

Anionic and Cationic Ring-Opening Polymerization of 2,2,4,4,6,6-Hexamethyl-8,8-divinylcyclotetrasiloxane

Conan J. Teng and William P. Weber*

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

Guoping Cai

Department of Polymer Science and Engineering, Zhejiang University, Hangzhou, ZJ 310028, P. R. China

Received March 7, 2003; Revised Manuscript Received May 15, 2003

ABSTRACT: Ring-opening polymerization (ROP) of 2,2,4,4,6,6-hexamethyl-8,8-divinylcyclotetrasiloxane (**I**) initiated by both 1-*tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)phosphoran-ylidenamino]-2,4,5-catenadi(phosphazene) (C₂₂H₆₃N₁₃P₄, P₄-*t*-Bu superbase) and trifluoromethanesulfonic acid (CF₃SO₃H, triflic acid) has been studied. Both reactions lead to mixtures of linear copolymer, low molecular weight co-oligomers and monomeric cyclosiloxanes. The composition, molecular weight distribution, microstructure, and thermal properties of the copolymers have been determined. The copolymer microstructure has been determined by ²⁹Si NMR spectroscopy. Monomeric cyclosiloxanes have been identified by GC/MS. Both copolymer microstructure and cyclosiloxanes formed depend on the particular catalyst system utilized. P₄-*t*-Bu superbase-initiated anionic ROP of **I** leads to a copolymer with a random microstructure and to a series of monomeric cyclotetra-, cyclopenta-, and cyclohexasiloxanes formed by random combination of dimethylsiloxane (D) and divinylsiloxane (V) units. On the other hand, triflic acid-initiated ROP of **I** occurs in a chemoselective manner. This leads to a copolymer with a more ordered microstructure. In this case, **I** is the only monomeric cyclosiloxane found.

Introduction

Polysiloxanes are important inorganic/organic materials. Poly(dimethylsiloxane) (PDMS) is commercially the most significant siloxane material. However, for some applications the properties of PDMS are short of those required. As a result, copolymers comprised of dimethylsiloxane and other siloxane units, e.g., vinylmethylsiloxane, divinylsiloxane, phenylmethylsiloxane, diphenylsiloxane, methylhydrosiloxane, and methyl-3,3,3-trifluoropropylsiloxane have been prepared to achieve the properties desired.^{1,2} The properties of copolymers depend on both the molar ratio and sequence of the monomer units. Alternating, block and random copolymers prepared from the same monomers can have distinct properties.²¹

We have been interested in the preparation, properties, and chemical modification of copolysiloxanes that have uniform distribution of the two different siloxane units along the copolymer chain, i.e., a regular microstructure. Kinetically controlled living anionic ROP of substituted cyclotrisiloxane has been shown, in favorable cases, to yield narrow molecular weight distribution copolymers with regular microstructures.^{3–5} To achieve such control, anionic ROP must occur regioselectively. This results when the propagating silanolate anion attacks a specific silyl center of the substituted cyclotrisiloxane. Subsequent ring opening must also occur in a specific manner. Finally, equilibration by redistribution and/or backbiting must be slow relative to chain propagation.

The requirement for chemoselective ROP of a cyclotrisiloxane is that all of the silyl units of the monomer be added to the growing polymer chain without scram-

bling. If one of the silyl centers of a cyclotrisiloxane is substituted, chemoselective ring opening can lead to three propagating triads.⁶

Since anionic ROP can be living, selective functionalization at one end of the copolymer chain can be achieved by use of a functionally substituted initiator or by quenching the reactive silanolate end group with suitable functionalized chlorosilane. In this way, narrow molecular weight distribution α,ω -functionalized copolysiloxanes can be prepared. We have previously reported the preparation of copoly(dimethylsiloxane/divinylsiloxane) (2:1 mole ratio) with a highly regular microstructure by low-temperature anionic ROP of 2,2,4,4-tetramethyl-6,6-divinylcyclotrisiloxane, initiated by dithiodiphenylsilanediolate in THF.⁷ This reaction occurs regiospecifically to yield regular poly(2,2,4,4-tetramethyl-6,6-divinyltrisiloxane). Despite this degree of control over copolymer microstructure, a narrow molecular weight distribution was not observed. By comparison, cationic ROP of this monomer occurs in a chemoselective manner.⁸

In this paper, we report the properties and microstructure of the copolysiloxanes produced by both cationic and anionic initiated ROP of 2,2,4,4,6,6-hexamethyl-8,8-divinylcyclotetrasiloxane (**I**). Triflic acid and P₄-*t*-Bu superbase were utilized to initiate ROP of **I** in separate experiments. The composition and structure of copoly(dimethylsiloxane/divinylsiloxane) (3:1 mole ratio) were characterized by ¹H, ¹³C, and ²⁹Si NMR as well as IR spectroscopy. Both ¹³C and ²⁹Si NMR were useful in determining copolymer microstructure. The molecular weights of the copolymers were determined by GPC. The thermal stabilities and glass transition temperatures of the copolymers were determined by TGA and DSC, respectively. In addition to copolymer,

* Corresponding author. E-mail: wpweber@usc.edu.

significant amounts of monomeric cyclosiloxanes were detected. These were characterized by GC/MS.

Experimental Section

Spectroscopic Analysis. ^1H , ^{13}C , and ^{29}Si NMR spectra of 5% w/v CDCl_3 solutions were obtained on a Bruker AMX-500 MHz spectrometer. ^{13}C NMR spectra were obtained with broad-band proton decoupling. ^1H and ^{13}C spectra were internally referenced to TMS and residual CHCl_3 . A heteronuclear gated decoupling pulse sequence (NONOE) with 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.

Gel permeation chromatographic (GPC) analysis of the molecular weight distribution (M_w/M_n) of the polymers carried out on a Waters system equipped with a 501 refractive index detector. Two 7.8 mm \times 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 0.6 mL/min. Toluene was utilized since the refractive indexes of THF and our siloxane polymers are quite close. The retention times were calibrated against known monodisperse polystyrene standards: 929 000, 114 200, 13 700, and 794 g/mol.

Thermogravimetric analysis (TGA) of the copolysiloxanes was carried out on a Shimadzu TGA-50 instrument with a flow rate of 40 cm³/min of nitrogen or air. The temperature was increased at a rate of 4 °C/min from 25 to 800 °C. Glass transition temperatures (T_g 's) of the copolymers were determined on a Perkin-Elmer DSC-7 or on a Shimadzu DSC-50. The differential scanning calorimeters (DSC) were calibrated against the heat of transition (−87.06 °C) and the melting point of cyclohexane (6.54 °C)⁹ as well as from the T_g of PDMS (−125 °C).¹⁰ Samples were equilibrated at −150 °C for 30 min. Thermal analysis was then carried out by increasing the temperature from −150 to 50 °C at a rate of 10 °C/min.

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 and a 30 m DB5 capillary column. High-resolution mass spectra were acquired at the University of California at Riverside Mass Spectroscopy Facility on a VG ZAB2SE instrument. Exact masses were calibrated determined against known mass peaks of perfluorokerosene.

Dimethyldichlorosilane, divinylchlorosilane, and 1,1,3,3-tetramethyldisiloxane were obtained from Gelest. Pd/C (5%) and phosphazene base, $\text{P}_4\text{-}t\text{-Bu}$ (1.0 M in *n*-hexane), were purchase from Fluka. THF, triethylamine, and diethyl ether were obtained from Aldrich. Triethylamine was dried over NaOH pellets. Diethyl ether was dried over activated 4 Å molecular sieves. 1,1,3,3-Tetramethyldisiloxane was purified by distillation. Other chemicals were used as obtained.

All reactions were run in flame-dried glassware under argon. Teflon-covered magnetic stir bars were used to agitate the reactions.

1,1,3,3,5,5-Hexamethyltrisiloxane (II).¹¹ 1,1,3,3-Tetramethyldisiloxane (281 g, 2.1 mol) and $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ (1 g, 3.7 mmol) were placed in a 500 mL two-neck round-bottom flask equipped with a rubber septum, a pressure-equalizing addition funnel. HCl gas was bubbled through the solution while dimethyldichlorosilane (127 g, 1 mol) was added dropwise from an addition funnel over 3 h. The reaction was stirred for 3 h at room temperature (rt). The mixture was then distilled through a 10 cm vacuum jacketed distillation column packed with glass saddles. A fraction bp 127 °C/760 mm, 80 g, 38% yield was obtained. ^1H NMR δ : 0.065 (s, 6H), 0.191 (d, 12H, $J = 2.5$ Hz), 4.70 (m, 2H). ^{13}C NMR δ : 0.64. ^{29}Si NMR δ : −17.56 (s, 1Si), −6.74 (d, 2Si, $J_{\text{Si-H}} = 2$ Hz). IR ν : 2128 (Si-H) and 1057 cm^{−1} (Si-O). GC/MS *m/e* (relative abundance): 207 (18%) (M−1)⁺, 193 (100%) (M−15)⁺, 133 (25%), 119 (16%), 103 (10%).

1,5-Dihydroxyhexamethyltrisiloxane (III).¹² Deionized water (8.0 g, 0.44 mol), THF (50 mL), and Pd/C (50 mg) were placed in a 250 mL Erlenmeyer flask equipped with a Teflon-

covered magnetic stir bar. The flask was placed in an ice bath, while **II** (30 g, 0.144 mol) was added via a 50 mL syringe slowly over 2 h. The solution was allowed to stir at room temperature until no more gas bubbles evolved. The solution was dried over anhydrous MgSO_4 and filtered, and the volatile solvents were removed by evaporation under reduced pressure. In this way, 36 g, 99% yield of **III** was obtained. ^1H NMR δ : 0.095 (s, 6H), 0.127 (s, 12H), 5.25 (m, 2H). ^{13}C NMR δ : 0.375, 0.89. ^{29}Si NMR δ : −19.9 (s, 1Si), −10.8 (s, 2Si). IR ν : 3275 (Si-OH), 2964, 1266 (Si-CH₃), 1051 cm^{−1} (Si-O).

2,2,4,4,6,6-Hexamethyl-8,8-divinylcyclotetrasiloxane (I). Diethyl ether (100 mL) and triethylamine (11.5 g, 114 mmol) were placed in a 250 mL three-neck round-bottom flask equipped with two pressure-equalizing addition funnels and a Tru-bore stirrer equipped with a Teflon paddle which was attached to a mechanical stirrer. Diethyl ether (15 mL) and **II** (6.7 g, 28 mmol) were placed in one addition funnel. Diethyl ether (15 mL) and divinylchlorosilane (4.3 g, 28 mmol) were placed in the other. Both solutions were added dropwise over 1 h. The reaction was allowed to stir for 3 h at room temperature. The reaction mixture was then washed with brine and water until it was neutral. The solution was dried over anhydrous MgSO_4 and filtered, and the volatile solvent was removed by evaporation under reduced pressure. The solution was then distilled through a 5 cm vacuum jacketed distillation column, which was packed with glass saddles. A fraction bp 109 °C/20 mm, 5 g, 56% yield was obtained. ^1H NMR δ : 0.092 (s, 6H), 0.121 (s, 12H), 5.874 (dd, 1H, $J = 13.5$ and 10 Hz), 6.0315 (d, 1H, $J = 13.5$ Hz), 6.035 (d, 1H, $J = 10$ Hz). ^{13}C NMR δ : 0.82, 0.854, 134.5, 135.0. ^{29}Si NMR δ : −48.2 (s, 1Si), −18.8 (s, 1Si), −18.0 (s, 2Si). IR ν : 3057, 2964, 1597 (C=C), 1074 cm^{−1} (Si-O). GC/MS *m/e* (rel. abundance): 320 (5%) M⁺, 305 (100%) (M−15)⁺, 277 (15%), 251 (17%). High-resolution mass spectra. Calcd for $\text{C}_{10}\text{H}_{24}\text{O}_4\text{Si}_4$: 320.07517. Found: 320.0748.

Anionic Polymerization of I, Copoly(dimethylsiloxane/divinylsiloxane) (3:1 Mole Ratio). **I** (1.5 g, 4.54 mmol) was placed in a 15 mL Ace pressure tube which was sealed with an O-ring and a threaded Teflon cap. $\text{P}_4\text{-}t\text{-Bu}$ superbase (3.1 mg, 5 μL , 5 μmol) was added. Argon was bubbled through the solution for 1 min, and the tube was then sealed. The polymerization was allowed to proceed at 80 °C for 20 min. Trimethylchlorosilane (8.85 mg, 10 μL , 79 μmol) and triethylamine (7.26 mg, 10 μL , 72 μmol) were added sequentially to quench the reaction. The polymer was precipitated three times from diethyl ether/methanol and was then dried under vacuum. In this way, 1.2 g, 80% yield, of polymer with $M_w/M_n = 87\ 300/43\ 500$ and $T_g = -125$ °C was obtained. ^1H NMR δ : 0.12 (s, 9H), 0.14 (s, 9H), 5.88–5.93 (m, 2H), 6.05–6.07 (m, 4H). ^{13}C NMR δ : 1.07, 1.08, 1.13, 1.21, 134.20, 134.21, 134.28, 134.37, 134.44, 134.45, 134.53, 134.60, 134.70, 134.72, 134.99, 135.05, 135.07, 135.16, 135.23, 135.24, 135.31, 135.33. ^{29}Si NMR δ : −50.12, −50.11, −50.07, −50.04, −50.01, −49.99, −49.97, −49.93, −49.92, −49.60, −49.58, −49.55, −49.53, −49.50, −49.43, −49.38, −49.02, −49.00, −48.93, −48.92, −21.89, −21.86, −21.83, −21.75, −21.73, −21.61, −21.60, −21.00, −20.98, 20.95, −20.88, −20.86, −20.74, −20.05, −20.02, −19.92, −19.79. IR ν : 2963, 1597, 1406, 1260, 1028 cm^{−1}.

Analysis of Methanol-Soluble Material. After evaporation of the methanol, approximately 0.3 g, 20% yield, of residue was obtained. This material was analyzed by a combination of GPC and GC/MS. Soluble oligomers, ~4% yield, $M_w/M_n = 3700/2640$ were obtained. In addition, a series of cyclotetra-, cyclopenta-, and cyclohexasiloxanes (~16% yield) were identified by GC/MS from their (M−15)⁺ ions. In this way, the following isomers of cyclosiloxanes containing D and V units were identified: octamethylcyclotetrasiloxane (D₄) (9.4%), **I** (D₃V) (20.3%), decamethylcyclopentasiloxane (D₅) (7.2%), D₂V₂ (6.7%), D₄V (26.9%), D₃V₂ (16.4%), D₂V₃ (1.7%), dodecamethylcyclohexasiloxane (D₆) (1.5%), D₅V (7.2%), D₄V₂ (2.7%). Yields reported here have been normalized so that the total amount of cyclosiloxanes equals 100%.

Cationic Polymerization of I, Copoly(dimethylsiloxane/divinylsiloxane). **I** (0.5 g, 1.56 mmol) was placed in a test tube which was sealed with a rubber septum. Dichlo-

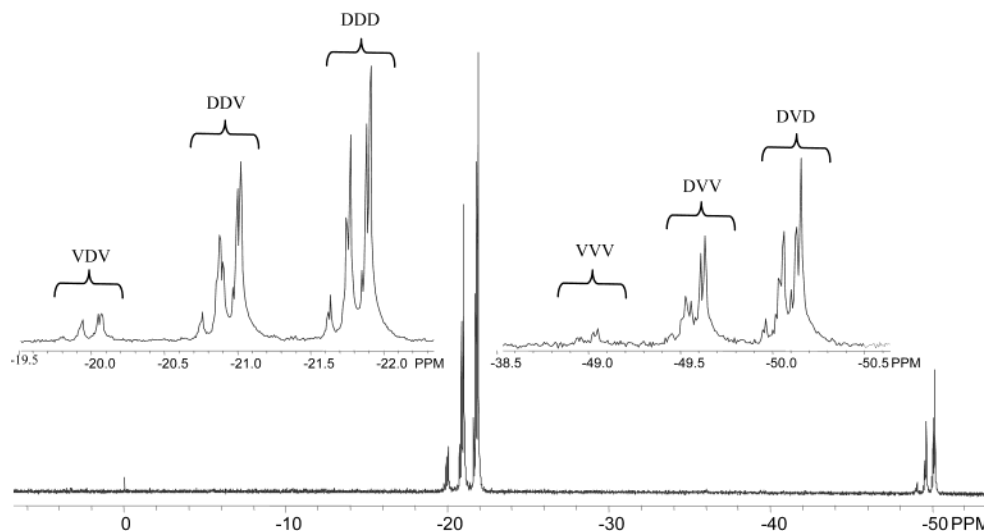


Figure 1. ^{29}Si NMR of copoly(dimethylsiloxane/divinylsiloxane) produced by P_4 -*t*-Bu-initiated ROP of **I**.

romethane (100 μL) and triflic acid (6.75 mg, 4 μL , 45 μmol) were injected into the test tube at 20 $^\circ\text{C}$. The polymerization was allowed to proceed for 15 min. At this time, hexamethyldisilazane (19 mg, 25 μL , 0.12 mmol) was added to quench the reaction. After 1 h, the polymer was precipitated three times from a mixture of diethyl ether and methanol and dried under vacuum. In this way, 0.25 g, 50% material with $M_w/M_n = 54\,650/24\,890$, and $T_g = -121.6$ $^\circ\text{C}$ was obtained. ^1H NMR δ : 0.07 (s, 5H), 0.09 (s, 12H), 0.12 (s, 1H), 5.86 (br dd 1H, $J = 15$ and 10 Hz), 6.01 (br d, 1H, $J = 10$ Hz), 6.02 (br dd, 1H, $J = 15$, and 10 Hz). ^{13}C NMR δ : 1.09, 1.14, 1.21, 134.21, 134.28, 134.36, 134.45, 135.25, 135.26, 135.33, 135.34. ^{29}Si NMR δ : -50.14, -50.12, -50.09, -50.05, -50.02, -49.61, -21.89, -21.86, -21.83, -21.75, -21.72, -21.62, -21.01, -20.98, -20.95, -20.86, -20.84, -20.06. IR ν : 3008, 3057, 2963, 2902, 1598, 1407, 1262, 1108, 1020, 965, 844, 802, 735 cm^{-1} .

Analysis of Methanol-Soluble Material. After evaporation of methanol, 0.24 g, 50% yield of **I** was recovered. Its structure was confirmed by GC/MS, ^1H NMR, and ^{13}C NMR.

Discussion

From a practical standpoint, ROP of octamethylcyclotetrasiloxane (D_4) is of greater industrial importance than ROP of hexamethylcyclotrisiloxane (D_3). This is usually accomplished with acid catalysis, since D_4 is much less reactive than D_3 under anionic ROP conditions.¹³ Dissociating solvents and large cations facilitate hydroxide-initiated ring-opening polymerization of D_4 .^{14–17} Recently, superbases P_4 -*t*-Bu has been shown to permit rapid anionic ring-opening polymerization of D_4 under relatively mild conditions.^{14,22} In this regard, no work has been yet reported on P_4 -*t*-Bu-initiated anionic ROP of substituted D_4 derivatives.

Despite the fact that the yield of copolymer is only 80%, the composition of copoly(dimethylsiloxane/divinylsiloxane) obtained by P_4 -*t*-Bu superbases-initiated anionic ROP of **I** has been determined by ^1H NMR. Specifically, the integration of the signals due to Si-methyl groups, D units, to the Si-vinyl groups, V units, are in a 3:1 ratio that is the same as their ratio in the starting monomer **I**. There has been no preferential incorporation of one type of siloxane unit into the copolymer. The band at 1597 cm^{-1} in the infrared spectrum is assigned to the C=C double bond of the Si-vinyl groups.

The microstructure of copoly(dimethylsiloxane/divinylsiloxane) has been analyzed by ^{13}C and ^{29}Si NMR spectroscopy. The ^{13}C NMR of the Si-vinyl groups can

be accounted for in terms of pentads formed by a random statistical arrangement of dimethylsiloxane (D) and divinylsiloxane (V) units in a 3:1 molar ratio. There are three V-centered triads: DVD, DVV, and VVV. Each are further split into pentads. The DVD triad is split into DDVDD, VD VDD, and VD VDV in a 81:54:9 statistical ratio. The DVV triad will be further split into a DDVVD, VD VVD, DDV VV, and VD V VV pentad in a 54:18:18:3 ratio. Finally, the VVV triad will be further split into a DVVVD, VVVVD, and VVV VV pentad in a 9:6:1 ratio. This leads to a prediction of 10 Si-vinyl groups. Since there are two distinct vinyl carbons $-\text{CH}=\text{CH}_2$, there should be a total of 20 vinyl carbon resonances observed. In fact, 18 vinyl carbon resonances are detected. While it is not possible to integrate ^{13}C NMR signals, it seems likely that the resonance due to the VVV VV pentad, which is statistically predicted to be the least probable, may not be detected. Only four signals are detected in the ^{13}C NMR due to the Si- CH_3 groups. Many more signals due to Si- CH_3 are expected. The reason for this lack of Si- CH_3 resonances is not understood.

The microstructure of copoly(dimethylsiloxane/divinylsiloxane) obtained by P_4 -*t*-Bu superbases-initiated anionic ROP of **I** has been also analyzed by ^{29}Si NMR. This spectrum can be accounted for in terms of heptads formed by a random statistical arrangement of D and V units in a 3:1 molar ratio. The chemical shift of these is primarily dependent on the central triad. Thus, there are three D-centered triads DDD, DDV, and VDV. The first is further split to three D-centered pentads: DDDDD, DDDDDV, and VDDDDV in a statistically expected intensity ratio of 81:54:9. The second, DDV, is split into four pentads: DDDVD, VDDVD, DDDVV, and VDDVV in a statistically expected ratio of 54:18:18:6. As can be seen in Figure 1, the VDDVD and DDDVV pentads apparently overlap. Finally, the third triad VDV is split into three pentads: DVDVD, VVDVD, and VVDVV in a ratio of 9:6:1. Each of these is further split into heptads. For example, the DDDDD pentad is split into three heptads: DDDDDDD (-21.89 ppm), VD DDDDD (-21.86 ppm), and VDDDDDDV (-21.83 ppm) in an intensity ratio of 729:486:81. The DDDDDV pentad is further split into four heptads DDDDDVD, VD DDDVD, DDDDDVV, and VDDDDVV in an intensity ratio of 243:81:81:27. Unfortunately, because of fortu-

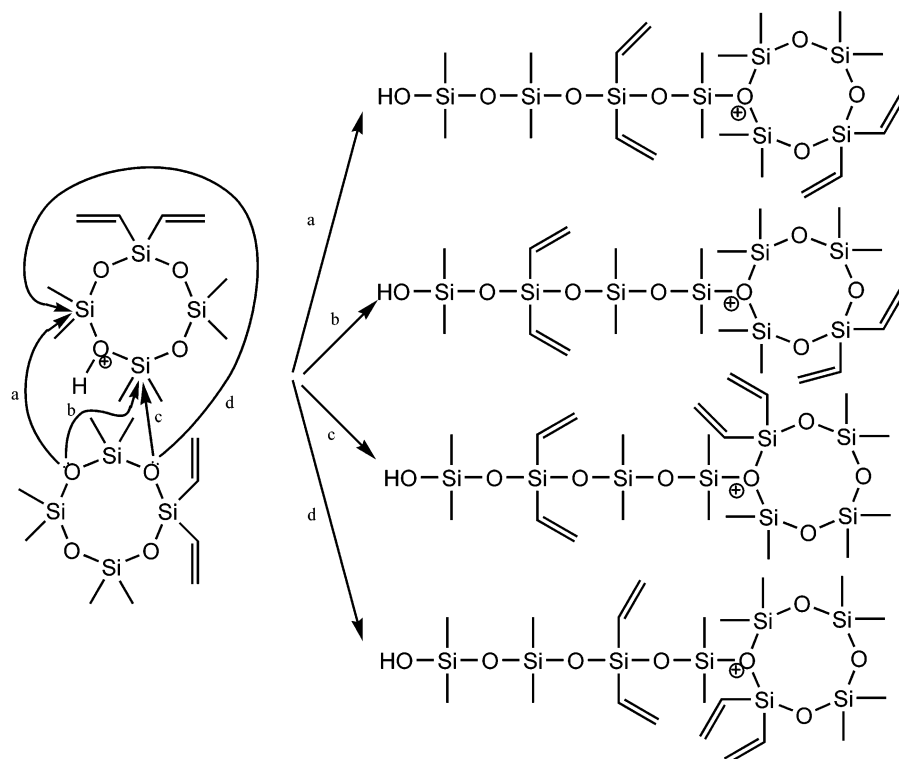


Figure 2. Mechanism of chemoselective triflic acid-initiated polymerization of **I**.

itous overlap, only two peaks are resolved at -21.75 and -21.73 ppm. The VDDDDV pentad is further split into three heptads: DVDDDVD (-21.61 ppm), VVDDDVD (-21.60 ppm), and finally VVDDDDV in a predicted intensity ratio of 81:54:9. Unfortunately, only two peaks are resolved. On the basis of their relative intensity, we suspect that we are unable to observe the peak due to the VVDDDDV heptad. Similar analysis can be applied to the VDD- and VDV-centered triads.

Similarly, there are three V-centered triads DVD, DVV, and VVV. These are further split into pentads which were further split into heptads. For example, the DVD triad is further split into DDVDD, VDVDD, and VDDVD pentads. These have a predicted intensity ratio of 81:54:9. Further analysis of the most probable pentad, DDVDD, follows. The DDVDD pentad can be further split into three heptads, DDDVDDD (-50.12 ppm), VDDVDDD (-50.11 ppm), and VDDVDDV (-50.07 ppm). Similar analysis can be applied to the other V-centered triads (see Figure 1 for ^{29}Si NMR).

Consistent with a random process, analysis of the methanol-soluble fraction shows the presence of a large number of cyclotetra-, cyclopenta-, and cyclohexasiloxanes made up of D and V units. The following cyclotetrasiloxanes were identified by GC/MS from the mass of their $(M-15)^+$ ion: D_4 , recovered **I** (D_3V), and D_2V_2 . The following cyclopentasiloxanes were found: decamethylcyclopentasiloxane (D_5), D_4V , D_3V_2 , and D_2V_3 . Finally, the following cyclohexasiloxanes were detected: dodecamethylcyclohexasiloxane (D_6), D_5V , and D_4V_2 . Since GC/MS does not differentiate between isomers, the latter cyclotetrasiloxane is probably a mixture of isomers; i.e., D_2V_2 can be 2,2,4,4-tetramethyl-6,6,8,8-tetravinylcyclotetrasiloxane and/or 2,2,6,6-tetramethyl-4,4,8,8-tetravinylcyclotetrasiloxane. Similarly, cyclopentasiloxanes D_3V_2 and D_2V_3 and cyclohexasiloxanes D_4V_2 and D_5V are probably mixtures of isomers.

Organosilicon compounds that have a methyl-Si bond are well-known to form siliconium ions in the mass

spectrometer by loss of a methyl from the silyl center.^{18,19} The number of silicon atoms in these ions was determined from the ratio of the $(M-15)^+$ to $(M-15+1)^+$ to the $(M-15+2)^+$ cluster of ions. These are due to the presence of naturally occurring ^{28}Si , ^{29}Si , and ^{30}Si isotopes.²⁰

Analysis of the ^{29}Si NMR spectrum of copoly(dimethylsiloxane/divinylsiloxane) (3:1) produced by triflic acid-initiated ring opening of **I** permits determination of the copolymer microstructure (see Figure 2). These results can be interpreted on the basis of a chemoselective ring-opening polymerization. The chemoselective ROP of 2,2,4,4-tetramethyl-6,6-diphenylcyclotrisiloxane initiated by triflic acid has been recently reported.²³ In such a process, the four siloxane units of **I** are added to the growing polymer. The connectivity of the siloxane units in **I** is preserved in the growing polymer. Two silyloxonium ions are involved as reactive intermediates. Polymer growth occurs by nucleophilic attack of a siloxane oxygen lone pair of electrons of **I** on a silyl center adjacent to the oxonium ion. In this process, the original oxonium ion undergoes ring opening, and a new silyloxonium ion is formed.

The analysis is somewhat complicated. There are two silyloxonium ions intermediates, each of which can undergo ring opening in two different ways, and there are two distinct types of siloxane oxygens in **I** (see Figure 2). This leads to a prediction of seven D-centered and three V-centered pentads. The D-centered pentads are DDDDD, VDDDD, VDDDDV, DVDDDD, VDDDDV, and DVDVD. These may be further split to heptads. In fact, only six types of D pentads are observed. No signals due to the VVDDDD pentad, whose chemical shift has been assigned from the copolymer obtained by $P_4-t\text{Bu}$ base catalysis, are detected (see Figure 3 for ^{29}Si NMR).

On the basis of this analysis, only three kinds of V-centered pentads are predicted: DDVDD, VDVDD, and DDVDD. The DDVDD pentad is further split into

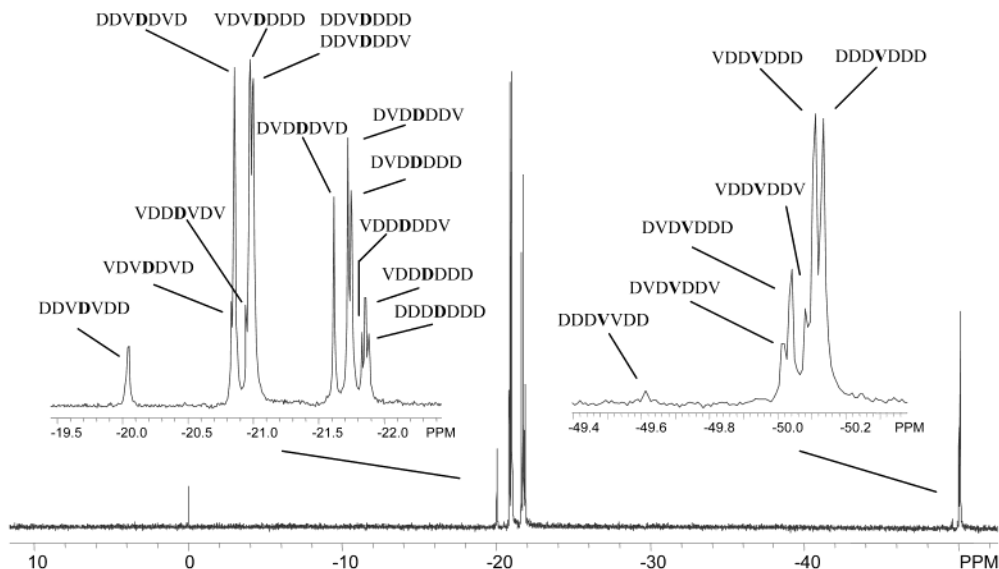


Figure 3. ^{29}Si NMR of copoly(dimethylsiloxane/divinylsiloxane) produced by triflic acid-initiated ROP of **I**.

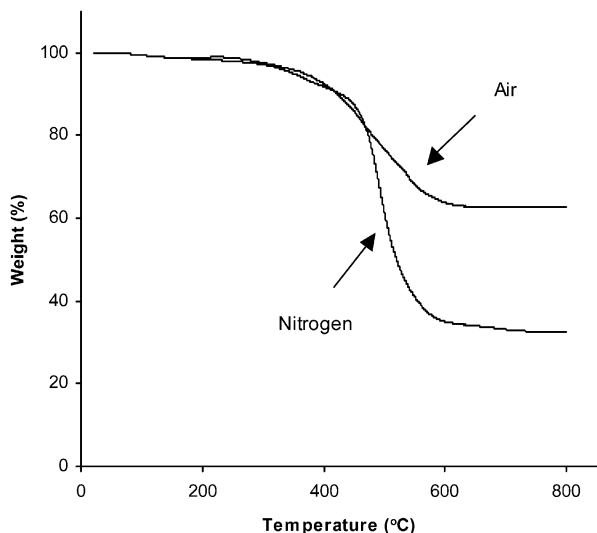


Figure 4. TGA of copoly(dimethylsiloxane/divinylsiloxane).

three kinds of heptads: DDDVDDD, VDDVDDD, and VDDVDDV. The VD VDD pentad should be split to four heptads. Only two signals, however, are observed. Finally, only a single signal from the DDVVD pentad is detected. Similar analysis can be applied to the other D-centered pentads (see Figure 3).

Consistent with this chemoselective process, the low molecular weight material obtained from the methanol-soluble fraction is only recovered starting material **I**.

The T_g 's for copoly(dimethylsiloxane/divinylsiloxane) (3:1 mole ratio) prepared by either acid or base catalysis are -121.6 and -125 °C, respectively. These are reasonable since we have previously found that the T_g of regular copoly(dimethylsiloxane/divinylsiloxane) (2:1 mole ratio) was -128 °C.⁸

Both of these copoly(dimethylsiloxane/divinylsiloxane) (3:1 mole ratio) materials are thermally stable to at least 350 °C. Above this temperature both decompose. In air, a residue of almost 70% remains above 600 °C, while in nitrogen a residue of more than 35% found at this temperature (see Figure 4). Thermogravimetric analysis of regular copoly(dimethylsiloxane/divinylsiloxane) (2:1 mole ratio) yields similar results.⁸

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

References and Notes

- (1) Kennan, J. J. In *Siloxane Copolymers in Siloxane Polymers*; Clarson, S. J., Semlyen, J. A., Eds.; Ellis Horwood PTR Prentice Hall: Englewood Cliffs, NJ, 1993; Chapter 2, p 72.
- (2) Kendrick, T. C.; Parbhoo, B.; White, J. W. *Siloxane Polymers and Copolymers*. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z. J. U., Eds.; Wiley & Sons: Chichester, 1989; p 1289.
- (3) Mazurek, M.; Zietera, J.; Sadowska, W.; Chojnowski, J. *Macromol. Chem.* **1980**, *181*, 777.
- (4) Hempenius, M. A.; Lammerting, M. G. H.; Vansco, G. L. *Macromolecules* **1997**, *30*, 266.
- (5) Rózga-Wijas, K.; Chojnowski, J.; Boileau, S. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 879.
- (6) Cypryk, M.; Kaźmierski, K.; Fortuniak, W.; Chojnowski, J. *Macromolecules* **2000**, *33*, 1536.
- (7) Battjes, K.; Kuo, C.-M.; Miller, R. L.; Saam, J. C. *Macromolecules* **1995**, *28*, 790.
- (8) Weber, W. P.; Cai, G. *Macromolecules* **2001**, *34*, 4355.
- (9) Aston, J. G.; Szabz, G. J.; Fink, H. L. *J. Am. Chem. Soc.* **1943**, *65*, 1135.
- (10) Clarson, S. J.; Dodgson, J.; Semlyen, J. A. *Polymer* **1985**, *26*, 930.
- (11) Zhdanov, A. A. *J. Gen. Chem. USSR* **1973**, *43*, 1265.
- (12) Zachernyuk, A. B.; Burlova, E. A.; Zhdanov, A. A. *J. Gen. Chem. USSR* **1985**, *55*, 1221.
- (13) Boileau, S. Anionic Polymerization of Cyclosiloxanes with Cryptates as Counterions. In *Ring Opening Polymerization, Kinetics, Mechanism and Synthesis*; McGrath, J. E., Ed.; ACS Symposium Series 286; American Chemical Society: Washington, DC, 1985.
- (14) Hupfield, P. C.; Taylor, R. G. *J. Inorg. Organomet. Polym.* **1999**, *9*, 17.
- (15) Molenberg, A.; Möeller, M. *Macromol. Rapid Commun.* **1995**, *16*, 449.
- (16) Van Dyke, M. E.; Clarson, S. J. *Am. Chem. Soc., Polym. Prepr.* **1996**, *37-II*, 668.
- (17) Van Dyke, M. E.; Clarson, S. J. *J. Inorg. Organomet. Polym.* **1996**, *8*, 111.
- (18) Weber, W. P.; Willard, A. K.; Boettger, H. G. *J. Org. Chem.* **1971**, *36*, 1620.
- (19) Swaim, R. E.; Weber, W. P. *J. Org. Mass Spectrosc.* **1980**, *15*, 304.
- (20) Biemann, K. *Isotope Peaks in Mass Spectrometry, Organic Chemical Applications*; McGraw-Hill Book Co., Inc.: New York, 1965; pp 59–69.
- (21) Odian, G. *Principles of Polymerization*, 3rd ed.; Wiley: New York, 1991; p 146.
- (22) Esswein, B.; Molenberg, A.; Möeller, M. *Macromol. Symp. Int. Symp. Ion. Polym.* **1995** (1996), 170.
- (23) Chojnowski, J.; Cypryk, M.; Kaźmierski, K. *Macromolecules* **2002**, *35*, 9904.