Synthesis and Properties of Novel Isomeric Regular Polysiloxanes That Contain Both Si−H and $RSiO_{3/2}$ (T) Units: Poly(1-hydrido-1-trimethylsiloxytetramethyltrisiloxane) and Poly(1-dimethylsiloxypentamethyltrisiloxane)

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Received July 21, 2000; Revised Manuscript Received September 20, 2000

ABSTRACT: Poly(1-dimethylsiloxypentamethyltrisiloxane) (**II**) has been prepared by anionic ring-opening polymerization (AROP) of 1-dimethylsiloxypentamethylcyclotrisiloxane (**I**) catalyzed by butyllithium and HMPA. The isomeric polysiloxane, poly(1-hydrido-1-trimethylsiloxytetramethyltrisiloxane) (**IV**), has been prepared by AROP of 1-hydrido-1-trimethylsiloxytetramethylcyclotrisiloxane (**III**) catalyzed by dilithiodiphenylsilanediolate. These are the first regular polysiloxanes that contain both Si−H and T groups. The polymers have been characterized by ^1H, ^{13}C, and ^{29}Si NMR as well as by IR spectroscopy and elemental analysis. Their molecular weight distribution (M_w/M_n) has been determined by GPC versus monodisperse polystyrene standards. M_n has also been determined by ^1H NMR end group analysis. The highly regular microstructures of these linear polysiloxanes has been determined by ^{29}Si NMR spectroscopy. Every third siloxane unit in these polymers is a $RSiO_{3/2}$ (T) group. Both copolymers contain reactive Si−H groups that permit chemical modification by hydrosilylation reactions. Quantitative hydrosilylation of **II** with benzophenone catalyzed by activated dihydridocarbonyltris(triphenylphosphine)ruthenium (Ru) yields poly(1-diphenylmethoxydimethylsiloxypentamethyltrisiloxane). Karstedt-catalyzed quantitative hydrosilylation of **II** with styrene gives copoly(1′-phenylethyldimethylsiloxypentamethyltrisiloxane/2′-phenylethyldimethylsiloxypentamethyltrisiloxane). These modified polysiloxanes also have regular microstructures. On the other hand, chemical modification of **IV** by hydrosilylation of benzophenone catalyzed by Ru or of styrene catalyzed by Karstedt catalyst proceeds slowly. It was not possible to obtain quantitative chemical modification of **IV** by either method.

Introduction

The properties of copolymers depend on both the sequence and molar ratio of the two components. Random, alternating, and block copolymers made from the same monomers can have distinct properties. Copoly(dimethylsiloxane/methylhydridosiloxane)s with a wide range of compositions [mole percent CH_3HSiO (D^H) from 0.5 to 55%)], molecular weight distributions, and random microstructures are commercially available.[1] These have been prepared either by cohydroylsis of dimethyldichlorosilane and methyldichlorosilane or by acid-catalyzed ring-opening equilibration polymerization of octamethylcyclotetrasiloxane (D_4) and 1,3,5,7-tetramethylcyclotetrasiloxane ($D^H{}_4$).[2−5] This latter process gives, in addition to the desired copolymer, significant amounts of cyclic siloxanes that must be separated from the copolymer. The terminal Si−OH groups of these are usually capped with trimethylsilyl groups to prevent the slow reaction of Si−H groups with Si−OH groups.[6]

Bases such as hydroxide are not used to prepare poly(methylhydridosiloxane)s, because nucleophilic attack by hydroxide on an Si−H center in the presence of water or other protic solvents results in formation of a silanolate, hydrogen, and regeneration of hydroxide.[7] Silanol and silanolate centers provide sites for polysiloxane cross-linking.[8,9]

Living AROP of cyclotrisiloxanes has been used to prepare narrow molecular distribution polysiloxanes.[11,12] This is possible because ring opening of the strained cyclotrisiloxane is generally faster than equilibration or redistribution reactions. Ring−chain equilibration of various polysiloxanes have been studied.[13] Regiospecific AROP of monosubstituted cyclotrisiloxanes has been used to prepare highly regular polysiloxanes.[10,14,15] For example, poly(1-hydridopentamethyltrisiloxane), a siloxane copolymer which has a highly regular [D−D−D^H] microstructure, results from AROP of 1-hydridopentamethylcyclotrisiloxane in an aprotic solvent at low temperature.[10] Under these conditions, the Si−H is not lost.

Herein we report the preparation of regular linear polysiloxanes that contain both reactive Si−H sites and T units. Trifunctional T units are usually found at branch points or at cross-links. 1-Dimethylsiloxypentamethylcyclotrisiloxane (**I**),[16,17] prepared by reaction of 1,1-dichloro-1,3,3-trimethyldisiloxane[18] with tetramethyldisiloxane-1,3-diol in the presence of triethylamine,[19] undergoes AROP catalyzed by amount of butyllithium/HMPA in THF at −25 °C to give poly(1-dimethylsiloxypentamethyltrisiloxane) (**II**) with a highly regular [D−D−T^{M^H}] microstructure (Figure 1).

In a similar manner, 1-hydrido-1-trimethylsiloxytetramethylcyclotrisiloxane (**III**), prepared by reaction of 1,1-dichloro-3,3,3-trimethyldisiloxane with tetramethyldisiloxane-1,3-diol in the presence of triethylamine, undergoes AROP catalyzed by dilithiodiphenylsilanediolate[11] to yield poly(1-hydrido-1-trimethylsiloxytetramethyltrisiloxane) (**IV**) with a regular [D−D−$T^{H,M}$] microstructure (Figure 2). The microstructure of **IV** is more regular than that of **II**; compare Figures 1 and 2.

Polysiloxanes **II** and **IV** both contain T units and reactive Si−H bonds. The T units of **II** and **IV** are unusual in that they are part of the linear polymer chain

10.1021/ma001276u CCC: $19.00

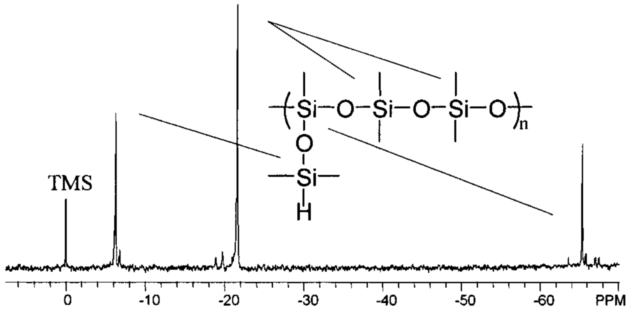


Figure 1. ^{29}Si NMR of **II**.

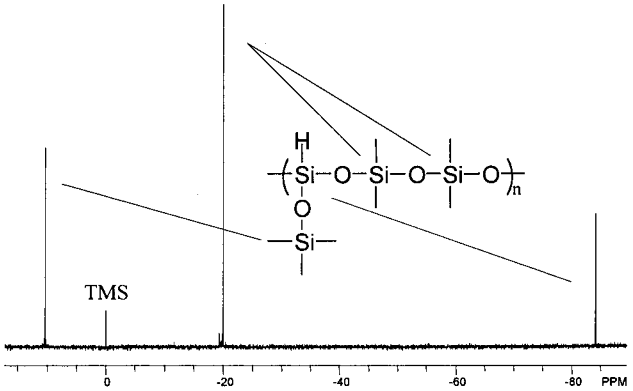


Figure 2. ^{29}Si NMR of **IV**.

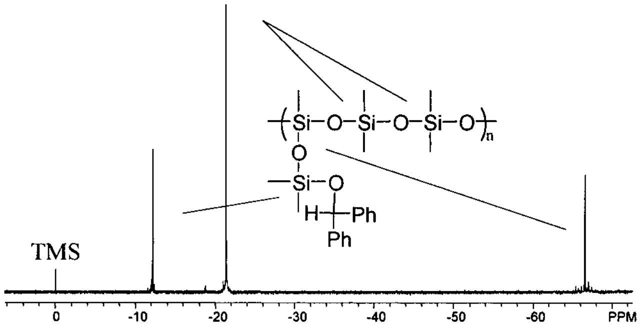


Figure 3. ^{29}Si NMR of poly(diphenylmethoxydimethylsiloxypentamethyltrisiloxane).

rather than cross-links. This is due to the fact that the branches at the T junctions are short. Chemical modification of the Si−H of **II** by a hydrosilylation with benzophenone was catalyzed by Ru,[20] which had been activated by prior treatment with styrene,[21] gave poly(1-diphenylmethoxydimethylsiloxypentamethyltrisiloxane) (Figure 3). We have previously reported that Ru catalyzes the hydrosilylation of C−O double bonds of ketones.[22,23] Hydrosilylation of **II** with styrene catalyzed by the Karstedt platinum catalyst was also successful. Unfortunately, hydrosilylation of styrene is not regiospecific. Thus, copoly(1′-phenylethyldimethylsiloxypentamethyltrisiloxane/2′-phenylethyldimetehylsiloxypentamethyltrisiloxane) is formed (Figure 4). In this connection, it should be noted that there is considerable interest in chemical modification of polymers.[24−27]

The Si−H bond of polymer **IV** is in a more sterically hindered environment than that of polymer **II**. For this reason, even with more rigorous conditions it is difficult to achieve high levels of hydrosilylation. Neither the hydrosilylation of **IV** with benzophenone catalyzed by Ru nor Karstedt-catalyzed hydrosilylation with styrene proceeded quantitatively. The NMR spectra of these partially chemically modified polysiloxanes are complex (Figure 5).

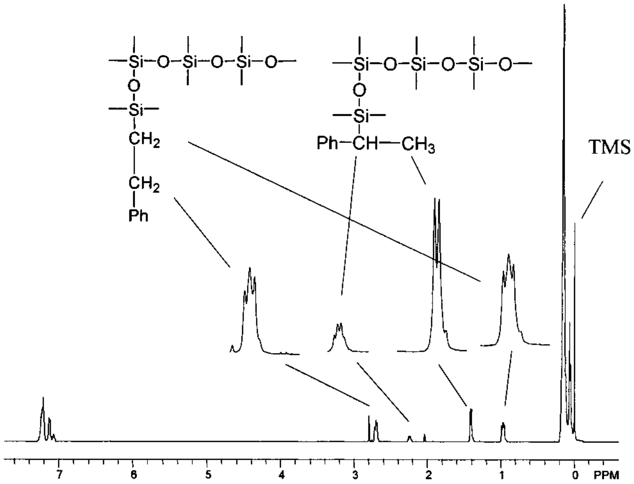


Figure 4. ^{1}H NMR of copoly(1′-phenylethyldimethylsiloxypentamethyltrisiloxane)/2′-phenylethyldimethylsiloxypentamethyltrisiloxane).

Experimental Section

^{1}H, ^{13}C, and ^{29}Si NMR spectra were obtained on a Bruker AMX-500 MHz spectrometer. ^{1}H and ^{13}C NMR spectra of 5% w/v acetone-d_6 (A), benzene-d_6 (B), or chloroform-d (C) solutions are reported. Twenty-five percent w/v solutions were used to obtain ^{29}Si NMR spectra.^{13}C NMR spectra were obtained with broad-band proton decoupling. A heteronuclear gated decoupling pulse program with a 60 s delay was used to acquire ^{29}Si NMR spectra. All spectra were referenced to internal TMS. IR spectra of neat films on KCl plates were recorded on a Perkin-Elmer Spectrum 2000 FT-IR spectrometer. UV spectra of cyclohexane solutions were run on a Shimadzu UV-260 spectrometer.

GPC analysis of the molecular weight distribution of the polymers was performed on a Waters system equipped with a 501 refractive index detector. Two 7.8 mm × 300 mm Styragel HT 6E and HMW 6E columns in series were used for the analysis. The eluting solvent was toluene at a flow rate of 0.5 mL/min. The retention times were calibrated against known monodisperse polystyrene standards: 929 000, 114 200, 13 700, and 794 g/mol.

The T_g of polymers was determined on a Perkin-Elmer DSC-7 instrument. The DSC was calibrated from the crystal transition temperature (−87.06 °C)[28] and mp (6.54 °C) of cyclohexane as well as from the T_g (−125 °C)[29] of poly(dimethylsiloxane). The analysis was begun by equilibration at −150 °C for 20 min, followed by an increase in temperature of 10 °C/min to 30 °C. Thermogravimetric analysis of the polymers was carried out on a Shimadzu TGA-50 instrument with a flow rate of 40 cm^3/min of nitrogen or air. The temperature was increased at 4 °C/min from 25 to 800 °C.

Low-resolution mass spectra were obtained by GC/MS on a Hewlett-Packard 5890 series II GC with a Hewlett-Packard 5971 series mass selective detector. Oneida Research Services Inc., Whitesboro, NY, carried out elemental analysis.

Diphenylsilanediol, methyltrichlorosilane (99%), trimethylchlorosilane (99%), *sym*-tetramethyldisiloxane, and Karstedt catalyst (4% w/w in xylene) were obtained from Gelest. Palladium on carbon (10%), ferric chloride hydrate, anhydrous diethyl ether, *p*-dioxane, butyllithium (2.5 M solution in hexanes), THF, HMPA, and triethylamine were purchased from Aldrich. THF was purified by distillation from sodium benzophenone ketyl immediately before use. *sym*-Tetramethyldisiloxane was redistilled through a 20 cm vacuum-jacketed Vigreux column. A fraction bp 71 °C was collected. All the other reagents were used as obtained. Reactions were conducted in flame-dried glassware under argon.

Initiator. Dilithium diphenylsilanediolate was prepared by titration of diphenylsilanediol with butyllithium in THF with styrene as an indicator.[11]

Dihydridocarbonyltris(triphenylphosphine)ruthenium (Ru) was prepared from ruthenium trichloride hydrate.[20]

1,1-Dichloro-1,3,3-trimethyldisiloxane was prepared by an acid-catalyzed equilibration reaction between *sym*-tetramethyldisiloxane and methyltrichlorosilane.[18]

1-Dimethylsiloxypentamethylcyclotrisiloxane (I).[16,17] Triethylamine (17.7 g, 175 mmol) and 250 mL of anhydrous diethyl ether were placed in a 1000 mL three-neck, round-bottom flask furnished with two pressure-equalizing addition funnels and a Tru-bore mechanical stirrer equipped with a Teflon paddle. The flask and its contents were cooled to 0 °C. A solution of 1,1-dichloro-1,3,3-trimethyldisiloxane (15.8 g, 83.6 mmol) in 50 mL of diethyl ether was placed in one addition funnel. A solution of tetramethyldisiloxane-1,3-diol[19] (13.9 g, 83.6 mmol) in 50 mL of diethyl ether was placed in the other. The two solutions were added dropwise simultaneously over 1 h. After stirring for 2 h, the triethylammonium chloride salts were removed by filtration. The diethyl ether solution was washed with water to remove excess triethylamine and residual triethylammonium chloride salts. It was dried over anhydrous magnesium sulfate and filtered, and the volatile solvents were removed by evaporation under reduced pressure. The residue was fractionally distilled through a 10 cm vacuum jacketed Vigreux column. A fraction bp 85 °C/42 mm, 18 g, 70% yield was obtained. ^{1}H NMR (A) δ: 0.15 (s, 3H), 0.17 (s, 6H), 0.19 (s, 6H), 0.23 (d, 6H, $J = 2.5$ Hz), 4.74 (sept, 1H, $J = 2.5$ Hz). ^{13}C NMR (A) δ: -3.02, 0.55, 0.74, 0.88. ^{29}Si NMR (A) δ: -5.21 (1Si), -8.12 (2Si), -55.94 (1Si). IR ν: 2966, 2907, 2133, 1406, 1260, 1089, 1020, 907, 862, 810, 770 cm^{-1}. Low-resolution MS m/z (relative intensity): 281 (10%) $(M-H)^+$, 267 (100%) $(M-CH_3)^+$, 193 (40%) $(M-OSi[(CH_3)_3])^+$.

Poly[1-dimethylsiloxypentamethyltrisiloxane] (II). I (1.0 g, 3.55 mmol) was placed in a test tube that was equipped with a Teflon-covered magnetic stir bar and sealed with a rubber septum. The system was purged with argon three times. THF (250 μL), HMPA (3.0 μL), and butyllithium hexane solution (5 μL, 7.5 μmol) were injected into the system. On the basis of the ratio of the monomer/initiator times the molecular weight of the monomer, a polymer with M_n equal to 133 000 is expected. The polymerization was allowed to proceed for 2.0 h at -25 °C. At this time, trimethylchlorosilane (5 μL) and triethylamine (5 μL) were added sequentially to quench the reaction. The polymer was precipitated three times from a mixture of diethyl ether and methanol. It was then dried under vacuum. In this way, 0.6 g, 60% yield, of material with $M_w/M_n = 6060/4120$ and $T_g = -131$ °C was obtained. It had the following spectral properties. ^{1}H NMR (A) δ: 0.12 (s, 3H), 0.15 (s, 12H), 0.24 (d, 6H, $J = 3.0$ Hz), 4.77 (br, 1.0H). ^{13}C NMR (A) δ: 1.30, 0.80, -2.12. ^{29}Si NMR (A) δ: -6.23 (1Si), -21.51 (2Si), -65.34 (1Si). In addition to these major signals in the ^{29}Si NMR small peaks were detected at δ -6.06, -6.73, -18.83, -19.69, -63.62, -65.65, -67.03, and -67.47 (Figure 1). IR ν: 2965, 2906, 2132, 1414, 1261, 1072, 1027, 909, 857. 801, 770 cm^{-1}. Elemental Anal. Calcd for $C_7H_{22}O_4Si_4$: C, 29.75; H, 7.85. Found: C, 29.78; H, 7.41.

Copoly(2′-phenylethyldimethylsiloxypentamethyltrisiloxane/1′-phenylethyldimethylsiloxypentamethyltrisiloxane). II (0.35 g, 1.24 mmol, $M_w/M_n = 6060/4120$), styrene (0.20 g, 1.86 mmol), toluene (1.5 mL), and Karstedt catalyst (50 μL) were placed in a 20 mL Ace pressure tube equipped with a Teflon-covered magnetic stir bar. The tube was sealed with a Teflon-threaded stopper. The reaction was allowed to proceed at room temperature for 3 h. The progress of the reaction was monitored by IR from the disappearance of the Si−H resonance of **II** at 2132 cm^{-1}. This was done by the periodic removal of small aliquots from the reaction. Toluene and other volatiles were removed under vacuum prior to obtaining the IR spectra. After 3 h, toluene was removed under vacuum. Ether (2 mL) was added, and a white solid (polystyrene) was removed by filtration. **III** was precipitated from the ether solution with methanol. The precipitate was dried in high vacuum for 24 h. In this way, 0.43 g, 90%, $M_w/M_n = 8025/5190$, $T_g = -93$ °C was obtained. UV λ_{max} nm (ϵ): 226 (680); 262 (242). ^{1}H NMR (A) δ: 0.05 (s, 1.2H), 0.07 (s, 1.8H), 0.15 (s, 12H), 0.16 (s, 6H), 0.97 (t, 1.2H, $J = 8$ Hz), 1.41 (d, 1.5H, $J = 7$ Hz), 2.24 (q, 0.33H, $J = 8$ Hz), 2.71 (t, 1.2H, $J = 9$ Hz), 7.06 (t, 0.4H, $J = 7.5$ Hz), 7.13 (br, s, 1.4H), 7.22 (m, 3.2H). ^{13}C NMR (C) δ: 145.05, 144.94, 128.25, 128.00, 127.75, 127.34, 125.45, 124.38, 31.38 (d), 29.27 (t), 20.07 (t), 14.39 (q), 1.02, 0.01, -1.49, -2.15, -2.28, -2.36. ^{29}Si NMR (A) δ: 7.68, 6.16, -21.77, -21.82, -21.85, -21.91, -21.95, -66.23, -66.24, -66.42, -66.43. IR ν: 3085, 3064, 3027, 2963, 2931, 2907, 2875, 1604, 1496, 1454, 1412, 1260, 1074, 1026, 903, 836, 799, 756, 699 cm^{-1}. Elemental Anal. Calcd for $C_{15}H_{30}O_4Si_4$: C, 46.58; H, 7.82. Found: C, 46.38; H, 7.81.

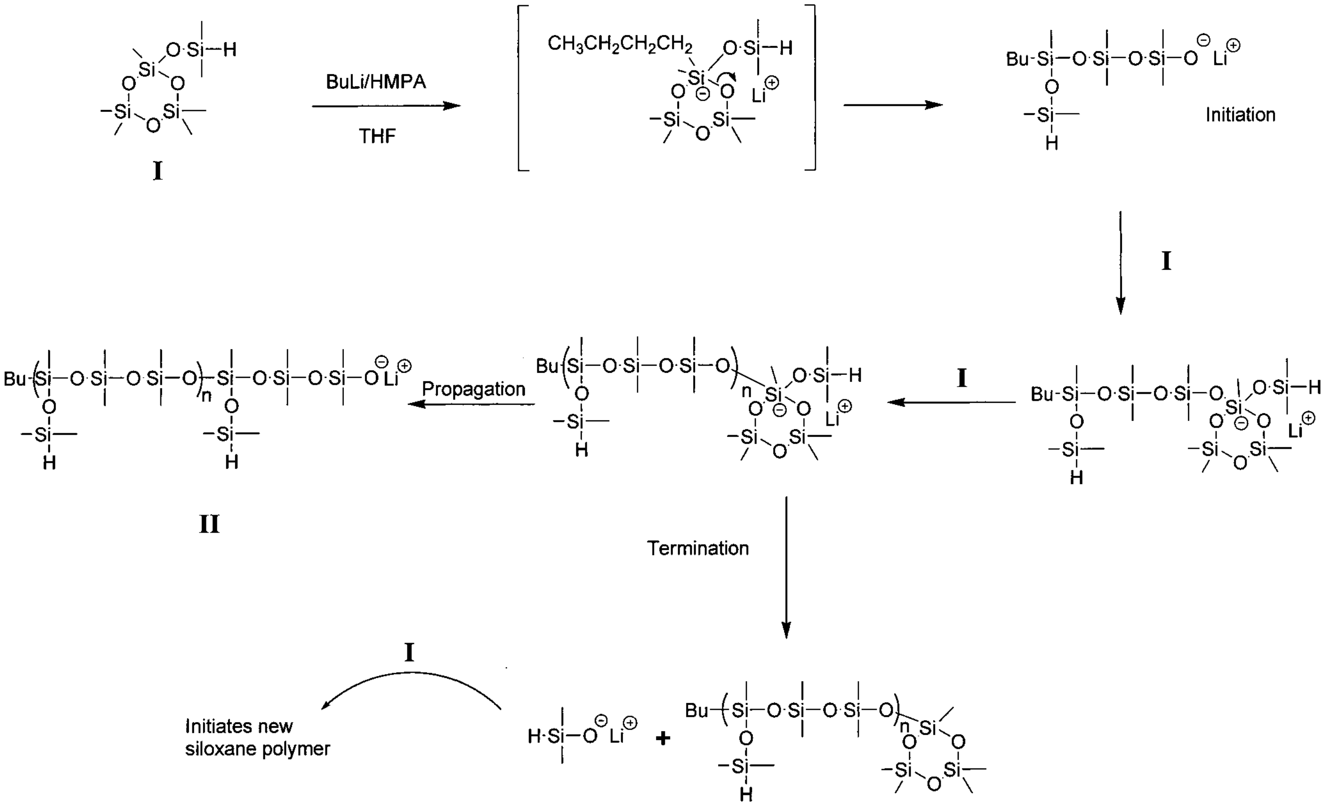
Poly(diphenylmethoxydimethylsiloxypentamethyltrisiloxane). In a 20 mL Ace pressure tube equipped with a Teflon-covered magnetic stir bar was placed 48.7 mg of Ru catalyst and 2 mL of toluene. A stoichiometrically equivalent amount of styrene was added (6.0 μL), and the tube was sealed with a Teflon-threaded stopper and heated to 80 °C for 5 min to activate the catalyst.[21] The tube was cooled to room temperature and opened, and **II** (0.4 g, 1.42 mmol, $M_w/M_n = 5460/3365$) and benzophenone (0.388 g, 2.12 mmol) were added. The tube was resealed and placed in oil bath (105 °C) for 3 h. After workup, the polymer was precipitated three times from diethyl ether/methanol and dried overnight under vacuum. In this way, 0.52 g, 75% yield, $M_w/M_n = 7450/4270 = 1.75$, $T_g = -71$ °C was obtained. It had the following properties: UV λ_{max} nm (ϵ): 226 (1865); 259 (685). ^{1}H NMR (A) δ: 7.41 (d, 4H, $J = 7.5$ Hz), 7.28 (br, s, 4H), 7.19 (br, s, 2H), 6.03 (s, 1H), 0.13 (s, 6H), 0.12 (s, 6H), 0.09 (s, 6H), 0.04 (s, 3H). ^{13}C NMR (A) δ: 145.69, 128.93, 127.80, 127.13, 76.71, 1.44, -0.08, -1.98. ^{29}Si NMR (A) δ: -12.10(1Si), -21.25 (2Si), -66.50 (1Si). IR ν: 3088, 3065, 3030, 2964, 2905, 1600, 1494, 1455, 1412, 1357. 1261, 1189, 1094, 1068, 1025, 921, 887, 858, 800, 754, 700 cm^{-1} Elemental Anal. Calcd for $C_{20}H_{32}O_5Si_4$: C, 51.68; H, 6.94. Found: C, 51.22; H, 6.62.

1,1-Dichloro-3,3,3-trimethyldisiloxane.[30] While 1,1-dichloro-3,3,3-trimethyldisiloxane has been reported in a 1967 German Patent, no experimental details or spectral data have been previously reported.

Trichlorosilane (100 g, 0.74 mol), hexamethyldisiloxane (59 g, 0.37 mol), and ferric chloride (0.05 g) were placed into a 500 mL round-bottom flask equipped with a Teflon-covered magnetic stir bar, and an acetone coldfinger condenser was attached to a drying tube filled with Drierite. Anhydrous HCl was slowly bubbled into the solution for 2 h. The reaction mixture was distilled through a 50 cm vacuum-jacketed column packed with stainless steel saddles. A fraction, bp 103 °C/760 mm, 15 g, 21% yield, was collected. It had the following spectral properties. ^{1}H NMR (A) δ: 0.164 (s, 9H), 5.56 (s, 1H). ^{13}C NMR (A) δ: 1.36. ^{29}Si NMR (A) δ: 18.37 [$(CH_3)_3\mathit{Si}$], -39.89 [$H\mathit{Si}Cl_2$]. IR ν: 2963, 2903, 2246, 1266, 1256, 1095, 876, 847, 827, 812, 758 cm $^{-1}$.

1-Hydrido-1-trimethylsiloxytetramethylcyclotrisiloxane (III). A solution of triethylamine (16.8 g, 167 mmol) in 300 mL of diethyl ether was placed in a 1000 mL three-neck round-bottom flask equipped with two 80 mL pressure-equalizing addition funnels and a Tru-bore mechanical stirrer fitted with a Teflon paddle. A solution of 1,1-dichloro-3,3,3-trimethyldisiloxane (15 g, 79.4 mmol) in 50 mL of diethyl ether was placed in one addition funnel. A solution of tetramethyldisiloxane-1,3-diol[19] (13.2 g, 79.4 mmol) in 50 mL of diethyl ether was placed in the other. The two solutions were added dropwise simultaneously over 2 h with stirring. After 2 h, triethylammonium chloride was removed by filtration. The ether solution was washed with water to remove excess triethylamine, dried over anhydrous magnesium sulfate, and filtered, and the volatile solvents were removed by evaporation under reduced pressure. The residue was purified by fractional distillation. A fraction, bp 45 °C/15 mm, 13.4 g, 60% yield, was obtained. ^{1}H NMR (A) δ: 0.15 (s, 9H), 0.186 (s, 6H), 0.192 (s, 6H), 4.37 (s, 1H). ^{13}C NMR (A) δ: 0.76, 0.94, 1.62. ^{29}Si NMR (A) δ: 11.25 (s, 1Si), -7.13 (s, 2Si), -75.67 (d, 1Si, $J_{Si-H} = 9$

Scheme 1. Mechanism of Chain Transfer versus Propagation of II



Hz). IR ν: 2964, 2904, 2225 (Si$-$H), 1408, 1262, 1095, 1027, 966, 897, 834, 808, 756 cm^{-1}. GC/MS *m/e* (rel intensity): 281 (5%) (M$-$1)$^+$, 267 (100%) (M$-$15)$^+$.

Poly(1-hydrido-1-trimethylsiloxytetramethyltrisiloxane) (IV). **III** (2.0 g, 7.09 mmol) was placed in a test tube equipped with a Teflon-covered magnetic stir bar and sealed with a rubber septum. The tube was purged three times with argon. THF (2.0 mL) and 50 μL of a THF solution of dilithiodiphenylsilanediolate (0.316 mol/L) (15.8 μmol) initiator were added. On the basis of the ratio of monomer/initiator concentration times the monomer molecular weight, a polymer with M_n = 126 000 is expected. The reaction was stirred for 2 h at -50 °C. Trimethylchlorosilane (10 μL) and triethylamine (10 μL) were sequentially added to quench the polymerization reaction. The polymer was taken up in a minimum amount of diethyl ether and was precipitated into methanol. This procedure was repeated three times. The polymer was dried under vacuum. In this way, 1.72 g, 86% yield, of material M_w/M_n = 17 890/11 810 = 1.51, $T_g = -120$ °C was obtained. ^{1}H NMR (B) δ: 0.23 (s, 9H), 0.30 (s, 12H), 4.69 (s, 1H). ^{13}C NMR (B) δ: 1.28, 1.29, 1.85. ^{29}Si NMR (B) δ: 10.25 (s, 1Si), -19.99 (s, 2Si), -84.09 (d, 1Si, J_{Si-H} = 7.7 Hz). IR ν: 2963, 2904, 2209, 1448, 1262, 1080, 1041, 901, 803, 707, 691 cm^{-1}.

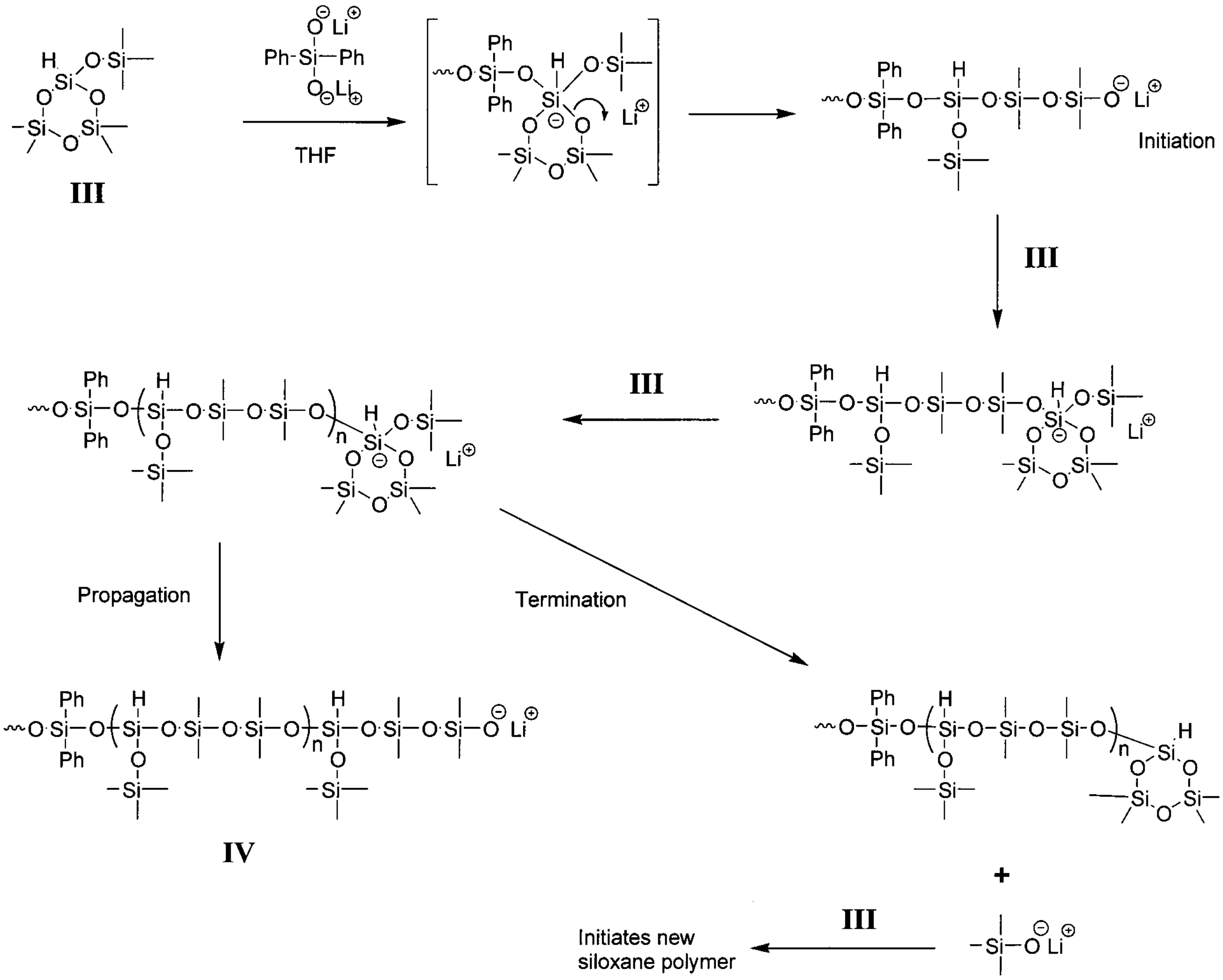
Partial Chemical Modification of IV by Platinum Karstedt-Catalyzed Hydrosilylation with Styrene. **IV** (0.50 g, 1.77 mmol), styrene (0.36 g, 3.54 mmol), toluene (2 mL), and Karstedt catalyst, 80 μL, was placed in a 20 mL Ace pressure tube equipped with a Teflon-covered magnetic stir bar. The tube was sealed with a Teflon-threaded stopper. The reaction was allowed to proceed at 110 °C. Additional styrene (2 × 100 μL) was added during the reaction. The progress of the reaction was monitored periodically by IR from the disappearance of the Si$-$H resonance of **II** at 2209 cm^{-1}. This was done by removal of small aliquots from the reaction. Toluene and other volatiles were removed under vacuum prior to obtaining the IR spectra. After 30 h, there is also a small band at 2208 cm^{-1} in IR due to Si$-$H. At this time, the toluene was removed under vacuum. Ether (2 mL) was added, and a white solid (polystyrene) was removed by centrifugation. The polymer was precipitated from the ether solution with MeOH. The precipitate was dried in high vacuum for 24 h. In this way, 0.58 g, 95% yield, M_w/M_n = 30 940/17 720, $T_g = -96$ °C was obtained. ^{1}H NMR (B) δ: 7.43 (m, 0.86 H), 7.26 (m, 1.36 H), 7.21 (m, 1.36 H), 4.76 (s, 0.4 H), 2.94 (br. s, 1.2 H), 1.13 (br. s., 1.2 H), 0.39 (s, 3.1 H), 0.35 (s, 4.7 H), 0.34 (s, 4.4 H), 0.28 (s, 4.8 H), 0.24 (s, 6.4 H). ^{13}C NMR (A) δ: 147.48, 145.50, 138.65, 129.44, 129.39, 129.12, 128.93, 128.77, 129.43, 127.38, 126.36, 122.59, 30.17, 17.38, 2.04, 1.94, 1.58, 146, 1.35. ^{29}Si NMR (A) δ: 10.21, 9.18, 8.38, -20.27, -20.37, -20.47, -20.86, -21.06, -21.37, -21.46, -24.56, -68.07, -78.49, -84.61. IR ν: 3084, 3063, 3027, 2962, 2931, 2905, 2852, 2208, 1604, 1495, 1453, 1413, 1261, 1072, 1029, 901, 842, 803, 770, 755, 737 cm^{-1}.

Partial Chemical Modification of IV by Ru-Catalyzed Hydrosilylation with Benzophenone. In a 20 mL Ace pressure tube equipped with a Teflon-covered magnetic stir bar was placed 48.7 mg of Ru and 2 mL of toluene. A stoichiometrically equivalent amount of styrene was added (6.0 μL), and the tube was sealed with a Teflon-threaded stopped and heated to 80 °C for 5 min to activate the catalyst. The tube was cooled to 25 °C and opened, and **IV** (0.5 g, 1.77 mmol) and benzophenone (0.48 g, 2.66 mmol) were added. The tube was resealed and heated to 110 °C for 30 h. After workup, the polymer was precipitated three times from diethyl ether and methanol and dried overnight under vacuum. In this way, 0.61 g, 85% yield, M_w/M_n = 37 930/16 850, $T_g = -88$ °C was obtained. ^{1}H NMR δ: 7.43 (d, 2.8 H, J = 4.5 Hz), 7.30 (t, 2.8 H, J = 3 Hz), 7.21 (t, 1.4 H, J = 6.5 Hz), 6.04 (d, 0.7 H, J = 3.5 Hz), 4.37 (s, 0.3 H), 0.17 (s, 10.7 H), 0.15 (s, 5.3 H), 0.10 (s, 2.1 H), 0.09 (s, 2.1 H), 0.08 (s, 4.5 H), 0.07 (s, 4.5H). ^{13}C NMR δ: 145.42, 128.94, 127.86, 127.11, 77.54, 77.53, 1.96, 1.75, 1.46, 1.37, 1.35, 1.26, 1.17. ^{29}Si NMR δ: 10.15, -20.16, -20.27, -84.67, -101.70. IR ν: 3090, 3067, 3031, 2962, 2903, 2207 (Si$-$H), 1948, 1495, 1454, 1414, 1261, 1084, 1068, 1029, 901, 842, 804, 755 cm^{-1}.

Results and Discussion

The highly regular microstructure of polysiloxanes **II** and **IV** may result from regioselective nucleophilic

Scheme 2. Mechanism of Chain Transfer versus Propagation of IV



attack on the T center of monomers **I** and **III**, respectively, rather than on the D centers of **I** and **III**. This results in formation of pentacoordinate T silyl centers. Ring opening of these leads to a T−D−D sequence that is terminated by a O−$(CH_3)_2$Si−O^- silanolate. This can subsequently attack another T center of monomer **I** or **III**. This regioselectivity results from the inherent differences between T and D centers. Thus, the silicon of a T center which is bonded to three electronegative oxygens is more electropositive than the silicon of a D center which is only bonded to two electronegative oxygens.

The molecular weight distribution of **II** determined by GPC is $M_w/M_n = 1.47$. An identical experiment was carried out in which the polymer was quenched with phenyldimethylchlorosilane rather than with trimethylchlorosilane. Resonances due to terminal Si−phenyl groups were detected in the ^{1}H NMR of this material at 7.62 and 7.38 ppm. Comparison of the integration of the signals due to Si−methyl groups to those of the terminal Si−phenyl groups permits determination of M_n by end group analysis. This gave a value of $M_n = 79\,500$. The value of M_n previously calculated on the basis of the ratio of [monomer]/[initiator] was 134 000. Both of these values are much larger than M_n obtained by GPC. NMR end group analysis is often used to calibrate M_n determined by GPC. Nevertheless, these large discrepancies suggest that despite the highly regular microstructure observed, significant chain transfer has occurred.

Similarly, the molecular weight distribution of **IV** determined by GPC is $M_w/M_n = 17\,890/11\,810 = 1.51$. In this case, dilithiodiphenylsilanediolate was used to initiate the polymerization. The expected value of M_n based on the ratio of [monomer]/[initiator] is 126 000. Resonances due to the initiator (Si−phenyl) can be detected in the ^{1}H NMR at 7.83, 7.61, and 7.53 ppm. Integration of these signals compared to those due to the Si−methyl groups gives a value of $M_n = 33\,700$. While NMR end group analysis is often used to calibrate GPC data, we suggest that this high value may also be due to chain transfer.

In the case of **II**, chain transfer can occur by loss of a dimethylsilanolate [H$(CH_3)_2$Si−O^-] from the intermediate pentacoordinate silyl T center rather than ring opening of the cyclotrisiloxane ring. This will result in a polysiloxane that is terminated by a pentamethylcyclotrisiloxane rather than by a phenyldimethylsilyl group (Scheme 1). The dimethylsilanolate lost is capable of initiating a new polysiloxane. Consistent with this interpretation, a small peak at −8.3 ppm is detected in the ^{29}Si NMR. The chemical shift of this peak is reasonable for a pentamethylcyclotrisiloxane.

Similarly, in the case of **IV**, chain transfer can occur by loss of a trimethylsilanolate from the intermediate pentacoordinate T center rather than ring opening. The trimethylsilanolate lost can also initiate a new polysiloxane chain. Consistent with this hypothesis, a small peak at −8.9 ppm is detected in the ^{29}Si NMR (Scheme 2).

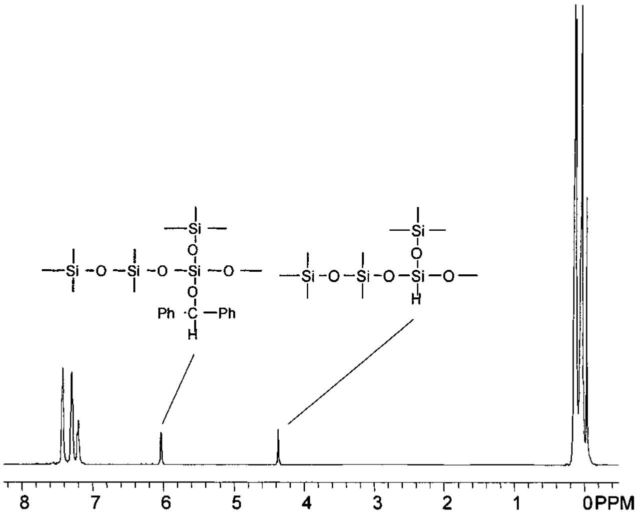


Figure 5. ^{1}H NMR of copoly(1-diphenylmethoxy-1-trimethylsiloxytetramethyltrisiloxane/1-hydrido-1-trimethylsiloxytetramethyltrisiloxane).

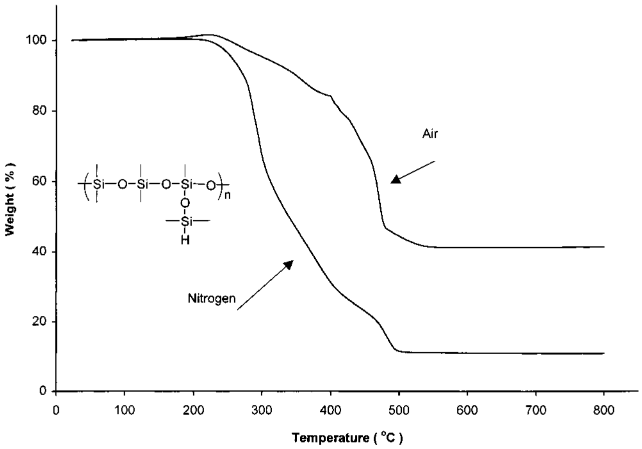


Figure 6. TGA of **II**.

Both polysiloxanes **II** and **IV** have very low glass transition temperatures. In fact, the T_g of **II** (−131 °C) is lower than that of poly(dimethylsiloxane) (−125 °C)[29] while that of **IV** is slightly higher T_g (−120 °C).

The thermal decomposition of poly(dimethylsiloxane) in both air and inert atmospheres has been thoroughly studied.[31,32] Polysiloxane **II** is thermally stable to only 220 °C in nitrogen. Above this temperature, catastrophic decomposition occurs in three stages. By 500 °C virtually only 10% of the initial sample weight remains. On the other hand, **II** is only stable to 170 °C in air. Between 170 and 230 °C the sample, in fact, gains a small amount of weight. Above 230 °C decomposition occurs. By 500 °C, only 40% of the initial sample weight remains. No additional weight is lost on heating the sample to 800 °C (Figure 6).

On the other hand, polysiloxane **IV** is thermally stable to 260 °C in both air and nitrogen atmospheres. Above 260 °C in nitrogen, **IV** undergoes catastrophic decomposition. By 450 °C only 5% of the initial sample remains. In air, on the other hand, between 260 and 380 °C, approximately 22% of the initial weight of the sample is lost. Above 380 °C weight loss occurs more rapidly. By 500 °C only 40% of the initial sample weight is left. No further weight loss occurs on heating the sample to 800 °C (Figure 7).

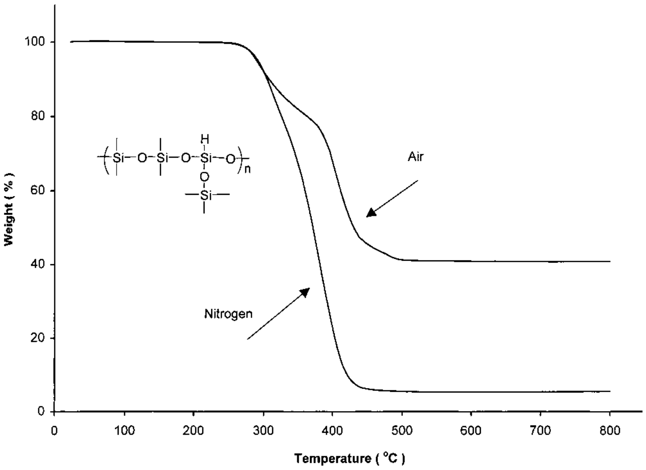


Figure 7. TGA of **IV**.

Hydrosilylation of **II** with styrene catalyzed by Karstedt catalyst proceeds in a quantitative yield to give a copolymer in which both 1′-phenylethyldimethylsiloxy (43%) and 2′-phenylethyldimethylsiloxy (57%) groups are formed. Thus, resonances in the ^{1}H NMR at 0.98(t) and 2.71(t) ppm due to the $-(CH_2-CH_2)-$ unit of the 2-phenylethyl group and at 1.41 (d) and 2.24 (q) ppm due to the $-(CH_3CH)-$ unit of the 1-phenylethyl group are observed. Likewise, two signals in the ^{29}Si NMR due to the 1-phenylethyldimethylsiloxy and 2-phenylethyldimethylsiloxy are observed at 7.68 and 6.16 ppm.

On the other hand, hydrosilylation of **IV** catalyzed by Karstedt catalyst requires higher temperature and longer reaction time. While it does not proceed quantitatively it is regioselective. Only 2′-phenylethyl groups attached to the T silyl center are formed. This regioselectivity may result from the greater steric hindrance of the T group Si−H bond of **IV** compared to the D group Si−H bond of **II**. Thus, it is easier to approach the terminal end of the styrene. Polystyrene is formed competitively.

Similarly, hydrosilylation of **II** with benzophenone catalyzed by Ru proceeds quantitatively. On the other hand, the hydrosilylation of **IV** with benzophenone catalyzed by Ru only proceeds to 60% conversion (Figure 5).

Conclusion

The first regular linear polysiloxanes which contain both Si−H and T units has been prepared by AROP of 1-dimethylsiloxypentamethylcyclotrisiloxane and by AROP of 1-hydrido-1-trimethylsiloxytetramethycyclotrisiloxane. These have been fully characterized. Significant differences between M_w/M_n determined by GPC and M_n determined by ^{1}H NMR end group analysis have been accounted for on the basis of chain transfer. This limits the molecular weights of polysiloxanes **II** and **IV**. Chemical modification of **II** and **IV** by Karstedt- and Ru-catalyzed hydrosilylation reactions is reported.

Acknowledgment. This work was supported in part by the Air Force Office of Scientific Research−MURI program.

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MA001276U