Anionic Ring-Opening Polymerization of Trimethylsiloxy-Substituted 1-Oxa-2,5-disilacyclopentanes: Synthesis of Trimethylsiloxy-Substituted Poly[1-oxa-2,5-disila-1,5-pentanylene]s†

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ABSTRACT: 2,5,5-Trimethyl-2-trimethylsiloxy-1-oxa-2,5-disilacyclopentane (**I**), *cis*- and *trans*-2,5-dimethyl-2,5-bis(trimethylsiloxy)-1-oxa-2,5-disilacyclopentane (**II**), and 2-methyl-2,5,5-tris(trimethylsiloxy)-1-oxa-2,5-disilacyclopentane (**III**) have been prepared from 1,3,5,7-tetramethylcyclotetrasiloxane (D_4^H) and vinylpentamethyldisiloxane, vinylmethylbis(trimethylsiloxy)silane, and vinyltris(trimethylsiloxy)-silane, respectively, by a two-step synthetic process. **I**, **II**, and **III** undergo anionic ring-opening polymerization (AROP) to yield poly[2,2,5-trimethyl-5-trimethylsiloxy-1-oxa-2,5-disila-1,5-pentanylene] (**IV**), poly[2,5-dimethyl-2,5-bis(trimethylsiloxy)-1-oxa-2,5-disila-1,5-pentanylene] (**V**), and poly[2-methyl-2,5,5-tris(trimethylsiloxy)-1-oxa-2,5-disila-1,5-pentanylene] (**VI**), respectively. **I**−**VI** have been characterized by ^{1}H, ^{13}C, and ^{29}Si NMR and IR spectroscopy. Polymer microstructures have been determined by ^{29}Si NMR. Molecular weights of **I**−**III** have been determined by GC/MS and by high-resolution mass spectrometry. Molecular weight distributions of **IV**−**VI** have been determined by GPC. M_n's have been independently determined by ^{1}H NMR analysis. The glass transition temperatures (T_g's) and thermal stability of these polymers have been determined by DSC and TGA, respectively. Chain transfer apparently limits the molecular weight of **VI**.

Introduction

There is interest in the synthesis of cyclosilaalkylenesiloxanes and in the cationic ring-opening polymerization of these to yield poly(silaalkylenesiloxane)s.[1] AROP of 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane has been reported,[2−5] and the kinetics of this process has been studied.[6] 2,2,5,5-Tetramethyl-1-oxa-2,5-disilacyclopentane has been used to prepare well-defined poly(α-methylstyrene)-*b*-poly(dimethylsiloxane) block copolymers by living anionic polymerization.[7] Polymerization of 2-(3′,3′,3′-trifluoropropyl)-2,5,5-trimethyl-1-oxa-2,5-disilacyclopentane and related systems gives elastomeric materials with excellent chemical resistance, electrical properties, and strength.[8,9] Bis(1-oxa-2,5-disilacyclopentane)s undergo AROP to yield nonshrinking polycarbosilane/siloxanes.[10,11] Despite this interest in 1-oxa-2,5-disilacyclopentanes and in AROP, no examples of polymerization of trimethylsiloxy (TMSO)-substituted 1-oxa-2,5-disilacyclopentanes have been reported.

Results

Herein, we report the preparation of **I**, **II**, and **III** by a two-step synthesis (Figure 1). Pt-catalyzed hydrosilylation of vinylpentamethyldisiloxane, vinylmethylbis(trimethylsiloxy)silane, or vinyltris(trimethylsiloxy)-silane with D_4^H yields the expected tetra-adducts. Alkaline pyrolysis of these tetra-adducts results in rearrangement and redistribution to yield **I**, **II**, and **III**. This sequence is modeled after one used by Frye to prepare 2-chloro-2,5,5-trimethyl-1-oxa-2,5-disilacyclopentane.[12,13]

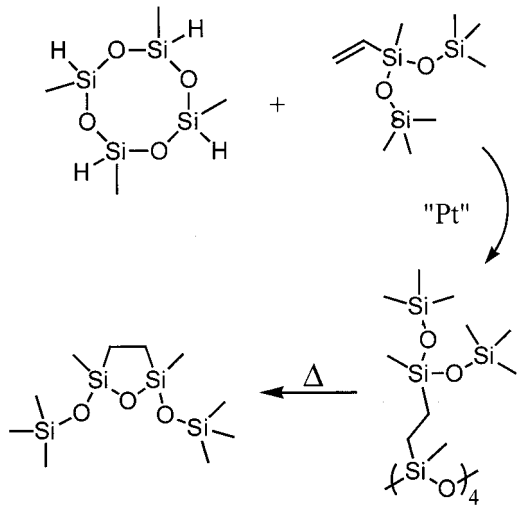

Figure 1. Synthesis of **II**.

AROP of **I**, **II**, or **III** in THF, catalyzed by dilithiodiphenylsilanediolate,[14] yields **IV**, **V**, or **VI**, respectively (Figure 2). The high reactivity of **I**, **II**, and **III** is the result of angle strain. Thus, the Si−O−Si bond angle of 1-oxa-2,5-disilacyclopentanes is appreciably less than of open chain disiloxanes, which are usually greater than 120°.[15]

Experimental Section

^{1}H, ^{13}C, and ^{29}Si NMR spectra were obtained on a Bruker AMX-500 MHz spectrometer. Five percent w/v $CDCl_3$ solutions were used to obtain ^{1}H NMR spectra. ^{13}C and ^{29}Si NMR spectra of 30% w/v $CDCl_3$ solutions were acquired. ^{13}C NMR spectra were obtained with broad-band proton decoupling. ^{1}H and ^{13}C NMR spectra were internally referenced to residual $CHCl_3$. A heteronuclear gated decoupling pulse sequence (NONOE) with

† This paper is dedicated to Dr. Cecil Frye.

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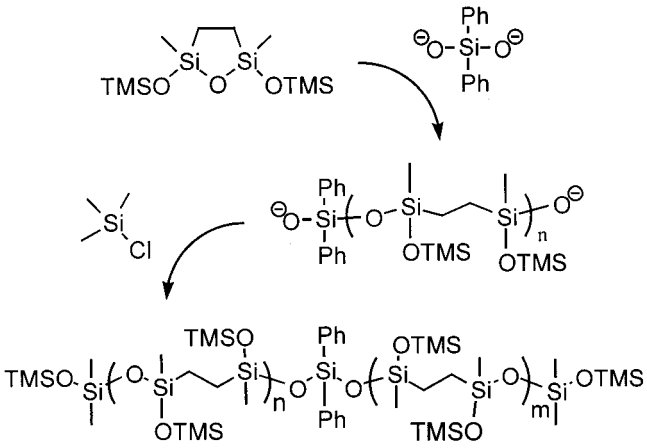

Figure 2. AROP of **II**.

a 60 s delay was used to acquire ^{29}Si NMR spectra. These were referenced to internal TMS. IR spectra of neat liquid films on NaCl plates were recorded on a Perkin-Elmer Spectrum 2000 FT-IR 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.

Thermogravimetric analysis (TGA) of **IV**, **V**, and **VI** was carried out on a Shimadzu TGA-50 instrument with a flow rate of 40 cm^3 of nitrogen or air per minute. The temperature was increased at 5 °C/min from 25 to 800 °C. The glass transition temperatures (T_g's) of **IV**, **V**, and **VI** were determined by DSC on a Perkin-Elmer DSC-7. The DSC instrument was calibrated against the heat of transition (−87.06 °C) and the melting point of cyclohexane (6.54 °C)[16] as well as from the T_g of poly(dimethylsiloxane) (−124 °C).[17] The temperature program for the analysis was begun at −150 °C and was increased at 10 °C/min to 50 °C.

Hexamethyldisiloxane, vinylpentamethyldisiloxane, vinylmethylbis(trimethylsiloxy)silane, vinyltris(trimethylsiloxy)silane, diphenylsilanediol, trimethylchlorosilane (TMS−Cl), D_4^H, and Karstedt catalyst (2% w/w in xylene) were obtained from Gelest. *n*-Butyllithium (2.0 M solution in pentanes), diethyl ether, THF, styrene, potassium hydroxide, and triethylamine (Et_3N) were purchased from Aldrich. Diethyl ether and THF were purified by distillation from sodium benzophenone ketyl immediately before use. All the other reagents were used as obtained.

High-resolution mass spectra were run at the University of California, Riverside, Mass Spectroscopy Facility on a VG-7070 EHF instrument. Exact masses of **I**−**III** were determined by peak matching against known masses of perfluorokerosene. A 70 eV beam of electrons was used to achieve electron impact ionization. Alternatively, ammonia was employed as the chemical ionization agent. Low-resolution mass spectra were obtained by GC/MS on a Hewlett-Packard 5890 series II GC equipped with a Hewlett-Packard 5971 series mass selective detector.

Elemental analysis of **IV**−**VI** was performed by Oneida Research Services Inc., Whitesboro, NY.

Reactions were conducted in flame-dried glassware under argon. Teflon-covered magnetic stir bars were used to stir the reactions.

2,5,5-Trimethyl-2-trimethylsiloxy-1-oxa-2,5-disilacyclopentane (I). Vinylpentamethyldisiloxane (20 g, 115 mmol) and Karstedt catalyst (200 μL) were placed in a 100 mL three-neck round-bottom flask equipped with a pressure equalizing addition funnel and a reflux condenser. D_4^H (6.8 g, 28 mmol) was placed in the addition funnel and was added dropwise over 1 h with refluxing to form the expected tetra-adduct. The solution was stirred for 2 h. *n*-Butyllithium (300 μL of 2.0 M hexane solution) was added. The reaction mixture was heated at 320−400 °C. Under these conditions, cracking occurred. Volatile material (20.3 g) was distilled from the system and was fractionally redistilled through a 15 cm vacuum jacketed Vigreux column. A fraction, bp 156−160 °C/760 mm, 14 g, 52% yield, was obtained. ^{1}H NMR δ: 0.10 (s, 9H), 0.13 (s, 3H), 0.14 (s, 3H), 0.20 (s, 3H), 0.56−0.65 (m, 1H), 0.70−0.80 (m, 3H). ^{13}C NMR δ: −0.63, 0.23, 0.39, 1.76, 8.68, 8.94. ^{29}Si NMR δ: −5.80 (1Si), 8.46 (1Si), 22.55 (1Si). IR ν: 2960, 2931, 2897, 2798, 1417, 1254 (Si−CH_3), 1216, 1078 (Si−O), 1060 (Si−O), 931 (strained Si−O−Si), 867, 842, 794, 770 cm^{-1}. High-resolution MS: Calcd for $C_8H_{22}O_2Si_3$ ($M^{\bullet+}$): 234.0928. Found: *m*/*z*: 234.0933. Low-resolution GC/MS *m*/*z* (relative intensity): 234 (5%) $M^{\bullet+}$, 219 (75%) $(M - 15)^+$, 205 (45%) $(M - 29)^+$, 191 (100%).

***cis*- and *trans*-2,5-Dimethyl-2,5-bis(trimethylsiloxy)-1-oxa-2,5-disilacyclopentane (II).** The Pt-catalyzed reaction of vinylmethylbis(trimethylsiloxy)silane (32 g, 0.13 mol) and D_4^H (7.6 g, 30 mmol) was carried out as above to give the expected tetra-adducts. These were not characterized but immediately subjected to pyrolysis at 360 °C in the presence of a trace of *n*-butyllithium. A 1:1 mixture of *cis*- and *trans*-**II** distilled from the flask. **II** was purified by fractional distillation through a 15 cm vacuum jacketed Vigreux column. **II**, bp 120 °C, 14 g, 45 mmol, ∼37% yield was obtained. ^{1}H NMR δ: 0.08 (s, 18H), 0.10 (s, 18H), 0.11 (s, 6H), 0.17 (s, 6H), 0.56−0.76 (br. m, 8H). ^{13}C NMR δ: −0.70, 1.70, 1.74, 8.83. ^{29}Si NMR δ: −8.25, −7.52, 8.56, 8.83. IR ν: 2960, 2899, 1416, 12150, 1218, 1063, 939, 843, 791, 770, 755 cm^{-1}. High-resolution MS: Calcd for $C_{10}H_{29}O_3Si_4$ $(M + 1)^+$: 309.1116. Found: 309.1194. GC/MS *m*/*e* (relative intensity): 293 (100%) $(M - 15)^+$, 279 (62%) $(M - 29)^+$, 265 (61%), 207 (47%).

2-Methyl-2,5,5-tris(trimethylsiloxy)-1-oxa-2,5-disilacyclopentane (III). The Pt-catalyzed reaction of vinyltris(trimethylsilyloxy)silane (20 g, 62 mmol) and D_4^H (3.75 g, 15 mmol) was carried out as above to give the expected tetra-adducts. ^{1}H NMR δ: 0.80−0.65 (br m, 4H), 0.16 (s, 3H), 0.13 (s, 9H), 0.111 (s, 9 H), 0.109 (s, 9H). ^{13}C NMR δ: 9.77, 5.84, 1.75, 1.65, −0.65, −0.67. ^{29}Si NMR δ: −52.13, −11.21, 8.92, 9.19, 9.54. IR ν: 2921, 2959, 2900, 1454, 1440, 1408, 1260, 1251, 1142, 1255, 909, 865, 841, 806, 795, 756, 707, 687, 666, 635, 593 cm^{-1}.

These were subjected to pyrolysis at 320−360 °C in the presence of a trace (0.3 mL) of *n*-butyllithium. Crude **III**, 15.5 g (60% purity), was distilled from the flask. **III** was purified by fractional distillation through a 15 cm vacuum jacketed Vigreux column. A fraction, bp 75−78 °C, 3.5 g (∼100% purity), 9.2 mmol, was obtained. ^{1}H NMR δ: 0.11 (s, 18H), 0.13 (s, 9H), 0.16 (s, 3H), 0.64−0.81 (br. m, 4H). ^{13}C NMR δ: −0.49, −0.47, 1.47, 1.67, 5.66, 9.59. ^{29}Si NMR δ: −52.13, −11.21, 8.92, 9.19, 9.54. IR ν: 2960, 2899, 1416, 1250, 1218, 1063, 939, 843, 791, 770, 755 cm^{-1}. High-resolution MS: Calcd for $C_{12}H_{35}O_4Si_5$ $(M + 1)^+$: 383.1303. Found: 383.1380. GC/MS *m*/*e* (rel intensity): 367 (100%) $(M - 15)^+$, 353 (52%) $(M - 29)^+$, 279 (85%), 265 (31%), 207 (29%), and 73 (66%).

Poly[2,2,5-trimethyl-5-trimethylsiloxy-1-oxa-2,5-disila-1,5-pentanylene] (IV). **I** (1.0 g, 4.27 mmol) was placed in a 10 mL round-bottom flask that was sealed with a rubber septum. THF (2.0 mL) and 20 μL of a THF solution of dilithiodiphenylsilanediolate initiator (0.308 mol/L) (6.16 μmol) were added. The polymerization proceed for 2.0 h at 0 °C. During this time, the solution became noticeably more viscous. At this time, TMS−Cl (7 μL) and Et_3N (7 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, 0.99 g, 99% yield of **IV**, M_w/M_n = 82 730/51 730 and T_g = −89 °C was obtained. **IV** had the following spectral properties. ^{1}H NMR δ: 0.004 (s, 1.5H), 0.026 (s, 1.5H), 0.031 (s, 3H), 0.057 (s, 3H), 0.086 (s, 5.5H), 0.089 (s, 4.5H), 0.315−0.487 (m, 4H), ^{13}C NMR δ: −1.19, −1.11, −0.48, −0.46, −0.34, 1.92, 9.00, 9.01, 9.57, 9.63. ^{29}Si NMR δ: −21.79, −21.73, −21.69, −21.64, −21.07, −21.00, 6.68, 6.79, 8.00, 8.01, 8.18, 8.19, 8.20 (Figure 3). IR ν:

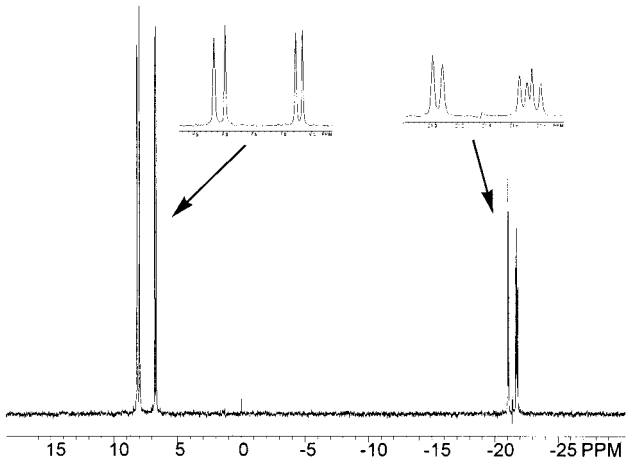

Figure 3. ^{29}Si NMR of **IV**.

2958, 2912, 2882, 2789, 1408, 1253 (Si−CH_3), 1136, 1048 (Si−O−Si), 873, 840, 778 cm^{-1}. Elemental Anal. Calcd for $C_8H_{22}O_2Si_3$: C, 40.97; H, 9.46. Found: C, 40.55; H, 9.63.

A similar polymerization was carried out at room temperature for 2 h. A 98.7% yield of **IV** was obtained, M_w/M_n = 124 100/51 360, T_g = −89 °C. It had identical spectral properties to that prepared above.

Poly[2,5-dimethyl-2,5-bis(trimethylsiloxy)-1-oxa-2,5-disila-1,5-pentanylene] (V). A 1:1 mixture of *cis*- and *trans*-**II**, 1.6 g (5.19 mmol), and 1 mL of THF was placed in a 10 mL round-bottom flask. Dilithiodiphenylsilanediolate in THF (20 μL) (6.16 μmol) was added at room temperature. The reaction was stirred for 4 h, during which time the solution became viscous. The reaction was quenched by the sequential addition of TMS−Cl and Et_3N. **V** was precipitated into methanol. The precipitate was dissolved in a minimum amount of THF and reprecipitated into methanol. In this way, 1 g, 63% yield of **V**, M_w/M_n = 30 700/17 300, T_g = −85 °C was obtained. ^{1}H NMR δ: 0.02 (br s, 6H), 0.09 (br s, 18 H), 0.40 (br s, 4H). ^{13}C NMR δ: −1.21, 1.94, 8.94. ^{29}Si NMR δ: −21.84, −21.65, 6.74, 6.78. IR ν: 2959, 2916, 2792, 1406, 1254, 1137, 1045, 841, 788, 754 cm^{-1}. Elemental Anal. Calcd for $C_{10}H_{28}O_3Si_4$: C, 38.37; H, 9.14. Found: C, 38.37; H, 8.98.

Poly[2-methyl-2,5,5-tris(trimethylsiloxy)-1-oxa-2,5-disila-1,5-pentanylene] (VI). **III**, 1 g (2.62 mmol), and THF (100 μL) were placed in a 10 mL round-bottom flask what was sealed with a rubber septum. Dilithiodiphenylsilanediolate in THF (20 μL, 0.30 M) was added at room temperature. After 1.5 h, the viscous reaction was quenched by sequential addition of 5 μL of TMS−Cl and 5 μL of Et_3N. The reaction mixture was dissolved in a minimum amount of diethyl ether and was precipitated with methanol three times. In this way 0.8 g, 80% yield, of **VI**, M_w/M_n = 6120/4990 and T_g = −96 °C, was obtained. ^{1}H NMR δ: 0.51−0.38 (br m, 4H), 0.10 (s, 18H), 0.09 (s, 9H), 0.03 (s, 3H). ^{13}C NMR δ: 9.26, 5.90, 1.97, 1.87, −1.35. ^{29}Si NMR δ: 7. 08, 7.02, 6.78, −22.06, -65.76. Additional small peaks were observed in the ^{29}Si NMR at δ: 7.24, 6.85, −20.83, -21.73, −55.00 (see Figure 4). IR ν: 2960, 2918, 2900, 2799, 1451, 1439, 1408, 1252, 1143, 1048 (br s), 945, 863, 840, 789, 756 cm^{-1}. Elemental Anal. Calcd for $C_{12}H_{34}O_4Si_5$: C, 37.65; H, 8.95. Found: C, 37.43; H, 8.65.

Discussion

AROP of **I**, **II**, and **III**, catalyzed by dilithiodiphenylsilanediolate, were carried out at room temperature. These conditions have been previously found to be successful for the AROP of 1,1-bis(trimethylsiloxy)-tetramethylcyclotrisiloxane.[16] The progress of the polymerizations were qualitatively monitored by an increase in the viscosity of the reaction solutions. A very high yield (99%) of high molecular weight **IV** is obtained

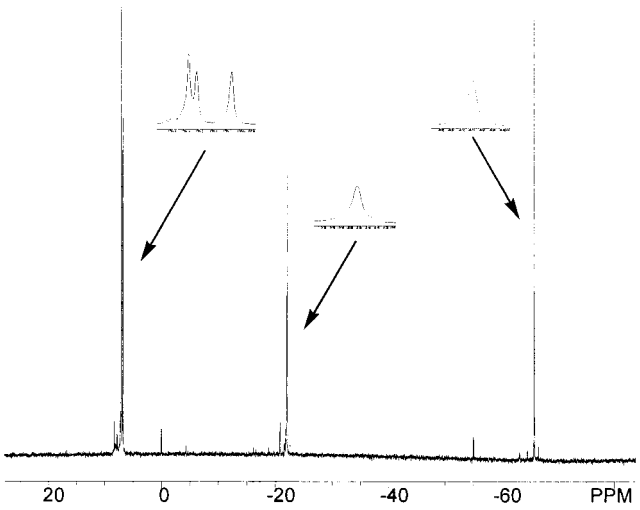

Figure 4. ^{29}Si NMR of **VI**.

in the AROP of **I**. Apparently, neither redistribution nor cyclization processes are important in this case.

Comparison of M_w/M_n Determined by GPC and M_n by End Group Analysis. Molecular weight distributions (M_w/M_n) have been determined by GPC. These were calibrated by comparison to narrow molecular weight distribution polystyrene standards. M_n has been independently determined by comparison of the ^{1}H NMR integration intensities of the signals due to Si−methyl groups, methylene groups, and diphenylsilanediolate initiator. Thus, high gain ^{1}H NMR of the aromatic region shows, in addition to the peak due to residual $CHCl_3$ in the $CDCl_3$ solvent, signals due to the diphenylsilanediolate initiator. For **I**, setting the value of the integration of the signals due to the initiator to 10H, the integration of the methylene protons gives a value of ∼1907H while the Si−methyl protons have an intensity equal to ∼7800H. The observed intensity ratio of the Si−methyl to methylene signals 4.1:1 is in close agreement with the expected value of 4.5:1 based on the structure of **I**. Comparison of the integration of the signal due to the diphenylsilanediolate initiator 10H to the methylene signals 1907H is consistent with a polymer whose degree of polymerization (DP) is ∼477. Similar comparison of the initiator signal to the Si−methyl signals is consistent with a polymer whose DP is ∼431. Using an average of these values, M_n is calculated to be 454 × 234 g/mol (molecular weight of **I**) or 106 000 g/mol. The value for M_n by GPC is 51 000.

If we assume the following in the AROP of **I**—initiation is fast, chain transfer does not occur, and termination does not happen prior to addition of TMS−Cl/Et_3N—then the DP can be calculated from the molar ratio of **I**/initiator. On this basis, the DP should be 693. Clearly, the molecular weight of **IV** is lower than predicted.

A similar analysis of the ^{1}H NMR of **V** has been carried out. The intensity of the signals due to the diphenylsilanediolate initiator has been set to 10H. This value has been used to calibrate the ^{1}H NMR integration intensity of the signals in the Si−methyl region. These are consistent with the presence of ∼3900H. Since each molecule of **II** has 24 Si−methyl hydrogens, the degree of polymerization of **V** based on this ^{1}H NMR analysis is ∼160. Since there are four methylene hydrogens in each monomer unit, a polymer with a DP of ∼160 should give an integration value for the

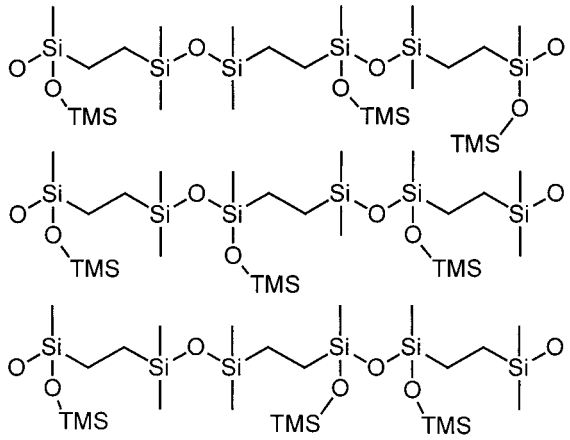

Figure 5. Analysis of microstructure of **IV**.

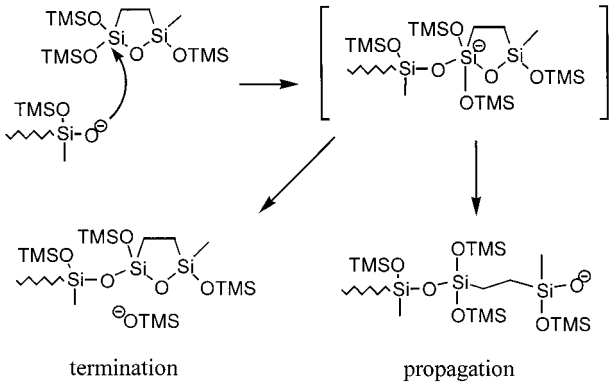

Figure 6. Competition between termination/chain transfer and propagation.

methylene groups of 640H. This is in close agreement with the observed value of 660H. On the basis of this analysis and the molecular weight of **II**, M_n is calculated to be 160 × 308 g/mol or ~49 300 g/mol. On the other hand, M_n by GPC is ~17 000. The DP predicted from the ratio of **II**/initiator is 840.

The AROP of **III** was quenched with TMS−Cl/Et_3N. The intensities due to Si−methyl and methylene signals were calibrated based on the intensity of the initiator signals (10H). Comparison of the integration of the signals due to the Si−methyl groups ~3750H to those due to the methylene groups ~515H gives a ratio of ~7.3:1, in reasonable agreement with the expected value of 7.5:1. The intensity of the Si−methyl signals is consistent with the presence of 125 monomer units in each polymer. The intensity of the signals due to the methylene groups is consistent with ~129 monomer units in each polymer. On this basis, we calculate that the polymer molecular weight M_n is 125 × (382 g/mol) = 47 750 g/mol. On the other hand, M_n observed by GPC is only ~5000 g/mol. The DP calculated based on the molar ratio of **III**/initiator is ~435. The reasons for these large discrepancies between M_n by GPC and ^{1}H NMR analysis are not understood.

By comparison with **IV** and **V**, the molecular weight of **VI**, based on GPC, is quite low and its distribution (M_w/M_n = 1.2) is quite narrow. By comparison, the minimum molecular weight distributions of **IV** and **V** are 1.6 and 1.8, respectively. In fact, **VI** might be considered an oligomer rather than a polymer. This may be due to chain transfer. Reactive hypervalent pentacoordinated siliconate species are key intermediates in the AROP of **I**, **II**, and **III**. These are formed by nucleophilic attack of a silanolate one of the silyl centers of the 1-oxa-2,5-disilacyclopentanes. Chain propagation occurs when heterolytic bond scission of the Si−O bond of the strained 1-oxa-2,5-disilacyclopentane siliconate occurs to yield a new reactive silanolate. On the other hand, chain transfer occurs if the hypervalent pentacoordinate siliconate species loses a trimethylsilanolate group. This results in termination and chain transfer if the trimethylsilanolate lost initiates growth of a new polymer chain growth (Figure 6).

A resonance (−55 ppm) consistent with terminal 1-oxa-2,5-silacyclopentanyl end groups is observed in the ^{29}Si NMR spectrum of **VI**; no extra signals are detected in the ^{29}Si NMR of **IV** or **V**. This may be due to the fact that the molecular weights of **IV** and **V** are significantly higher than that of **VI**. AROP of 1,1-bis(trimethylsiloxy)-3,3,5,5-tetramethylcyclotrisiloxane also yields low molecular weight polymer, which has also been attributed to chain transfer. Apparently, two trimethylsiloxy groups substituted on a silyl center facilitate chain transfer.[16]

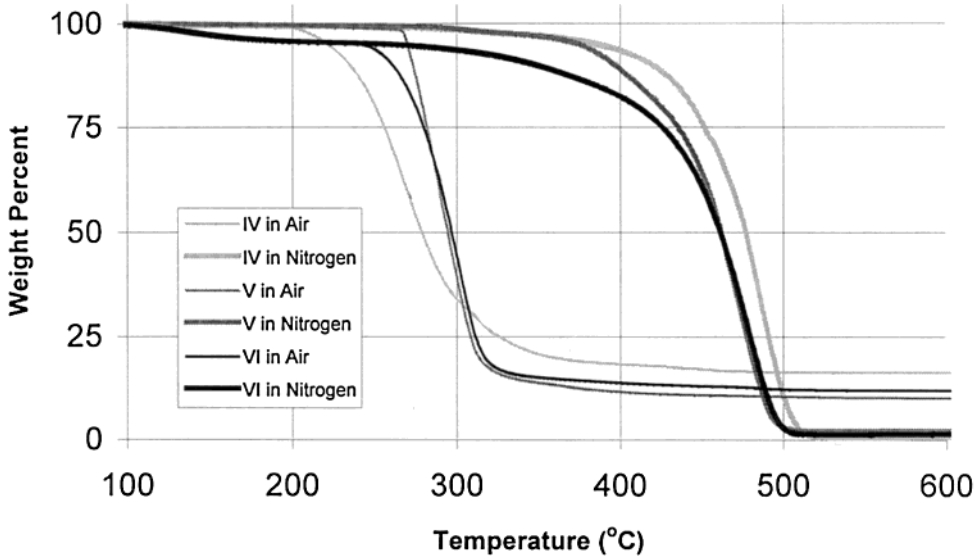

Figure 7. Thermal stability of **IV**, **V**, and **VI** in air and nitrogen.

^{1}H NMR analysis of **IV**, **V**, and **VI** consistently yields higher values of M_n than those obtained by GPC. This may be due to the fact that the hydrodynamic volume of branched polymers is smaller than that of similar linear materials. In this regard, the pendant trimethylsiloxy substituents of **IV**, **V**, and **VI** may function as branching groups.

Determination of the Polymer Microstructures. We expected that AROP of **I** would lead to **IV** with a regular microstructure. This hypothesis was based on the assumption that nucleophilic attack by the silanolate would occur preferentially on the TMSO-substituted silicon. This silyl center is substituted by two electronegative oxygen atoms. This electronic inductive effect makes this silicon more positive and thus more susceptible to nucleophilic attack than the other silicon atom that is only substituted by one oxygen. Similarly, AROP of 1,1-bis(trimethylsiloxy)tetramethylcyclotrisiloxane leads to poly[1,1-bis(trimethylsilyloxy)-3,3,5,5-tetramethyltrisiloxane] with a completely regular microstructure.[16] If such a regioselective AROP of **I** had occurred, **IV** would be predicted to have three ^{29}Si NMR resonances and six ^{13}C NMR. The two methyl groups in $(CH_3)_2$Si units are diastereotopic. In fact, 10 ^{13}C signals and 12 ^{29}Si NMR resonances (Figure 5) are observed. These can be accounted for if AROP of **I** is not regioselective. Apparently, nucleophilic attack occurs on both of the silyl centers of **I** with almost equal facility. This leads to head-to-head, head-to-tail, and tail-to-tail units (Figure 5). Four of the ^{29}Si signals are due to $-(CH_3)_2$SiO$-$ (A) units, six to $-CH_3$Si(OTMS)O$-$ (B) units, and two to the pendant OTMS groups. The silicon atom of B units is a center of chirality. On the basis of a triad analysis, there are two types of B units (ABA or BBA) to which the TMSO groups can be bonded. Pentad analysis predicts four A-centered units (AB**A**BA, BA**A**BA, BA**A**BB, BB**A**BA). Finally, pentad analysis predicts four types of B-centered units (BA**B**AB, BA**B**BA, AA**B**AB, AA**B**BA). The chiral silyl centers of pentads BA**B**BA and AA**B**BA interact with one another. This results in two resonances for each pentad due to existence of both RR,SS and RS,SR diastereoisomers. Thus, six resonances result from B units. This analysis predicts 12 ^{29}Si resonances, as is observed. Similar analysis predicts 10 ^{13}C signals. In fact, 10 are detected. The lack of regiospecificity in AROP of **I** may be due to its increased reactivity compared to cyclotrisiloxanes.

The ^{1}H and ^{13}C NMR spectra of **V** are quite simple. On the other hand, the ^{29}Si NMR spectra are more complex. A total of four resonances are observed. Two of these at 6.74 and 6.78 ppm are due to the TMSO groups. The other two at -21.84 and -21.65 ppm are due to the chiral silyl centers $-CH_3$**Si**(OTMS)O$-$. Two adjacent chiral silyl centers interact to form a pair of diastereoisomers RR,SS and RS,SR. Apparently, this diastereoisomeric relationship also affects the TMSO silyl centers.

The ^{1}H, ^{13}C, and ^{29}Si NMR of **VI** are very simple and consistent with a highly regular microstructure: $-[CH_3[(CH_3)_3SiO]Si-CH_2CH_2-Si(OSi(CH_3)_3)_2]-O]_n-$. In the ^{1}H NMR spectrum, the singlet at 0.10 ppm (18H) is due to the two equivalent TMSO groups of the $[(CH_3)_3SiO]_2$Si units. The singlet at 0.09 ppm (9H) is due to the TMSO group of the $CH_3[(CH_3)_3SiO]Si-$ units, and the singlet at 0.03 ppm is due to the Si$-$methyl group of the $CH_3[(CH_3)_3SiO]Si-$ units. In the ^{13}C NMR, five resonances are observed. Those at 9.26 and 5.90 ppm are due to the nonequivalent methylene groups, while the two resonances at 1.97 and 1.87 ppm are due to the TMSO groups. The signal at -1.35 ppm can be assigned to the Si$-$methyl group. Five resonances are observed in the ^{29}Si NMR rather than the four which might be expected. This is apparently due to the fact that the silyl center of the $CH_3[(CH_3)_3SiO]Si-$ unit is chiral. This causes the TMSO groups of the $Si(OSi(CH_3)_3)_2-$ unit to be diastereotopic (Figure 4).

Thermal Stability of Polymers. IV is quite thermally stable as measured by TGA. In nitrogen, it does not decompose until 315 °C. Above this temperature, it undergoes catastrophic decomposition. By 515 °C, virtually no residue remains. On the other hand, in air, decomposition begins at 190 °C. By 350 °C only 20% of the initial sample weight remains. Above this temperature, a 5% weight loss occurs. On heating to 800 °C, a residue amounting to ~15% of the initial sample weight remains.

V is also quite thermally stable. In nitrogen, **V** does not begin to decompose until ~290 °C. Above this temperature, it undergoes catastrophic decomposition. By 500 °C, none of the starting polymer sample remains. Surprisingly, unlike **IV**, **V** is almost as thermally stable in air as it is in nitrogen. It does not begin to decompose until 265 °C. Above this temperature, the polymer undergoes rapid decomposition. By 320 °C, only ~12% of the initial polymer sample weight remains. No further loss of weight occurs on heating the sample to 800 °C.

The thermal decomposition of **VI** is similar to that of **V**. In nitrogen, **VI** is thermally stable to 300 °C. Above this temperature, catastrophic decomposition occurs. By 500 °C, only a few percent of residue remains. In air, **VI** is thermally stable to 250 °C. Above this temperature, **VI** undergoes rapid catastrophic decomposition. By 300 °C, 95% of the initial sample weight has been lost. Between 300 and 800 °C a few percent additional weight loss is observed. Given the low molecular weight of **VI**, its relatively high thermal stability is unexpected (Figure 7).

***T*$_g$'s of Polymers.** Both **IV** and **V** have similar T_g's, -89 and -85 °C, respectively. The T_g of **VI**, on the other hand, is lower at -96 °C. This may reflect the low molecular weight of **VI**.

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