Macromolecules 1993, *26*, 969–974 969

Synthesis and Properties of Novel Comb Polymers: Unsaturated Carbosilane Polymers with Pendant Oligo(oxyethylene) Groups

Liming Wang and William P. Weber*

Donald P. and Katherine B. Loker Hydrocarbon Research Institute, Department of Chemistry, University of Southern California, Los Angeles, California 90089-1661

Received September 3, 1992; Revised Manuscript Received October 26, 1992

ABSTRACT: 1-[ω-Methoxyoligo(oxyethylene)propyl]-1-methyl-1-silacyclopent-3-enes have been prepared by the dissolving-metal reaction of [ω-methoxyoligo(oxyethylene)propyl]methyldichlorosilane with magnesium and 1,3-butadiene or by the platinum-catalyzed hydrosilation reaction between the Si–H bond of 1-methyl-1-silacyclopent-3-ene and the C–C double bond of oligo(ethylene glycol) allyl methyl ether. Anionic ring-opening polymerization of these monomers yields poly[1-[ω-methoxyoligo(oxyethylene)propyl]-1-methyl-1-sila-*cis*-pent-3-enes]. These comb polymers have low T_gs (−70 to −75 °C). Complex formation between the pendant oligo(oxyethylene) chains and lithium cations has been studied by ^{13}C NMR and differential scanning calorimetry.

Introduction

While there has been considerable work, over the last 50 years, on silicone polymers,[1,2] there has been much less effort on polycarbosilanes. We have been interested in the preparation of unsaturated carbosilane polymers by anionic ring-opening polymerization of 1-silacyclopent-3-enes.[3–6] In this paper, we report the preparation and properties of polymers which have unsaturated carbosilane backbones and hydrophilic oligo(oxyethylene) pendant groups bonded to the silyl centers via strong hydrolytically stable C–Si bonds.

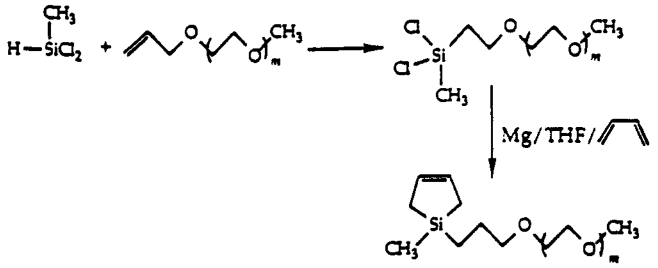
Significant work has been done on polysiloxanes with hydrophilic, nonionic oligo(oxyethylene) pendant groups. These low T_g comb polymers are able to complex lithium salts to form solvent-free polymer electrolytes[7–10] as well as to serve as polymeric surfactants.[11]

The low T_gs of poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene) (−63 °C)[12] and poly(oxyethylene) (−41 °C)[13] suggest that comb polymers comprised of a poly(1-methyl-1-sila-*cis*-pent-3-ene) backbone with oligo(oxyethylene) pendant groups would likewise have low T_gs.

Two main approaches exist for the preparation of functional polymers: polymerization of suitably functionalized monomers and chemical modification of preformed polymers.[14,15] This latter has been used for the preparation of comb polymers with a siloxane backbone and oligo(oxyethylene) pendant groups. Thus zinc or stannous salts or triethylamine catalyzes the reactions of poly(methylhydrosiloxane) with oligo(ethylene glycol) monomethyl ethers.[7–10,16,17] Unfortunately, the Si–O–C bonds of these are susceptible to hydrolytic cleavage.[11] Alternatively, comb polymers in which oligo(oxyethylene) pendant groups are joined to the silicon atoms of the polysiloxane chain via Si–C bonds have been prepared by the platinum-catalyzed hydrosilation graft reactions of the Si–H bonds of poly(methylhydrosiloxane) with the C–C double bonds of oligo(ethylene glycol) allyl ethers.[7,11,18–20]

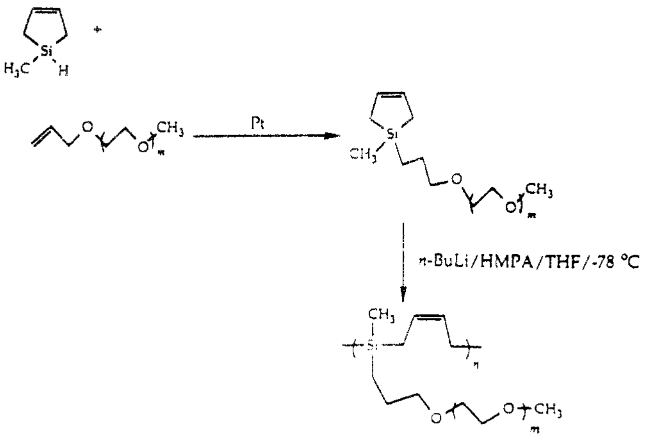
The low molecular weight of poly(1-methyl-1-sila-*cis*-pent-3-ene) prepared by the anionic ring-opening polymerization (AROP) of 1-methyl-1-silacyclopent-3-ene[6] limits the molecular weight of graft polymers which can be prepared by hydrosilation reactions between poly(1-methyl-1-sila-*cis*-pent-3-ene) and oligo(ethylene glycol) allyl methyl ethers. In addition, platinum-catalyzed intramolecular hydrosilation reactions between the Si–H and C–C double bonds of poly(1-methyl-1-sila-*cis*-pent-3-ene) can result in cross-linking.[21]

For these reasons, the alternative approach, namely, the preparation of functionalized monomers and their polymerization was undertaken. A two-step reaction sequence was used to prepare a series of silacyclopent-3-ene monomers in which ω-alkoxyoligo(oxyethylene)propyl groups are bonded to the silyl center via stable Si–C bonds. [ω-Methoxyoligo(oxyethylene)propyl]methyldichlorosilanes were prepared by the platinum-catalyzed hydrosilation reaction of methyldichlorosilane with the C–C double bond of oligo(ethylene glycol) allyl methyl ethers. These were then converted to the desired 1-[ω-methoxyoligo(oxyethylene)propyl]-1-methyl-1-silacyclopent-3-enes by the dissolving-metal reaction of [ω-methoxyoligo(oxyethylene)propyl]methyldichlorosilanes with magnesium and 1,3-butadiene. Unfortunately, the yield is low and decreases as the length of the oligo(oxyethylene) chain increases.



To improve overall monomer yields, a more direct route was developed. This involves the platinum-catalyzed hydrosilation reaction of the Si–H bond of 1-methyl-1-silacyclopent-3-ene with the terminal C–C double bond of oligo(ethylene glycol) allyl methyl ether. Fortunately, the hydrosilation reaction of 1-methyl-1-silacyclopent-3-ene with itself was not a problem.[22] AROP of 1-[ω-methoxyoligo(oxyethylene)propyl]-1-methyl-1-silacyclopent-3-enes proceeded to give the desired high molecular weight poly[1-[ω-methoxyoligo(oxyethylene)propyl]-1-methyl-1-sila-*cis*-pent-3-enes].

0024-9297/93/2226-0969$04.00/0



Experimental Section

^{1}H and ^{13}C NMR spectra were run on a Bruker AM-250 spectrometer operating in the Fourier transform (FT) mode. ^{13}C NMR spectra were run with broad-band proton decoupling. ^{29}Si NMR spectra were recorded on a IBM-Bruker 270-SY spectrometer. ^{29}Si NMR spectra were obtained by use of a heteronuclear gated decoupling pulse sequence (NONOE) with a pulse delay of 15 s.[23] ^{13}C and ^{29}Si NMR spectra were obtained on a 10% solution in chloroform-*d*. ^{1}H NMR spectra were obtained on a 5% solution in chloroform-*d*. Chloroform was utilized as an internal standard for ^{1}H and ^{13}C NMR spectra. ^{29}Si NMR spectra were externally referenced to TMS. IR spectra were recorded on an IBM FT IR/30S, DTGS/CSI spectrometer. Spectra were taken of neat films on NaCl plates.

The molecular weight distribution of the polymers was determined by gel permeation chromatography on a Waters system. This is comprised of a U6K injector, a 510 HPLC solvent delivery system, an R401 differential refractometer, and a Maxima 820 control system. A Waters 7.8 mm × 30 cm Ultrastyragel linear column packed with <10-μm particles of mixed pore size cross-linked styrene divinylbenzene copolymer was utilized for analysis. The column was maintained at 20 °C. The eluting solvent was HPLC grade THF at a flow rate 0.6 mL/min. Retention times were calibrated against known monodisperse polystyrene standards: 929 000, 114 200, 47 500, 13 700, 5120, and 2200, whose M_w/M_n values are <1.09.

Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer TGS-2 instrument with a nitrogen flow rate of 40 mL/min. The temperature program for the analysis was 50 °C for 2 min. The temperature was then increased at a rate of 4 °C/min to 100 °C. The temperature was held at 100 °C for 5 min. This was followed by an increase of 4 °C/min to 750 °C. The glass transition temperatures (T_gs) were determined by differential calorimetry (DSC) on a Perkin-Elmer DSC-7 instrument. The melting points of indium (mp 156 °C) and spectral grade *n*-hexane (mp −95 °C) were used to calibrate the DSC. After equilibration at −100 °C for 20 min, scans were conducted by increasing the temperature at a rate of 20 °C/min to 150 °C.

Low-resolution mass spectra were recorded on a Finnigan MAT Incos 50 GC/MS instrument at either an ionizing voltage of 70 eV or under chemical ionization. Methane was used as the chemical ionization gas. A Varian 3400 GLPC equipped with a 0.25 mm × 30 m, DB-5 capillary column served as the inlet. High-resolution mass spectra were obtained at the University of California Riverside Mass Spectrometry Facility on a VG-7070 EHF mass spectrometer at an ionizing voltage of 20 eV. Exact masses were determined by peak matching against known masses of perfluorokerosene.

Elemental analysis was performed by Galbraith Laboratories, Knoxville, TN.

Tetrahydrofuran (THF) was distilled immediately prior to use from a deep blue solution of sodium benzophenone ketyl. Hexamethylphosphoramide (HMPA) was distilled from calcium hydride and stored over 4-Å molecular sieves. Methyldichlorosilane and platinum divinyltetramethyldisiloxane complex were obtained from Hüls America. *n*-Butyllithium, allyl chloride, chloroplatinic acid, ethylene glycol monoethyl ether, di(ethylene glycol) monomethyl ether, tri(ethylene glycol) monomethyl ether, and poly(ethylene glycol) monomethyl ether (average molecular weight 350) were obtained from Aldrich. 1,3-Butadiene was obtained from Matheson Gas Products Inc.

All glassware was dried overnight in an oven at 120 °C. It was then assembled and flame-dried under an atmosphere of purified nitrogen. All reactions and transfers were conducted under an atmosphere of purified nitrogen.

Methyl-[1-ω-ethoxy(oxyethylene)propyl]dichlorosilane (I). A 100-mL round-bottom flask equipped with a Teflon-covered magnetic stirring bar and reflux condenser was charged with allyl ethyl ethylene glycol[24] (4.16 g, 32 mmol) and a catalytic amount of chloroplatinic acid. Methyldichlorosilane (11.5 g, 100 mmol) was added to the reaction mixture at room temperature. The mixture was heated to reflux with stirring for 3 h. The color of the reaction turned black. Volatiles were removed by evaporation under reduced pressure. The residue was purified by fractional distillation through a 15-cm vacuum-jacketed Vigreux column. A fraction with bp 98–99 °C (2 mmHg), 5.33 g, 68% yield, was obtained: ^{1}H NMR δ 0.75 (s, 3 H), 1.14 (m, 2 H), 1.17 (t, 3 H, J = 7.16 Hz), 1.76 (m, 2 H), 3.46 (t, 2 H, J = 6.5 Hz), 3.49 (q, 2 H, J = 7.16 Hz), 3.55 (s, 4 H); ^{13}C NMR δ 5.12, 15.10, 18.06, 22.64, 66.61, 69.70, 70.09, 72.35; ^{29}Si NMR δ 33.07.

1-Methyl-1-[ω-ethoxy(oxyethylene)propyl]-1-silacyclopent-3-ene (II). A 100-mL three-necked round-bottom flask equipped with a Teflon-covered magnetic sitrring bar and a reflux condenser was charged with activated magnesium powder (1 g, 42 mmol), THF (10 mL), and I (5 g, 20.4 mmol). The reflux condenser was connected to a refrigeration unit. Isopropyl alcohol, cooled to −20 °C, was circulated through the reflux condenser. 1,3-Butadiene (10 mL, 0.11 mol) was condensed into a flask containing anhydrous calcium chloride at −78 °C and was transferred to the reaction via a cannula. The reaction was stirred at room temperature for 5 days. Ether was added to the reaction. The organic layer was decanted from the excess of magnesium and magnesium chloride salts and was washed with water. The aqueous layer was extracted with ether. The combined organic layer was dried over anhydrous magnesium sulfate and filtered. The volatile solvents were removed by evaporation under reduced pressure. The residue was purified by fractional distillation through a 15-cm vacuum-jacketed Vigreux column. A fraction with bp 105 °C (0.8 mmHg), 1.9 g, 41% yield, was obtained: IR ν 3018, 2976, 2868, 1609, 1456, 1443, 1402, 1377, 1350, 1252, 1204, 1117, 1053, 945, 844, 787, 722, 618 cm^{-1}; ^{1}H NMR δ 0.11 (s, 3 H), 0.61 (m, 2 H), 1.17 (t, 3 H, J = 7.0 Hz), 1.22 (m, 4 H, J = 6.1 Hz), 1.59 (m, 2 H), 3.39 (t, 2 H, J = 7.02 Hz), 3.48 (q, 2 H, J = 7.0 Hz), 3.53 (s, 4 H), 5.79 (s, 2 H); ^{13}C NMR δ −3.77, 10.55, 15.06, 16.30, 24.09, 66.56, 69.77, 70.00, 74.00, 130.93; ^{29}Si NMR δ 18.1; GC/MS *m/e* (rel intensity) 229 (1), 228 (2) $M^{\bullet+}$, 133 (1), 132 (4), 131 (14), 118 (4), 117 (8), 105 (4), 104 (3), 103 (36), 102 (5), 101 (23), 77 (3), 75 (3), 74 (5), 73 (43), 72 (10), 45 (100); high-resolution MS $M^{\bullet+}$. Anal. Calcd for $C_{12}H_{24}O_2Si$: 228.1539. Found: 228.1545.

Poly[1-methyl-1-[ω-ethoxy(oxyethylene)propyl]-1-sila-*cis*-pent-3-ene] (III). A 100-mL round-bottom flask equipped with a Teflon-covered magnetic stirring bar was filled with HMPA (6–7 drops), THF (50 mL), and II (1.2 g, 5.26 mmol). The flask was sealed with a rubber septum. The solution was cooled to −78 °C. *n*-Butyllithium (0.1 mL, 2.5 M in hexane) was injected into the flask. The solution became pale yellow in color. It was stirred for 1.5 h. The reaction was quenched at −78 °C by addition of saturated aqueous ammonium chloride (20 mL). The aqueous layer was extracted with ether (2 × 20 mL). The organic layer was washed with water (20 mL), dried over anhydrous magnesium sulfate, and filtered. The volatile solvents were removed by evaporation under reduced pressure. A viscous material was obtained. It was redissolved in a minimum amount of THF, and the polymer was precipitated by addition of pentane. This process was repeated and the polymer was dried under vacuum. A white material, 0.96 g, 80% yield, M_w/M_n = 75 760/43 340, T_g = −71 °C, was obtained: IR ν 3006, 2975, 2927, 2866, 1443, 1411, 1377, 1350, 1250, 1116, 1053, 1023, 991, 930, 846, 747, 666 cm^{-1}; ^{1}H NMR δ −0.05 (s, 3 H), 0.48 (m, 2 H), 1.19 (t, 3 H, J = 7.0 Hz), 1.40 (d, 4 H, J = 6.3 Hz), 1.58 (m, 2 H), 3.38 (t, 2 H, J = 7.1 Hz), 3.51 (q, 2 H, J = 7.1 Hz), 3.55 (s, 4 H), 5.26 (t, 2 H, J = 5.6 Hz); ^{13}C NMR δ −5.36, 9.42, 14.88, 15.17, 23.94, 66.64, 69.84, 70.06, 74.47, 123.04; ^{29}Si NMR δ 3.43. Anal. Calcd for $C_{12}H_{24}O_2Si$: C, 63.10; H, 10.59. Found: C, 62.41; H, 10.67.

Allyl Methyl Diethylene Glycol.[25] Into a 500-mL three-necked round-bottom flask equipped with a Teflon-covered magnetic stirring bar were placed sodium hydride (14.4 g, 0.6 mol) and THF (150 mL). Diethylene glycol monomethyl ether (35.6 mL, 0.3 mol) was added dropwise. After the evolution of hydrogen had ceased, allyl chloride (49.8 mL, 0.6 mol) was added dropwise to the reaction. The reaction was stirred at room temperature for 16 h. Excess sodium hydride was destroyed by the cautious addition of water (6 mL). The aqueous layer was extracted with ether (3 × 70 mL). The combined organic layer was washed with water (2 × 70 mL), dried over anhydrous magnesium sulfate, and filtered. The volatile solvents were removed by evaporation under reduced pressure. The product was purified by fractional distillation through a 15-cm vacuum-jacketed Vigreux column. A fraction with bp 90–94 °C (10 mmHg), 25 g, 52% yield, was collected: ^{1}H NMR δ 3.36 (s, 3 H), 3.52–3.54 (m, 2 H), 3.57–3.60 (m, 2 H), 3.61–3.65 (m, 4 H), 3.99 (dt, 2 H, J = 5.62, 1.33 Hz), 5.15 (ddd, 1 H, J = 10.2, 2.0, 1.0 Hz), 5.24 (ddd, 1 H, J = 17.2, 2.2, 1.0 Hz), 5.89 (ddd, 1 H, J = 17.2, 10.8, 6.0 Hz); ^{13}C NMR δ 59.00, 69.34, 70.53, 70.62, 71.92, 72.24, 117.06, 134.73.

Methyl[ω-methoxydi(oxyethylene)propyl]dichlorosilane (IV). A 250-mL three-necked round-bottom flask equipped with a Teflon-covered magnetic stirring bar and a reflux condenser was charged with a catalytic amount of chloroplatinic acid (200 mg) and methyldichlorosilane (26.1 mL, 0.25 mol). Allyl methyl diethylene glycol (20 g, 0.125 mol) was slowly added to the reaction mixture at 40 °C. It was stirred for 4 h. The reaction became deep red. Volatiles were removed by evaporation under reduced pressure. The product was purified by fractional distillation through a 15-cm vacuum-jacketed Vigreux column. A fraction with bp 108–110 °C (1 mmHg), 17.5 g, 51% yield, was obtained: ^{1}H NMR δ 0.76 (s, 3 H), 1.15 (m, 2 H), 1.77 (m, 2 H), 3.36 (s, 3 H), 3.47 (t, 2 H, J = 6.5 Hz), 3.51–3.64 (m, 8 H); ^{13}C NMR δ 5.16, 18.13, 22.72, 59.03, 70.07, 70.54, 70.60, 71.93, 72.38; ^{29}Si NMR δ 32.97.

1-Methyl-1-[ω-methoxydi(oxyethylene)propyl]-1-silacyclopent-3-ene (V). A 250-mL three-necked round-bottom flask was equipped with a Teflon-covered magnetic stirring bar, an efficient reflux condenser, and a 0.5-in. ultrasound probe. The probe was connected to a Tekmar 500-W, 20-kHz high-intensity ultrasound generator and was sealed to the reaction flask with a rubber septum. The reflux condenser was connected to a refrigeration unit as above. Magnesium powder (1.83 g, 74.2 mmol), IV (14 g, 50.9 mmol), and THF (100 mL) were added to the reaction flask. 1,3-Butadiene (44 mL, 0.51 mol) was condensed into a flask at −78 °C and transferred to the reaction flask via a cannula. The reaction was activated by ultrasound (40% duty cycle at 20% energy output) for 5 days. Ether was added to the reaction. The organic layer was decanted from excess magnesium and magnesium chloride salts and was washed with water. The aqueous layer was extracted with ether. The combined organic layer was dried over anhydrous magnesium sulfate and filtered. The volatile solvents were removed by evaporation under reduced pressure. The product was purified by fractional distillation through a 15-cm vacuum-jacketed Vigreux column. A fraction with bp 110–112 °C (1 mmHg), 3.4 g, 26% yield, was collected: IR ν 3017, 2875, 1608, 1457, 1401, 1352, 1251, 1203, 1100, 944, 843, 787, 722, 614 cm^{-1}; ^{1}H NMR δ 0.12 (s, 3 H), 0.63 (m, 2 H), 1.20 (d, 2 H, J = 12.5 Hz), 1.28 (d, 2 H, J = 12.5 Hz), 1.60 (m, 2 H), 3.35 (s, 3 H), 3.40 (t, 2 H, J = 6.9 Hz), 3.52 −3.64 (m, 8 H), 5.82 (s, 2 H); ^{13}C NMR δ −3.70, 10.65, 16.39, 24.19, 59.02, 70.01, 70.53, 70.65, 71.94, 74.03, 131.0; ^{29}Si NMR δ 18.63. Anal. Calcd for $C_{13}H_{26}O_3Si$: C, 60.42; H, 10.14. Found: C, 60.24; H, 9.44.

Preparation of V via Hydrosilation. V was also prepared by a hydrosilation reaction between allyl methyl diethylene glycol (2.3 g, 14.4 mmol) and 1-methyl-1-silacyclopent-3-ene[6] (2.2, 22.4 mmol) catalyzed by chloroplatinic acid at 40 °C for 4 h. A fraction with bp 105 °C (0.7 mmHg), 2.98 g, 80.5% yield, was collected. It had spectral properties identical to these of V prepared above.

Poly[1-methyl-1-[ω-methoxydi(oxyethylene)propyl]-1-sila-*cis*-pent-3-ene] (VI). Into a 100-mL round-bottom flask equipped with a Teflon-covered magnetic stirring bar were placed THF (40 mL), 7 drops of HMPA, and V (0.63 g, 2.44 mmol). The solution was cooled to −78 °C. *n*-Butyllithium (0.1 mL, 2.5 M in hexane) was injected into the flask. The reaction solution became pale yellow. The reaction was maintained at −78 °C for 1.5 h. The reaction was quenched by addition of saturated aqueous ammonium chloride. The aqueous layer was extracted with ether (2 × 20 mL). The combined organic layer was washed with water (20 mL), dried over anhydrous magnesium sulfate, and filtered. The solvents were removed by evaporation under reduced pressure. The viscous material was dissolved in a minimum amount of THF, and the polymer was precipitated from pentane. The polymer was redissolved in THF, precipitated by addition of pentane, and dried under vacuum. A sticky material, M_w/M_n = 189 000/96 600, T_g = −71 °C, 0.56 g, 88.9% yield, was obtained: IR ν 2992, 2908, 2816, 1456, 1400, 1367, 1336, 1227, 1192, 1134, 1066, 999, 910, 774, 718, 519 cm^{-1}; ^{1}H NMR δ −0.51 (s, 3 H), 0.48 (m, 2 H), 1.41 (d, 4 H, J = 6.2 Hz), 1.57 (m, 2 H), 3.36 (s, 3 H0, 3.38 (t, 2 H, J = 7.2 Hz), 3.51–3.65 (m, 8 H), 5.26 (t, 2 H, J = 5.5 Hz); ^{13}C NMR δ −5.33, 9.43, 14.91, 23.99, 59.02, 70.12, 70.54, 70.65, 71.96, 74.42, 123.07; ^{29}Si NMR δ 2.49. Anal. Calcd for $C_{13}H_{26}O_3Si$: C, 60.42; H, 10.14. Found: C, 59.33; H, 10.23.

Allyl Methyl Triethylene Glycol.[26] Into a 500-mL three-necked round-bottom flask equipped with a Teflon-covered magnetic stirring bar were placed sodium hydride (14.4 g, 0.6 mol) and THF (150 mL). Triethylene glycol monomethyl ether (50.5 mL, 0.3 mol) was added dropwise to the reaction. After the hydrogen evolution had ceased, allyl chloride (49.8, 0.6 mol) was added dropwise to the reaction. The reaction was stirred at room temperature for 16 h. Excess sodium hydride was destroyed by the cautious addition of water. The aqueous layer was extracted with ether (3 × 70 mL). The combined organic layer was washed with water (2 × 70 mL), dried over anhydrous magnesium sulfate, and filtered. The volatile solvents were removed by evaporation under reduced pressure. The product was purified by fractional distillation as above. A fraction with bp 145 °C (0.2 mmHg), 55 g, 89.8% yield, was collected: ^{1}H NMR δ 3.32 (s, 3 H), 3.48–3.51 (m, 2 H), 3.52–3.58 (m, 2 H), 3.61 (s, 8 H), 3.99 (dt, 2 H, J = 5.67, 1.7 Hz), 5.16 (dd, 1 H, J = 10.24, 1.6 Hz), 5.24 (dd, 1 H, J = 17.15, 1.7 Hz), 5.89 (ddd, 1 H, J = 17.2, 10.0, 5.6 Hz); ^{13}C NMR δ 58.94, 69.33, 70.44, 70.54, 71.85, 72.13, 116.95, 134.70.

Methyl-1-[ω-methoxytri(oxyethylene)propyl]dichlorosilane (VII). VII was prepared by a hydrosilation reaction of allyl methyl triethylene glycol (25 g, 123 mmol) and methyldichlorosilane (25.7 mL, 0.25 mol) catalyzed by chloroplatinic acid at 40 °C as above. After removal of excess methyldichlorosilane the product was obtained by fractional distillation. A fraction with bp 125–130 °C (0.1 mmHg), 25 g, 64% yield, was collected: ^{1}H NMR δ 0.76 (s, 3 H), 1.15 (m, 2 H), 1.75 (m, 2 H), 3.36 (s, 3 H), 3.46 (t, 2 H, J = 6.4 Hz), 3.51–3.63 (m, 4 H), 3.64 (s, 8 H); ^{13}C NMR δ 5.16, 18.12, 22.71, 59.03, 70.06, 70.52, 70.56, 70.59, 71.92, 72.35; ^{29}Si NMR δ 33.03.

1-Methyl-1-[ω-methoxytri(oxyethylene)propyl]-1-silacyclopent-3-ene (VIII). A 250-mL three-necked round-bottom flask was equipped with a Teflon-covdered magnetic stirring bar, an efficient reflux condenser, and a 0.5-in. ultrasound probe. The condenser was connected to a refrigeration unit and the probe to a Tekmar ultrasound generator as above. Magnesium powder (2.7 g, 112.5 mmol), VII (24 g, 75 mmol), and THF (100 mL) were added to the reaction flask. 1,3-Butadiene (33 mL, 375 mmol) was condensed into a flask at −78 °C and transferred to the reaction flask via a cannula. The reaction was activated by ultrasound (40% duty cycle at 20% energy output) for 5 days. Ether was added to the reaction. The organic layer was decanted from excess magnesium and magnesium chloride salts and was washed with water. The aqueous layer was extracted with ether. The combined organic layer was dried over anhydrous magnesium sulfate and filtered. The volatile solvents were removed by evaporation under reduced pressure. The product was purified by fractional distillation. A fraction with bp 126 °C (0.03 mmHg), 4.5 g, 20% yield, was collected: IR ν 30.17, 2875, 1608, 1456, 1402, 1350, 1325, 1299, 1251, 1203, 1101, 989, 945, 844, 787, 768, 723, 618 cm^{-1}; ^{1}H NMR δ 0.10 (s, 3 H), 0.60 (m, 2 H), 1.17 (d, 2 H, J = 16.8 Hz), 1.27 (d, 2 H, J = 17.8 Hz), 1.58 (m, 2 H), 3.33 (s, 3 H), 3.38 (t, 2 H, J = 7.0 Hz), 3.48–3.55 (m, 4 H), 3.58–3.61 (m, 4 H), 3.62 (s, 4 H), 5.79 (s, 2 H); ^{13}C NMR δ −3.75, 10.58, 16.32, 24.13, 58.95, 69.94, 70.44, 70.54, 71.85, 73.94, 130.94; ^{29}Si NMR δ 18.57. Anal. Calcd for $C_{15}H_{30}O_4Si$: C, 59.56; H, 10.00. Found: C, 59.56; H, 9.90.

1-Methyl-1-[ω-methoxytri(oxyethylene)propyl]-1-silacyclopent-3-ene and -2-ene (VIII and IX). Into a 100-mL round-bottom flask equipped with a Teflon-covered magnetic stirring bar and a reflux condenser were placed 1-methyl-1-silacyclopent-

3-ene (8.82 g, 88% in ether, 74 mmol) and allyl methyl triethylene glycol (11 g, 54 mmol). A catalytic amount of platinium divinyltetramethyldisiloxane complex (3 drops) was added at room temperature. The reaction was stirred for 2 h. The product was purified by fractional distillation. A fraction with bp 130 °C (0.03 mmHg), 10 g, 63% yield, was obtained. NMR analysis showed that the product was a mixture of two isomers. The ratio of VIII to IX (62:38) was determined by integration of the vinyl ^{1}H NMR signals. For spectral properties of VIII, see above. The spectral properties of IX were determined by subtraction of signals due to VIII. The IR spectrum of the mixture of VIII and IX was essentially identical to that of VIII. For IX: ^{1}H NMR δ 0.09 (s, 3 H), 0.61 (m, 4 H), 1.57 (m, 2 H), 2.43 (m, 2 H), 3.33 (s, 3 H), 3.38 (t, 2 H, J = 7.0 Hz), 3.48–3.55 (m, 4 H), 3.58–3.61 (m, 4 H), 3.62 (s, 4 H), 5.86 (dt, 1 H, J = 10.1, 2.3 Hz), 6.76 (dt, 1 H, J = 10.16, 2.62 Hz); ^{13}C NMR δ −2.73, 7.07, 11.59, 24.59, 32.05, 58.95, 69.94, 70.44, 70.54, 71.85, 73.94, 128.97, 153.6; ^{29}Si NMR δ 20.28. Anal. Calcd for $C_{15}H_{30}O_4Si$ (the isomers): C, 59.56; H, 10.00. Found: C, 59.33; H, 9.75.

Poly[1-methyl-1-[ω-methoxytri(oxyethylene)propyl]-1-sila-*cis*-pent-3-ene] (X). A 100-mL round-bottom flask equipped with a Teflon-covered magnetic stirring bar and reflux condenser was charged with THF (60 mL), 6–7 drops of HMPA, and VIII (0.75 g, 2.48 mmol). The solution was cooled to −78 °C. n-Butyllithium (60 μL, 2.5 M in hexane) was injected into the solution. The reaction solution became pale yellow. It was stirred for 1.5 h. The reaction was quenched by addition of saturated aqueous ammonium chloride. The aqueous layer was extracted with ether (2 × 20 mL). The organic layer was washed with water, dried over anhydrous magnesium sulfate, and filtered. The volatile solvents were removed by evaporation under reduced pressure. The viscous residue was dissolved in a minimum amount of THF, and the polymer was precipitated by addition of pentane. The polymer was redissolved in THF and was precipitated from pentane. It was dried under vacuum. A white polymer, M_w/M_n = 41 200/24 280, T_g = −70 °C, 0.6 g, 79.7% yield, was obtained: IR ν 3006, 2870, 1457, 1376, 1351, 1250, 1199, 1112, 1027, 847 cm^{-1}; ^{1}H NMR δ −0.06 (s, 3 H), 0.47 (m, 2 H), 1.40 (d, 4 H, J = 5.1 Hz), 1.56 (m, 2 H), 3.34 (s, 3 H), 3.37 (t, 2 H, J = 5.0 Hz), 3.50–3.60 (m, 8 H), 3.64 (s, 4 H), 5.25 (t, 2 H, J = 5.5 Hz); ^{13}C NMR δ −5.35, 9.43, 14.87, 23.97, 59.02, 70.00, 70.50, 70.56, 70.59, 71.92, 74.44, 123.04; ^{29}Si NMR δ 3.41. Anal. Calcd for $C_{15}H_{30}O_4Si$: C, 59.56; H, 10.00. Found: C, 58.51; H, 10.00.

The polymerization of the mixture of VIII and IX as above also gave X and recovered IX in the supernatant. The polymer M_w/M_n = 55 950/26 680 was formed in 66% yield. IX was recovered in 30% yield. X had spectral properties identical to that prepared by polymerization of pure VIII.

Allyl Methyl Poly(ethylene glycol).[7] Allyl methyl methyl poly(ethylene glycol) was synthesized from poly(ethylene glycol) monomethyl ether (average molecular weight 350) and allyl chloride as above. The mass spectrum analysis of the product by chemical ionization showed that in addition to allyl methyl hepta(ethylene glycol) (7), M_w = 380, allyl methyl octa(ethylene glycol) (8), M_w = 424, and allyl methyl nona(ethylene glycol) (9), M_w = 468, are also present. The ratio of 7:8:9 = 46:41:13.

1-Methyl-1-[ω-methoxyoligo(oxyethylene)propyl]-1-silacyclopent-3-ene (XI). Into 100-mL three-necked round-bottom flask equipped with a Teflon-covered magnetic sitrring bar and a reflux condenser were placed 1-methyl-1-silacyclopent-3-ene (2 g, 20.4, mmol) and allyl methyl poly(ethylene glycol) (5 g, 12.8 mmol). A catalytic amount of chloroplatinic acid was added at room temperature. The reaction was stirred for 3 h. The reaction turned brown. The product was purified by flash column chromatography on aluminum oxide using ether as eluent. After evaporation of the solvent, a colorless liquid (5.8 g, 92% yield) was obtained. The liquid was dried under vacuum at 60 °C for 24 h and then used without further purification: IR ν 3017, 2870, 1608, 1454, 1402, 1349, 1324, 1298, 1251, 1203, 1105, 945, 842, 722, 617; ^{1}H NMR δ 0.12 (s, 3 H), 0.62 (m, 6 H), 1.23 (m, 4 H), 1.59 (m, 2 H), 3.35 (s, 3 H), 3.39 (t, 2 H, J = 7.2), 3.50–3.56 (m, 8 H), 3.59–3.63 (m, 24 H), 5.81 (s, 2 H); ^{13}C NMR δ −3.72, 10.65, 16.39, 24.18, 58.97, 69.13, 70.21, 71.63, 71.89, 73.10, 74.00, 131.00; ^{29}Si NMR δ 18.55. Anal. Calcd for $C_{23}H_{46}O_8Si$ (calculation is based on the assumption that m = 7): C, 57.71; H, 9.69. Found: C, 56.68; H, 9.79.

Poly[1-methyl-1-[ω-methoxyoligo(oxyethylene)propyl]-1-sila-*cis*-pent-3-ene] (XII). A 100-mL round-bottom flask equipped with a Teflon-covered magnetic stirring bar was charged with THF (60 mL), 8–9 drops of HMPA, and XI (0.9 g, 1.84 mmol). The solution was cooled to −78 °C. n-Butyllithium (100 μL), 2.5 M in hexane) was injected into the solution. The reaction solution became pale yellow. It was stirred for 2 h. The reaction was quenched by addition of saturated aqueous sodium chloride. If no separation of the aqueous and organic layers occurred, sodium chloride was added. The aqueous layer was extracted with ether (2 × 30 mL). The organic layer was washed with water (sodium chloride may be needed), dried over anhydrous magnesium sulfate, and filtered. The volatile solvents were removed by evaporation under reduced pressure. The viscous residue was dissolved in a minimum amount of THF, and the polymer was precipitated by addition of pentane. The polymer was redissolved in THF and was precipitated with pentane. It was dried under vacuum. A white polymer, M_w/M_n = 42 600/23 280, T_g = −76 °C, 0.6 g, 60% yield, was obtained: IR ν 3006, 2870, 1455, 1412, 1376, 1350, 1299, 1250, 1198, 1111, 1030, 944, 8467, 749 cm^{-1}; ^{1}H NMR δ −0.06 (s, 3 H), 0.48 (m, 2 H), 1.40 (d, 4 H, J = 5.0 Hz), 1.57 (m, 2 H), 3.35 (s, 3 H), 3.37 (t, 2 H, J = 7.2 Hz), 3.51–3.57 (m, 8 H), 3.60–3.64 (m, 24 H), 5.25 (t, 2 H), J = 5.5 Hz); ^{13}C NMR δ −5.32, 9.47, 14.89, 23.98, 59.01; 69.99, 70.56, 71.93, 74.46, 123.06; ^{29}Si NMR δ 3.41. Anal. Calcd for $C_{23}H_{46}O_8Si$: C, 57.71; H, 9.69. Found: C, 57.07; H, 9.84.

Methylene-16-crown-5 was prepared according to a literature procedure.[30]

The product, bp 140–145 °C (0.2 mmHg), 14.8 g, 30.1% yield, was obtained by fractional distillation: ^{1}H NMR δ 3.60–3.68 (m, 16 H), 4.12 (t, 4 H, J = 1.1 Hz), 5.12 (t, 2 H, J = 1.09 Hz); ^{13}C NMR δ 69.18, 70.36, 70.64, 70.91, 72.00, 113.36, 143.15.

1-Methyl-1-(methylene-16′-crown-5′)-1-silacyclopent-3-ene and -2-ene (XIII and XIV). Into a 100-mL round-bottom flask equipped with a Teflon-covered magnetic stirring bar and a reflux condenser were charged with methylene-16-crown-5 (5 g, 20 mmol) and 1-methyl-1-silacyclopent-3-ene (3 g, 30 mmol). Platinum divinyltetramethyldisiloxane complex (3 drops) was added at room temperature. The temperature was increased to 40 °C, and reaction was continued for 3 h. The product was purified by fractional distillation. A fraction with bp 140 °C (0.01 mmHg), 4.5 g, 56.7% yield, was obtained. NMR analysis showed that the product was a mixture of two isomers. The ratio of XIII to XIV (70:30) was determined by integration of the vinyl ^{1}H NMR signals: IR (mixture of isomers) ν 3015, 2866, 1608, 1473, 1451, 1403, 1354, 1296, 1250, 1204, 1130, 1038, 988, 945, 875, 834, 729, 616 cm^{-1}. For isomer XIII: ^{1}H NMR δ 0.14 (s, 3 H), 0.70 (d, 2 H, J = 7.39 Hz), 1.27 (m, 2 H), 2.03 (m, 1 H), 3.40 (dd, 2 H, J = 9.14, 5.05 Hz), 3.50 (dd, 2 H, J = 9.12, 5.05 Hz), 3.64 (s, 16 H), 5.81 (s, 2 H); ^{13}C NMR δ −2.82, 14.53, 17.44, 36.06, 70.05, 70.50, 70.69, 70.80, 73.49, 131.02; ^{29}Si NMR δ 17.46. For isomer XIV: ^{1}H NMR δ 0.12 (s, 3 H), 0.65 (d, 2 H), J = 7.31 Hz), 0.65 (m, 2 H), 2.03 (m, 1 H), 2.44 (m, 2 H), 3.40 (dd, 2 H, J = 9.14, 5.05 Hz), 3.50 (dd, 2 H, J = 9.12, 5.05 Hz), 3.64 (s, 16 H), 5.89 (dt, 1 H, J = 10.2, 2.4 Hz), 6.75 (dt, 1 H, J = 10.2, 2.4 Hz); ^{13}C NMR δ −1.98, 8.00, 15.39, 31.96, 35.95, 73.28, 73.56, 130.00, 153.27; three other ^{13}C lines are coincident with three of four signals (δ 70.05, 70.50, 70.69, 70.80) from XIII; ^{29}Si NMR δ 18.97. Anal. Calcd for $C_{17}H_{32}O_5Si$ (mixture of XIII and XIV): C, 59.27; H. 9.36. Found: C, 58.52; H, 9.22.

XIII was also prepared by hydrosilation reaction of methylene-16-crown-5 with 1-methyl-1-silacyclopent-3-ene catalyzed by chloroplatinic acid at 40 °C. ^{1}H NMR of the crude product showed only XIII. The yield after fractional distillation was 80%. Isomerization occurred during distillation. The percentage of isomer XIII after distillation was 84%.

Poly[1-methyl-1-(methylene-16′-crown-5′)-1-sila-*cis*-pent-3-ene] (XV). A 100-mL round-bottom flask equipped with a Teflon-covered magnetic stirring bar was charged with THF (40 mL), 6–7 drops of HMPA, and a 70:30 mixture of XIII:XIV (0.95 g, 2.76 mmol). The reaction solution was cooled to −78 °C. n-Butyllithium (0.1 mL, 2.5 M in hexane) was injected into the reaction. The reaction solution became pale yellow. The reaction was continued for 2 h and was quenched by addition of saturated aqueous ammonium chloride (30 mL). The aqueous layer was extracted with ether (2 × 30 mL). The organic layer was washed with water, dried over anhydrous magnesium sulfate, and filtered.

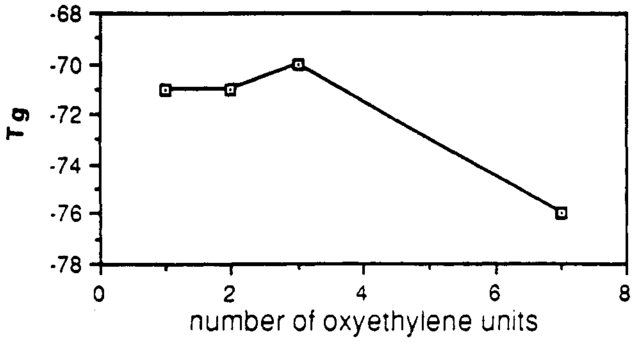


Figure 1. Dependence of T_g of poly[1-ω-methoxyoligo(oxyethylene)propyl]-1-methyl-1-sila-1-*cis*-pent-3-enes on the number of oxyethylene units in pendant groups.

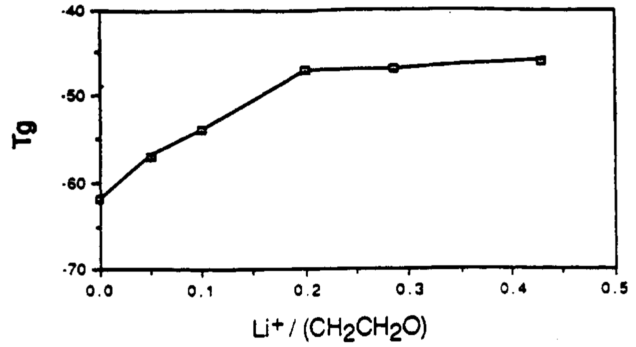


Figure 2. T_g (°C) versus the molar ratio of Li^+ to oxyethylene units in X.

The volatile solvents were removed by evaporation under reduced pressure. The viscous residue was dissolved in a minimum amount of THF, and the polymer was precipitated by addition of pentane. The isomer XIV was recovered from the supernatant. The polymer was redissolved in THF and was precipitated from pentane. It was dried under vacuum. A white polymer, 0.5 g, 75% yield based on the XIII in the starting materials, was obtained: T_g = −78 °C; IR ν 3006, 2866, 1451, 1377, 1355, 1296, 1250, 1127, 1034, 990, 941, 843, 755 cm^{-1}; ^1H NMR δ −0.02 (s, 3 H), 0.55 (d, 2 H, J = 7.01 Hz), 1.42 (d, 2 H, J = 5.7 Hz), 1.96 (m, 1 H), 3.38–3.50 (m, 4 H), 3.56–3.61 (m, 4 H), 3.64 (s, 12 H), 5.27 (t, 2 H, J = 5.41 Hz); ^{13}C NMR δ −4.35, 12.98, 15.65, 35.56, 70.14, 70.57, 70.79, 70.81, 73.34, 123.23; ^{29}Si NMR δ 2.93. Anal. Calcd for $C_{17}H_{32}O_6Si$: C, 59.27; H, 9.36. Found: C, 58.79; H, 9.04.

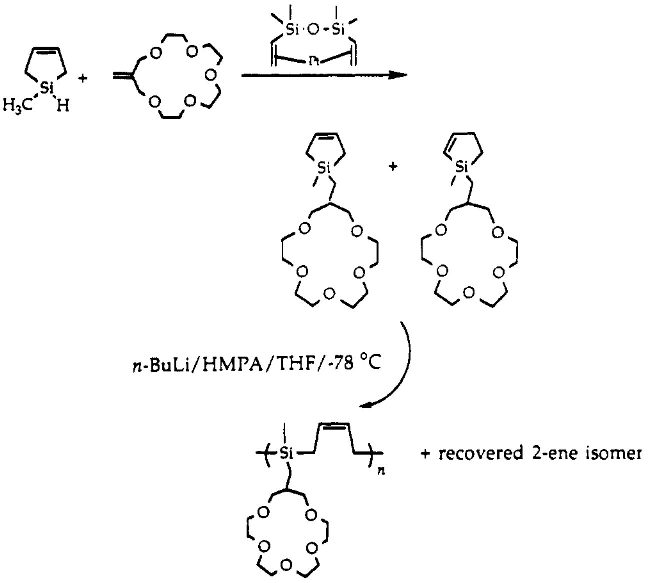
DSC and ^{13}C NMR of Lithium Cation/Polymer Complexes. The samples were prepared by dissolving the polymers (X or XII, respectively) and $LiClO_4$ in THF at different molar ratios of oxyethylene units to $LiClO_4$ (see Figures 1 and 2 in Results and Discussion). The solution was placed in an aluminum DSC pan. The solvent was removed by evaporation under vacuum for 7 days. DSC measurement was run on these samples. The sample was then dissolved in chloroform-*d*; no residual THF solvent was detected by NMR.

Polymer/lithium cation complexes for ^{13}C NMR were prepared by dissolving the polymer (X or XII, respectively) and lithium perchlorate in acetonitrile-d_3 in a 1:1 molar ratio (for data see Results and Discussion).

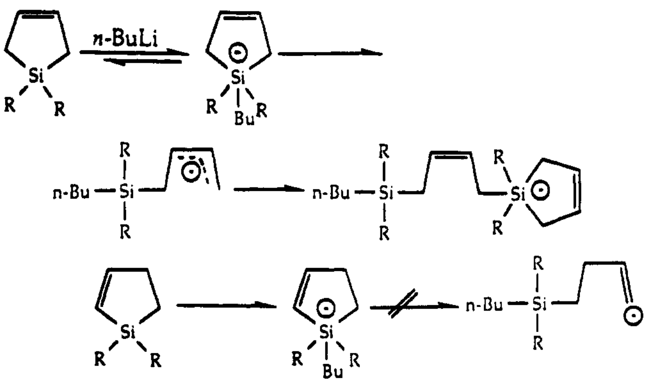
Results and Discussion

Synthesis of 1-[ω-methoxyoligo(oxyethylene)propyl]-1-methyl-1-silacyclopent-3-ene monomers by hydrosilation gave an isomeric mixture comprised of 1-[ω-methoxyoligo(oxyethylene)propyl]-1-methyl-1-silacyclopent-3-ene and -2-ene. The formation of the undesired 2-ene isomer depends on temperature and the presence of platinum. Purification by fractional distillation requires relatively high temperature. Under these conditions the 3-ene isomer is partially converted to the 2-ene isomer. While preparative separation of the 3-ene and 2-ene isomers is difficult, the isomeric mixture undergoes successful AROP to yield the desired poly[1-ω-methoxyoligo(oxyethylene)propyl]-1-methyl-1-sila-*cis*-pent-3-enes. The 2-ene isomer is unreactive under the polymerization conditions and can be recovered in the supernatant liquid after precipitation of the polymer.

A comb polymer with an unsaturated carbosilane backbone and pendant crown ether groups has been prepared in a similar manner.



The failure of the 2-ene isomer to undergo AROP is consistent with the probable mechanism of this reaction. Thus is has been proposed that the alkyllithium initiator adds to the silyl center of the 1-silacyclopent-3-ene ring to yield a hypervalent siliconate anion. Propagation occurs by ring opening to give an allylic anion, which rapidly adds to the silyl center of another molecule of 1-silacyclopent-3-ene.[28] While alkyllithium reagents probably add to the silyl center of 1-silacyclopent-2-ene to yield hypervalent siliconates, ring opening of this species to yield a vinyl anion apparently does not occur. Possibly the difference in stability of allyl and vinyl anions[29] may account for this difference.



While we can rationalize the failure of 1-silacyclopent-2-ene to undergo anionic ring-opening polymerization,[30] it is surprising that alkyllithium reagents apparently do not add to the C–C double bond of 1-silacyclopent-2-enes to give a carbanion α to silicon.[31,32]

Unlike poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene), which is a hydrophobic material that is soluble in common organic solvents, the solubility of these unsaturated carbosilane polymers with pendant oligo(oxyethylene) groups depends on the specific number of oxyethylene units in the side chain. For example, while polymers X and XII cannot be purified by precipitation from THF with methanol, they precipitate from THF on addition of pentane.

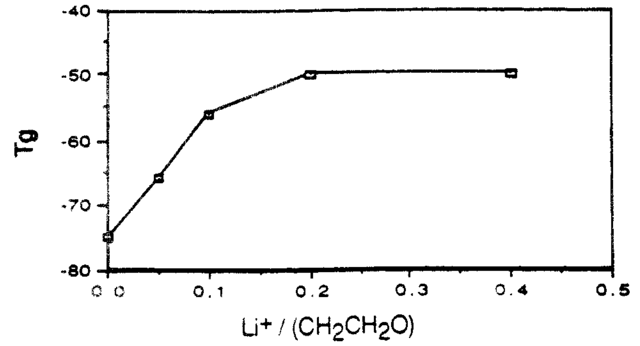


Figure 3. T_g °C versus the molar ratio of Li^+ to oxyethylene units in XII.

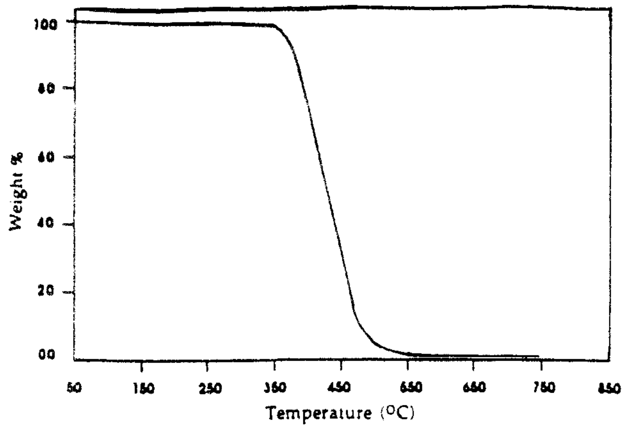
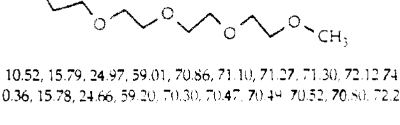


Figure 4. TGA of polymer VI.

As anticipated, these comb polymers have low T_gs in the range of −70 to −75 °C. Addition of lithium perchlorate to these polymers results in an increase in their T_gs. Similar increases in T_gs have been observed when lithium salts have been added to poly[1-methyl-1-oligo(oxyethylene)siloxane].[7,8] This has been accounted for in terms of multisite complexation between the lithium cation and the oligo(oxyethylene) pendant chain which impedes the segmental motion of the side chain[33] and thus increases the T_g.[34-36]

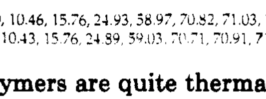
Complex formation between the pendant oligo(oxyethylene) side chains of these unsaturated carbosilane polymers and lithium cations has also been studied by ^{13}C NMR. While it is not possible to assign the ^{13}C resonances observed for the oxyethylene units to specific carbons, it is apparent that these signals are significantly shifted when 1 equiv of lithium perchlorate is added for each pendant oxyethylene chain. On the other hand, the ^{13}C resonances due to carbons of the unsaturated carbosilane chain are virtually unchanged.



X

X: −4.79, 10.52, 15.79, 24.97, 59.01, 70.86, 71.10, 71.27, 71.30, 72.12 74.77, 124.14

X·$LiClO_4$: −4.83, 10.36, 15.78, 24.66, 59.20, 70.30, 70.47, 70.49 70.52, 70.80, 72.22, 74.55, 124.15



XII

XII: −4.80, 10.46, 15.76, 24.93, 58.97, 70.82, 71.03, 71.21, 72.65, 74.77, 124.12

XII·$LiClO4$: −4.82, 10.43, 15.76, 24.89, 59.03, 70.71, 70.91, 71.07, 71.16, 72.48, 74.77, 124.12

These polymers are quite thermally stable. Polymers III, VI, X, XII, and XV lose between 1 and 5% of their initial weights between 50 and 350 °C. Above 350 °C, all of these polymers undergo rapid thermal decomposition. In the case of III, VI, X, and XII, by 500 °C between 2 and 6% of the initial sample weight remains. By 750 °C very little residue is left (1–5%). A residue of 12% is found for polymer XV at 750 °C. See Figure 4 for the TGA of polymer VI.

These polymers should have numerous applications due to their low T_gs, high thermal and hydrolytic stability, and the possibility of controlling solubility properties by appropriate choice of oligo(oxyethylene) pendant group. Further studies on these systems are in progress.

Acknowledgment. This work was supported in part by the Office of Naval Research/DARPA.

References and Notes

(1) Noll, W. *Chemistry and Technology of Silicones*; Academic Press: New York, 1968.
(2) Kendrick, T. C.; Parbhoo, B.; White, J. W. Siloxane Polymers and Copolymers. In *Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; J. Wiley and Sons: Chicester, England, 1989.
(3) Zhang, X.; Zhou, Q.; Weber, W. P.; Horvath, R. F.; Chan, T. H.; Manuel, G. *Macromolecules* **1988**, *21*, 1563.
(4) Park, Y. T.; Zhou, Q.; Weber, W. P. *Polym. Bull.* **1989**, *22*, 349.
(5) Park, Y. T.; Manuel, G.; Weber, W. P. *Macromolecules* **1990**, *23*, 349.
(6) Zhou, S. Q.; Weber, W. P. *Macromolecules* **1990**, *23*, 1915.
(7) Fish, D.; Khan, I. M.; Wu, E.; Smid, J. *Br. Polym. J.* **1988**, *20*, 281.
(8) Fish, D.; Khan, I. M.; Smid, J. *Makromol. Chem., Rapid Commun.* **1986**, *7*, 115.
(9) Spindler, R.; Shriver, D. F. *Macromolecules* **1988**, *21*, 648.
(10) Hall, P. G.; Davies, G. R.; McIntyre, J. E.; Ward, I. M.; Bannister, D. J.; LeBrocq, K. M. F. *Polym. Commun.* **1986**, *27*, 98.
(11) Kanner, B.; Reid, W. G.; Petersen, I. H. *Ind. Eng. Chem., Prod. Res. Dev.* **1967**, *6*, 88.
(12) Zhou, S. Q.; Wang, L.; Liao, X.; Manuel, G.; Weber, W. P. *J. Inorg. Organomet. Polym.* **1991**, *1*, 199.
(13) *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; J. Wiley & Sons: New York, Vol. 6, p 229.
(14) *Chemical Reactions on Polymers*; Benham, J. L., Kinstle, J. F., Eds.; ACS Symposium Series 364; American Chemical Society: Washington, DC, 1988.
(15) *Modification of Polymers*; Carraher, C. E., Jr., Moore, J. A., Eds.; Plenum Press: New York, 1983.
(16) Bannister, D. J.; Doyle, M.; MacFarlane, D. R. *J. Polym. Sci., Polym. Lett. Ed.* **1985**, *23*, 465.
(17) Kohama, S.; Umeki, Y. *J. Appl. Polym. Sci.* **1977**, *21*, 863.
(18) Wu, E.; Khan, I. M. Smid, J. *Polym. Bull.* **1988**, 455.
(19) Lestel, L.; Boileau, S.; Cheradame, H. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1989**, *30* (1), 133.
(20) Lestel, L.; Cheradame, H.; Boileau, S. *Polymer* **1990**, *31*, 1154.
(21) Liao, C. X.; Weber, W. P., Patent Pending.
(22) Lu, J.; Wang, G.; Manuel, G.; Weber, W. P., unpublished results.
(23) Freeman, R.; Hill, H. D. W.; Kaptein, R. *J. Magn. Reson.* **1972**, *7*, 327.
(24) Mikhant'ev, B. I.; Mikhant'eva, O. N.; Mikhant'ev, V. B.; Voishcheva, O. V. *J. Org. Chem. USSR* **1972**, *8*, 450.
(25) Feibush, B.; Cohen, M. J.; Karger, B. *J. Chromatogr.* **1983**, *282*, 2.
(26) Birchall, J. D.; Carey, J. G.; Howard, A. J. *Nature* **1977**, *266*, 154.
(27) Tomoi, M.; Abe, O.; Ikeda, M.; Kihara, K.; Kakiuchi, H. *Tetrahedron Lett.* **1978**, 3031.
(28) Weber, W. P.; Park, Y. T.; Zhou, S. Q. *Makromol. Chem., Macromol. Symp.* **1991**, *42/43*, 259.
(29) Cram, D. J. *Fundamentals of Carbanion Chemistry*; Academic Press: New York, 1965; pp 25, 26.
(30) Sargeant, S. J.; Weber, W. P. *Macromolecules*, submitted.
(31) Cason, L. F.; Brooks, H. G. *J. Am. Chem. Soc.* **1952**, *74*, 4582.
(32) Cason, L. F.; Brooks, H. G. *J. Org. Chem.* **1954**, *19*, 1278.
(33) Vogtle, F.; Weber, E. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 814.
(34) Killis, A.; LeNest, J. F.; Cheradame, H.; Gandini, S. *Makromol. Chem.* **1982**, *183*, 2835.
(35) Blonsky, P. M.; Shriver, D. F.; Austin, P. E.; Allock, H. R. *J. Am. Chem. Soc.* **1984**, *106*, 6854.
(36) Tonge, J. S.; Shriver, D. F. *J. Electrochem. Soc.* **1987**, *134*, 269.