Macromolecules **2001,** *34,* 4355−4360

Anionic and Cationic Ring-Opening Polymerization of 2,2-Divinyl-4,4,6,6-tetramethylcyclotrisiloxane. Synthesis of Regular Poly[2,2-bis(perfluoroalkyl-1′*H*,1′*H*,2′*H*,2′*H*-dimethylsilylethyl)-4,4,6,6-tetramethyltrisiloxanes] by Chemical Modification of Regular Poly(2,2-divinyl-4,4,6,6-tetramethyltrisiloxane)

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 February 16, 2001; Revised Manuscript Received April 17, 2001

ABSTRACT: Anionic ring-opening polymerization of 2,2-divinyl-4,4,6,6-tetramethylcyclotrisiloxane yields regular poly(2,2-divinyl-4,4,6,6-tetramethyltrisiloxane), while cationic ring-opening polymerization of 2,2-divinyl-4,4,6,6-tetramethylcyclotrisiloxane yields copoly(dimethylsiloxane/divinylsiloxane). The mechanisms of both anionic and cationic ring-opening polymerizations are discussed. Chemical modification of poly(2,2-divinyl-4,4,6,6-tetramethyltrisiloxane) has been achieved by platinum-catalyzed hydrosilylation reactions with both 3,3,3-trifluoropropyldimethylsilane and perfluorooctyl-1′*H*,1′*H*,2′*H*,2′*H*-dimethylsilane. Polymers and monomer have been characterized by ^{1}H, ^{13}C, ^{19}F, and ^{29}Si NMR as appropriate. Molecular weight distributions of polymers have been determined by GPC and their thermal properties measured by DSC and TGA.

Introduction

The properties of copolymers depend on both the molar ratio and sequence of the two components. Random, alternating, and block copolymers prepared from the same monomers can have distinct properties. We have been interested in the preparation, properties, and chemical modification of copoly(siloxanes) that have regular microstructures. For example, we have previously reported the preparation of poly(2-hydrido-2,4,4,6,6-pentamethyltrisiloxane) with an extremely regular microstructure by anionic ring-opening polymerization (AROP) of 2-hydridopentamethylcyclotrisiloxane. The reactive Si−H bonds of this material permit chemical modification by both platinum-catalyzed hydrosilylation reactions with terminal alkenes as well as by ruthenium-catalyzed hydrosilylation reaction with ketones.[1] There is considerable interest in chemical modification of polymers.[2,3]

This paper reports the preparation of poly(2,2-divinyl-4,4,6,6-tetramethyltrisiloxane) which has an extremely regular microstructure and the chemical modification of this material by platinum-catalyzed hydrosilylation reactions with both 3,3,3-trifluoropropyldimethylsilane and perfluorooctyl-1*H*,1*H*,2*H*,2*H*-dimethylsilane. While copoly(dimethylsiloxane/vinylmethylsiloxanes) in which the mole percent of vinylmethylsiloxane groups varies from 1 to 13% are commercially available,[4] no copoly(dimethylsiloxane/divinylsiloxanes) have been previously reported.

Kinetically controlled living AROP of cyclotrisiloxanes can lead to polysiloxanes that have narrow molecular weight distributions. For example, AROP of vinylpentamethylcyclotrisiloxane yields narrow molecular weight material which has predominantly a regular 2-vinyl-2,4,4,6,6-pentamethyltrisiloxane microstructure.[5,6] This material has also been prepared by heterofunctional polycondensation of vinylmethyldichlorosilane and tetramethyldisiloxane-1,3-diol[7] in the presence of triethylamine and a catalytic amount of 4-(*N*,*N*-dimethylamino)pyridine. Unfortunately, neither approach yields perfectly regular poly(2-vinyl-2,4,4,6,6-pentamethyltrisiloxane).[8]

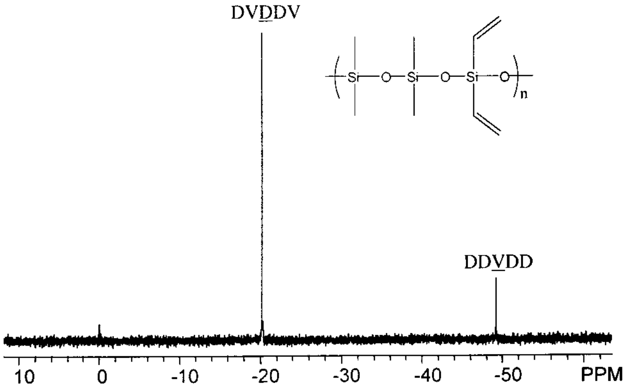

Figure 1. ^{29}Si NMR of poly(2,2,-divinyl-4,4,6,6-tetramethyltrisiloxane).

Results and Discussion

We should like to report that anionic ring-opening polymerization of 2,2-divinyl-4,4,6,6-tetramethylcyclotrisiloxane catalyzed by dilithiodiphenylsilanediolate[9] leads to perfectly regular poly(2,2-divinyl-4,4,6,6-tetramethyltrisiloxane). The regularity of the polymer microstructure has been determined by ^{29}Si NMR spectrum (see Figure 1). Only two signals are observed in the ^{29}Si

10.1021/ma010288s CCC: $20.00

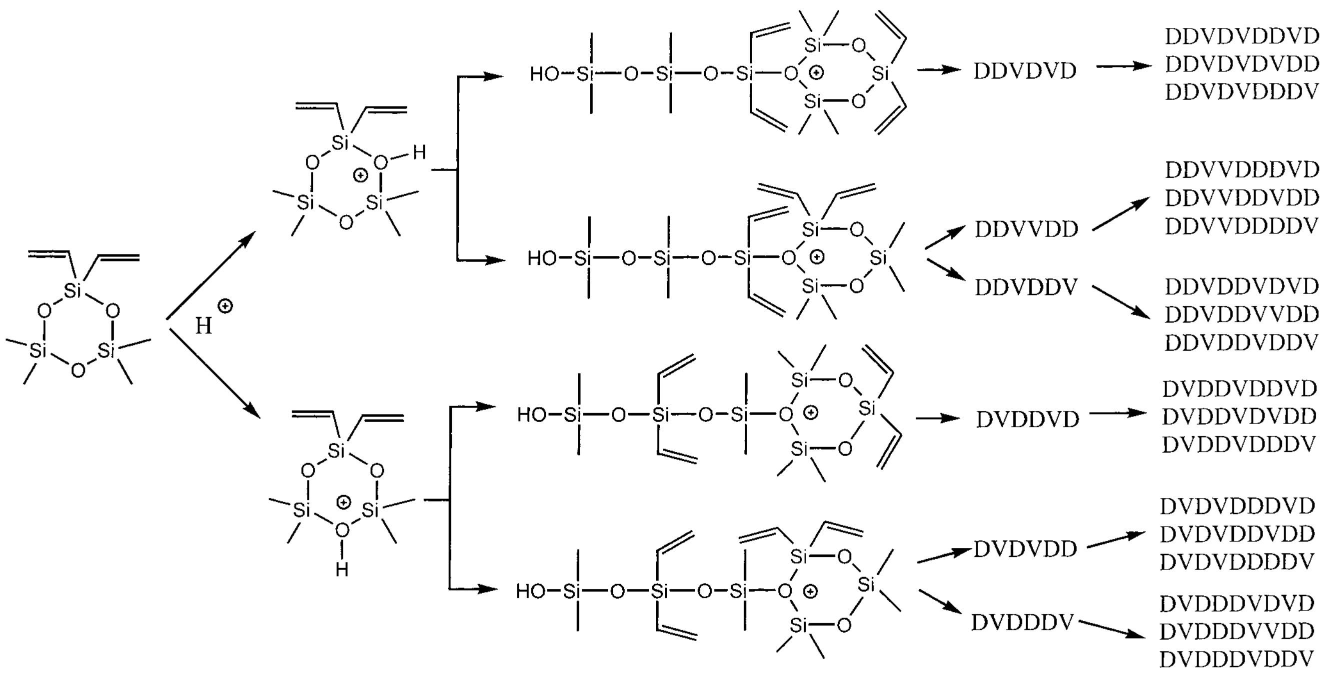

Figure 2. Chemoselective cationic ring-opening polymerization of 2,2-divinyl-4,4,6,6-tetramethylcyclotrisiloxane.

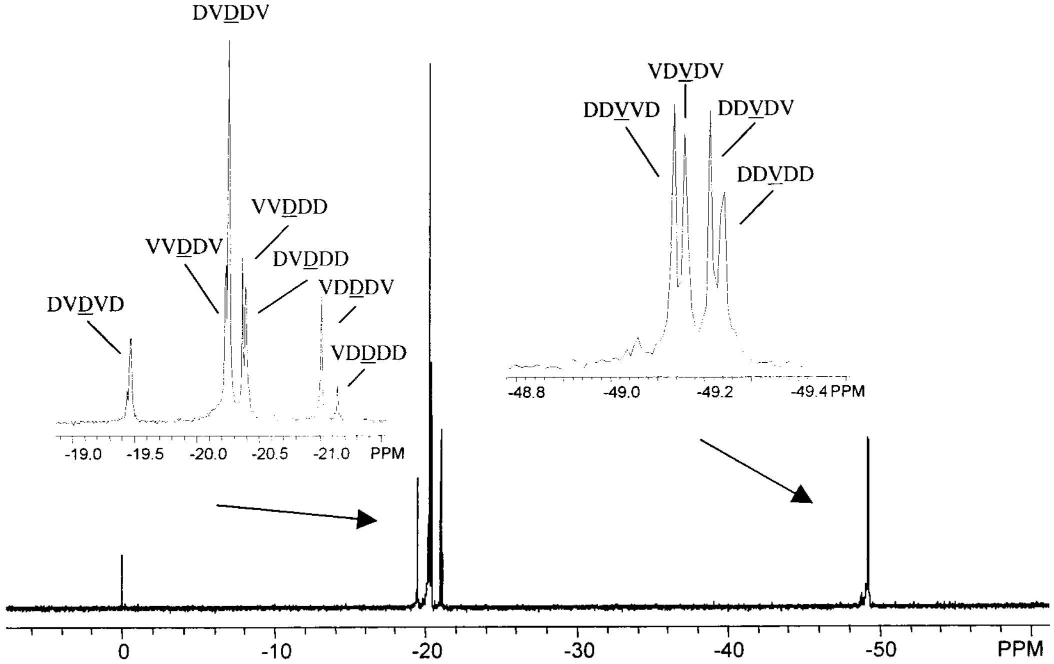

Figure 3. ^{29}Si NMR of copoly(dimethylsiloxane/divinylsiloxane) formed by cationic ring-opening polymerization of 2,2-divinyl-4,4,6,6-tetramethylcyclotrisiloxane.

NMR: one at −49.17 ppm due to the divinylsiloxane units (V) of the DD**V**DD pentads and one at −20.20 ppm due to the dimethylsiloxane units (D) of the DV**D**DV pentads. Both low molecular weight polymer M_w/M_n = 12 300/9200 and higher molecular weight polymer M_w/M_n = 39 000/19 600 have equally regular microstructures. Clearly, neither of these has the narrow molecular weight distribution expected for a living anionic polymerization in which redistribution processes are much slower than chain propagation. While redistribution results in broader molecular weight distributions, it does *not* result in loss of regularity of the polymer microstructure.

By comparison, cationic ring-opening polymerization of 2,2-divinyl-4,4,6,6-tetramethylcyclotrisiloxane catalyzed by triflic acid yields copoly(dimethylsiloxane/divinylsiloxane) with a significantly more complex microstructure. While all three of the oxygen atoms of 2,2-divinyl-4,4,6,6-tetramethylcyclotrisiloxane form oxonium ions, chemoselective ring opening occurs. Addition of triad units to the polymer without scrambling leads to a prediction of four V-centered pentads and seven D-centered pentads (see Figures 2 and 3). These peaks have been assigned by comparison with previously reported model monomeric, oligomeric, and polymeric siloxanes.[8,10] Chemoselective ring opening with addition

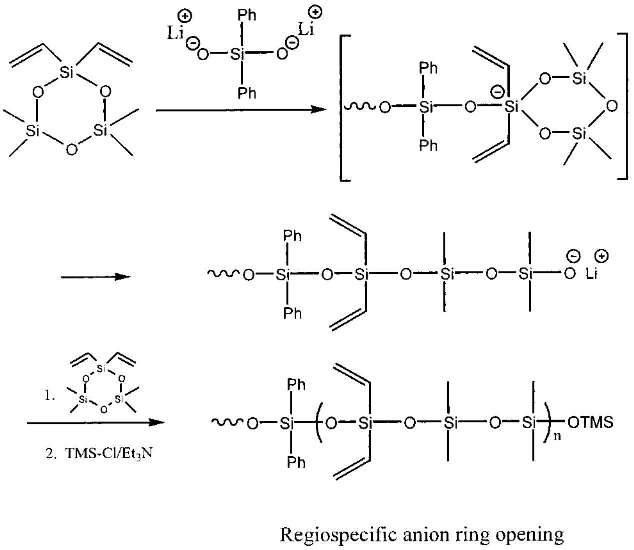

Figure 4. Mechanism of anionic ring-opening polymerization of 2,2-divinyl-4,4,6,6-tetramethylcyclotrisiloxane.

of triad units without scrambling has also been reported in the triflic acid-catalyzed cationic ring-opening polymerization of 2,2-diphenyl-4,4,6,6-tetramethylcyclotrisiloxane.[11]

The regular microstructure of the poly(2,2-divinyl-4,4,6,6-tetramethyltrisiloxane) formed by AROP of 2,2-divinyl-4,4,6,6-tetramethylcyclotrisiloxane may result from a strong preference for nucleophilic attack on the divinylsiloxane center of 2,2-divinyl-4,4,6,6-tetramethylcyclotrisiloxane. Anionic ring opening of 2,2-divinyl-4,4,6,6-tetramethylcyclotrisiloxane forms a single propagating silanolate triad $\mathrm{In{-}Vin_2SiO{-}Me_2SiO{-}Me_2SiO^-}$ (see Figure 4).

By comparison, AROP of 2,2-diphenyl-4,4,6,6-tetramethylcyclotrisiloxane leads to material with a much less regular microstructure.[12] The sequence of siloxane units found in copoly(dimethylsiloxane/diphenylsiloxane) has been accounted for in terms of three propagating triads: $\mathrm{In{-}Ph_2SiO{-}Me_2SiO{-}Me_2SiO^-}$, $\mathrm{In{-}Me_2SiO{-}Me_2SiO{-}Ph_2SiO^-}$, and finally $\mathrm{Me_2SiO{-}Ph_2SiO{-}Me_2SiO^-}$, each of which can attack both dimethylsiloxane and diphenylsiloxane centers of 2,2-diphenyl-4,4,6,6-tetramethylcyclotrisiloxane.

Both vinyl and phenyl substituents are electron withdrawing by inductive effects. This favors nucleophilic attack on divinylsiloxane or diphenylsiloxane centers, respectively. However, the larger size of the phenyl groups may partially hinder nucleophilic attack. For this reason, nucleophilic attack at the dimethylsiloxane centers of 2,2-diphenyl-4,4,6,6-tetramethylcyclotrisiloxane may become competitive. This is apparently not a problem with the smaller vinyl substituents of 2,2-divinyl-4,4,6,6-tetramethylcyclotrisiloxane.

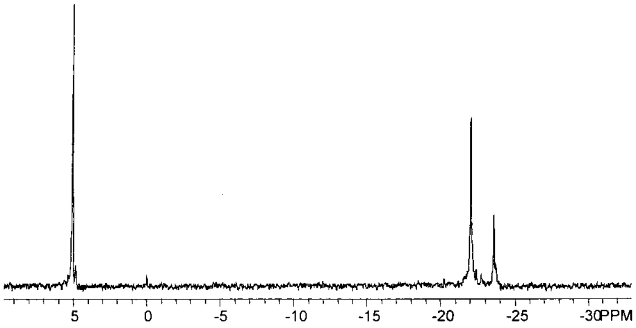

Figure 6. ^{29}Si NMR of poly[2,2-bis(3′,3′,3′-trifluoropropyldimethylsilylethyl)-4,4,6,6-tetramethyltrisiloxane].

We have also carried out the chemical modification of poly(2,2-divinyl-4,4,6,6-tetramethyltrisiloxane) by platinum-catalyzed hydrosilylation with both 3,3,3-trifluoropropyldimethylsilane and perfluorooctyl-1*H*,1*H*,2*H*,2*H*-dimethylsilane (see Figure 5). In both cases, ^{29}Si NMR of the chemically altered polymers indicates complete chemical modification. Unfortunately, the hydrosilylation is not completely regiospecific. Thus, while anti-Markovnikov addition of the Si−H bonds of the both 3,3,3-trifluoropropyldimethylsilane and tetrahydroperfluorooctyl-1*H*,1*H*,2*H*,2*H*-dimethylsilane across the carbon−carbon double bonds of the polymer to form $\mathrm{CF_3CH_2CH_2{-}(CH_3)_2Si{-}CH_2CH_2{-}}$ or $\mathrm{CF_3(CF_2)_5{-}(CH_3)_2Si{-}CH_2CH_2{-}}$ pendant units, respectively, is predominant, a small amount (∼10%) of Markovnikov addition occurs. This leads respectively to $\mathrm{CF_3CH_2CH_2(CH_3)_2Si{-}(CH_3)CH{-}}$ and $\mathrm{CF_3(CF_2)_5{-}(CH_3)_2Si{-}(CH_3)CH{-}}$ pendant groups. Consistent with this interpretation, a doublet at 1.115 ppm is seen in the ^{1}H NMR. Nevertheless, ^{29}Si NMR indicates that the regular microstructure of the starting siloxane polymer backbone has been retained in the chemically modified polymers (see Figure 6). The microstructures of these materials have significantly more regular siloxane polymer backbones than those which we have previously reported from the AROP of either 2,2-bis(perfluorooctyl-1′*H*,1′*H*,2′*H*,2′*H*)-4,4,6,6-tetramethylcyclotrisiloxane, 3,3,3-trifluoropropylpentamethylcyclotrisiloxane, or perfluorooctyl-1*H*,1*H*,2*H*,2*H*-pentamethylcyclotrisiloxane.[13,14]

These chemically modified materials are quite remarkable. The molar mass of the pendant side chains is comparable $\mathrm{CF_3CH_2CH_2Si(CH_3)_2}$ (155 g/side chain) or $\mathrm{CF_3(CF_2)_5{-}CH_2CH_2Si(CH_3)_2{-}}$ (405 g/side chain) to that of a unit of poly(2,2-divinyl-4,4,6,6-tetramethyltrisiloxane) (246 g/unit). Thus, it should not be surprising that some of the properties of these materials are determined by the nature of the pendant side chains

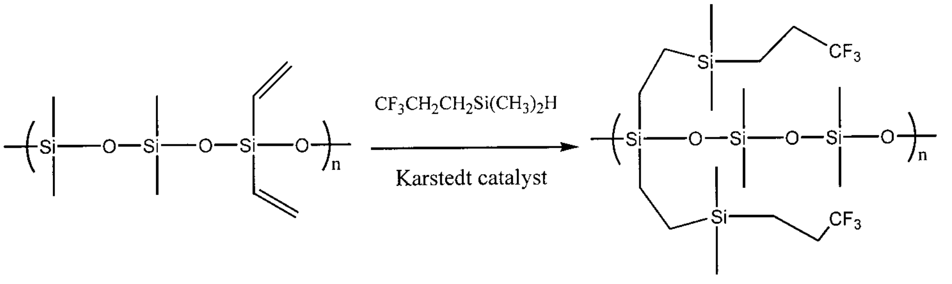

Figure 5. Chemical modification of poly(2,2-divinyl-4,4,6,6-tetramethyltrisiloxane) by Pt-catalyzed hydrosilylation with 3,3,3-trifluoropropyldimethylsilane.

while others are determined by the flexible siloxane backbone. The low T_g's of these materials are probably due to the flexible siloxane backbone. On the other hand, these chemical modified polyfluorinated materials have significantly different solubility properties. For this reason, it was necessary to use 1,1,2-trifluoro-1,2,2-trichloroethane (CFC-113) as a solvent for GPC analysis. Unfortunately, monodispersed polystyrene standards are not soluble in this system. Calibration of GPC results for the modified polymers is a challenge. The starting polymer had a molecular weight distribution $M_w/M_n = 38\,900/19\,000$. Thus, we expected poly[2,2-bis(3′,3′,3′-trifluoropropyldimethylsilylethyl)-4,4,6,6-tetramethyltrisiloxane] to have an $M_w/M_n = 88\,000/43\,000$. In fact, the M_w/M_n observed is 70 000/25 500. In the case of poly[2,2-bis(perfluorooctyl-1′*H*,1′*H*,2′*H*,2′*H*-dimethylsilylethyl)-4,4,6,6-tetramethyltrisiloxane], we expect a molecular weight distribution of $M_w/M_n = 167\,000/82\,000$, whereas in fact we observed $M_w/M_n = 98\,000/61\,000$. We believe these differences are the result of problems comparing GPC results obtained with two very different solvent systems and different standards. The fact that branched materials are well-known to have lower hydrodynamic radii and thus to give lower apparent molecular weights by GPC may be even more significant.

The thermal stability of the poly(2,2-divinyl-4,4,6,6-tetramethyltrisiloxane) and its chemically modified derivatives have been determined by TGA in both air and nitrogen atmospheres. Poly(2,2-divinyl-4,4,6,6-tetramethyltrisiloxane) is thermally stable to 300 °C in nitrogen. Above this temperature, it loses weight so that by 800 °C a residue to 65% of the initial sample weight remains. Poly(2,2-divinyl-4,4,6,6-tetramethyltrisiloxane is thermally stable to 200 °C in air. Above this temperature, it gains a small amount of weight until 350 °C. Above this temperature, it loses weight so that by 800 °C a residue of 75% of the initial sample weight remains. This high yield of residue may result from cross-linking that occurs during the initial weight gain oxidation process (200−350 °C). Poly(2,2-bis(3′,3′,3′-trifluoropropyldimethylsilyethyl)-4,4,6,6-tetramethyltrisiloxane) is thermally stable in both air and nitrogen to 280 °C. Above this temperature, it undergoes catastrophic decomposition in nitrogen. By 800 °C less than 15% residue remains. On the other hand, in air, a residue of 35% remains. Poly(2,2-bis(perfluoroctyl-1′*H*,1′*H*,2′*H*,2′*H*-dimethylsilylethyl)-4,4,6,6-tetramethyltrisiloxane) is thermally stable in both air and nitrogen to 280 °C. Above this temperature weight loss occurs so that by 800 °C only a small amount of residue remains (see Figure 7). The presence of trace amounts of platinum catalyst in both of the perfluoroalkyl siloxane polymers may affect their thermal stability.

Of note, the T_g (−128 °C) of poly(2,2-divinyl-4,4,6,6-tetramethyltrisiloxane) is lower than that of poly(dimethylsiloxane) (PDMS) ($T_g = -124$ °C). Needless to say, these measurements were checked by careful calibration of our DSC instrument with authentic samples of PDMS.

Experiment

^{1}H, ^{13}C, ^{19}F, and ^{29}Si NMR spectra were obtained on a Bruker AMX-500 MHz spectrometer. Five percent w/v chloroform-*d* or benzene-d_6 solutions were used to acquire ^{1}H, ^{13}C, and ^{19}F spectra. Twenty percent w/v CFC-113 solutions were used as solvent to acquire NMR data of polyfluorinated siloxane polymers. ^{29}Si NMR spectra were procured of 25% w/v chloroform-*d* or benzene-d_6 solutions. ^{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 liquid films on NaCl plates were recorded on a Perkin-Elmer Spectrum 2000 FT-IR spectrometer. 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 DB-5 capillary column.

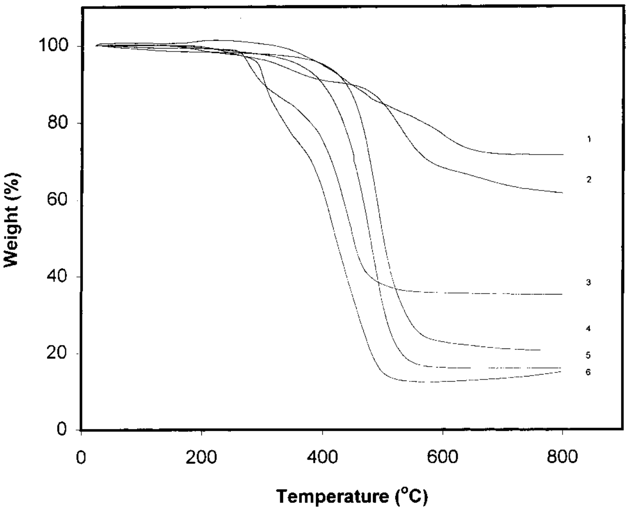

Figure 7. TGA of poly(2,2-divinyl-4,4,6,6-tetramethyltrisiloxane) (1 in air, 2 in nitrogen), poly[2,2-bis(3′,3′,3′-trifluoropropyldimethylsilylethyl)-4,4,6,6-tetramethyltrisiloxane] (3 in air, 4 in nitrogen), and poly[2,2-bis(perfluorooctyl-1′*H*,1′*H*,2′*H*,2′*H*-dimethylsilylethyl)-4,4,6,6-tetramethyltrisiloxane (6 in air and 5 in nitrogen).

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 with toluene solvent at a flow rate of 0.5 mL/min were used for the analysis of poly(2,2-divinyl-4,4,6,6-tetramethylsiloxane). The retention times were calibrated against known monodisperse polystyrene standards: 929 000, 114 200, 13 700, and 794 g/mol. Two 7.8 mm × 300 mm Styragel HR3 and HR4 columns in series with CFC-113 solvent at a flow rate of 0.7 mL/min was used for the analysis of polyfluorinated siloxane polymers. The retention times were calibrated against known poly(dimethylsiloxane) broad standard ($M_w/M_n = 52\,100/32\,800$).

Thermogravimetric analysis of the polymers 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 the rate of 4 °C/min from 25 to 800 °C. The glass transition temperature (T_g) of the polymers was determined on a Perkin-Elmer DSC-7. The DSC was calibrated from the heat of transition (−87.06 °C) and the melting point of cyclohexane (6.54 °C)[15] as well as from the T_g of poly(dimethylsiloxane) (−125 °C).[16] The temperature program for the analysis was begun at −150 °C and was increased at a rate of 10 °C/min to 50 °C.

Divinyldichlorosilane, hexamethyldisilazane, *sym*-tetramethyldisiloxane, 3,3,3-trifluoropropyldimethylchlorosilane, perfluorooctyl-1*H*,1*H*,2*H*,2*H*-dimethylchlorosilane, and Karstedt catalyst were obtained from Gelest. Lithium aluminum hydride, palladium on carbon (10%), HMPA, CFC-113, and triethylamine were purchased from Aldrich. All reactions were run in flame-dried glassware under argon.

Tetramethyldisiloxane-1,3-diol was prepared by oxidation of *sym*-tetramethyldisiloxane with water over a palladium on carbon catalyst.[17]

3,3,3-Trifluoropropyldimethylsilane. Lithium aluminum hydride (0.8 g, 26 mmol) was placed in a three-necked round-bottom flask furnished with a pressure equaling addition funnel and a reflux condenser. Anhydrous diethyl ether (50 mL) was added by syringe to the flask. A solution of 3,3,3-trifluoropropyldimethylchlorosilane (9 g, 47 mmol) in anhydrous diethyl ether (20 mL) was added dropwise at room temperature. After stirring for an additional hour, the mixture was filtered. The solution was fractionated by distillation through a 10 cm vacuum jacketed Vigreux column. In this way, 3,3,3-trifluoropropyldimethylsilane (4.7 g), bp 78 °C, was obtained in 64% yield.[18] ^{1}H NMR δ: 0.06 (d, 6H, $J = 3.5$ Hz), 0.76 (dt, 2H, $J = 3.5$ and 8.5 Hz), 2.01 (m, 2H), 3.84 (septet, 1H, $J = 3.5$ Hz). ^{13}C NMR δ: -4.92, 5.98, 29.25 (q, $J_{\mathrm{C-F}} = 30$ Hz), 127.64 (q, $J_{\mathrm{C-F}} = 276$ Hz). ^{19}F NMR δ: -69.19 (t, $J_{\mathrm{F-H}} = 10.4$ Hz). ^{29}Si NMR δ: -11.62. IR ν: 2964, 2908, 2122 (Si$-$H). 1444, 1427, 1366, 1316, 1266, 1212, 1203, 1127, 1069, 1031, 919, 890, 838, 771 cm^{-1}.

Perfluorooctyl-1*H*,1*H*,2*H*,2*H*-dimethylsilane. Perfluorooctyl-1*H*,1*H*,2*H*,2*H*-dimethylchlorosilane and lithium aluminum hydride were reacted as above. Perfluorooctyl-1*H*,1*H*,2*H*,2*H*-dimethylsilane was obtained in 91% yield; bp 77 °C/28 mmHg.[19] ^{1}H NMR δ: 0.13 (d, 6H, $J = 4.0$ Hz), 0.84 (dt, 2H, $J = 4.0$ and 8.5 Hz), 2.07 (m, 2H), 3.93 (septet, 1H, $J = 4.0$ Hz). ^{13}C NMR δ: -4.82, 3.90, 26.62 (t, $J_{\mathrm{C-F}} = 24.1$ Hz), 108.98 (m), 109.29 (m), 111.17 (m), 111.44 (m), 117.56 (qt, $J_{\mathrm{C-F}} = 288$ and 33.3 Hz), 118.61 (tt, $J_{\mathrm{C-F}} = 286$ and 31.5 Hz). ^{19}F NMR δ: -126.84, -123.99, -123.52, -122.57, -116.74 (t, 2F, $J_{\mathrm{F-H}} = 16$ Hz), -81.58 (t, 3F, $J_{\mathrm{F-H}} = 3$ Hz). ^{29}Si NMR δ: -11.31. IR ν: 2965, 2911, 2126 (Si$-$H), 1443, 1424, 1361, 1351, 1318, 1241, 1210, 1195, 1166, 1145, 1121, 1070, 1018, 918, 892, 880, 839, 813, 770 cm^{-1}.

2,2-Divinyl-4,4,6,6-tetramethylcyclotrisiloxane. Triethylamine (6.9 g, 69 mmol) and 40 mL of anhydrous diethyl ether were placed in a 250 mL three-neck round-bottom flask equipped 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 divinyldichlorosilane (5 g, 33 mmol) and 15 mL of anhydrous diethyl ether was placed in one addition funnel. A solution of tetramethyldisiloxane-1,3-diol (5.4 g, 33 mmol) and 15 mL of anhydrous diethyl ether was placed in the other. The two solutions were added dropwise simultaneously over 3 h. Triethylammonium chloride was removed by filtration. The diethyl ether solution was washed with water, dried over anhydrous magnesium sulfate, and filtered, and the volatile solvents removed by evaporation under reduced pressure. The residue was fractionally distilled through a 10 cm vacuum jacketed Vigreux column. In this way, 3.5 g of 2,2-divinyl-4,4,6,6-tetramethylcyclotrisiloxane was obtained in 44% yield; bp 67 °C/1.5 mmHg. ^{1}H NMR δ: 0.20 (s, 12H), 5.94 (dd, 2H, $J = 16.5$ and 8 Hz), 6.08 (d, 2H, $J = 16.5$ Hz), 6.09 (d, 2H, $J = 8$ Hz). ^{13}C NMR δ: 0.89, 134.1, 135.4. ^{29}Si NMR δ: -38.6 (s, 1Si), -7.2 (s, 2Si). IR ν: 3059, 3015, 2965, 2906, 1597 (C$=$C), 1406, 1261, 1016, 965, 856, 807, 742 cm^{-1}. GC-MS m/z (rel int): 246 (5%) ($\mathrm{M}^{\bullet+}$), 231 (100%) $(\mathrm{M-CH_3})^+$, 219 (19%) (M$-$vinyl)$^+$.

Poly(2,2-divinyl-4,4,6,6-tetramethyltrisiloxane) (AROP). 2,2-Divinyl-4,4,6,6-tetramethylcyclotrisiloxane (1 g, 4.06 mmol) was placed in a 10 mL round-bottom flask that was equipped with a Teflon-covered magnetic stir bar and sealed with a rubber septum. THF (500 μL), HMPA (4 μL), and 25 μL of a THF solution of dilithiodiphenylsilanediolate (0.33 mol/L, 8.25 μmol) initiator were added. The reaction was stirred for 2 h at room temperature. Trimethylchlorosilane (10 μL) and triethylamine (10 μL) were sequentially added to quench the 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, 0.96 g of poly(2,2-divinyl-4,4,6,6-tetramethyltrisiloxane) was obtained in 96% yield; $M_w/M_n = 38\,900/19\,600$ by GPC. The calculated value of M_n based on the [monomer]/[initiator] molar concentration is approximately 120 000 g/mol; $T_g = -128$ °C. ^{1}H NMR δ: 0.30 (s, 12H), 6.037 (dd, 2H, $J = 14.5$ and 4.5 Hz), 6.059 (dd, 2H, $J = 20.5$ and 4.5 Hz), 6.221 (dd, 2H, $J = 20.5$ and 14.5 Hz). ^{13}C NMR δ: 1.49, 134.7, 135.7. ^{29}Si NMR δ: -49.17, -20.20. IR ν: 3057, 3016, 2964, 2903, 1598 (C$=$C), 1406, 1261, 1094 (Si$-$O$-$Si), 1022 (Si$-$O$-$Si), 1007, 962, 846, 799, 744 cm^{-1}.

Poly(2,2-divinyl-4,4,6,6-tetramethyltrisiloxane) (AROP). A similar experiment was carried out at 0 °C for 2 h. A 96% yield of polymer was obtained; $M_w/M_n = 12\,300/9200$, $T_g = -128$ °C. It had identical spectral properties to that prepared above.

Copoly(dimethylsiloxane/divinylsiloxane) (ACROP). 2,2-Divinyl-4,4,6,6-tetramethylcyclotrisiloxane (0.5 g, 2 mmol) was placed in a test tube that was equipped with a Teflon-covered magnetic stir bar and sealed with a rubber septum. CFC-113 (100 μL) was injected into the flask that was cooled to -10 °C. Triflic acid (4 μL, 0.045 mmol) was added into the system. The polymerization was allowed to proceed for 1.0 h at -10 °C. At this time, hexamethyldisilazane (25 μL, 0.12 mmol) was added to quench the reaction. The polymer was precipitated three times from a mixture of diethyl ether and methanol and dried under vacuum. In this way, 0.48 g of 80% yield of material with $M_w/M_n = 106\,300/53\,100$ and $T_g = -128$ °C was obtained. It had the following spectral properties. ^{1}H NMR δ: 0.28 (s, 0.84H), 0.29 (s, 2.44H), 0.30 (s, 1.66H), 0.31 (s, 1.06H), 6.21 (m, 1H), 6.05 (m, 2H). ^{13}C NMR δ: 1.48, 1.53, 134.66, 134.72, 135.62, 135.67. ^{29}Si NMR δ: -49.14, -49.17, -49.23, -49.25, -21.16, -21.02, -20.40, -20.38, -20.27, -20.24, -19.48.

Poly[2,2-bis(perfluorooctyl-1′*H*,1′*H*,2′*H*,2′*H*-dimethylsilylethyl)-4,4,6,6-tetramethyltrisiloxane)]. [Poly(2,2-divinyl-4,4,6,6-tetramethyltrisiloxane)] (0.24 g, 0.98 mmol, $M_w/M_n = 38\,900/19\,600$), perfluorooctyl-1*H*,1*H*,2*H*,2*H*-dimethylsilane (0.85 g, 2.1 mmol), CFC-113 (3 mL), and Karstedt catalyst (5 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 85 °C overnight. The polymer was precipitated from a mixture of CFC-113/$\mathrm{Et_2O}$/MeOH (1:1:5). It was dried under vacuum. In this way, 0.97 g, 94%, yield of material with $T_g = -67$ °C and $M_w/M_n = 97\,700/61\,100$ was obtained. ^{1}H NMR δ: 0.054 (s, 12H), 0.149 (s, 12H), 0.538 (m, 8H), 0.800 (m, 4H), 1.115 (d, 0.66 H, $J = 6.0$ Hz), 2.035 (m, 4H). ^{13}C NMR δ: -4.28, 1.711, 4.714, 7.096, 7.966, 26.813 (t, $J_{\mathrm{C-F}} = 24$ Hz), multiplets center at 112.50, 112.26, 112.01, 111.70, 118.26 (qt, $J_{\mathrm{C-F}} = 257$ and 31 Hz), 119.53 (tt, $J_{\mathrm{C-F}} = 254$ and 32 Hz). ^{19}F NMR δ: -127.5 (br.s, 2F), -124.5 (br.s, 2F), -124.1 (br.s, 2F), -123.1 (br.s, 2F), -117.5 (br.s, 2F), -82.5 (br.s, 3F). ^{29}Si NMR δ: 5.59 (2Si), -21.98 (2Si), -23.59 (1Si). IR ν: 2962, 2911, 2883, 1443, 1426, 1408, 1360, 1351, 1317, 1238, 1209, 1194, 1166, 1145, 1118, 1100, 1069, 1020, 898, 844, 804 cm^{-1}.

Poly[2,2-bis(3′,3′,3′-trifluoropropyldimethylsilylethyl)-4,4,6,6-tetramethyltrisiloxane)]. Poly(2,2-divinyl-4,4,6,6-tetramethyltrisiloxane) (0.4 g, 1.63 mmol) and 3′,3′,3′-trifluoroproyldimethylsilane (0.55 g, 3.5 mmol) were reacted as above. In this way, 0.87 g, 96%, yield of material with $M_w/M_n = 70\,100/29\,500$ and $T_g = -81$ °C was obtained. ^{1}H NMR δ: 0.042 (s, 12H), 0.149 (s, 12H), 0.526 (m, 8H), 0.773 (m, 4H), 1.102 (d, 0.56H, $J = 6.0$ Hz), 1.993 (m, 4H). ^{13}C NMR δ: -4.242, 1.739, 6.922, 7.067, 7.875, 29.710 (t, $J_{\mathrm{C-F}} = 31$ Hz), 128.4 (q, $J_{\mathrm{C-F}} = 275.8$ Hz). ^{19}F NMR δ: -70.3. ^{29}Si NMR δ: 5.08 (2Si), -20.00 (2Si), -23.56 (1Si). IR ν: 2961, 2911, 2880, 2789, 1447, 1408, 1365, 1317, 1262, 1212, 1199, 1124, 1099, 1068, 1021, 901, 847, 803, 769 cm^{-1}.

References and Notes

(1) Paulasaari, J. K.; Weber, W. P. *Macromolecules* **1999**, *32*, 5217.

(2) Carraher, C. E., Jr.; Moore, J. A. *Modification of Polymers*; Plenum: New York, 1983.

(3) Benham, J. L.; Kinstle, J. F. *Chemical Reactions On Polymers*; ACS Symposium Series 364; American Chemical Society, Washington, DC, 1988.

(4) Arkles, B. *Silicon, Germanium, & Tin Compounds, Metal Alkoxides, Metal Diketonates, Silicones*; Gelest, Inc.: Tullytown, PA, 1998; p 488.

(5) Hempenius, M. A.; Lammertink, R. G. H.; Vancso, G. J. *Macromol. Rapid Commun.* **1996**, *17*, 299.
(6) Hempenius, M. A.; Lammertink. R. G. H.; Vancso, G. J. *Macromolecules* **1997**, *30*, 266.
(7) Harris, G. I. *J. Chem. Soc.* **1963**, 5978.
(8) Rozga-Wijas, K.; Chojnowski, J.; Zundel, T.; Boileau, S. *Macromolecules* **1996**, *29*, 2711.
(9) Battjes, K.; Kuo, C.-M.; Miller, R. L.; Saam, J. C. *Macromolecules* **1995**, *28*, 790.
(10) Ziemelis, M. J.; Saam, J. C. *Macromolecules* **1989**, *22*, 2111.
(11) Chojnowski, J.; Kazmierski, K Cypryk, M.; Fortuniak, W. *Silicones and Silicone Modified Materials*; ACS Symposium Series 729; American Chemical Society: Washington, DC, 2000.
(12) Cypryk, M.; Kazmierski, K.; Fortuniak, W.; Chojnowski, J. *Macromolecules* **2000**, *33*, 1536.
(13) Paulasaari, J. K.; Weber, W. P. *Polym. Prepr.* **2000**, *41* (1), 133.
(14) Paulasaari, J. K.; Weber, W. P. *Polym. Mater. Sci. Eng.* **2000**, *82*. 71.
(15) Aston, J. G.; Szabz, G. J.; Fink, H. L. *J. Am. Chem., Soc.* **1943**, *65*, 1135.
(16) Clarson, S. J.; Dodgson, K.; Semlyen, J. A. *Polymer* **1985**, *26*, 930.
(17) Barnes, G. H., Jr.; Daughenbaugh, N. E. *J. Org. Chem.* **1966**, *31*, 885.
(18) Steward, O. W.; Pierce, O. R. *J. Am. Chem. Soc.* **1961**, *83*, 1916.
(19) Ameduri, B.; Boutevin, B.; Nouiri, M.; Talbi, M. *J. Fluorine Chem.* **1995**, *74*, 191.

MA010288S