*Macromolecules* **1999,** *32,* 5217−5221

# Preparation and Orthogonal Polymerizations of 1-Hydrido-1-vinyldimethylsiloxy-3,3,5,5-tetramethylcyclotrisiloxane

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*Received February 26, 1999; Revised Manuscript Received May 17, 1999*

ABSTRACT: 1-Hydrido-1-vinyldimethylsiloxy-3,3,5,5-tetramethylcyclotrisiloxane (**IV**) was prepared by reaction of tetramethyldisiloxane-1,3-diol and 1,1-dichloro-1-hydrido-3,3-dimethyl-3-vinyldisiloxane (**III**). Ring-opening polymerization of **IV** catalyzed by either triflic acid or dilithium diphenylsilanediolate yields high molecular weight poly[1-hydrido-1-vinyldimethylsiloxy-3,3,5,5-tetramethyl-1,3,5-trisiloxanylene] (**V**), which has an exceptionally low $T_g$. On the other hand, hydrosilylation polymerization of **IV** catalyzed by the 1,3-divinyltetramethyldisiloxane platinum complex (Karstedt catalyst) gives high molecular weight *alt*-copoly(3,3,5,5-tetramethylcyclotrisiloxane-1,1-ylene/2,2-dimethyl-1-oxa-2-sila-1,4-butanylene) (**VI**). The structures of **V** and **VI** were confirmed by IR, $^1$H, $^{13}$C, and $^{29}$Si NMR spectroscopy as well as by elemental analysis. Differences in the microstructure of **V**, formed by acid- or base-catalyzed ring opening of **IV**, were detected by $^{29}$Si NMR. The molecular weight distributions of **V** and **VI** were determined by GPC. The thermal stability and glass transition temperatures of **V** and **VI** were measured by TGA and DSC, respectively. As expected, these polymers are easily cross-linked.

## Introduction

Over 30 years ago, Andrianov et al. reported the preparation of 1-hydrido-3-vinyl-1,3,5,5,7,7-hexamethylcyclotetrasiloxane (**I**) by cohydrolysis of 1,3-dichlorotetramethyldisiloxane and 1,3-dichloro-1-hydrido-1,3-dimethyl-3-vinyldisiloxane. Chloroplatinic acid-catalyzed hydrosilylation polymerization of **I** gave low molecular weight *alt*-copoly(1,3,5,5,7,7-hexamethylcyclotetrasiloxan-1,3-ylene/ethylene) (**II**).[1]

While cyclotetrasiloxanes are well-known to undergo acid-catalyzed ring-opening polymerization,[2] neither acid-catalyzed ring-opening polymerization of **I** nor acid-catalyzed cross-linking of **II** by ring opening of the cyclotetrasiloxane ring of **II** has been reported.

We report, herein, the preparation of 1-hydrido-1-vinyldimethylsiloxy-3,3,5,5-tetramethylcyclotrisiloxane (**IV**). This is the first cyclotrisiloxane that has been orthogonally polymerized. **IV** has been prepared by the reaction of 1,1-dichloro-1-hydrido-3,3-dimethyl-3-vinyldisiloxane (**III**) with tetramethyldisiloxane-1,3-diol in the presence of triethylamine. We have recently prepared **III** by a Lewis/Brønsted acid-catalyzed equilibration of 1,3-divinyltetramethyldisiloxane with trichlorosilane. Hydrosilylation polymerization[3] of **IV** using Karstedt catalyst involves the platinum-catalyzed anti-Markovnikov addition of the Si−H from one molecule of **IV** across the C−C double bond of the vinyl group another to yield high molecular weight *alt*-copoly(3,3,5,5-tetramethylcyclotrisiloxan-1,1-ylene/2,2-dimethyl-1-oxa-2-sila-1,4-butanylene) (**VI**). On the other hand, acid- or base-catalyzed ring-opening polymerization of the cyclotrisiloxane ring of **IV** by triflic acid or dilithium diphenylsilanediolate yields poly[1-hydrido-1-vinyldimethylsiloxy-3,3,5,5-tetramethyl-1,3,5-trisiloxanylene] (**V**).

While cyclotrisiloxanes are significantly more reactive toward acid or base-catalyzed ring-opening polymerization than cyclotetrasiloxanes,[2] these results are unexpected. Specifically, Si−H bonds are usually unstable to base. For example, reaction of hydroxide with Si−H bonds in 95% ethanol results in loss of hydrogen and formation of Si−OH bonds which can undergo further condensation to yield Si−O−Si bonds and water.[4,5] Further, Si−vinyl bonds undergo protodesilylation reactions on treatment with HX. This results in ethylene and formation of an Si−X bond.[6] Neither of these possible side reactions prevents the polymerization of **IV** under the experimental conditions used. Apparently, the acid-catalyzed ring opening of the cyclotrisiloxane of **IV** occurs faster than protodesilylation. Further, base-catalyzed polymerization of IV by dilithium diphenylsilanediolate has been carried out in the polar aprotic solvent THF.

## Experimental Section

**Spectroscopic Analysis.** $^1$H, $^{13}$C, and $^{29}$Si NMR spectra were obtained on a Bruker AMX-500 MHz spectrometer operating in the FT mode, using 40% w/v solutions in acetone-$d_6$. $^{13}$C NMR spectra were obtained with broad-band proton decoupling. An inverse gated $^1$H decoupling pulse program with a 60 s delay was used to acquire $^{29}$Si NMR spectra.[7] All spectra were referenced to an internal TMS standard. IR spectra of neat films on NaCl plates were recorded on a Perkin-Elmer Spectrum 2000 FT-IR spectrometer.

Gel permeation chromatography (GPC) analysis of the molecular weight distribution of **V** and **VI** was performed on a Waters system. Two 7.8 mm × 300 mm Styragel columns, HMW 6E and HT 6E, in series were used for the analysis. The eluting solvent was toluene at a flow rate of 0.6 mL/min. The retention times were calibrated against known monodisperse polystyrene standards: $M_w$ 929 000, 114 200, 13 700, and 794 whose polydispersity is less than 1.14.

The TGA of **V** and **VI** was measure on a Shimadzu TGA-50 instrument. The temperature program was 4 °C/min from 25 to 850 °C. The temperature was held at 850 °C for an additional 5 min. The glass transition temperatures ($T_g$) and melting temperatures ($T_m$) of the polymers were determined on a Perkin-Elmer DSC-7 instrument. The DSC was calibrated by measurement of the heat of transition (−87.06 °C)[8] and melting point (6.54 °C) of cyclohexane as well as by determi-

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10.1021/ma990293k CCC: $18.00

nation of the $T_g$ (−125 °C)[9] of poly(dimethylsiloxane) $M_w/M_n$ = 504 000/311 000. The analysis program was begun by equilibration at −150 °C for 20 min. This was followed by an increase in temperature of 10 °C/min to 30 °C.

Elemental analysis was carried out by Oneida Research Services Inc., Whitesboro, NY.

**Reagents.** Trichlorosilane, dimethyldichlorosilane, trimethylchlorosilane, hexamethyldisilazane, diphenylsilanediol, and 1,3-divinyltetramethyldisiloxane were procured from Gelest and distilled before use. Ferric chloride was purchased from Mallinckrodt. Triflic acid was obtained from the 3M Co. 1,3-Divinyltetramethyldisiloxane−platinum complex, 3−3.5% in xylene, was acquired from Hüls.

All reactions were carried out under an inert atmosphere in flame-dried glassware.

**1,1-Dichloro-1-hydrido-3,3-dimethyl-3-vinyldisiloxane (III).** Trichlorosilane (56 g, 0.42 mol), 1,3-divinyltetramethyldisiloxane (42 g, 0.22 mol), and ferric chloride (0.05 g, 180 $\mu$mol) were placed into a 120 mL round-bottomed flask equipped with a Teflon-covered magnetic stir bar and sealed with a rubber septum. Dry HCl was slowly bubbled into solution. An exothermic reaction occurred. Excess pressure was relieved through a syringe needle attached to a drying tube filled with Drierite. The contents of the flask warmed to ~35 °C in 10 min. The addition of HCl was continued for 2 h. The reaction mixture was distilled through a 50 cm vacuum jacketed column which was packed with stainless steel saddles. A fraction, bp 56 °C/40 mm, 9.0 g, 20% yield, was collected. $^1$H NMR $\delta$: 0.31 (s, 6H), 5.66 (s, 1H), 5.86 (dd, 1H, $J$ = 20 and 4 Hz), 6.06 (dd, 1H, $J$ = 15 and 4 Hz), 6.19 (dd, 1H, $J$ = 20 and 15 Hz). $^{13}$C NMR $\delta$: −0.04, 134.02, 137.03. $^{29}$Si NMR $\delta$: −39.58 (1Si), 5.77 (1Si). IR $\nu$: 3058, 2965, 2248, 1598, 1409, 1261, 1098, 1007, 845, 811, 792, 714, 570 cm$^{-1}$. Elemental Anal. Calcd for $C_4H_{10}Cl_2OSi_2$: C, 23.88; H, 5.01; Cl, 35.24. Found: C, 24.43; H, 4.99; Cl, 37.03.

**1-Hydrido-1-vinyldimethylsiloxy-3,3,5,5-tetramethylcyclotrisiloxane (IV).** A solution of triethylamine (14.2 g, 140 mmol) and 150 mL of diethyl ether was placed in a 150 mL three-neck round-bottomed flask equipped with two 50 mL pressure equalizing addition funnels and a Tru-bore mechanical stirrer fitted with a Teflon paddle. A solution of **III** (13.0 g, 64 mmol) and 15 mL of diethyl ether was placed in one addition funnel. A solution of tetramethyldisiloxane-1,3-diol[10] (10.8 g, 64 mmol) and 15 mL of diethyl ether was placed in the other addition funnel. The two solutions were added simultaneously dropwise for 1 h at room temperature to the well-stirred solution of diethyl ether and triethylamine. Stirring was continued for 1 h. The solution was then washed three times with saturated aqueous $NaHCO_3$. It was then dried over anhydrous magnesium sulfate and filtered. Distillation gave a fraction, bp 88 °C/20 mm, 12.1 g, 64% yield. $^1$H NMR $\delta$: 0.145 (s, 6H), 0.149 (s, 6H), 0.19 (s, 6H), 4.37 (s, 1H), 5.78 (dd, 1H, $J$ = 21 and 3.5 Hz), 5.94 (dd, 1H, $J$ = 14.5 and 4 Hz), 6.12 (dd, 1H, $J$ = 21 and 14.5 Hz). $^{13}$C NMR $\delta$: 0.19, 0.77, 0.93, 132.40, 138,63. $^{29}$Si NMR $\delta$: −75.90 (1Si, $J_{Si-H}$ = 306 Hz), −7.72 (2Si), −1.15 (1Si). IR $\nu$: 3055, 2965, 2226, 1597, 1408, 1261, 1096, 1025, 963, 896, 809, 710, 620 cm$^{-1}$. Elemental Anal. Calcd for $C_8H_{22}O_4Si_4$: C, 32.62; H, 7.53. Found: C, 31.90; H, 7.66.

**Poly[1-hydrido-1-vinyldimethylsiloxy-3,3,5,5-tetramethyl-1,3,5-trisiloxanylene] (V). Anionic Polymerization. IV** (0.53 g, 1.8 mmol) and 0.2 mL of THF were placed into a 18 × 70 mm test tube equipped with a Teflon magnetic stir bar and sealed with a rubber septum. The system was cooled to 0 °C and 30 $\mu$L initiator (dilithium diphenylsilanediolate in THF,[11] 0.294 mol/L) was injected into the solution. Polymerization was continued for 1 h. Trimethylchlorosilane (11 $\mu$L, 8.7 $\mu$mol) and $Et_3N$ (11 $\mu$L, 7.9 $\mu$mol) were then added to stop the polymerization. The polymer was precipitated three times from $Et_2O$/MeOH and then dried in a vacuum. In this way, 0.41 g, 77%, $M_w/M_n$ = 74 000/26 250, $T_g$ = −130 °C, and $T_m$ = −62.5 °C were obtained. $^1$H NMR $\delta$: 0.15 (s, 12H) 0.21 (s, 6H), 4.36 (s, 0.8H), 4.37 (s, 0.2H), 5.80 (dd, 1H, $J$ = 20 and 3.3 Hz), 5.96 (dd, 1H, $J$ = 15 and 3.5 Hz), 6.15 (dd, 1H, $J$ = 20 and 15 Hz). $^{13}$C NMR $\delta$: 0.34, 1.18, 132.52, 139.05, 139.07. $^{29}$Si NMR $\delta$: −84.65 (s, 0.86Si), −84.59 (s, 0.14 Si), −20.38 (s, 1.54Si), −20.31 (s, 0.26Si), −20.03 (s, 0.07Si), −19.65 (s, 0.09Si), −1.68 (s, 0.81Si), −1.60 (s, 0.16Si), −1.18 (s, 0.03Si). IR $\nu$: 3054, 3015, 2964, 2905, 2211, 1597, 1408, 1261, 1037 (br), 957, 900, 803, 709 cm$^{-1}$. Elemental Anal. Calcd for $C_8H_{22}O_4Si_4$: C, 32.62; H, 7.53. Found: C, 32.55; H, 7.39.

**Poly[1-hydrido-1-vinyldimethylsiloxy-3,3,5,5-tetramethyl-1,3,5-trisiloxanylene] (V). Triflic Acid-Catalyzed Polymerization. IV** (0.9 g, 3.1 mmol) was placed in a 18 × 70 mm test tube equipped with a Teflon-covered magnetic spin bar and a rubber septum. The tube was cooled to −5 °C, and triflic acid (6 $\mu$L, 6.8 $\mu$mol) was injected into the solution. After 30 min, hexamethyldisilazane (30 $\mu$L, 144 $\mu$mol) was added to stop the reaction. The polymer was purified by precipitation three times from $Et_2O$/MeOH. It was then allowed to dry in a vacuum for 12 h. In this way, 0.65 g, 67%, $M_w/M_n$ = 52 800/19 000, $T_g$ = −130 °C, and $T_m$ = −65 °C were obtained. $^1$H NMR $\delta$: 0.12 (s, 1.5H) 0.13 (s, 3H), 0.14 (s, 6H), 0.165 (s, 1.5H), 0.21 (s, 6H), 4.36 (s, 0.5H), 4.37 (s, 0.4H), 4.38 (s, 0.1H), 5.79 (dd, 1H, $J$ = 19.5 and 3 Hz), 5.95 (dd, 1H, $J$ = 14 and 3 Hz), 6.14 (dd, 1H, $J$ = 19.5 and 14 Hz). $^{13}$C NMR $\delta$: 0.09, 0.90, 132.18, 138.73. $^{29}$Si NMR $\delta$: −85.18 (s, 0.12Si), −84.68 (s, 0.5 Si), −84.62 (s, 0.4Si), −21.46 (s, 0.06Si), −21.40 (s, 0.02Si), −21.13 (s, 0.12Si), −21.07 (s, 0.06Si), −20.86 (s, 0.07Si), −20.77 (s, 0.26Si), −20.72 (s, 0.17Si), −20.46 (s, 0.64Si), −20.40 (s, 0.26Si), −20.13 (s, 0.06Si), −19.98 (s, 0.04Si), −19.77 (s, 0.15Si), −19.72 (s, 0.05Si), −3.99 (s, 0.015Si), −3.55 (s, 0.03Si), −1.94 (s, 0.05Si), −1.80 (s, 0.17Si), −1.78 (s, 0.28Si), −1.72 (s, 0.17Si), −1.69 (s, 0.16Si), −1.62 (s, 0.02Si), −1.31 (s, 0.11Si). IR $\nu$: 3054, 3015, 2964, 2905, 2211, 1597, 1408, 1262, 1052 (br), 900, 803, 709, 518 cm$^{-1}$. Elemental Anal. Calcd for $C_8H_{22}O_4Si_4$: C, 32.62; H, 7.53. Found: C, 32.50; H, 7.35.

***alt*-Copoly(3,3,5,5-tetramethylcyclotrisiloxane-1,1-ylene/2,2-dimethyl-1-oxa-2-sila-1,4-butanylene) (VI). IV** (1.0 g, 3.4 mmol) was placed into a 18 × 70 mm rubber-sealed test tube equipped with a Teflon magnetic stir bar. A Karstedt catalyst solution (5 $\mu$L) was injected. The temperature was kept between 35 and 45 °C. After 20 min, 100 $\mu$L of toluene was injected to allow proper mixing. The reaction was continued for 2 h, after which it was stopped, and the polymer was purified by precipitation three times from $Et_2O$/MeOH. The polymer was dried for 24 h in a vacuum. In this way, 0.71 g, 71% yield, $M_w/M_n$ = 70 800/14 200, $T_g$ = −66 °C, and $T_m$ = −47 °C were obtained. $^1$H NMR $\delta$: 0.11 (s, 6H), 0.13 (s, 6H), 0.16 (s, 6H), 0.55 (m, 3H), 0.97 (m, 0.5H), 1.14 (m, 0.5H). $^{13}$C NMR $\delta$: −0.61, 0.85, 1.04, 5.45, 9.70. $^{29}$Si NMR $\delta$: −57.74 (1Si), −8.51 (2Si), 9.80 (1Si). IR $\nu$: 2963, 1408, 1260, 1142, 1074, 1018, 839, 806, 764, 640, 466 cm$^{-1}$. Elemental Anal. Calcd for $C_8H_{22}O_4Si_4$: C, 32.62; H, 7.53. Found: C, 32.65; H, 7.40.

## Results and Discussion

Comparatively few heteropolyfunctional disiloxanes are known. Among these, bis(trimethylsiloxy)chlorosilane has been prepared by photochemical or palladium-catalyzed chlorination of bis(trimethylsiloxy)silane,[12] while 1,3-dichloro-1,3-dihydrido-1,3-dimethyldisiloxane has been formed by reaction of methyldichlorosilane with ferric oxide.[13] 1,3-Dichloro-1-hydrido-1,3-dimethyl-3-vinyldisiloxane has been prepared by cohydrolysis of methyldichlorosilane and vinylmethyldichlorosilane.[1] Recently, several unsymmetrical heteropolyfunctional disiloxanes have been synthesized by reaction of lithium vinylmethylsilaneloate with various chlorosilanes.[14,15]

We have used the combination of ferric chloride, a Lewis acid, and HCl, a Brønsted acid, to catalyze an equilibration reaction between 1,3-divinyltetramethyldisiloxane and trichlorosilane to yield **III**. (Ferric chloride and HCl are known to combine to form a superacid ($H_o$ < −12), $HFeCl_4$.[16] The reaction may occur by protonation of the oxygen of 1,3-divinyltetramethyldisiloxane, which leads to an oxonium ion. Nucleophilic attack by chloride ion on a vinyldimethylsilyl center of the oxonium ion may lead to vinyldimethylchlorosilane

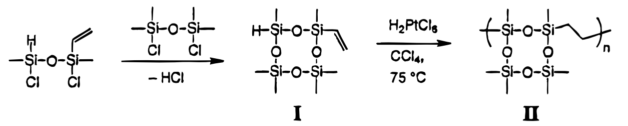


**Figure 1.** Preparation and $H_2PtCl_6$-catalyzed hydrosilylation polymerization of 1-hydrido-3-vinyl-1,3,5,5,7,7-hexamethylcyclotetrasiloxane (**I**).

and vinyldimethylsilanol. Subsequent reaction of vinyldimethylsilanol with trichlorosilane gives **III**.

The synthesis of polycarbosilanes by chloroplatinic acid-catalyzed hydrosilylation polymerization was first reported by Curry.[3,17,18] The fact that the hydrosilylation polymerization of **I**, reported by Andrianov, gives low molecular weight **II** is not surprising. Chloroplatinic acid-catalyzed step-growth hydrosilylation copolymerization of α,ω-divinylsiloxane and α,ω-dihydridosilanes also produces low molecular weight copoly(carbosilane/siloxanes).[19,20] Step-growth copolymerization reactions are well-known to require exact stoichiometric balance to achieve high molecular weight materials. Stoichiometric imbalance may result from loss of vinyl groups from **I**. Loss of vinyl groups from the α,ω-divinyldisiloxane by a protodesilylation reaction with HCl, which is generated by reaction of the chloroplatinic acid with 2-propanol solvent, has been observed.[6] We have been able to polymerize **IV** to give high molecular weight **VI** by use of the Karstedt catalyst, which is neutral.

Success of the triflic acid-catalyzed ring-opening polymerization of **IV** to yield **V** must result from the high rate of the acid-catalyzed ring opening of the strained cyclotrisiloxane ring compared to the rate of loss of a vinyl group by protodesilylation.

While high molecular weight polymers are obtained, the yields obtained are less than quantitative. The yields reported (~70%) for polymers **V** and **VI** are based on material isolated by precipitation three times. No analysis of the soluble materials has been carried out. It is expected that low molecular weight cyclic oligomers are formed in both the acid-catalyzed ring-opening polymerization and in the Karstedt catalyzed hydrosilylation polymerizations.

The molecular weight distributions of both **V** and **VI** are quite large. The reasons for the molecular weight distributions observed are not well understood. Nevertheless, the following comments provide some insight. For acid-catalyzed siloxane ring-opening polymerization $M_w/M_n$ is usually two. While acid-catalyzed ring opening of **IV** is very rapid, protodesilylation of pendant vinyl groups of **V** may occur. This would yield Si−OH groups which can undergo condensation. This would increase the value of $M_w/M_n$. Living anionic polymerization of hexamethylcyclotrisiloxane can yield extremely narrow molecular weight distributions which approach one.[21] Nevertheless, **V** formed by ring-opening polymerization of **IV** by dilithium diphenylsilanedioate has an $M_w/M_n$ greater than two. This would be expected, if the polymerization quenching reaction with trimethylchlorosilane/triethylamine of the reactive silanolate end groups is not stoichiometric. Subsequent hydrolysis would yield reactive Si−OH groups that could undergo condensation. Finally, step-growth hydrosilylation polymerizations are expected to have a molecular weight distribution of two. The reasons why $M_w/M_n$ is greater than two in the hydrosilylation polymerization of **IV** are not understood.

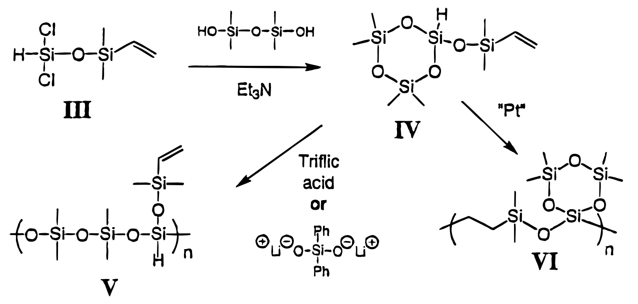


**Figure 2.** Synthesis and orthogonal polymerization of 1-hydrido-1-vinyldimethylsiloxy-3,3,5,5-tetramethylcyclotrisiloxane (**IV**).

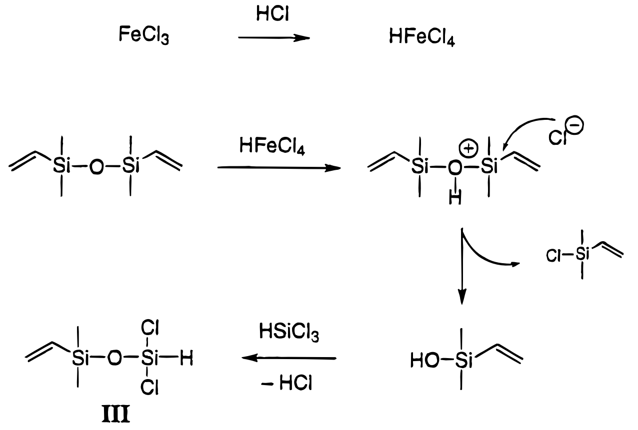


**Figure 3.** Proposed mechanism for the superacid-catalyzed equilibration of trichlorosilane and 1,3-divinyltetramethyldisiloxane.

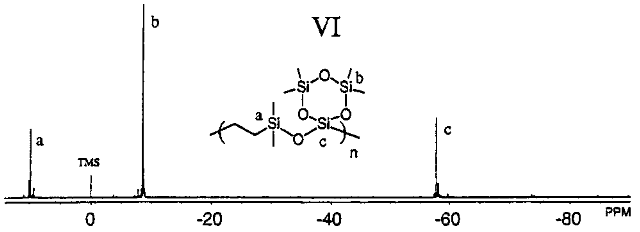
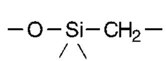


**Figure 4.** $^{29}$Si NMR of **VI**.

The structure of **VI** has been confirmed by $^{29}$Si NMR. Thus, three major resonances are observed: 9.80, −8.51, and −57.74 ppm. The first at 9.80 ppm is due to $(CH_3)_2$-Si units of the polymer backbone, while the resonance at −8.51 ppm is due to the two $(CH_3)_2SiO$ units of the cyclotrisiloxane ring, and finally the signal at −57.74 ppm is due to the



$-O-\underset{O\ \ O}{Si}-CH_2-$

unit of the cyclotrisiloxane ring (Figure 4).

While cyclotrisiloxanes are much more reactive than cyclotetrasiloxanes, both are known to undergo acid- or base-catalyzed ring-opening polymerization.[2] Thus, it is not surprising that **IV** undergoes both facile triflic acid-catalyzed ring-opening polymerization and base-catalyzed anionic ring-opening polymerization by dilithium diphenylsilanediolate to yield **V**. Neither acid- nor base-catalyzed ring-opening polymerization of **II** has been reported.

The structure of **V** produced by anionic ring-opening polymerization has been confirmed by $^{29}$Si NMR. The presence of a Si−H bond is confirmed by the signal at 2211 cm$^{-1}$ in the IR spectrum as well as by signals centered at 4.37 ppm in the $^1$H NMR (Figure 5). Three

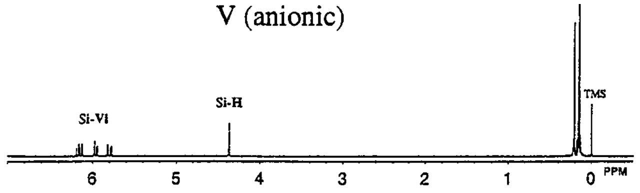


**Figure 5.** $^1$H NMR of **V** (anionic).

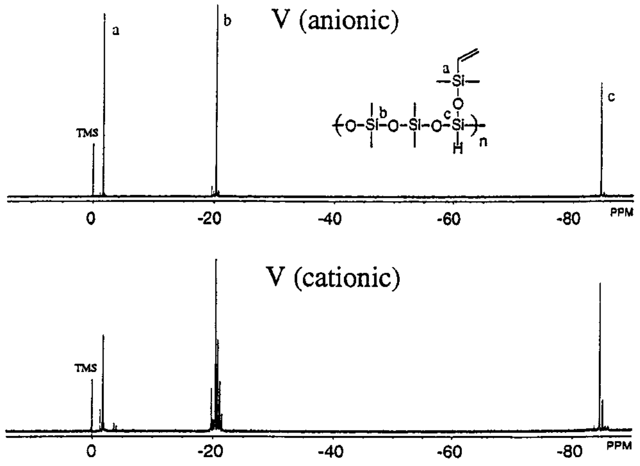
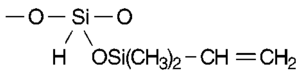


**Figure 6.** $^{29}$Si NMR of **V** (anionic and cationic).

sets of resonances are observed in the $^{29}$Si NMR. The peaks centered at −1.68 ppm are due to the vinyldimethylsiloxy (Vin−M) unit, while those centered at −20.3 ppm are due to dimethylsiloxy groups (D) in the polymer backbone. Finally, the resonances centered at −84.6 ppm are due to the units (T)



$$\underset{\mathrm{H}\qquad \mathrm{OSi(CH_3)_2{-}CH{=}CH_2}}{-\mathrm{O}-\mathrm{Si}-\mathrm{O}}$$

Differences in the $^{29}$Si NMR of **V** prepared by acid- and base-catalyzed ring-opening polymerizations are observed (Figure 6). These reflect differences in the polymer microstructure of **V**. The $^{29}$Si NMR of **V** produced by base-catalyzed ring opening is significantly simpler than that produced by triflic acid catalysis. These can be understood on the basis of a pentad analysis. The polymer is apparently formed chemoselectively by addition of the monomer **IV** to the active silanolate end of the polymer chain without equilibration.[22,23] This analysis is similar to that reported by Chojnowski and Boileau for the ring-opening polymerization of vinylpentamethylcyclotrisiloxane.[24]

**Pentad Analysis of Anionic Polymerization of IV.** A propagating silanolate anion attacks either the T silicon atom or one of the two D silicon atoms of the strained cyclotrisiloxane ring of **IV**. Attack on the Vin−M silicon atom of **IV** does not occur. Attack on T will lead to a TDD silanolate triad. Alternatively, attack on D can lead to to either a DTD or a DDT propagating silanolate anions depending on how the cyclotrisiloxane ring opens. Attack of the TDD silanolate triad on another molecule of **IV** can lead to TDDTDD, to TDDDTD, or to TDDDDT silanolates. Similarly, attack by the DTD propagating silanolate on another molecule of **IV** yields DTDTDD, DTDDTD, and DTDDDT propagating silanolates. Finally, the DDT silanolate can attack another molecule of **IV** to yield DDTTDD, DDTDTD, and DDTDDT propagating silanolates (Figure 7).

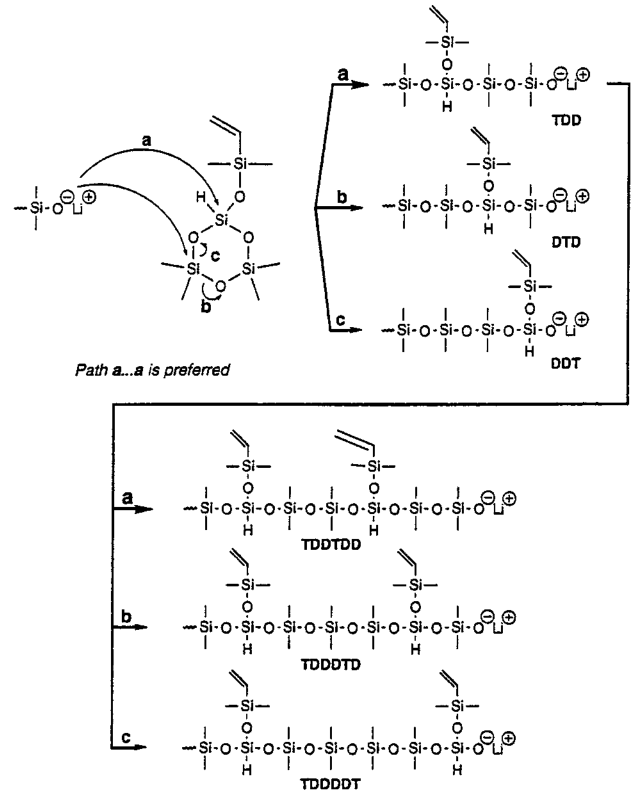


**Figure 7.** Pentads formed by preferential anionic ring opening of **IV**.

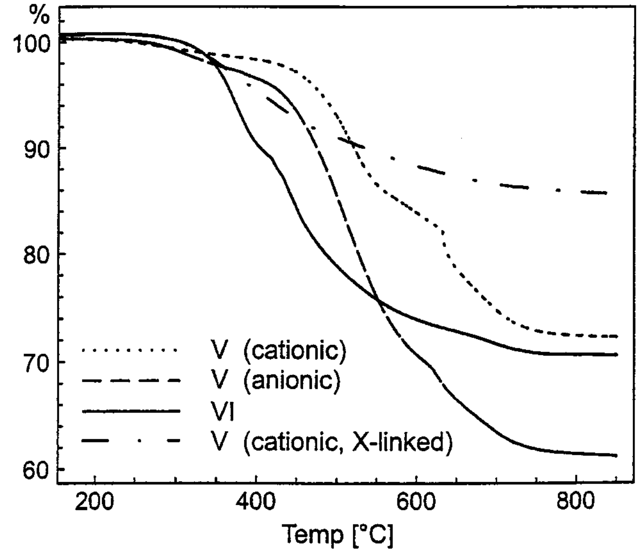


**Figure 8.** TGA of **V**, **VI**, and cross-linked **V**.

If scrambling does not occur, there are predicted to be four different T-centered pentads environments: DDTDD, TDTDD, DDTTD, and TDTDT. A similar analysis applied to the D units leads to the prediction of seven allowed D centered pentads: DTDTD, TTDDT, DTDDT, TTDDD, DTDDD, TDDDT, TDDDD. These are expected to have different $^{29}$Si NMR chemical shifts. In fact, only two $^{29}$Si NMR resonances due to a T unit are observed in **V** produced by base-catalyzed ring opening of **IV** in an intensity ratio of 86:14. Likewise, two resonances are observed in the $^1$H NMR for Si−H units in a ratio of 8:2. Four resonances due to D units and three resonances due to Vin−M units are observed. These resonances are not of equal intensity. The three following resonances—T (−84.65 ppm), D (−20.38 ppm), and VinM (−1.68 ppm)—dominate the $^{29}$Si NMR spectrum. We believe that this results from the significant preference (~90%) for silanolate attack on the T silyl centers of **IV** compared to the D silyl centers. Thus, TDD propagating silanolates are preferentially formed. While four T-centered pentads can be formed, DDTDD is preferred. The predominant VinM unit is bonded to the T of this pentad. Further, while seven D-centered pentads can be formed, the DTDDT pentad is formed preferentially. Silanolate attack on the silyl center of the T units may occur preferenially for steric reasons due to the small size of the Si−H.

Acid-catalyzed ring-opening polymerization of **IV** leads to **V**, which has a more complex microstructure. While only three resonances are observed for T units, 13 signals are detected for D units and nine are seen for VinM units in the $^{29}$Si NMR. This may be due to acid-catalyzed equilibration (scrambling) which leads to pentads in which two T units are adjacent. The presence of adjacent T units can lead to meso and D,L stereochemical environments. Clearly, acid-catalyzed ring-opening polymerization of the cyclotrisiloxane ring of **IV** is not regioselective.

Despite microstructure differences **V** produced by acid- or base-catalyzed polymerization, the polymers have similar properties as measured by DSC. Both have extremely low $T_g = -130$ °C for high molecular weight polymers and almost identical $T_m$ values (−62.5 and −65 °C). The $T_g$ of **V** is remarkable low. It is even lower than poly(dimethylsiloxane), which has been independently measured for calibration. The low $T_g$ of **V** may be due to the size difference between the Si−H and vinyldimethylsiloxy groups.

The glass transition temperature of polymers is related to the segmental motion of the polymer backbone. The backbone of **V** is a polysiloxane whereas that of **VI** is a copoly(carbosilane/siloxane). Thus, it is reasonable that the glass transition temperature of **V** is lower than that for **VI** (−66 °C).

Both **V** and **VI** are thermally stable to 300 °C. Between 300 and 600 °C, **VI** loses 25% of its initial sample weight. An additional 4% weight loss occurs by 800 °C. At 800 °C, a residue of 70% remains. **V**, produced by either acid- or base-catalyzed ring-opening polymerization, is thermally stable. Between 300 and 450 °C only a 5% weight loss is observed. Above 450 °C, rapid weight loss of 20−30% occurs. By 800 °C, 74% of the initial sample weight of **V** acid catalyzed remains, while 64% of initial weight of **V** base catalyzed is still present.

Both **V** and **VI** possess reactive functionality, which can be utilized to form multiple cross-links and thus insoluble materials. Triflic acid-catalyzed ring opening of the cyclotrisiloxane rings of **VI** results in extremely rapid cross-linking via formation of new siloxane bonds to yield a rubberlike material whose $T_g$ is −64 °C and $T_m$ −38 °C. On the other hand, the reactive Si−vinyl and Si−H bonds of **V** permit slower cross-linking by Karstedt-catalyzed hydrosilylation reactions. After curing in an oven at 100 °C for 30 min, it yields a brittle material whose $T_g$ is −68 °C. These cross-linked materials are thermally stable to 350 °C. Above this temperature, 15% of the initial sample weight is lost. The materials give ~85% yields of thermally stable residue.

## Conclusions

Orthogonal polymerization of **IV** has been achieved. Platinum-catalyzed step-growth hydrosilylation polymerization, involves the addition of the Si−H bond of a molecule of **IV** across the C−C double bond of another, leads to polymer **VI**. The high molecular weights achieved are the result of neutral character of the Karstedt catalyst. On the other hand, triflic acid- or base-catalyzed ring-opening polymerization of the strained cyclotrisiloxane ring of **IV** leads to polymer **V**. While Si−H bonds react with base in protic solvents, the Si−H bonds of **IV** and **V** are not affected by the basic catalyst, dilithium diphenylsilanediolate, in THF. Both polymers **V** and **VI** are potentially reactive and can be cross-linked. **VI** can be cross-linked by acid-catalyzed ring opening of its reactive cyclotrisiloxane rings, while **V** can be cross-linked by platinum-catalyzed hydrosilylation.

**Acknowledgment.** This work was supported in part by the National Science Foundation. Jyri K. Paulasaari thanks the Neste Foundation for fellowship support.

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MA990293K