropylidene methyl proton. Similarly, C11 was coupled to silylmethyl protons.

Tables II and III list the ^{1}H and ^{13}C resonances for ortho-sulfone silylated PSf and PPSf and include comparative data[2] for PSf and PPSf that we reported previously. Figure 5 shows the simple partial ^{1}H NMR spectrum for disubstituted PSf—$SiMe_3$ (**3a**). The effect of the $SiMe_3$ group in **3a** relative to PSf is to shield H9, as shown by a considerable upfield shift, and to deshield H12. The shielding environment for H9 is far less marked in monosubstituted PSf—$SiMe_3$ polymer, suggesting a different conformational environment around the sulfone in disubstituted PSf—$SiMe_3$. A similar shielding effect on H9 is also evident in Figure 5, which shows the aromatic region of PPSf—$SiMe_3$ (**3b**). The partial ^{13}C spectra for **3a** and **3b** in Figure 6 show fully disubstituted polymers. The most significant difference from PSf and PPSf is the expected approximately 13.4-ppm downfield shift for C11 attached to silicon.

The PSf—$SiMe_2Ph$ (**4a**) and PPSf—$SiMe_2Ph$ (**4b**) derivatives exhibited a larger upfield shift of over 0.60 ppm for H9, compared with the $SiMe_3$ derivatives, due to the shielding effect of the phenyl ring on the side chain. The aromatic ^{1}H NMR and ^{13}C NMR spectra of **4a** are shown in Figure 7. Long-range coupling of the SiMe proton was used to confirm C13.

The ^{1}H NMR spectra of PSf—$SiMePh_2$ (**5a**) and PPSf—$SiMePh_2$ (**5b**) consist of overlapping multiplets in the aromatic region that could not be readily assigned to individual protons. For each polymer, the upfield SiMe were notable for having three large signals. One possible explanation is a combination of substituent size and restrictive ortho-sulfone geometry that most likely causes rotational hindrance around both the sulfone linkage and the silyl side group, resulting in three different environments for SiMe, at least at room temperature. The DS of **5a** was 1.20, suggesting

Table IV. Proton Shift Assignments for Tricyclic Polysulfones and Polyphenylsulfones

Proton	**8a** R: Isopropylidene, Y: $SiMe_2$	**9a** R: Isopropylidene, Y: SiMePh	**8b** R: Bond, Y: $SiMe_2$	**9b** R: Bond, Y: SiMePh
H2, H6	6.95 J8.8	6.85 J8.8	7.13 J8.4	7.04 J8.8
H3, H5	7.26 J8.8	7.14 J8.6	7.61 J8.6	7.51 J8.6
H8	6.98 J2.5, J8.6	7.01 J2.4, J8.8	7.06 J2.4, J8.6	7.07 J2.5, J8.8
H9	8.09 J8.6	8.14 J8.4	8.14 J8.6	8.18 J8.6
H12	7.33 J2.5	7.04 J2.4	7.38 J2.6	7.13 J2.4
H14	—	7.52–7.50	—	7.57–7.54
H15	—	7.37–7.33	—	7.41–7.39
H16	—	7.42–7.40	—	7.46–7.44
—C—CH_3	1.71	1.64	—	—
—Si—CH_3	0.65	0.97	0.67	1.00

disubstituted repeat units were difficult to obtain. In the sterically more bulky PSf—$SiPh_3$ (**6a**) and PSf—Si(isobutyl)$_3$ (**7a**) derivatives, only low DS values of 0.4–0.5 were obtained. A partial upfield ^{1}H NMR spectrum of **5a** in Figure 8 shows three distinct SiMe singlets and an isopropylidene proton consisting of several singlets of very similar chemical shifts.

Tables IV and V list the ^{1}H and ^{13}C resonances, respectively, for the silicon-bridged tricyclic polymers. Partial ^{1}H NMR spectra of **8a** and **8b** are shown in Figure 9. The most noteworthy differences in both these spectra in comparison with those of **3a** and **3b** are the downfield shift of H8 by approximately 0.15 ppm and the large downfield shift of H9 by approximately 0.70 ppm. The quasiplanar tricyclic ring gives H9 shift values more comparable to H9 of PSf, in contrast to **3a** and **3b**, where the steric configuration of the rings strongly shields H9. The $SiMe_2$ signals have

Table V. Carbon Shift Assignments for Tricyclic Polysulfones and Polyphenylsulfones

Carbon Atom	**8a** R: Isopropylidene, Y: $SiMe_2$	**9a** R: Isopropylidene, Y: SiMePh	**8b** R: Bond, Y: $SiMe_2$	**9b** R: Bond, Y: SiMePh
C1	153.1	152.9	154.9	154.8
C2	119.4	119.3	120.2	120.1
C3	128.4	128.3	128.6	128.5
C4	146.9	146.8	136.7	136.7
C5	128.4	128.3	128.6	128.5
C6	119.4	119.3	120.2	120.1
C7	160.1	160.0	160.0	159.8
C8	117.4	117.8	117.9	118.1
C9	127.1	127.1	127.2	127.1
C10	140.8	141.2	141.0	141.4
C11	140.6	139.4	140.8	139.5
C12	124.0	125.3	124.1	125.5
C13	—	131.5	—	131.4
C14	—	135.6	—	135.5
C15	—	128.2	—	128.3
C16	—	130.6	—	130.7
—*C*—CH_3	42.4	42.3	—	—
—C—*C*H_3	30.9	30.9	—	—
—Si—*C*H_3	−2.4	−3.4	−2.3	−3.4

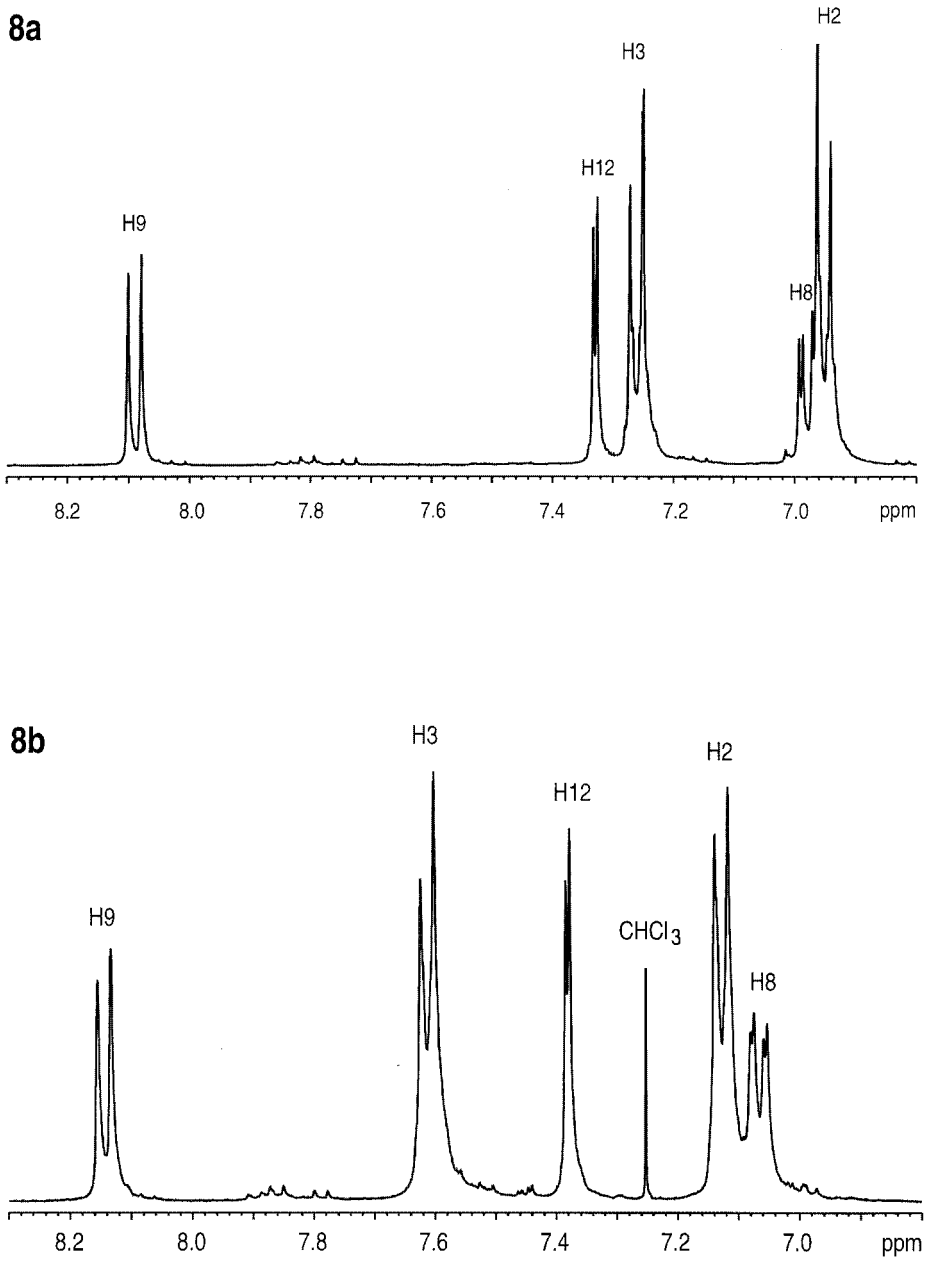

Figure 9. Aromatic-region ^{1}H NMR for tricyclic PSf—$SiMe_2$ (**8a**) and PPSf—$SiMe_2$ (**8b**).

chemical shifts of approximately 0.65 as a result of the attachment of two phenyl rings to the silicon atom. The chemical shift values are similar to those of the $SiMe_2Ph$ side-group derivatives **4a** and **4b**, which also have two phenyl rings attached to the silicon atom. The ^{13}C NMR spectra of **8a** and **8b** (Fig. 10) show only minor impurities, indicating that almost all of the polymer repeat units contain the silyl-bridged tricyclic ring system. A low percentage of uncyclized repeat units are evident from the relatively simple spectra (not shown) of the SiMePh tricyclic derivatives **9a** and **9b**.

Table VI lists ^{1}H and ^{13}C chemical shifts for the ortho-ether derivatives substituted with $SiMe_3$ (**12a**) and with $SiMe_2Ph$ (**13a**). The ^{1}H NMR spectrum of **12a** shown in Figure 11 indicates a DS of about 1.80. The substituted bisphe-

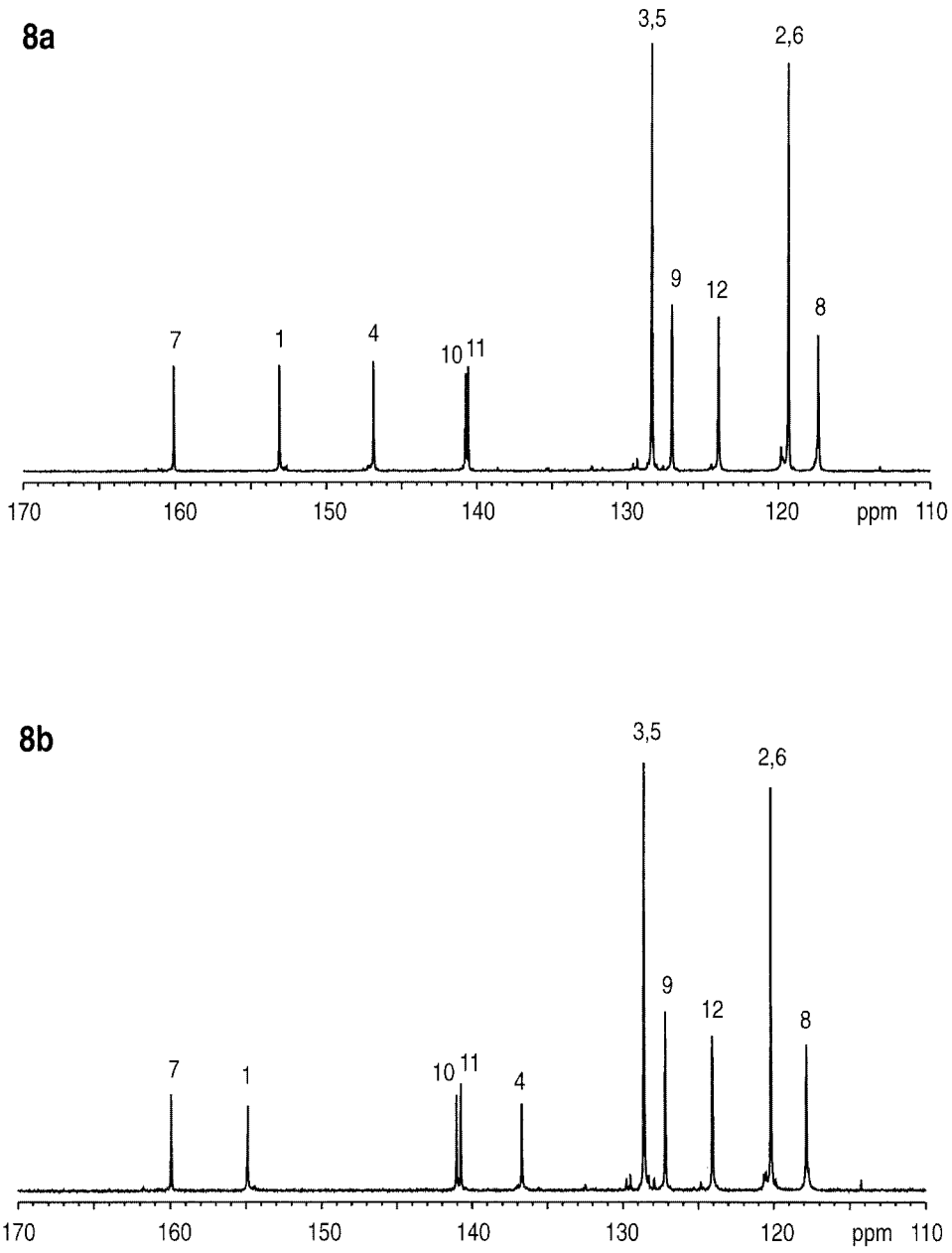

Figure 10. Aromatic-region ^{13}C NMR for tricyclic PSf—$SiMe_2$ (**8a**) and PPSf—$SiMe_2$ (**8b**).

nol ring has the characteristic pattern of an upfield 2H doublet (H2) coupled with the 2H doublet of doublets (H3), itself long-range-coupled to the 2H doublet (H5). Some minor signals and a small singlet at δ 0.36 indicate that a small percentage of the repeat units are substituted ortho to sulfone (DS $\sim$ 0.1). The ^{13}C NMR spectrum (Fig. 11) of **12a** also shows some minor signals indicating the presence of other structural repeat units.

The proton and carbon spectra of **13a** (not shown) indicate a high DS of about 1.90, and there is also evidence for a small percentage of substitution on the phenylsulfone ring. The proton spectrum of **14a** indicates that the $SiMePh_2$ derivative has a higher DS of 1.45 compared with the value obtained for the ortho-sulfone analogue **5a** (DS $\sim$ 1.20), probably because of the sterically more accessible site. There are two closely spaced

Table VI. Proton and Carbon Shift Assignments for Ortho-Ether Disubstituted Polysulfones and Polyphenylsulfones

Proton	**12a** R: Isopropylidene, X: $SiMe_3$	**13a** R: Isopropylidene, X: $SiMe_2Ph$	Carbon Atom	**12a** R: Isopropylidene, X: $SiMe_3$	**13a** R: Isopropylidene, X: $SiMe_2Ph$
—	—	—	C1	157.6	157.7
H2	6.77 J8.5	6.74 J8.5	C2	118.8	118.9
H3	7.22 J2.3, J8.5	7.20 J2.3, J8.5	C3	129.5	129.7
—	—	—	C4	146.4	146.5
H5	7.33 J2.4	7.27 J2.3	C5	133.8	134.7
—	—	—	C6	130.9	129.5
—	—	—	C7	162.1	161.7
H8	6.98 J8.8	6.78 J8.9	C8	117.6	117.4
H9	7.85 J8.8	7.70 J8.9	C9	129.7	129.4
—	—	—	C10	135.1	135.1
H11	7.85 J8.8	7.70 J8.9	C11	129.7	129.4
H12	6.98 J8.8	6.78 J8.9	C12	117.6	117.4
—	—	—	C13	—	137.4
H14	—	7.34–7.32	C14	—	133.8
H15	—	7.12–7.09	C15	—	127.5
H16	—	7.12–7.09	C16	—	128.9
—	—	—	—*C*—CH_3	42.5	42.4
—C—CH_3	1.71	1.63	—C—*C*H_3	31.0	30.8
—Si—CH_3	0.15	0.46	—Si—*C*H_3	−0.9	−2.4

methyl singlets shifted upfield, approximately in a 1/2 ratio (upfield). These upfield chemical shifts for methyls presumably arise from a through-space shielding effect of the silyl phenyl rings on the isopropylidene unit. We hypothesize that the two singlets arise from the presence of monosubstituted and disubstituted repeat units rather than from rotational steric hindrance. The proton spectrum of **15a** (not shown) with a DS of 0.33 is characterized by overlapping multiplets, similar to the spectrum of **6a**.

IR

Significant IR absorptions and their assignments for silyl PSf are listed in Table VII. Strong absorptions attributed to aromatic C—O—C stretching appear between 1254 and 1241 cm^{-1} but are less strong for the modified polymers compared with the starting materials **1a** and **1b**. The presence of a very strong absorption from symmetrical bending vibrations of Si—Me was observed at 1229 cm^{-1} for ortho-sulfone-substituted polymers only and at 1222 cm^{-1} for the cyclic polymers. These absorptions are at lower wave numbers than the expected typical range of 1275–1260 cm^{-1}. In the ortho-ether derivatives **12a** and **13a**, these absorptions are apparently absent or underlying the C—O—C stretching absorptions at 1241 cm^{-1}. The weak absorptions at 1383 and 1377 cm^{-1} are attributed to asymmetric bending vibrations of the Si—Me group. Characteristic strong absorptions for the SiMe group were observed between 855 and 816 cm^{-1}, although absorption intensities are lower for the cyclic series. Polymers **4a**, **13a**, and **9a** give characteristic medium and strong absorptions from SiPh vibrations at 1428 and 700 cm^{-1}, respectively. Both absorptions are characteristic of all phenyl-containing side groups, as shown in Table VII.

GPC

The effect of chemical modification on the MW distribution was determined by GPC. In Figure 12, the ortho-sulfone series **3a** to **5a** for PSf are compared with **1a** and **3b**. The PPSf series had very similar profiles (not shown) to those of the PSf series. Polymers **1a**, **3a**, and **4a** had very similar profiles and MW distributions, but with a small amount of a high MW tail on the profile and with a shift to a higher MW with each increase in

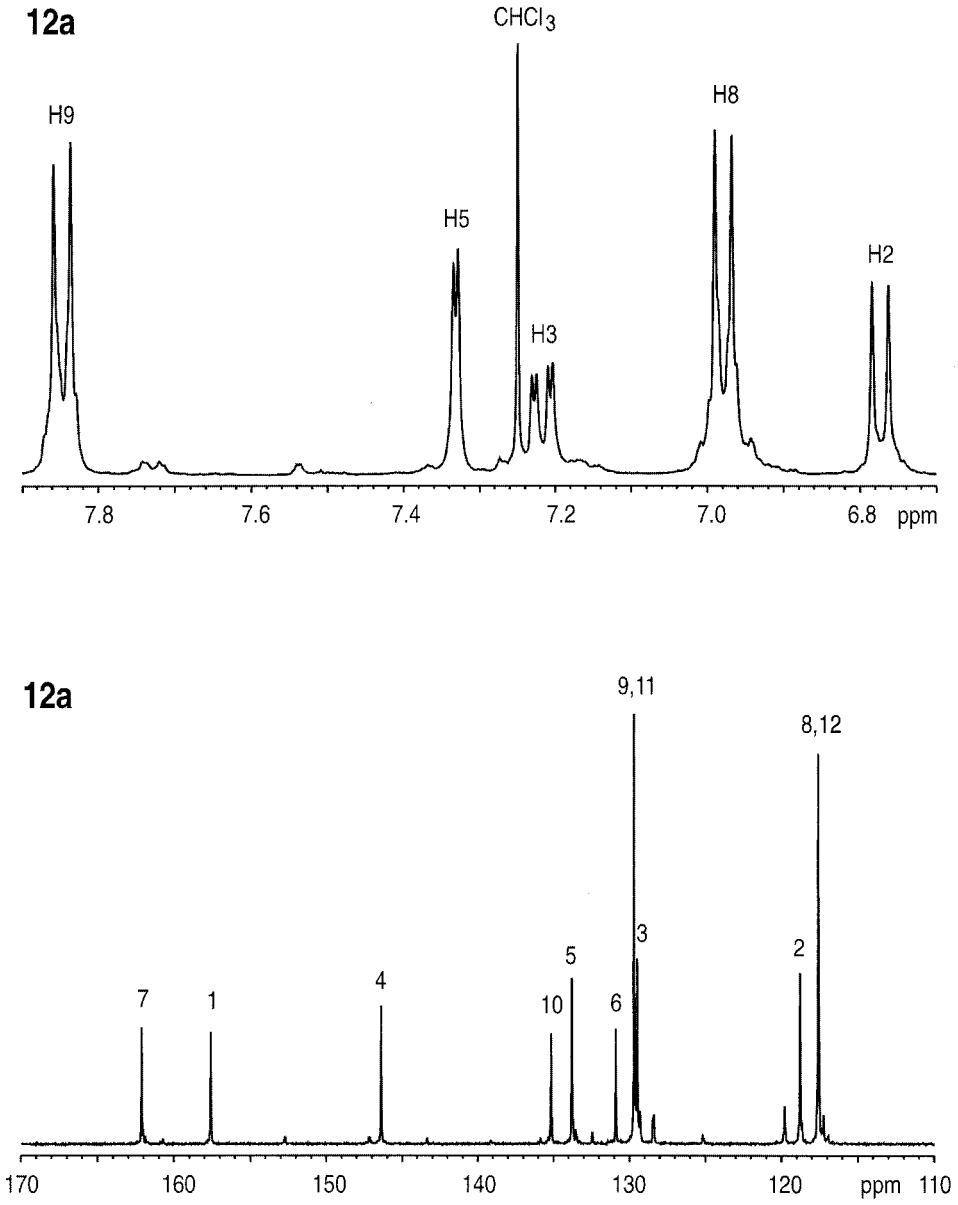

Figure 11. Aromatic-region ^{1}H and ^{13}C NMR for PSf—$SiMe_3$ (**12a**).

the size of the silyl group. The MW increase is believed to be due to the increase in the MW of the repeat unit brought about by the substitution of increasingly large silyl substituents. In addition, it is most likely that the side groups change the hydrodynamic volume and dimensions of the polymer chain. The result for **5a** (and **5b**) is unexpected and shows the additional presence of a large high MW fraction from chain extension or crosslinking. Both **5a** and **5b** are soluble in THF and do not have the appearance of crosslinked polymer. It appears that the reaction of only the ortho-sulfone lithiated polymer **2** with $ClSiMePh_2$ somehow causes chain extension or crosslinking, but no mechanism for this is proposed here. Compared with the ortho-ether series in Figure 12, the analogous reaction with the lithiated polymer **11** does not give a similar high MW fraction. Polymers **12a** to **14a** show the regular incremental increases in MW through the series and increases in the MW distribution. In some derivatives, notably **12a**, there is also the presence of a small fraction of high MW polymer. The MW profiles for the cyclic polymers **8a** and **9a** are also shown in

Table VII. Significant New IR Absorptions for Silylated Polymers

Polymer	Si—Ph	Si—CH_3	Asymmetric Stretching C—O—C	1,2,4-Trisubstituted C—C Stretching
1a	—	—	1248 (ss)	—
3a	—	1383 (w), 1229 (ss), 842 (ss), 771 (m), 758 (w)	1248 (s)	1454 (m)
4a	1428 (m), 700 (s)	1383 (w), 1229 (ss), 822 (ss), 784 (m)	1248 (s)	1454 (m)
7a		1383 (w), 855 (w), 835 (w), 771 (m)		1454 (m)
8a	—	1383 (w), 1222 (ss), 848 (m), 829 (m), 803 (s), 790 (m)	1254 (s)	1448 (m)
9a	1428 (m), 700 (s)	1383 (w), 1222 (ss), 855 (m), 835 (s), 790 (m)	1254 (s)	1448 (m)
12a	—	1383 (w), 835 (ss), 752 (w)	1241 (ss)	1473 (m)
13a	1428 (m), 700 (s)	1383 (w), 835 (s), 816 (s), 777 (m)	1241 (ss)	1473 (m)
1b	—	—	1241 (ss)	—
3b	—	1383 (w), 1229 (ss), 842 (ss), 771 (m), 758 (w)	1248 (s)	1454 (m)
4b	1428 (m), 700 (s)	1377 (w), 1229 (ss), 822 (s), 777 (m), 739 (m)	1241 (m)	1454 (m)
5b	1428 (m)	1377 (w), 790 (m), 700 (s)		1454 (m)
8b	—	1383 (w), 1222 (ss), 848 (w), 816 (m), 790 (m)	1254 (s)	1448 (m)
9b	1428 (w), 700 (s)	1383 (w), 1222 (ss), 848 (m), 816 (m), 790 (m)	1254 (s)	1448 (m)

Figure 12. The profiles for the PPSf series **8b** and **9b** are very similar and are not shown. Because these polymers were prepared by an intramolecular ring-closing reaction of **2** with a difunctional silyl electrophile, it was expected that some crosslinking or chain extension would occur by the competing intermolecular reaction. The derivatives were prepared under conditions that would minimize the undesired competing reaction. Although the derivatives appeared to be completely soluble but highly viscous in THF, the profiles show the presence of some very high MW fraction resulting from the intermolecular reaction. The sharp slope on the high MW side of the profiles is due to the cutoff of the GPC column.

Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) T_g Data

The thermal stability of the silicon derivatives was determined by TGA. Table VIII lists both the actual onset of degradation temperatures and the extrapolated onsets of degradation at a heating rate of 10 °C/min in nitrogen. All the silyl-modified polymers were thermally less stable than the respective parent polymers. The ortho-ether series were thermally more stable than the analogous ortho-sulfone derivatives, and the tricyclic ring-closed polymers had the highest thermal stability. A possible explanation for the lower thermal stability of the ortho-sulfone derivatives could be a combination of steric hindrance about the diphenylsulfone site and a bulky side group as well as the strong electron withdrawing ability of the sulfone group, resulting in a weakening of the carbon–silicon bond. This explanation supports the two-step degradation readily observed in the derivative curves for the ortho-sulfone PSf polymer and less easily observed in the PPSf derivatives. The initial weight loss is believed to be due to the loss of the silicon functional groups because the initial weight loss in polymer **3a** is consistent with the calculated value of 25% for the loss of two trimethylsilyl groups. For **3a** (DS = 1), the initial weight loss is respectively less. The ortho-ether and tricyclic derivatives displayed one-step degradation profiles with the exception of the PPSf derivative **9b**.

The T_g of the silicon derivatives obtained by DSC are also shown in Table VIII. For all the

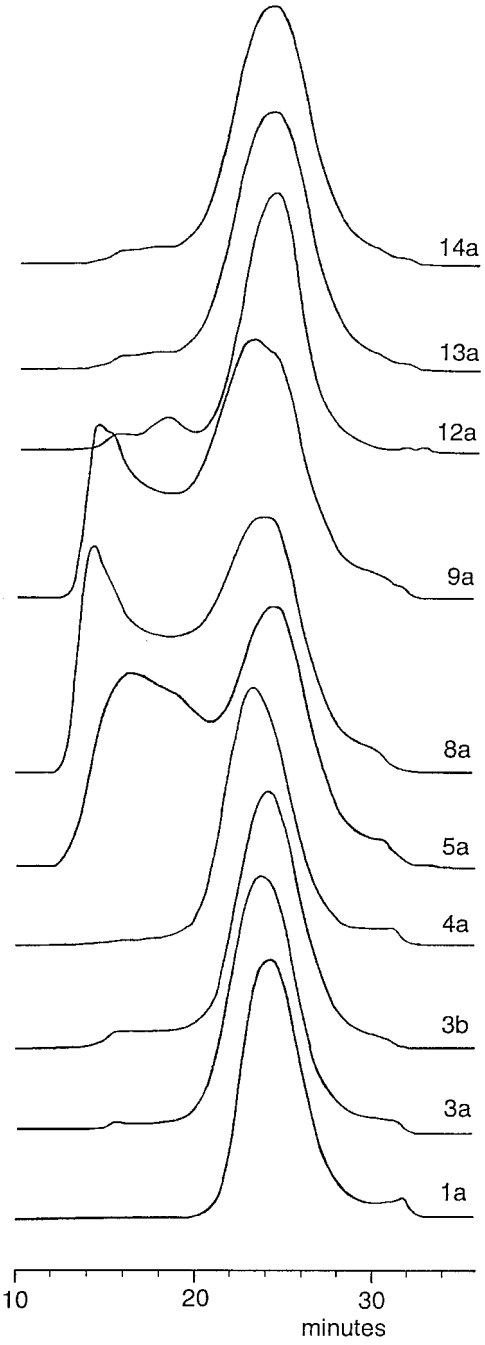

Figure 12. GPC profiles for selected polymers with different silyl side groups.

derivatives with pendant silyl substituents, there was a decrease in T_g. The $SiMe_3$ group resulted in the smallest decreases within the substituent groups $SiMe_3$, $SiMe_2Ph$, and $SiMePh_2$ for each respective polymer, whereas $SiMe_2Ph$ gave the largest decrease in T_g. However, for the $SiMePh_2$ group, the T_g trend is reversed with values similar to the $SiMe_3$ group. In a comparison of the same three silyl substituents for the ortho-sulfone and ortho-ether PSfs, the ortho-ether series exhibited the largest decrease in T_g, suggesting that substitution on the ortho-ether bisphenol A site has the greatest effect on polymer mobility. However, in the case of ortho-sulfone substitution on PPSf, decreases of the order of the ortho-ether PSf series were observed. It was anticipated that the larger silyl substituents would increase the stiffness of the backbone and would ultimately increase T_g, although this effect was not observed.

The cyclic polymers had higher T_g's than the unmodified polymers because the tricyclic ring structure increases the stiffness of the polymer chain by removing a rotational linkage site and by making the rotation about the ether linkage more difficult. The dimethylsilane bridge (**8a**, **8b**) derivatives had higher T_g's than the methylphenylsilane bridge derivatives. The glass-transition curves of the cyclic polymers showed some unusual behavior. Polymer **8a** showed an initial T_g at 217 °C and a large exothermic decomposition peak after T_g. After **8a** was heated to 250 °C, quenched, and then reheated, a well-defined T_g of 221 °C was observed. Similar to **8a**, polymer **9a** had a large exotherm after T_g of the first heating (ca. 250 °C). However, unlike **8a**, the **9a** exotherm disappeared after the quenching and reheating of the sample. Because the onset of thermal decomposition is above 300 °C, this exotherm could be the result of crystallinity. By contrast, polymer **8b** showed no exotherm after T_g. Polymer **9b** showed a broad exothermic peak around 260 °C after both the first and second heatings; however, T_g was not altered from the first to second heatings. This does not represent thermal decomposition because the onset of decomposition occurs above 300 °C. Some crystallinity is possible, but the typically well-defined exotherm is not evident.

CONCLUSIONS

PSf and PPSf modified with silyl groups were prepared to investigate the effect of incrementally increasing silyl substituent size on gas permeation and other properties of the polymers.[25] Three types of modified polymers containing different silyl functional groups were prepared by a general two-stage process entailing lithiation of the polymer followed by the addition of an appropriate silicon electrophile. Polymers with pendant

Table VIII. Degradation Temperatures and Glass-Transition Temperatures for Silylated Polymers

	TGA				
	Actual Onset		Extrapolated Onset		
Polymer	Weight (%)	Temperature (°C)	Temperature (°C)	T_g by DSC (°C)	Change in T_g (°C)
1a	99.8	453	518	188.1	—
3a	98.9	386	436	163.6	−24.5
4a	99.3	383	436	138.4	−49.7
5a	98.6	361	445	164.2	−23.9
1b	99.9	475	518	225.6	—
3b	98.7	383	425	184.5	−41.1
4b	98.3	366	425	152.1	−73.5
5b	96.5	358	405	179.1	−46.5
8a	97.7	438	500	221.2	+33.1
9a	97.0	418	481	213.4	+25.3
8b	98.1	425	480	264.0	+38.4
9b	98.5	373	483	253.7	+28.1
12a	97.9	417	491	154.9	−33.2
13a	99.4	421	497	116.7	−71.4
14a	96.3	435	488	137.5	−50.6

silyl groups at the ortho-sulfone site were prepared from the corresponding dilithiated PSf or PPSf polymer. Reactions to produce the $SiMe_3$ and $SiMe_2Ph$ derivatives were close to quantitative, whereas the one to produce the $SiMePh_2$ derivative gave a polymer with a DS considerably less than 2 because of the lower reactivity of the electrophile or steric hindrance. Reactions to produce the $SiPh_3$ derivatives gave only low DS values for the same reason. The second types of polymers with pendant silyl groups at the ortho-ether site were prepared from the corresponding dilithiated PSf, itself prepared by a lithium–halogen exchange reaction with **10a**. As before, the $SiMe_3$ and $SiMe_2Ph$ derivatives had DS values close to 2. Attempts to prepare the same series of PPSf derivatives were not successful because of practical difficulties associated with the anomalous solubility behavior of the starting material, dibrominated PPSf. The third type of polymers were prepared by an intramolecular cyclization reaction between ortho-sulfone dilithiated PSf and a dichlorosilane electrophile, effectively introducing silyl groups into the main chain. Because of the nature of the reaction, some degree of crosslinking occurred with the competing intermolecular reaction, although the polymers appeared to be fully soluble.

Detailed NMR data and spectral assignments are given to support the chemical structures of the silyl derivatized polymers as well as IR and elemental analyses. MW distributions of the modified polymers were compared to starting materials by GPC. As expected, the cyclic types contained a high MW fraction, indicating that some chain lengthening or crosslinking occurred. Apart from the $SiMePh_2$ derivatives of both the ortho-sulfone PSf and PPSf, which showed a similar high MW fraction, the GPC profiles generally showed small increases in MW with incremental increases in the substituent size. The silyl-modified polymers were thermally less stable than the respective parent polymers. The ortho-ether series were thermally more stable than the analogous ortho-sulfone derivatives, and the tricyclic ring-closed polymers had the highest thermal stability. The T_g's of PSf and PPSf with pendant silyl substituents decreased generally in the order of $SiMe_3 > SiMePh_2 > SiMe_2Ph$. The cyclic polymers had higher T_g's than PSf and PPSf because the tricyclic ring structure increased the stiffness of the polymer backbone by removing a rotational linkage.

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