Macromolecules **2001,** *34,* 931−936

Highly Conductive Siloxane Polymers

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Received October 26, 2000; Revised Manuscript Received December 7, 2000

ABSTRACT: A series of double-comb, disubstituted polysiloxane polymers have been prepared containing oligoethylene oxide units, $CH_3(OCH_2CH_2)_n(CH_2)_3-$, in the side chains. These polymers were doped with $LiN(SO_2CF_3)_2$ (LiTFSI, **1**), and conductivities of the polymer-salt complexes were determined as a function of temperature and doping level. Conductivities increase with n up to $n = 6$ and then decrease. The maximum conductivity of the polymer with $n = 6$ at 25 °C was 4.5×10^{-4}, the highest value yet recorded for a lithium-doped polymer electrolyte.

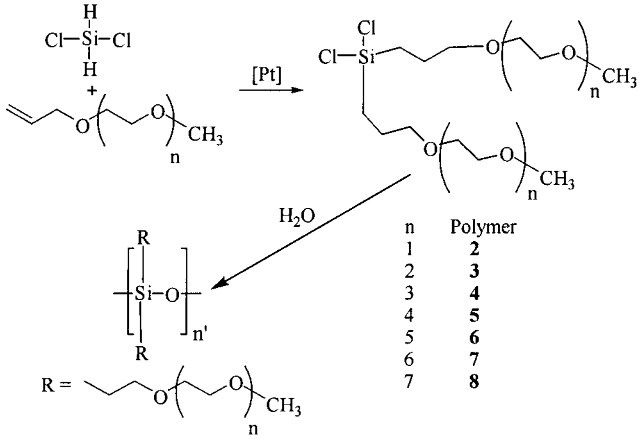
Introduction

Over the past decade, there has been interest in generating solid polymer electrolytes for high energy density lithium batteries.[1] Since the pioneering work by Wright et al. in the early 70's, it has been known that alkali metal salt complexes with poly(ethylene oxide) (PEO) act as conductors, but for practical applications the room temperature conductivity is too low ($\sim 10^{-7}$ S cm^{-1}).[2−4] Better results are obtained for polymers with highly flexible backbones, bearing oligoethylene oxide (EO) substituents as side chains. Polyphosphazenes of this type have been studied extensively, especially by Allcock, Shriver, and co-workers.[5,6] The maximum conductivity at 25 °C with $LiSO_3CF_3$ as dopant was near 5×10^{-5} S cm^{-1}.[7] Similarly, other inorganic comb polymers, polysilanes,[8] and polycarbosilanes[9] have been prepared and tested as conductive electrolytes, but in all cases, they have shown lower room temperature results. The overall potential of these systems as practical materials for applied electrochemistry has been recognized, and a number of reviews on this field are available.[10]

The polysiloxanes, like the polyphosphazenes, have highly flexible backbones, with the barrier to bond rotation being only 0.8 kJ mol^{-1}, as well as very low glass-transition energies (T_g) and high free volumes. They should therefore be good hosts for lithium ion transport, if properly substituted. Smid and co-workers have investigated several families of polysiloxanes, made by replacing the hydrogen atoms in the commercial polymer $[MeSi(H)O]_n$ with oligoethylene oxide substituents.[11,12] These have shown some promise as solid-state electrolytes,[13] but all were monocomb polymers, bearing a methyl group as well as an EO group on each silicon.

We began our studies to investigate the possibility that double-comb polysiloxanes might prove superior to their monosubstituted analogues. Previously we reported that a bis-substituted polysiloxane polymer, of the type $-[R_2SiO]_n-$, is superior to its monosubstituted analogue, $-[CH_3RSiO]_n-$, when doped with LiTFSI (**1**).[14] We now report the syntheses of a complete series of double-comb, disubstituted polysiloxane polymers that incorporate an increasing number of ethylene oxide units in the side chains. These polymers generally show an increased conductivity compared to that of the monocomb polysiloxanes, and have provided us with the highest ambient temperature conductivity yet recorded for any polymer electrolyte.

Scheme 1. Synthesis of Linear Polysiloxanes 2−8



n	Polymer
1	**2**
2	**3**
3	**4**
4	**5**
5	**6**
6	**7**
7	**8**

Results and Discussion

The series of polysiloxanes, $\{[CH_3O(CH_2CH_2O)_n(CH_2)_3]_2SiO\}_m$, where $n = 1-7$, (**2**−**8**, respectively) were prepared from readily accessible starting materials, as shown in Scheme 1.[6a,15] Rather than using the classical pyridine method for preparing the intermediate tosylate compounds,[16] we instead chose an elegant, and quantitative, tosylation procedure which involved sodium hydroxide as the base in the presence of both THF and

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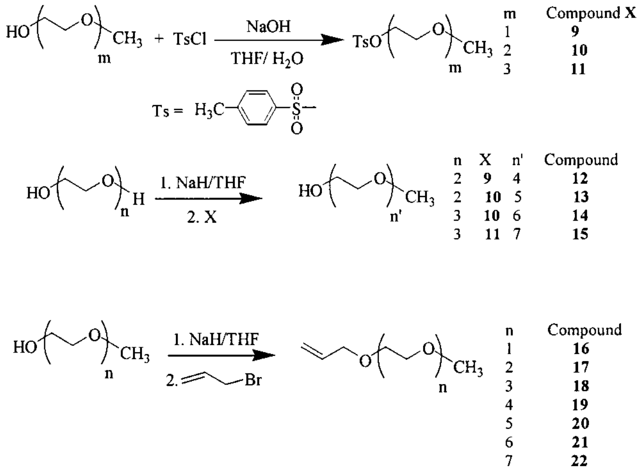
10.1021/ma0018446 CCC: $20.00

Table 1. Charaterization Data for 2−8

	NMR data, δ, ppm vs $CDCl_3$					elemental analysis		GPC	DSC
polymer	^1H				^{29}Si	calculated C/H	found C/H	M_w (PDI)	T_g (°C)
2	3.70−3.5 (m,12H)	3.35 (s, 6H)	1.75 (m, 4H)	0.60 (m, 4H)	−21.0	$C_{12}H_{26}SiO_5$ 51.76:9.43	51.51:9.45	7.3×10^3 (1.25)	−55.0
3	3.70−3.50 (m, 20H)	3.35 (s, 6H)	1.75 (m, 4H)	0.60 (m, 4H)	−22.6	$C_{16}H_{34}SiO_7$ 52.43:9.37	52.51:9.32	7.6×10^3 (1.30)	−63.4
4	3.70−3.50 (m, 28H)	3.35 (s, 6H)	1.75 (m, 4H)	0.60 (m, 4H)	−21.0	$C_{20}H_{42}SiO_9$ 52.84:9.31	52.35:9.47	8.0×10^3 (1.35)	−69.2
5	3.70−3.50 (m, 36H)	3.35 (s, 6H)	1.75 (m, 4H)	0.60 (m, 4H)	−23.0	$C_{24}H_{50}SiO_{11}$ 53.11:9.30	53.08:9.33	2.5×10^4 (1.22)	−69.8
6	3.70−3.50 (m, 44H)	3.35 (s, 6H)	1.75 (m, 4H)	0.60 (m, 4H)	−21.0	$C_{28}H_{58}SiO_{13}$ 53.31:9.29	53.29:9.29	1.5×10^4 (1.15)	−69.7
7	3.70−3.50 (m, 52H)	3.35 (s, 6H)	1.75 (m, 4H)	0.60 (m, 4H)	−21.0	$C_{32}H_{66}SiO_{15}$ 53.46:9.27	53.51:9.26	1.5×10^4 (1.20)	−68.9
8	3.70−3.50 (m, 60H)	3.35 (s, 6H)	1.75 (m, 4H)	0.60 (m, 4H)	−21.0	$C_{36}H_{74}SiO_{17}$ 53.60:9.18	53.59:9.18	2.5×10^4 (1.20)	−66.4

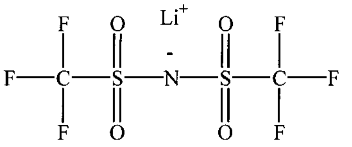
Scheme 2. Preparation of Linear Side Chain Ethylene Oxides



water.[15] From these building blocks and commercially available poly(ethylene glycols), we were able to systematically prepare a complete series of poly(ethylene glycol)allyl methyl ethers where the oxygen content was a known integer, Scheme 2. The polymers themselves were then obtained by a condensation route from intermediate dichlorosilanes, which were accessed through a hydrosilylation reaction, Scheme 1.[14] Each polymer was fractionated from low-molecular-weight material and unwanted hydrogenated byproducts by washing with hexane. All polymers were characterized by multinuclear NMR spectroscopy, gel permeation chromatography, and differential scanning calorimetry, Table 1.

Conductivity Results

All polymer samples were doped with lithium bis((trifluoromethyl)sulfonyl)imide (**1**) using THF as the solvent. The polymers all formed homogeneous amorphous salt complexes with this salt, which were dried overnight on a standard Schlenk line ($\sim 10^{-3}$ atm) and then for a further 24 h on a high vacuum line ($<10^{-6}$ atm). Each sample was next transferred to an argon-filled glovebox where further manipulation was performed with Teflon-coated instruments. Each polymer complex was analyzed at ambient temperature, followed by a variable temperature run between 0 and 70 °C.


$\mathrm{CF_3{-}SO_2{-}N^{-}(Li^{+}){-}SO_2{-}CF_3}$

(1)

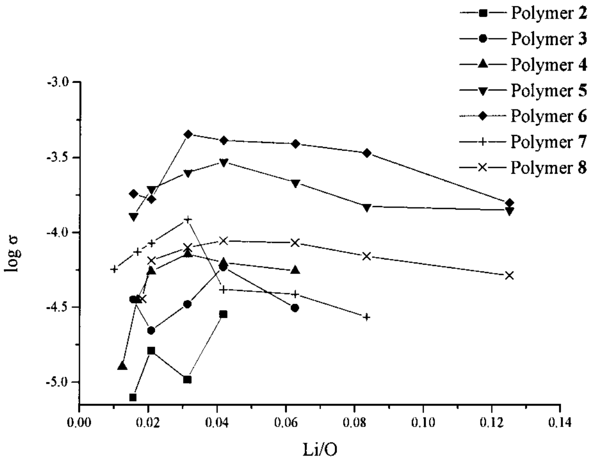


Figure 1. Ionic conductivities of $(LiN(SO_3CF_3)_2)_x/[SiOR_2]_n$ complexes for polymers **2**−**8** at room temperature.

Table 2. Maximum Ambient Conductivities for 2−8

polymer	ambient conductivity, σ (S cm^{-1})	doping level	M_w
2	2.83×10^{-5}	24	7.3×10^3
3	5.87×10^{-5}	24	7.6×10^3
4	7.20×10^{-5}	32	8.0×10^3
5	2.96×10^{-4}	24	2.5×10^4
6	4.54×10^{-4}	32	1.5×10^4
7	1.22×10^{-4}	32	1.5×10^4
8	8.70×10^{-5}	24	2.5×10^4

The results we observed are consistent with those reported for the polyphosphazenes.[7] With low oxygen content, the conductivities of the polymers at room temperature are quite poor, but gradually, as the side chain lengthens, the conductivity increases approaching a maximum and then tails away, Figure 1.[17] The best conductivities are found for polymers that contain five and six EO units in the side chain, polymers **5** and **6**. The highest ambient temperature conductivities are presented in Table 2; the average optimum doping level was found to be between 24:1 and 32:1 (O/Li). The conductivities range from 2.8×10^{-5} to 4.5×10^{-4} S cm^{-1}, as shown in Table 2. The latter value is observed from the polymer poly[bis(2-(2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)ethoxy)ethoxy)propyl siloxane], **6**, where each sidearm has six coordinating EO oxygens, doped at a 32:1 level. This polymer−salt complex shows the

Table 3. VFT Data for 2−8

	polymer						
	2	**3**	**4**	**5**	**6**	**7**	**8**
doping level	24	24	32	24	32	32	24
A (S cm^{-1}K$^{1/2}$)	4.4×10^{-5}	0.61	1.40	2.09	1.97	7.55	2.36
B (K^{-1})	656.8	655.47	868.6	755.6	702.6	1379.7	816.0
T_0 (K)	189.8	195.5	174.4	172.3	171.1	128.3	187
E_a (kJ mol^{-1})	5.46	5.45	7.22	6.28	5.84	11.47	6.78
T_g (K)	195.2	209.6	204.62	198.01	193.71	204.1	214.2

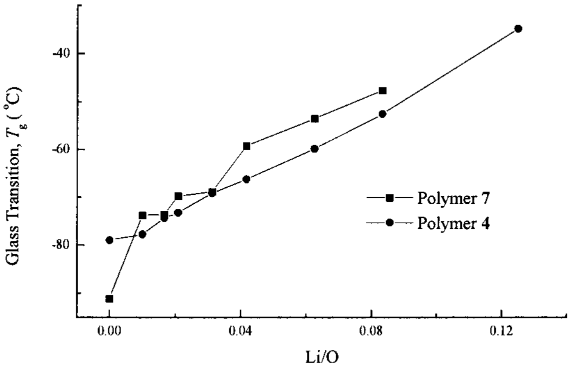


Figure 2. Glass transition (T_g) of $(LiN(SO_3CF_3)_2)_x/[SiOR_2]_n$ complexes for polymers **4** and **7**.

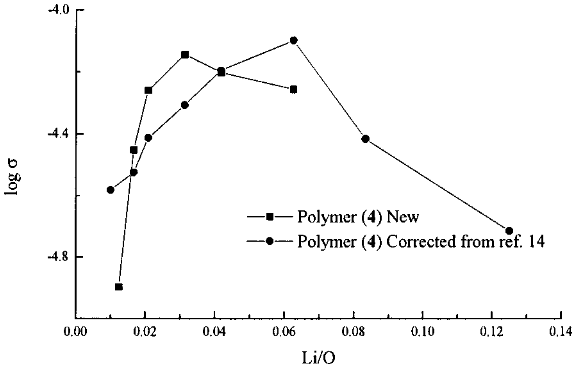


Figure 3. Ionic conductivity of $(LiN(SO_3CF_3)_2)_x/[SiOR_2]_n$ complexes for polymer **4** (corrected from Hooper et al.[14]) and a new sample of **4**.

highest reported conductivity to date for a polymer electrolyte.

The doped samples become quite viscous but are still nonsolid in nature. This we believe is a function of molecular weight, and we are currently investigating procedures to increase the molecular weights of all of our linear disubstituted polymers. Most of the polymer complexes show typical behavior as ionic conductors: the conductivities increase to an optimum value as the salt content increases, with the conductivity dropping off at higher salt levels, Figure 1. This is not true for the polymers with lowest oxygen content in the side chains; these polymers are quite low in molecular weight and have low viscosities, and we attribute their erratic behavior to these factors.

The variable-temperature experiments that were recorded showed a clear trend, whereby conductivities increased with increasing temperature. The Arrhenius plots of the data all had the curvature characteristic of polymer-assisted ion motion. The data were fit to the Vogel−Tamman−Fulcher[18] equation $\sigma = AT^{1/2}\exp[-B/(T - T_0)]$, (VTF) and the parameters T_0 and E_a for all samples, as well as glass-transition temperatures (T_g), are highlighted in Table 3. These clearly correlate well with the conductivity plots; as the lithium ion content increases, the glass-transition temperature increases, Figure 2. The activation energies range from 5.45 to 11.47 kJ/mol, and the T_0 values are closer to the actual T_g than the usual 50 K difference.

As we observed previously,[14] these disubstituted polysiloxanes show only a glass-transition endotherm at low temperatures; this temperature steadily increases with higher lithium ion content, Figure 3 for polymer **4**. This is in contrast to the thermal properties of monocomb polysiloxanes previously reported which show crystallization exotherms and melt endotherms.[11,12] Such behavior is indicative of a fully amorphous polymer system and is partly responsible for the high conductivities we observe.

Conclusions

A series of linear disubstituted (double-comb) polysiloxanes has now been prepared and their conductivities measured when doped with a lithium salt, **1**. Some thermal properties of the polymers and their salt complexes have been measured and compared to single-comb polysiloxanes. All polymers exhibited low glass-transition temperatures that rose slowly with increasing salt content. The double-comb polymers all form amorphous polymer−salt complexes with LiTSFI (**1**). The optimum ionic conductivity increased with increasing length of side chains, up to a maximum of six oxygens, before tailing off at higher ethylene oxide content. The highest reported ambient temperature conductivity for an inorganic polymer electrolyte has been observed for polymer **6** (4.5×10^{-4} S cm^{-1}), which contains six oxygens in each side chain. For each polymer system, the conductivity steadily increased to a maximum at a certain salt concentration; above this concentration, the conductivity decreased. The average optimum doping level was found to be between 24:1 and 32:1 (O/Li) for most polymer−salt complexes.

Experimental Section

All synthetic manipulations were carried out under an atmosphere of dry dinitrogen gas using standard vacuum-line Schlenk techniques. All solvents were degassed and purified prior to use according to standard literature methods: diethyl ether, hexanes, and tetrahydrofuran were distilled from sodium/benzophenone ketal. NMR grade deuteriochloroform was stored over 4 Å molecular sieves. All other reagents (Aldrich, Gelest) were used as received or distilled prior to use.

All NMR chemical shifts are reported in parts per million (δ ppm); downfield shifts are reported as positive values from tetramethylsilane (TMS) as standard at 0.00 ppm. The ^{1}H and ^{13}C chemical shifts are reported relative to the NMR solvent as an internal standard, and the ^{29}Si chemical shifts are reported relative to an external TMS standard. NMR spectra were recorded using samples dissolved in $CDCl_3$, unless otherwise stated, on the following instrumentation. Carbon-13 NMR were recorded as proton decoupled spectra, and ^{29}Si NMR were recorded using an inverse gate pulse sequence with a relaxation delay of 30 s.

^{1}H NMR Bruker AC300
(300.1 MHz) with Grant NIH 1 S10 RRO 8389-01

^{13}C NMR Bruker AC300
(75.5 MHz) with Grant NIH 1 S10 RRO 8389-01

^{29}Si NMR Bruker Avance 360
(71.54 MHz) with Grant NSF CHE-9013030

Varian Unity 500
(99.2 MHz) with Grants NIH 1 S10 RRO4981-01 &
NIH CHE-9629688

Gel permeation chromatography (GPC) polydispersity measurements were recorded on a Waters 745 liquid chromatograph using American Polymer Laboratories 100, 500, and 1000 Å columns. HPLC-grade THF, containing 0.5 wt % of tetra-*n*-butylammonium nitrate, was used as eluent at 2 mL/min, and fractions were detected by a differential refractometer.

Elemental microanalyses were obtained by Galbraith Laboratories, Knoxville, TN. Fast atom bombardment (FAB) mass spectra were recorded using a Micromass Autospec, with added NaI. Differential scanning calorimetry (DSC) measurements were recorded on a Perkin-Elmer DSC7 series scanning calorimeter. Samples were sealed in aluminum pans prepared in the drybox. A scanning rate of 10 °C/min was used over the range −100 to +80 °C.

Impedance measurements were performed under computer control using an EG&G Princeton Applied Research model 273A potentiostat/galvanostat, EG&G Princeton Applied Research model 5210 lock-in amplifier for frequency control (0.01 Hz to 10 kHz), and EG&G Princeton Applied Research model 388 impedance software for data acquisition. Subsequently, the data obtained was analyzed on a PC with Microsoft Excel. Room temperature conductivity measurements were at 23 ± 1 °C while variable-temperature measurements (0−70 °C) were made by placing the electrochemical cell in a jacketed holder and circulating ethylene glycol/water from a Lauda RMT6 circulating bath. Actual temperatures were determined via an Omega thermocouple attached directly to the cell.

2-Methoxyethyl *p*-Toluenesulfonate (9). Compound **9** was prepared according to the method described by Ouchi et al.[15] 2-Methoxyethanol (110 mL, 1.4 mol) in 300 mL of THF was added dropwise to a solution of NaOH (80 g, 2 mol) in water and THF (400 mL and 300 mL) at 0 °C. This mixture was stirred for a further 30 min before the dropwise addition of *p*-toluenesulfonyl chloride (tosyl chloride) (247 g, 1.3 mol) in 500 mL of THF. After being stirred at room temperature for a further 2 h, the mixture was poured onto 200 mL of ice. This solution was extracted with 3 × 500 mL of dichloromethane that was subsequently dried with magnesium sulfate, and all volatile materials were removed by rotary evaporation, yielding a colorless oil (**9**) which was used without further purification, 300 g (100%): ^{1}H NMR ($CDCl_3$), δ (ppm) 7.8 (d, 2H), 7.3 (d, 2H), 4.1 (m, 2H), 3.65−3.45 (m, 2H), 3.3 (s, 3H), 2.40 (s, 3H); ^{13}C NMR ($CDCl_3$), δ (ppm) 146.8, 141.5, 129.7, 127.8, 71.7, 70.6, 61.4, 21.5; mass spectroscopy *m*/*e* 231 MH^{+} base peak.

2-(2-Methoxyethoxy)ethyl *p*-Toluenesulfonate (10). Compound **10** was prepared in a manner similar to that used for **9**. The following reagents and quantities were used: diethlyene glycol monomethyl ether (165 mL, 1.4 mol), NaOH (80 g, 2 mol), and tosyl chloride (247 g, 1.3 mol). The final product was isolated as a colorless oil, which was used without further purification, 356 g (100%): ^{1}H NMR ($CDCl_3$), δ (ppm) 7.8 (d, 2H), 7.3 (d, 2H), 4.1 (m, 2H), 3.65−3.45 (m, 6H), 3.3 (s, 3H), 2.40 (s, 3H); ^{13}C NMR ($CDCl_3$), δ (ppm) 146.8, 141.5, 129.7, 127.8, 71.7, 70.6, 70.3−70.0, 61.4, 21.5; mass spectroscopy *m*/*e* 275 MH^{+} base peak.

2-(2-(2-Methoxyethoxy)ethoxy)ethyl *p*-Toluenesulfonate (11). Compound **11** was prepared in a manner similar to that used for **9**. The following reagents and quantities were used: triethlyene glycol monomethyl ether (224 mL, 1.4 mol), NaOH (80 g, 2 mol), and tosyl chloride (247 g, 1.3 mol). The final product was isolated as a colorless oil, which was used without further purification, 415 g (100%): ^{1}H NMR ($CDCl_3$), δ (ppm) 7.8 (d, 2H), 7.3 (d, 2H), 4.1 (m, 2H), 3.65−3.45 (m, 10H), 3.3 (s, 3H), 2.40 (s, 3H); ^{13}C NMR ($CDCl_3$), δ (ppm) 146.8, 141.5, 129.7, 127.8, 71.7, 70.6, 70.3−70.0, 61.4, 21.5; mass spectroscopy *m*/*e* 319 MH^{+} base peak.

2-(2-(2-(2-Methoxyethoxy)ethoxy)ethoxy)ethanol (12). Compound **12** was prepared according to a method similar to that described by Allcock et al.[6a] Triethylene glycol (33 mL, 0.25 mol) in 200 mL of THF was added dropwise to a suspension of NaH (80% dispersion in mineral oil) (9.75 g, 0.325 mol) in 500 mL of THF at 0 °C. This mixture was stirred for a further 60 min at 0 °C, and then a solution of **9** (57.6 g, 0.25 mol) in 200 mL of THF was added dropwise. This mixture was stirred overnight and allowed to warm to room temperature. The reaction mixture was filtered, and all volatile materials were removed by rotory evaporation. The yellow oil was dissolved into toluene (100 mL), and the organic layer was extracted with 3 × 150 mL of water. The aqueous layer was next extracted with 3 × 150 mL of chloroform. The remaining organic layer was dried with $MgSO_4$, and the solvent was removed by rotory evaporation. The yellow oil that remained was distilled under vacuum (90 °C, 5 mmHg) to give a colorless oil, 46.8 g (90%): ^{1}H NMR ($CDCl_3$), δ (ppm) 3.65−3.45 (m, 16H), 3.27 (s, 3H), 3.00 (b, 1H); ^{13}C NMR ($CDCl_3$), δ (ppm) 72.3, 71.6, 70.3−70.0, 61.4, 58.7; mass spectroscopy *m*/*e* 165 MH^{+} base peak.

2-(2-(2-(2-(2-Methoxyethoxy)ethoxy)ethoxy)ethoxy)ethanol (13). Compound **7** was prepared in a manner similar to that used for **12**. The following reagents and quantities were used: diethylene glycol (47.5 mL, 0.5 mol), NaH (16.5 g, 0.55 mol), and **10** (128.7 g, 0.47 mol). The yellow oil that remained was distilled under vacuum (120 °C, 5 mmHg) to give a colorless oil, 88 g (90%): ^{1}H NMR ($CDCl_3$), δ (ppm) 3.65−3.45 (m, 20H), 3.27 (s, 3H), 3.00 (b, 1H); ^{13}C NMR ($CDCl_3$), δ (ppm) 72.3, 71.6, 70.3−70.0, 61.4, 58.7; mass spectroscopy *m*/*e* 209 MH^{+} base peak.

2-(2-(2-(2-(2-(2-Methoxyethoxy)ethoxy)ethoxy)ethoxy)ethoxy)ethanol (14). The preparation was similar to that used for **12**. The following reagents and quantities were used: triethylene glycol (33 mL, 0.25 mol), NaH (9.75 g, 0.325 mol), and **10** (57.6 g, 0.25 mol). The yellow oil that remained was distilled under vacuum (165 °C, 5 mmHg) to give a colorless oil, 46.8 g (64%): ^{1}H NMR ($CDCl_3$), δ (ppm) 3.65−3.45 (m, 24H), 3.27 (s, 3H), 3.00 (b, 1H); ^{13}C NMR ($CDCl_3$), δ (ppm) 72.3, 71.6, 70.3−70.0, 61.4, 58.7; mass spectroscopy *m*/*e* 253 MH^{+} base peak.

2-(2-(2-(2-(2-(2-(2-Methoxyethoxy)ethoxy)ethoxy)ethoxy)ethoxy)ethoxy)ethanol (15). Compound **15** was prepared similarly. The following reagents and quantities were used: triethylene glycol (33 mL, 0.25 mol), NaH (9.75 g, 0.325 mol), and **11** (79.5 g, 0.25 mol). The yellow oil that remained was distilled under vacuum (220 °C, 5 mmHg) to give a colorless oil, 40.7 g (55%): ^{1}H NMR ($CDCl_3$), δ (ppm) 3.65−3.45 (m, 24H), 3.27 (s, 3H), 3.00 (b, 1H); ^{13}C NMR ($CDCl_3$), δ (ppm) 72.3, 71.6, 70.3−70.0, 61.4, 58.7; mass spectroscopy *m*/*e* 297 MH^{+} base peak.

Ethylene Glycol Allyl Methyl Ether (16). A solution of 2-methoxyethanol (79 mL, 1 mol) in 250 mL of THF was added dropwise to a suspension of NaH (80% dispersion in mineral oil) (36 g, 1.2 mol) in THF (1.5 L) chilled to 0 °C. This solution was stirred for a further 2 h followed by the dropwise addition of allyl bromide (104 mL, 1.2 mol) in 250 mL of THF. The resulting mixture was stirred at room temperature for 3 h and then filtered to remove unreacted NaH. All volatile materials were removed by rotary evaporation to yield an orange oil. This oil was dissolved into water, and unreacted alcohol was extracted using 3 × 75 mL portions of toluene. The desired product was then extracted into chloroform by washing the water layer with 3 × 200 mL of $CHCl_3$, this was dried with magnesium sulfate, and all volatile materials were removed by rotary evaporation. The resulting yellow oil was distilled

(100 °C) to yield ethylene glycol allyl methyl ether, 106 g (92%): ^{1}H NMR (CDCl$_3$), δ (ppm) 5.85 (m, 1H), 5.15 (dd, 2H), 3.95 (d, 2H), 3.65−3.45 (m, 8H), 3.30 (s, 3H); ^{13}C NMR (CDCl$_3$), δ (ppm) 134.6, 116.8, 72.1, 71.8, 69.2, 58.9; mass spectroscopy *m/e* 117 MH$^+$ base peak.

Diethylene Glycol Allyl Methyl Ether (17). Compound **17** was prepared in a manner similar to that described for **16**. The following reagents and quantities were used: diethylene glycol methyl ether (120 mL, 1 mol), NaH (36 g, 1.2 mol), and allyl bromide (130 mL, 1.5 mol). The resulting yellow oil was distilled (50 °C, 5 mmHg) to yield diethylene glycol allyl methyl ether, 136 g (85%): ^{1}H NMR (CDCl$_3$), δ (ppm) 5.85 (m, 1H), 5.15 (dd, 2H), 3.95 (d, 2H), 3.65−3.45 (m, 12H), 3.30 (s, 3H); ^{13}C NMR (CDCl$_3$), δ (ppm) 134.6, 116.8, 72.1, 71.8, 70.3, 70.0, 69.2, 58.9; mass spectroscopy *m/e* 161 MH$^+$ base peak.

Triethylene Glycol Allyl Methyl Ether (18). Compound **18** was prepared in a manner similar to that described for **16**. The following reagents and quantities were used: triethylene glycol methyl ether (96 mL, 0.6 mol), NaH (21 g, 0.7 mol), and allyl bromide (61 mL, 0.7 mol). The resulting yellow oil was distilled (90 °C, 5 mmHg) to yield 111 g (90%): ^{1}H NMR (CDCl$_3$), δ (ppm) 5.85 (m, 1H), 5.15 (dd, 2H), 3.95 (d, 2H), 3.65−3.45 (m, 16H), 3.30 (s, 3H); ^{13}C NMR (CDCl$_3$), δ (ppm) 134.6, 116.8, 72.1, 71.8, 70.3−70.0, 69.2, 58.9; mass spectroscopy *m/e* 205 MH$^+$ base peak.

Tetraethylene Glycol Allyl Methyl Ether (19). Compound **19** was prepared in a manner similar to that described for **16**. The following reagents and quantities were used: tetraethylene glycol methyl ether **12** (35.6 g, 0.17 mol), NaH (6.7 g, 0.22 mol), and allyl bromide (19.2 mL, 0.22 mol). The resulting yellow oil was distilled (120 °C, 5 mmHg) to yield 30.5 g (72%): ^{1}H NMR (CDCl$_3$), δ (ppm) 5.85 (m, 1H), 5.15 (dd, 2H), 3.95 (d, 2H), 3.65−3.45 (m, 20H), 3.30 (s, 3H); ^{13}C NMR (CDCl$_3$), δ (ppm) 134.6, 116.8, 72.1, 71.8, 70.3−70.0, 69.2, 58.9; mass spectroscopy *m/e* 249 MH$^+$ base peak.

Pentaethylene Glycol Allyl Methyl Ether (20). Compound **20** was prepared in a manner similar to that described for**16**. The following reagents and quantities were used: pentaethylene glycol methyl ether **13** (25.5 g, 0.1 mol), NaH (4.5 g, 0.15 mol), and allyl bromide (13 mL, 0.15 mol). The resulting yellow oil was distilled (140 °C, 5 mmHg) to yield 24.8 g (85%): ^{1}H NMR (CDCl$_3$), δ (ppm) 5.85 (m, 1H), 5.15 (dd, 2H), 3.95 (d, 2H), 3.65−3.45 (m, 24H), 3.30 (s, 3H); ^{13}C NMR (CDCl$_3$), δ (ppm) 134.6, 116.8, 72.1, 71.8, 70.3−70.0, 69.2, 58.9; mass spectroscopy *m/e* 293 MH$^+$ base peak.

Hexaethylene Glycol Allyl Methyl Ether (21). Compound **21** was prepared in a manner similar to that described for **16**. The following reagents and quantities were used: hexaethylene glycol methyl ether **14** (24.8 g, 83.5 mmol), NaH (3.26 g, 0.11 mol), and allyl bromide (14 mL, 0.16 mol). The resulting yellow oil was distilled (183 °C, 5 mmHg) to yield 20.9 g (74%): ^{1}H NMR (CDCl$_3$), δ (ppm) 5.85 (m, 1H), 5.15 (dd, 2H), 3.95 (d, 2H), 3.65−3.45 (m, 28H), 3.30 (s, 3H); ^{13}C NMR (CDCl$_3$), δ (ppm) 134.6, 116.8, 72.1, 71.8, 70.3−70.0, 69.2, 58.9; mass spectroscopy *m/e* 337 MH$^+$ base peak.

Heptaethylene Glycol Allyl Methyl Ether (22). Compound **22** was prepared in a manner similar to that described for **16**. The following reagents and quantities were used: heptaethylene glycol methyl ether **15** (95 g, 0.25 mol), NaH (7.2 g, 0.3 mol), and allyl bromide (26 mL, 0.3 mol). The resulting yellow oil was distilled (220 °C, 5 mmHg) to yield 50.3 g (53%): ^{1}H NMR (CDCl$_3$), δ (ppm) 5.85 (m, 1H), 5.15 (dd, 2H), 3.95 (d, 2H), 3.65−3.45 (m, 32H), 3.30 (s, 3H); ^{13}C NMR (CDCl$_3$), δ (ppm) 134.6, 116.8, 72.1, 71.8, 70.3−70.0, 69.2, 58.9; mass spectroscopy *m/e* 381 MH$^+$ base peak.

Poly[bis(2-methoxyethoxy)propyl siloxane] (2). Dichlorosilane (6.52 g, 65 mmol, 25% solution in xylene) was added to a solution of **16** (15 g, 0.13 mol) and chloroplatinic acid (20 μmol) in THF (50 mL) at 0 °C. The mixture was heated at 60 °C for 12 h, after which time the solvents were removed by heating under reduced pressure to yield a light yellow oil, 20.9 g (97%); ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.70−3.50 (m, 12 H, O−CH_2), 3.35 (s, 6 H, OCH_3), 1.85 (m, 4 H, CH$_2$CH_2CH$_2$), 1.15 (m, 4 H, SiCH_2); ^{29}Si NMR (99 MHz, CDCl$_3$) δ 32.6; no residual Si−H functionality could be detected by ^{1}H,^{29}Si NMR, or IR spectroscopy. Anal. Calcd for C$_{12}$H$_{26}$SiO$_4$Cl$_2$: Cl, 21.27. Found: Cl, 21.20. This product was rapidly added to a water/triethylamine solution to yield a brown oil. This oil was dissolved into 30 mL of diethyl ether, to precipitate triethylammonium hydrochloride, and was filtered. Removal of solvent under reduced pressure yielded a yellow oil. The polymer was purified by repeatedly washing with hexane, yield 7.5 g (42%).

Poly[bis(2-(2-methoxyethoxy)ethoxy)propyl siloxane] (3). Polymer **3** was prepared by a method similar to that described for **2**. The following reagents and quantities were used: dichlorosilane (5.83 g, 57.8 mmol, 25% solution in xylene), diethylene glycol allyl methyl ether **17** (18.5 g, 0.12 mol), and chloroplatinic acid (20 μmol) and THF (50 mL). The mixture was heated at 60 °C for 12 h, after which time the solvents were removed by heating under reduced pressure to yield a light yellow oil, 23.1 g (95%): ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.70−3.50 (m, 20 H, O−CH_2), 3.35 (s, 6 H, OCH_3), 1.85 (m, 4 H, CH$_2$CH_2CH$_2$), 1.15 (m, 4 H, SiCH_2); ^{29}Si NMR (99 MHz, CDCl$_3$) δ 32.6; no residual Si−H functionality could be detected by ^{1}H,^{29}Si NMR, or IR spectroscopy. Anal. Calcd for C$_{16}$H$_{34}$SiO$_6$Cl$_2$: Cl, 16.82. Found: Cl, 16.93. This product was rapidly added to a water/triethylamine solution to yield a brown oil. This oil was dissolved into 30 mL of diethyl ether, to precipitate triethylammonium hydrochloride, and was filtered. Removal of solvent under reduced pressure yielded a yellow oil. The polymer was purified by repeatedly washing with hexane, yield 16.6 g (90%).

Poly[bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)propyl siloxane] (4). Polymer **4** was prepared by a method similar to that described for **2**. The following reagents and quantities were used: dichlorosilane (40 g, 0.1 mol, 25% solution in xylene), **18** (41.12 g, 0.2 mol), chloroplatinic acid (20 μmol), and THF (50 mL). The mixture was heated at 60 °C for 12 h, after which time the solvents were removed by heating to 150 °C under reduced pressure to yield a brown oil, 40.1 g (80%): ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.70−3.50 (m, 28 H, O−CH_2), 3.35 (s, 6 H, OCH_3), 1.85 (m, 4 H, CH$_2$CH_2CH$_2$), 1.15 (m, 4 H, SiCH_2); ^{29}Si NMR (99 MHz, CDCl$_3$) δ 32.6; no residual Si−H functionality could be detected by ^{1}H,^{29}Si NMR, or IR spectroscopy. Anal. Calcd for C$_{20}$H$_{42}$SiO$_8$Cl$_2$: Cl, 13.92. Found: Cl, 14.04. To 10 g of this product, a water/pyridine solution (1:4) was rapidly added to yield a brown oil. This oil was dissolved into 30 mL of diethyl ether, to precipitate pyridinium hydrochloride, and was filtered. Removal of solvent under reduced pressure yielded a yellow oil. The polymer was purified by repeatedly washing with hexane, yield 8.5 g (95%).

Poly[bis(2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)ethoxy)propyl siloxane] (5). Polymer **5** was prepared by a method similar to that described for **2**. The following reagents and quantities were used: dichlorosilane (2.82 g, 28 mmol, 25% solution in xylene), **19** (13.8 g, 0.56 mol), chloroplatinic acid (20 μmol), and THF (50 mL). The mixture was heated at 60 °C for 12 h, after which time the solvents were removed by heating under reduced pressure to yield a light yellow oil, 14.9 g (90%): ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.70−3.50 (m, 36 H, O−CH_2), 3.35 (s, 6 H, OCH_3), 1.85 (m, 4 H, CH$_2$CH_2CH$_2$), 1.15 (m, 4 H, SiCH_2); ^{29}Si NMR (99 MHz, CDCl$_3$) δ 32.6; no residual Si−H functionality could be detected by ^{1}H,^{29}Si NMR, or IR spectroscopy. Anal. Calcd for C$_{24}$H$_{50}$SiO$_{10}$Cl$_2$: Cl, 11.86. Found: Cl, 11.85. This product was rapidly added to a water/triethylamine solution to yield a brown oil. This oil was dissolved into 30 mL of diethyl ether, to precipitate triethylammonium hydrochloride, and was filtered. Removal of solvent under reduced pressure yielded a dark yellow oil. The polymer was purified by repeatedly washing with hexane, yield 9.4 g (69%).

Poly[bis(2-(2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)ethoxy)ethoxy)propyl siloxane] (6). Polymer **6** was prepared by a method similar to that described for **2**. The following reagents and quantities were used: dichlorosilane (2.38 g, 23 mmol, 25% solution in xylene), **20** (13.8 g, 47 mmol), chloroplatinic acid (20 μmol), and THF (50 mL). The mixture was heated at 60 °C for 12 h, after which time the solvents were removed by heating under reduced pressure to yield a dark yellow oil, 15.3 g (95%): ^{1}H NMR (300 MHz, CDCl$_3$) δ

3.70−3.50 (m, 44 H, $\mathrm{O{-}C}H_2$), 3.35 (s, 6 H, $\mathrm{OC}H_3$), 1.85 (m, 4 H, $\mathrm{CH_2C}H_2\mathrm{CH_2}$), 1.15 (m, 4 H, $\mathrm{SiC}H_2$); ^{29}Si NMR (99 MHz, $CDCl_3$) δ 32.6; no residual Si−H functionality could be detected by ^{1}H,^{29}Si NMR, or IR spectroscopy. Anal. Calcd for $C_{28}H_{58}SiO_{12}Cl_2$: Cl, 10.34. Found: Cl, 10.40. This product was rapidly added to a water/triethylamine solution to yield a brown oil. This oil was dissolved into 30 mL of diethyl ether, to precipitate triethylammonium hydrochloride, and was filtered. Removal of solvent under reduced pressure yielded a yellow oil. The polymer was purified by repeatedly washing with hexane, yield 13.8 g (93%).

Poly[bis(2-(2-(2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)ethoxy)ethoxy)ethoxy)propyl siloxane] (7). Polymer **7** was prepared by a method similar to that described for **2**. The following reagents and quantities were used: dichlorosilane (2.36 g, 23 mmol, 25% solution in xylene), **21** (15.7 g, 47 mmol), chloroplatinic acid (20 μmol), and THF (50 mL). The mixture was heated at 60 °C for 12 h, after which time the solvents were removed by heating under reduced pressure to yield a light yellow oil, 17.1 g (96%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.70−3.50 (m, 52 H, $\mathrm{O{-}C}H_2$), 3.35 (s, 6 H, $\mathrm{OC}H_3$), 1.85 (m, 4 H, $\mathrm{CH_2C}H_2\mathrm{CH_2}$), 1.15 (m, 4 H, $\mathrm{SiC}H_2$); ^{29}Si NMR (99 MHz, $CDCl_3$) δ 32.6; no residual Si−H functionality could be detected by^{1}H,^{29}Si NMR or IR spectroscopy. Anal. Calcd for $C_{32}H_{66}SiO_{14}Cl_2$: Cl, 9.16. Found: Cl, 9.20. This product was rapidly added to a water/triethylamine solution to yield a brown oil. This oil was dissolved into 30 mL of diethyl ether, to precipitate triethylammonium hydrochloride, and was filtered. Removal of solvent under reduced pressure yielded a yellow oil. The polymer was purified by repeatedly washing with hexane, yield 15.1 g (95%).

Poly[bis(2-(2-(2-(2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)ethoxy)ethoxy)ethoxy)ethoxy)propyl siloxane] (8). Polymer **8** was prepared by a method similar to that described for **2**. The following reagents and quantities were used: dichlorosilane (2.52 g, 25 mmol, 25% solution in xylene), **22** (19 g, 50 mmol), chloroplatinic acid (20 μmol), and THF (50 mL). The mixture was heated at 60 °C for 12 h, after which time the solvents were removed by heating under reduced pressure to yield a dark yellow oil, 20.4 g (95%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.70−3.50 (m, 60 H, $\mathrm{O{-}C}H_2$), 3.35 (s, 6 H, $\mathrm{OC}H_3$), 1.85 (m, 4 H, $\mathrm{CH_2C}H_2\mathrm{CH_2}$), 1.15 (m, 4 H, $\mathrm{SiC}H_2$); ^{29}Si NMR (99 MHz, $CDCl_3$) δ 32.6; no residual Si−H functionality could be detected by ^{1}H,^{29}Si NMR, or IR spectroscopy. Anal. Calcd for $C_{36}H_{74}SiO_{16}Cl_2$: Cl, 8.23. Found: Cl, 8.22. This product was rapidly added to a water/triethylamine solution to yield a brown oil. This oil was dissolved into 30 mL of diethyl ether, to precipitate triethylammonium hydrochloride, and was filtered. Removal of solvent under reduced pressure yielded a yellow oil. The polymer was purified by repeatedly washing with hexane, yield 17.7 g (88%).

Acknowledgment. This work was supported by the National Science Foundation and by the sponsors of the Organosilicon Research Center. We also thank 3M Co. for the gift of $LiN(SO_2CF_3)_2$. Work at Grinnell was supported by NSF-REU Site Grant DUE- 0097531.

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MA0018446