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Poly(silyl ether)s by Ruthenium-Catalyzed Hydrosilylation Polymerization of Aliphatic ω-Dimethylsilyloxy Ketones and Copolymerization of Aliphatic α,ω-Diketones with α,ω-Dihydridooligodimethylsiloxanes

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ABSTRACT: The hydrosilylation polymerization of aliphatic ω-dimethylsilyloxy ketones is catalyzed by activated dihydridocarbonyltris(triphenylphosphine)ruthenium (**Ru**) to yield unsymmetrical poly(silyl ether)s. Likewise, **Ru** catalyzes the copolymerization of aliphatic α,ω-diketones with α,ω-dihydridooligodimethylsiloxanes to yield symmetrical poly(silyl ether)s. These polymers have been characterized by ^{1}H, ^{13}C, and ^{29}Si NMR as well as IR spectroscopy. Their molecular weight distributions (M_w/M_n) have been determined by GPC. End group analysis by ^{1}H NMR provides an independent measure of M_n. Their thermal stability was measured by TGA, and their glass transition temperatures (T_g's) were determined by DSC. Chiral centers affect the NMR spectra of these poly(silyl ether)s. The effect of siloxane chain length on copolymer T_g has been evaluated.

Introduction

Poly(dimethylsiloxane) (PDMS) has a melting point (T_m) of approximately −40 °C and a glass transition temperature (T_g) of approximately −125 °C.[1] Many copolymers, which contain oligodimethylsiloxane (ODMS) units, no longer exhibit detectable T_m's but still have T_g's close to that of PDMS.[1] While PDMS is biocompatible,[2] the strength of the Si−O−Si bond makes it relatively resistant to hydrolysis and thus to biodegradation. Poly(silyl ether)s, on the other hand, contain Si−O−C bonds, which are more susceptible to acid- or base-catalyzed hydrolysis.[3] This hydrolytic instability may make them attractive as materials whose degradation will limit their long-term environmental impact or for the controlled release of drugs.[4] There is also interest in the possible utility of poly(silyl ether)s as sensor materials,[5] membranes,[6] and elastomers.[7] The stability to high temperatures and ultraviolet radiation of some poly(silyl ether)s may make them useful in space applications.[8] Certain poly(silyl ether)s exhibit flame-retardant properties.[9]

A general method to prepare symmetrical poly(silyl ether)s is the condensation polymerization of diols with either dialkoxysilanes,[10] diaminosilanes,[8,11] or dihalosilanes.[10] Unsymmetrical poly(silyl ether)s have been prepared by acid-catalyzed ring-opening polymerization of 2-sila-1-oxacyclopentanes.[12] Because of the instability of poly(silyl ether)s to acid or base, synthetic methods, which utilize neutral conditions, are favored. These include transition-metal catalysis. There is considerable interest in the application of transition-metal catalysis in both synthetic organic and polymer chemistry. High molecular weight symmetrical poly(silyl ether)s have been obtained by rhodium- or palladium-catalyzed cross-dehydrocoupling of aliphatic and aromatic α,ω-bis(Si−H) compounds with α,ω-diols.[13−16] Quaternary ammonium chloride-catalyzed reaction of bis(oxetane)s or bis(epoxide)s with dichlorosilanes yields poly(silyl ether)s containing pendant chloromethyl groups.[17−20] Palladium-catalyzed condensation copolymerization of α,ω-bis(Si−H) compounds with para-quinones has also been utilized.[21] We have reported the $RuH_2(CO)(PPh_3)_3$ (**Ru**)-catalyzed dehydrogenative silylation condensation copolymerization of ortho-quinones with α,ω-dihydridooligodimethylsiloxanes to yield aromatic poly(silyl ether)s.[22] We have also reported the **Ru**-catalyzed hydrosilylation copolymerization of aromatic α,ω-diketones with α,ω-dihydridooligodimethylsiloxanes to yield poly(silyl ether)s.[23]

Herein, we report the **Ru**-catalyzed polymerization of aliphatic ω-dimethylsilyloxy ketones to yield unsymmetrical poly(silyl ether)s and the **Ru**-catalyzed hydrosilylation copolymerization of aliphatic α,ω-diketones with α,ω-dihydridooligodimethylsiloxanes to yield symmetrical poly(silyl ether)s.

Results

Ru, activated with a stoichiometric amount of styrene, catalyzes the hydrosilylation copolymerization reactions of 2,5-hexanedione (**I**) or 2,7-octanedione (**II**) with 1,1,3,3-tetramethyldisiloxane (**III**) to yield symmetrical aliphatic poly(silyl ether)s: *alt*-copoly[2,2,4,4-tetramethyl-1,3,5-trioxa-2,4-disila-1,5-pentanylene/2,5-hexanylene] (**VII**) and *alt*-copoly[2,2,4,4-tetramethyl-1,3,5-trioxa-2,4-disila-1,5-pentanylene/2,7-octanylene] (**XI**), respectively. Similar copolymerizations of **I** or **II** with 1,1,3,3,5,5-hexamethyltrisiloxane (**IV**), 1,1,3,3,5,5,7,7-octamethyltetrasiloxane (**V**), or 1,1,3,3,5,5,7,7,9,9-decamethylpentasiloxane (**VI**) yield the expected symmetrical poly(silyl ether)s (Figure 1). **Ru**-catalyzed polymerization of 5-dimethylsilyloxy-2-pentanone (**XV**) yields unsymmetrical poly(2,2,7-trimethyl-1,3-dioxa-2-sila-1,7-heptanylene) (**XVII**). 4-Dimethylsilyloxy-2-butanone (**XVI**) was polymerized in a manner similar to give poly(2,2,6-trimethyl-1,3-dioxa-2-sila-1,6-hexanylene) (**XVIII**).

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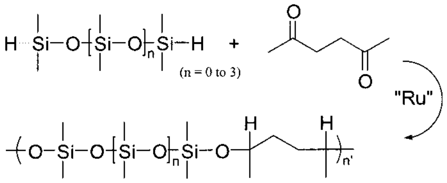

Figure 1. **Ru**-catalyzed hydrosilylation copolymerization.

Experimental Section

^{1}H, ^{13}C, and ^{29}Si NMR spectra were obtained on a Bruker AMX-500 MHz spectrometer operating in the FT mode. ^{1}H and ^{13}C NMR spectra of 5% w/v $CDCl_3$ solutions were obtained. ^{29}Si NMR spectra of 25% w/v $CDCl_3$ solutions were acquired. ^{13}C NMR spectra were obtained with broad-band proton decoupling. A heteronuclear gated decoupling pulse sequence (NONOE) with a 60 s delay was used to acquire ^{29}Si NMR spectra. Residual $CHCl_3$ was used as an internal standard for ^{1}H and ^{13}C NMR. ^{29}Si NMR spectra were referenced to internal TMS. IR spectra of neat films on NaCl plates were recorded using a Perkin-Elmer Spectrum 2000 FT-IR spectrometer.

GPC analyses of the molecular weight distributions (M_w/M_n) of the polymers were performed on a Waters system equipped with a 401 refractive index detector. Two 7.8 × 300 mm Styragel columns packed with <5 μm divinylbenzene cross-linked polystyrene HR4 and HR2 in series were used for the analysis. The eluting solvent was toluene at a flow rate of 0.3 mL/min. The retention times were calibrated against known monodisperse polystyrene standards: (929 000, 212 400, 47 400, 13 700, and 794). Low-resolution GC-MS analysis was performed on a Hewlett-Packard 4107 gas/liquid-phase chromatograph equipped with a mass selective Quadrupole detector and a 30 m DB-5 capillary column.

High-resolution mass spectra were run at the University of California, Riverside, Mass Spectroscopy Facility on a VG-7070 EHF instrument. Exact masses were determined by peak matching against known masses of perfluorokerosene. Ammonia was employed as the chemical ionization agent.

TGA of the polymers was measured on a Shimadzu TGA-50 instrument at a flow rate of 40 cm^3 of nitrogen/min. The temperature was increased 4 °C/min from 25 to 800 °C. The T_g's of the polymers were determined on a Perkin-Elmer DSC-7. The DSC was calibrated using the thermal transition temperature (−87.06 °C) and melting point (6.54 °C) of cyclohexane.[24] The temperature was increased 10 °C/min from −150 to 25 °C.

All reactions were conducted in flame-dried glassware under argon with a Teflon-covered magnetic stir bar.

I, 1,7-octadiene, 5-hydroxy-2-pentanone, toluene, and styrene were obtained from Aldrich. 4-Hydroxy-2-butanone was purchased from Lancaster. Hexamethylcyclotrisiloxane (**D$_3$**), 1,1,3,3-tetramethyldisilazane, **III**, **IV**, and **V** were purchased from Gelest.

Dihydridocarbonyltris(triphenylphosphine)ruthenium (Ru) was prepared from ruthenium trichloride hydrate.[25] It was activated as follows. **Ru** (0.04 g, 43.6 μmol), toluene (0.25 mL), and an equimolar amount of styrene (5.0 μL, 43.6 μmol) were placed in a 20 mL Ace pressure tube. The tube was sealed and heated at 125 °C for 3 min. The color of the activated catalyst is red.[26]

2,7-Octanedione (II) was prepared by oxymercuration−demercuration of 1,7-octadiene,[27] followed by oxidation of 2,7-octanediol with a chromium trioxide bis(pyridine) complex in CH_2Cl_2.[28]

1,1,3,3,5,5,7,7,9,9-decamethylpentasiloxane (VI) was prepared by the triflic acid-catalyzed reaction of **D$_3$** with **III**.[23]

***alt*-Copoly[2,2,4,4-tetramethyl-1,3,5-trioxa-2,4-disila-1,5-pentanylene/2,5-hexanylene] (VII).** **I** (1.14 g, 10.0 mmol), **III** (1.34 g, 10.0 mmol), and activated **Ru** catalyst were placed in an Ace pressure tube. The tube was sealed and heated to 125 °C. After 5 min, the color of the reacting solution was brown. After 18 h at 125 °C, the reaction was stopped. The polymer was dissolved in a minimum amount of THF and precipitated from methanol. In this way, 2.1 g (84.5% yield) of polymer with M_w/M_n = 11 100/7800, T_g = −83 °C, was obtained. ^{1}H NMR δ: 0.04 (s, 12H), 1.15 (d, 6H, J = 6 Hz), 1.34 (m, 2H), 1.49 (m, 2H), 3.84 (m, 2H). ^{13}C NMR δ: −0.48, −0.21, 23.64, 23,45, 35.44, 35.94, 68.21, 68.58. ^{29}Si NMR δ: −14.84 (s, 0.5Si), −14.83 (s, 0.5Si), −14.76 (s, 0.5Si), −14.75 (s, 0.5Si). IR ν: 2967, 2932, 2906, 2870, 1445, 1410, 1374, 1326, 1258, 1212, 1131, 1050, 984, 893, 834 cm^{-1}. TGA: **VII** is stable to 275 °C. Between 275 and 425 °C, catastrophic decomposition occurs. Ninety percent of initial weight is lost.

***alt*-Copoly[2,2,4,4,6,6-hexamethyl-1,3,5,7-tetraoxa-2,4,6-trisila-1,7-heptanylene/2,5-hexanylene] (VIII)** was prepared by a **Ru**-catalyzed reaction of **I** (1.14 g, 10.0 mmol) and **IV** (2.09 g, 10.0 mmol) as above. In this way, 2.8 g (86.8% yield) of polymer with M_w/M_n = 85 500/67 500, T_g = −90 °C, was obtained. ^{1}H NMR δ: 0.07 (s, 12H), 0.09 (s, 6H), 1.15 (d, 6H, J = 6 Hz), 1.39 (m, 2H), 1.53 (m, 2H), 3.93 (m, 2H). ^{13}C NMR δ: −0.29, −0.06, 1.15, 24.01, 24.06, 35.84, 36.11, 68.36, 68.72. ^{29}Si NMR δ: −22.33 (s, 1Si), −15.55 (s, 2Si). IR ν: 2966, 2934, 2906, 2871, 1446, 1413, 1377, 1326, 1261, 1214, 1132, 1082, 1045, 983, 894, 831, 800 cm^{-1}. TGA: **VIII** is stable to 200 °C. Between 200 and 425 °C, catastrophic decomposition occurs. Ninety percent of initial weight is lost.

***alt*-Copoly[2,2,4,4,6,6,8,8-octamethyl-1,3,5,7,9-pentaoxa-2,4,6,8-tetrasila-1,9-nonanylene/2,5-hexanylene] (IX)** was prepared by a **Ru**-catalyzed reaction of **I** (0.80 g, 7.0 mmol) and **V** (1.98 g, 7.0 mmol) as above. After precipitation, 2.29 g, 82.5% yield, M_w/M_n = 12 800/6400, T_g = −96 °C, was obtained. ^{1}H NMR δ: 0.05 (s, 12H), 0.06 (s, 12H), 1.14 (d, 6H, J = 6 Hz), 1.37 (m, 2H), 1.49 (m, 2H), 3.86 (m, 2H). ^{13}C NMR δ: −0.51, −0.22, 1.02, 23.65, 23.84, 35.45, 35.96, 68.18, 68.58. ^{29}Si NMR δ: −22.07 (s, 1Si), −22.04 (s, 1Si), −14.71 (s, 1Si), −14.64 (s, 1Si). IR ν: 2962, 2931, 2906, 2870, 1445, 1412, 1374, 1258, 1212, 1080, 1032, 890 cm^{-1}. TGA: **IX** is stable in nitrogen to 225 °C. Between 225 and 450 °C, catastrophic decomposition occurs. Ninety percent of initial weight is lost. **IX** is stable in air to 175 °C. Between 175 and 550 °C, gradual decomposition occurs. Seventy-five percent of initial weight is lost.

***alt*-Copoly[2,2,4,4,6,6,8,8,10,10-decamethyl-1,3,5,7,9,11-hexaoxa-2,4,6,8,10-pentasila-1,11-dodecanylene/2,5-hexanylene] (X)** was prepared as above by reaction of **I** (0.80 g, 7.0 mmol) and **VI** (2.50 g, 7.0 mmol) as above. After precipitation, 2.8 g, 85.0% yield, M_w/M_n = 20 050/18 900, T_g = −106 °C, was obtained. ^{1}H NMR δ: 0.037 (s, 6H), 0.042 (s, 12H), 0.05 (s, 12H), 1.13 (d, 6H, J = 6 Hz), 1.35 (m, 2H), 1.50 (m, 2H), 3.86 (m, 2H). ^{13}C NMR δ: −0.50, −0.22, 1.03, 23.66, 23.85, 35.46, 35.98, 68.18, 68.58. ^{29}Si NMR δ: −22.08 (s, 1Si), −22.15 (s, 1Si), −21.99 (s, 1Si), −14.76 (s, 1Si), −14.68 (s, 1Si). IR ν: 2961, 2928, 2906, 2867, 1446, 1413, 1374, 1258, 1211, 1093, 1032, 894, 861 cm^{-1}. TGA: **X** is stable to 250 °C. Between 250 and 500 °C, catastrophic decomposition occurs. Ninety percent of initial weight is lost.

***alt*-Copoly[2,2,4,4-tetramethyl-1,3,5-trioxa-2,4-disila-1,5-pentanylene/2,7-octanylene] (XI)** was prepared by a **Ru**-catalyzed reaction of **II** (0.250 g, 1.76 mmol) and **III** (0.236 g, 1.76 mmol) as above. In this way, 0.37 g (76.1% yield) of polymer with M_w/M_n = 16 700/9100, T_g = −87 °C, was obtained. ^{1}H NMR δ: 0.07 (s, 12H), 1.13 (d, 6H, J = 6 Hz), 1.23 (m, 2H), 1.35 (m, 4H), 1.45 (m, 2H), 3.87 (m, 2H). ^{13}C NMR δ: −0.42, −0.016, 23.70, 25.98, 39.63, 68.41. ^{29}Si NMR δ: −14.77 (s, 2Si). IR ν: 2965, 2938, 2906, 2868, 1449, 1409, 1376, 1258, 1191, 1137, 1086, 1046, 833, 796, 707 cm^{-1}. TGA: **XI** is stable to 150 °C. Between 150 and 530 °C, catastrophic decomposition occurs. Ninety-seven percent of initial weight is lost.

***alt*-Copoly[2,2,4,4,6,6-hexamethyl-1,3,5,7-tetraoxa-2,4,6-trisila-1,7-heptanylene/2,7-octanylene] (XII)** was prepared as above by reaction of **II** (0.250 g, 1.76 mmol) and **IV** (0.367 g, 1.76 mmol) as above. In this way, 0.33 g (53.5% yield) of polymer with M_w/M_n = 22 000/10 500, T_g = −94 °C, was obtained. ^{1}H NMR δ: 0.06 (s, 18H), 1.13 (d, 6H, J = 6 Hz), 1.22 (m, 2H), 1.35 (m, 4H), 1.45 (m, 2H), 3.86 (m, 2H). ^{13}C NMR δ: −0.42, −0.16, 1.04, 23.70, 25.98, 39.64, 68.40. ^{29}Si NMR δ: −22.16 (s, 1Si), −14.75 (s, 2Si). IR ν: 2965, 2938, 2906, 2863,

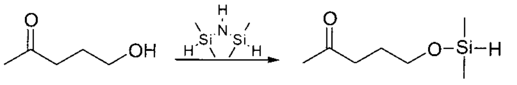

Figure 2. Synthesis of 5-dimethylsilyloxy-2-pentanone.

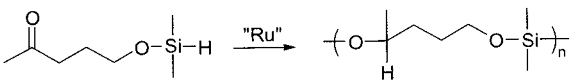

Figure 3. Polymerization of 5-dimethylsilyloxy-2-pentanone.

1446, 1411, 1374, 1258, 1137, 1089, 1038, 798, 710 cm^{-1}. TGA: **XII** is stable to 190 °C. Between 190 and 575 °C catastrophic decomposition occurs. Ninety-five percent of initial weight is lost.

***alt*-Copoly[2,2,4,4,6,6,8,8-octamethyl-1,3,5,7,9-pentaoxa-2,4,6,8-tetrasila-1,9-nonanylene/2,7-octanylene] (XIII)** was prepared as above by reaction of **II** (0.250 g, 1.76 mmol) with **V** (0.497 g, 1.76 mmol) as above. In this way, 0.60 g (80.0% yield) of polymer with M_w/M_n = 11 700/5300, T_g = −98 °C, was obtained. ^{1}H NMR δ: 0.056 (s, 12H), 0.061 (s, 12H), 1.13 (d, 6H, J = 6 Hz), 1.22 (m, 2H), 1.34 (m, 4H), 1.43 (m, 2H), 3.86 (m, 2H). ^{13}C NMR δ: −0.44, −0.16, 1.04, 23.67, 25.97, 39.64, 68.39. ^{29}Si NMR δ: −22.11 (s, 2Si), −12.67 (s, 2Si). IR ν: 2964, 2927, 2906, 2863, 1446, 1411, 1379, 1255, 1188, 1089, 1035, 866, 798 cm^{-1}. TGA: **XIII** is stable to 195 °C. Between 195 and 530 °C, catastrophic decomposition occurs. Ninety-seven percent of initial weight is lost.

***alt*-Copoly[2,2,4,4,6,6,8,8,10,10-decamethyl-1,3,5,7,9,11-hexaoxa-2,4,6,8,10-pentasila-1,11-dodecanylene/2,7-octanylene] (XIV)** was prepared as above by reaction of **II** (0.250 g, 1.76 mmol) with **VI** (0.627 g, 1.76 mmol) as above. In this way, 0.65 g (70.5% yield) of polymer with M_w/M_n = 35 550/20 700, T_g = −104 °C, was obtained. ^{1}H NMR δ: 0.056 (s, 18H), 0.062 (s, 12H), 1.13 (d, 6H, J = 6 Hz), 1.22 (m, 2H), 1.34 (m, 4H), 1.43 (m, 2H). ^{13}C NMR δ: −0.44, −0.16, 1.04, 23.69, 25.97, 39.64, 68.39. ^{29}Si NMR δ: −22.02 (s, 2Si), −21.89 (s, 1Si), −14.67 (s, 2Si). IR ν: 2960, 2938, 2906, 2863, 1446, 1411, 1379, 1261, 1099, 1024, 866, 796 cm^{-1}. TGA: **XIV** is stable to 190 °C. Between 190 and 560 °C, catastrophic decomposition occurs. Ninety-eight percent of initial weight is lost.

5-Dimethylsilyloxy-2-pentanone (XV) was prepared by reaction of 5-hydroxy-2-pentanone (4.09 g, 40 mmol) and 1,1,3,3-tetramethyldisilazane (5.87 g, 44 mmol) (Figure 2). **XV** was purified by fractional distillation through a 10 cm vacuum-jacketed Vigreux column. A fraction, bp 52−54 °C/2.5 mm, 5.9 g, 82% yield, was collected. ^{1}H NMR δ: 0.10 (d, 6H, J = 3 Hz), 1.71 (pent, 2H, J = 7 Hz), 2.05 (s, 3H), 2.42 (t, 2H, J = 7 Hz), 3.53 (t, 2H, J = 7 Hz), 4.50 (sept, 1H, J = 3 Hz) ppm. ^{13}C NMR δ: −1.64, 26.34, 29.87, 40.01, 63.15, 208.25 ppm. ^{29}Si NMR δ: 5.60 ppm. IR ν: 2958, 2933, 2903, 2869, 2110, 1719, 1477, 1420, 1365, 1314, 1253, 1166, 1094, 1006, 904, 836, 783, 766, 743, 714 cm^{-1}. GC-MS of **XV** m/z (rel int): 160 (3%) ($M^{\bullet+}$), 159 (10%) $(M - 1)^+$, 145 (27%) $(M - 15)^+$, 116 (50%), 75 (100%). High-resolution mass spectra calculated for $C_7H_{15}O_2Si$ $(M-H)^+$, 159.0841; found, 159.0837.

4-Dimethylsilyloxy-2-butanone (XVI) was prepared by reaction of 4-hydroxy-2-butanone (3.52 g, 40 mmol) and 1,1,3,3-tetramethyldisilazane (5.87 g, 44 mmol). **XVI** was purified by fractional distillation as above. A fraction, bp 85−87 °C/64 mmHg, 5.1 g, 87% yield, was collected. ^{1}H NMR δ: 0.15 (d, 6H, J = 3 Hz), 2.13 (s, 3H), 2.61 (t, 2H, J = 6.5 Hz), 3.85 (t, 2H, J = 6.5 Hz), 4.55 (sept, 1H, J = 3 Hz) ppm. ^{13}C NMR δ: −1.70, 30.51, 46.19, 59.43, 207.02 ppm. ^{29}Si NMR δ: 6.48 ppm. IR ν: 2962, 2908, 2879, 2116, 1717, 1422, 1393, 1360, 1317, 1255, 1172, 1102, 1077, 1030, 974, 947, 902, 836, 768, 720 cm^{-1}. GC-MS of **XVI** m/z (rel int.): 146 (3%) ($M^{\bullet+}$), 145 (16%) $(M - 1)^+$, 131 (76%) $(M - 15)^+$, 115 (25%), 101 (100%). High-resolution mass spectra calculated for $C_6H_{13}O_2Si$ $(M-H)^+$, 145.0685; found, 145.0686.

Poly(2,2,7-trimethyl-1,3-dioxa-2-sila-1,7-heptanylene) (XVII) was prepared by an activated **Ru**-catalyzed hydrosilylation polymerization of 5-dimethylsilyloxy-2-pentanone (3.2 g, 20 mmol) (Figure 3). In this way, 3.0 g (93.8% yield) of polymer with M_w/M_n = 9900/5900, T_g = −81 °C, was obtained. ^{1}H NMR δ: 0.07 (s, 6H), 1.15 (d, 3H, J = 6 Hz), 1.44 (m, 2H), 1.49 (m, 1H), 1.60 (m, 1H), 3.63 (m, 2H), 3.90 (m, 1H) ppm. ^{13}C NMR δ: −2.45, −2.23, 23.89, 29.12, 35.97, 62.71, 68.58 ppm. ^{29}Si NMR δ: −5.45 ppm. IR ν: 2964, 2929, 2869, 1446, 1376, 1257, 1207, 1090, 1056, 943, 921, 848, 830, 794, 720 cm^{-1}. TGA: **XVII** is stable to 130 °C. Between 130 and 510 °C, catastrophic decomposition occurs. Ninety-seven percent of initial weight is lost.

Poly(2,2,6-trimethyl-1,3-dioxa-2-sila-1,6-hexanylene) (XVIII) was prepared as above by an activated **Ru**-catalyzed reaction of 4-dimethylsilyloxy-2-butanone (2.9 g, 20 mmol). In this way, 2.5 g (86.2% yield) of polymer with M_w/M_n = 4800/4400, T_g = −88 °C, was obtained. ^{1}H NMR δ: 0.06 (s, 6H), 1.16 (d, 3H, J = 6 Hz), 1.63 (m, 1H), 1.67 (m, 1H), 3.70 (m, 2H), 4.05 (m, 1H) ppm. ^{13}C NMR δ: 1.18, 1.22, 24.05, 42.42, 59.27, 65.55 ppm. ^{29}Si NMR δ: −5.10 ppm. IR ν: 2964, 2929, 2874, 1473, 1447, 1436, 1374, 1257, 1144, 1084, 1041, 1001, 982, 962, 905, 858, 834, 796 cm^{-1}. TGA: **XVIII** is stable to 140 °C. Between 140 and 620 °C, catastrophic decomposition occurs. Ninety-five percent of initial weight is lost.

Discussion

Styrene activates $RuH_2(CO)(PPh_3)_3$ (**Ru**) by removal of hydrogen and production of ethylbenzene. One triphenylphosphine ligand is also lost. This produces the highly coordinately unsaturated active catalyst "$Ru(CO)(PPh_3)_2$".[26] Approximately 1 mol % of **Ru** was routinely used. Among the advantages of the **Ru** catalyst is that it does not equilibrate the ODMS units. Siloxane equilibration is observed in many cation- and anion-catalyzed reactions.[29] The mechanism of this reaction is believed to be similar to that reported for Wilkinson's catalyst.[30] **Ru** is at least as effective as $RhCl(PPh_3)_3$ for the hydrosilylation of ketones.[31] The catalyst remains active on subsequent additions of monomer while still in solution. However, purification of the polymers by precipitation into methanol and column chromatography destroys the catalyst. In these reactions, no color change occurs as previously reported with aromatic α,ω-diketones.[23]

The NMR spectra for these *alt*-copolymers are complicated by the presence of chiral centers. The **Ru**-catalyzed addition of the Si−H bond across the C−O double bond of the carbonyl group results in formation of a single chiral center, so each polymer unit contains two chiral centers. This results in two different stereochemical environments for the adjacent atoms.

In the copolymers, splitting is clearly visible in the ^{13}C NMR spectra. Surprisingly, in the case of the 2,5-hexanedione copolymers, every ^{13}C NMR signal resulting from the aliphatic portion of the copolymers is split into two peaks. The terminal Si-methyl signals are also split due to their close proximity to the chiral centers. The internal Si-methyl peaks of copolymers containing more than two silicon atoms are too far removed from the chiral centers for splitting to occur. Therefore, in copolymer **VII**, every peak in the ^{13}C NMR spectrum is split. The copolymer has four nonequivalent carbon atoms; however, there are eight peaks in the ^{13}C NMR spectrum. In the ^{13}C NMR spectrum for **VIII**, all peaks are also split, with the exception of the internal Si-methyl peak, which may be too far removed from the chiral centers to be affected (Figure 4). Interestingly, copolymers of 2,7-octanedione only show terminal Si-methyl splitting in ^{13}C NMR spectra, as do the ω-dimethylsilyloxy ketone polymers.

Copolymer **VII** also exhibits interesting splitting in its ^{29}Si NMR spectrum. The signal is split into two peaks by the nearest chiral center. It is then split again by

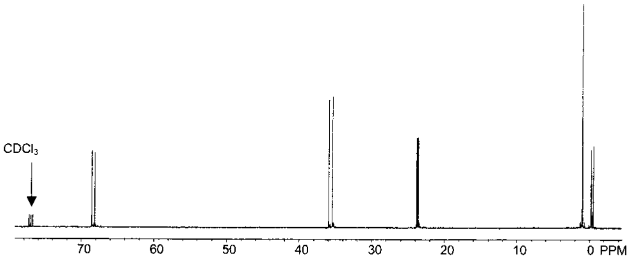

Figure 4. ^{13}C NMR spectrum of **VIII**.

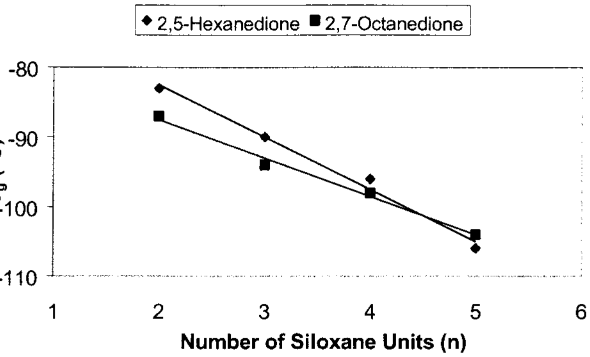

Figure 5. Plots of T_g vs number of siloxane units.

the more remote chiral center, producing four peaks from two chemically equivalent silicon atoms. Such splitting is not seen in copolymers with longer siloxane segments. This may be because, as the siloxane chain gets longer, there is less effect from the more remote chiral center.

End group analysis by ^1H NMR provides a valuable tool for determination of M_n. End group analysis was carried out before and after the completion of the copolymerization reactions to compare the values of M_n obtained by GPC with those obtained by ^1H NMR. For example, the copolymerization of **I** and **V** was analyzed *prior to its completion*. The integration of peaks at 2.11 and 2.47 ppm, assigned to the $-CH_2-CO-CH_3$ end group, was compared to the integration of the peak at 3.87 ppm, assigned to the methine protons in the polymer backbone. According to the integration, there should be 6.5 monomer units per oligomer, provided each oligomer has a ketone group at one end. The number of monomer units multiplied by the monomer molecular weight gives M_n of the oligomer. This was calculated to be 2100. Analysis of the integration of the peak at 4.69, from an Si$-$H end group, and the peak at 3.87 ppm likewise, gives a M_n value of 2100. End group analysis of the two different end groups give identical results. Comparison of the Si$-$H to the $CH_2-CO-CH_3$ end groups is consistent with the existence of proper stoichiometric balance. The M_n determined by GPC (1900) was in good agreement ($\pm$10%) with that determined by ^1H NMR end group analysis at this stage in the reaction.

The T_g's for these copolymers decrease linearly as the length of the siloxane chain between the aliphatic units increases (Figure 5). This decrease is expected because of the added flexibility provided by the longer ODMS unit.[32] The decrese in T_g's of similar aromatic copolymers, previously reported, is asymptotic.[23] Perhaps, with longer ODMS monomers, the decrease in the T_g's of these copolymers will be less rapid.

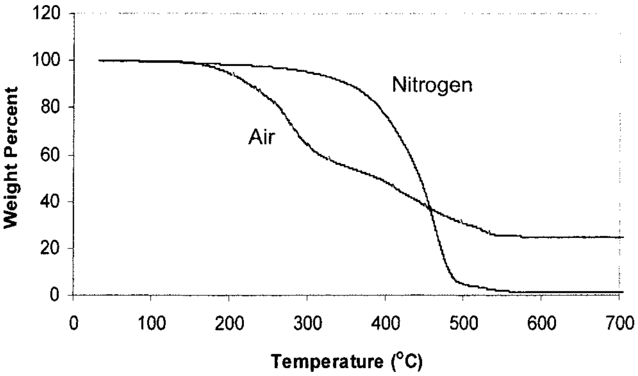

Figure 6. TGA of **IX** in nitrogen and air.

While the T_g's of the copolymers depend on the length of the ODMS monomers, their thermal stability does not. The mechanism for thermal degradation is most likely the same for all copolymers, regardless of the length of the ODMS unit. All TGA analyses began at ambient temperature. The temperature was increased 4 °C/min and continued to 800 °C. The thermal stability of these polymers in a nitrogen atmosphere is rather low. In particular, polymers **XVII** and **XVIII**, which begin to degrade below 150 °C. This may be due to their lower molecular weights. Each also contains a primary silyl ether linkage. The copolymers of **I** appear to be the most stable. All are stable in nitrogen to over 200 °C. All polymers decompose catastrophically in nitrogen, with little or no residue. **VIII** begins to degrade in nitrogen at 200 °C, which is the lowest temperature of all copolymers of **I**. This may be due to the presence of a catalytic impurity, which alters the degradation pathway. **IX** degrades in air at a lower temperature than in nitrogen (Figure 6). This is typical of all copolymers reported. The degradation of **IX** in air occurs in two phases with a 25% yield of white char. PDMS is known to undergo a two-step thermal decomposition in air to yield SiO_2.[33] Redistribution of ODMS segments with loss of small cyclic siloxanes such as D_3 apparently occurs in competition with formation of silica.

The aliphatic ω-dimethylsilyloxy ketone polymers (and monomers) are much less hydrolytically stable than any of the copolymers. Silyl ethers are well-known to undergo both acid- and base-catalyzed hydrolysis and methanolysis. In general, silyl ethers are more susceptible to acid-catalyzed hydrolysis than to basic hydrolysis.[34,35] The rate of these reactions depends not only on the concentration of acid or base but also on the nature of the substituents bonded to silicon and on the character of the alkyl or aryl group of the ether. In particular, if the carbon of the Si$-$O$-$C bond is secondary, the silyl ether is considerably more resistant to hydrolysis and methanolysis than if it is primary.[36] Polymers **XVII** and **XVIII** each contain an Si$-$O$-$C bond linkage in which the oxygen is bonded to a primary carbon. Even though precipitation was done under neutral conditions, these polymers are quite unstable. They were hydrolyzed at room temperature in a matter of hours. This makes polymer purification by precipitation from methanol impossible due to immediate methanolysis. All copolymers were purified by repeated precipitation from THF and methanol. Instability has been previously observed in polymers produced by the **Ru**-catalyzed hydrosilylation of aldehydes, which also produce primary poly(silyl ether) products.[23,31] A theoretical study of the hydrolysis and condensation of silyl ethers indicates that hydrolysis of the Si$-$O$-$C bond linkage, even under neutral conditions, is facile.[37]

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