Preparation of Highly Regular Poly(1-hydrido-1,3,3,5,5-pentamethyltrisiloxane) and Its Chemical Modification by Hydrosilylation

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ABSTRACT: High molecular weight poly(1-hydrido-1,3,3,5,5-pentamethyltrisiloxane) (**II**) with a highly regular microstructure has been prepared by dilithium diphenylsilanediolate-catalyzed ring-opening polymerization of 1,3,3,5,5-pentamethylcyclotrisiloxane. The microstructure of **II** was determined by ^{29}Si NMR. Chemical modification of **II** has been achieved. Quantitative hydrosilylation of **II** with benzophenone can be catalyzed by activated dihydridocarbonyltris(triphenylphosphine)ruthenium. Karstedt-catalyzed hydrosilylation of **II** with pentafluorostyrene has been achieved. The high molecular weight modified copolymers also have regular microstructures.

Introduction

High molecular weight (M_w/M_n = 84 600/53 200) poly(1-hydrido-1,3,3,5,5-pentamethyltrisiloxane) (**II**), a siloxane copolymer which has *a regular microstructure* as determined by ^{29}Si NMR, has been prepared by anionic ring-opening polymerization of 1-hydrido-1,3,3,5,5-pentamethylcyclotrisiloxane (**I**). Chemical modification of **II** by activated dihydridocarbonyltris(triphenylphosphine)ruthenium (Ru)-catalyzed hydrosilylation with benzophenone as well as by Karstedt (Pt)-catalyzed hydrosilylation with pentafluorostyrene is reported.

The properties of copolymers depend on both the sequence and the molar ratio of the two components. Random, alternating, and block copolymers made from the same monomers have distinct properties. Commercially available copoly(dimethylsiloxane/methylhydridosiloxane)s have broad molecular weight distributions and significant variations in microstructure.

These have been prepared either by cohydrolysis of dimethyldichlorosilane and methyldichlorosilane or by triflic or trifluoroacetic acid-catalyzed equilibration polymerization of octamethylcyclotetrasiloxane (D_4) and 1,3,5,7-tetramethylcyclotetrasiloxane (D^H_4).[1−5] This gives in addition to the desired copolymer significant amount of cyclic siloxanes that must be separated from the copolymer. The terminal Si−OH groups of these are usually capped with trimethylsilyl groups to prevent the slow reaction of Si−H groups with Si−OH groups.[6] These copolymers do not have a regular microstructure.

Acid-catalyzed ring opening of mono- or 1,1-disubstituted permethylcyclotrisiloxanes or cyclotetrasiloxanes leads to copolysiloxanes with partially random microstructure due to equilibration.[7] At low temperature, polymerization occurs via ring opening with no significant equilibration. Unfortunately, despite high chemoselectivity, cationic ring-opening polymerization does not have significant regioselectivity.[8]

Bases are not commonly used to prepare polymethylhydridosiloxanes, because nucleophilic attack by hydroxide on an Si−H center in the presence of water or other protic solvents results in formation of a silanolate, hydrogen, and regeneration of hydroxide.[9] Silanol and silanolate centers provide sites for polysiloxane crosslinking.[10,11]

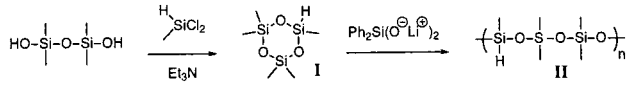

Figure 1. Preparation of **I** and **II**.

Living anionic ring-opening polymerization gives little or no cyclics and leads to siloxane copolymers with fairly regular microstructure since nucleophilic attack preferentially occurs on the silicon atom that bears the most electron-withdrawing substituents. For example, 1-vinyl-1,3,3,5,5-pentamethylcyclotrisiloxane undergoes anionic ring-opening polymerization in which 76% of the attack occurs on the silicon that bears the vinyl group.[12] However, since 24% of the attack occurs on the two dimethylsilyl centers, the polymer backbone is far from regular. We have obtained similar results with 1-(2′-pentafluorophenylethyl)-1,3,3,5,5-pentamethylcyclotrisiloxane.[13] No examples of high molecular weight regular siloxanes copolymers have been reported.

Attachment of pendent functionalized groups to the silyl centers of the backbone polymethylhydridosiloxanes or copolymers via Pt-catalyzed hydrosilylation reactions is well-known. For example, liquid crystalline mesogens have been attached to poly(siloxane)s in this way.[14]

Results and Discussion

Reaction of methyldichlorosilane and tetramethyldisiloxane-1,3-diol in the presence of triethylamine yields **I**, which undergoes rapid anionic ring-opening polymerization at −78 °C. Polymer, **II** (Figure 1), has *a highly regular microstructure*. Only two peaks (dimethylsiloxy unit D and methylhydridosiloxy unit D^H) are observed in ^{29}Si NMR (Figure 2). The resonance at −37.6 ppm has been previously assigned to a D^H unit in a pentad DD*D*^{H}DD.[15] The ^{13}C NMR of **II** shows three resonances for the Si−CH_3 groups. The chiral D^H center makes the adjacent methyl groups of each D unit diastereotopic.[16] This accounts for two of the resonances. The third ^{13}C resonance is due to the methyl group of the D^H unit

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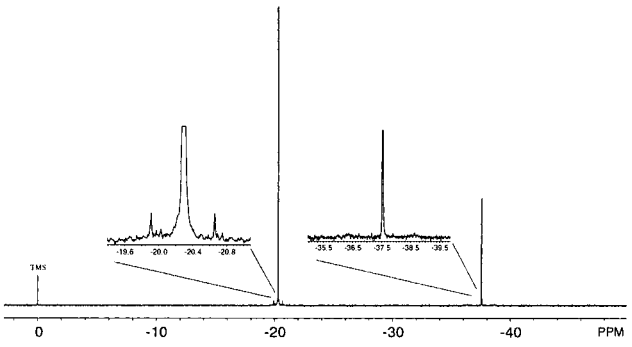

Figure 2. ^{29}Si NMR of **II**.

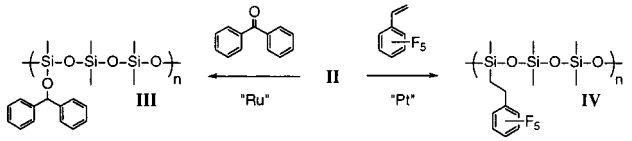

Figure 3. Preparation of **III** and **IV**.

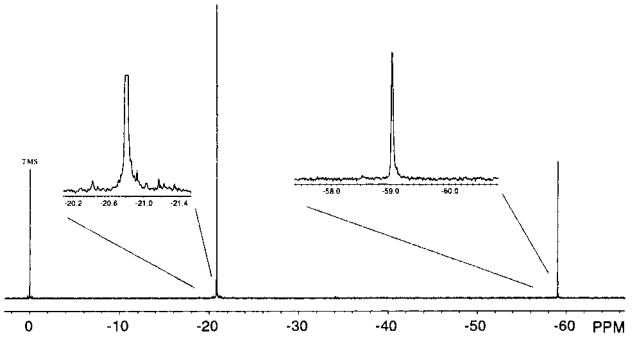

Figure 4. ^{29}Si NMR of **III**.

itself. Apparently, anionic nucleophilic attack takes place exclusively on the D^H unit of **I**. No cross-linking was observed. The silanolate base does not affect the Si−H bonds.

Chemical modification of **II** was carried out by Ru-catalyzed hydrosilylation reactions with ketones such as benzophenone (Figure 3). There is considerable interest in chemical modification of polymers.[17−20] We have reported that Ru catalyzes the hydrosilylation of the C−O double bonds of ketones.[21,22] The high molecular weight modified polymer, poly(1-diphenylmethoxy-1,3,3,5,5-pentamethyltrisiloxane) (**III**), has a regular structure as determined by ^{29}Si NMR (Figure 4). Three resonances are observed in the ^{13}C NMR of **III** due to Si−CH_3 groups. This is similar to the ^{13}C NMR of **II**.

Chemical modification of **II** has also been achieved by Karstedt (Pt)-catalyzed hydrosilylation of terminal alkenes, albeit at slower rate. Hydrosilylation with pentafluorostyrene yields poly[1-(2′-pentafluorophenylethyl)-1,3,3,5,5-pentamethyltrisiloxane] (**IV**). After 24 h, approximately 95% of Si−H have reacted. Neither equilibration nor cross-linking is observed (Figure 5). Polymer **IV** is significantly more regular and has a higher molecular weight than that obtained via anionic ring-opening polymerization of 1-(2′-pentafluorophenylethyl)-1,3,3,5,5-pentamethylcyclotrisiloxane.[13]

Analysis of Results

While the Ru-catalyzed hydrosilylation of **II** with benzophenone is fast and quantitative and gives perfectly regular high molecular weight **III**, the Karstedt-catalyzed hydrosilylation of pentafluorostyrene is much

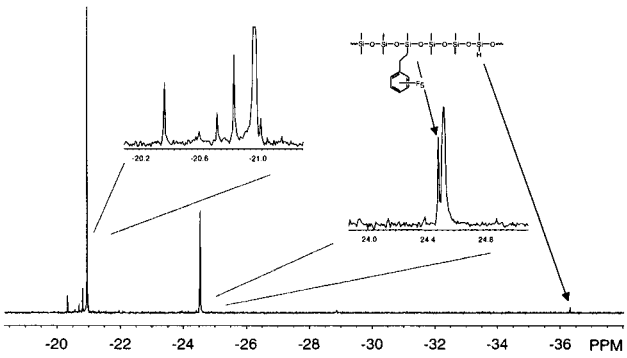

Figure 5. ^{29}Si NMR of **IV**.

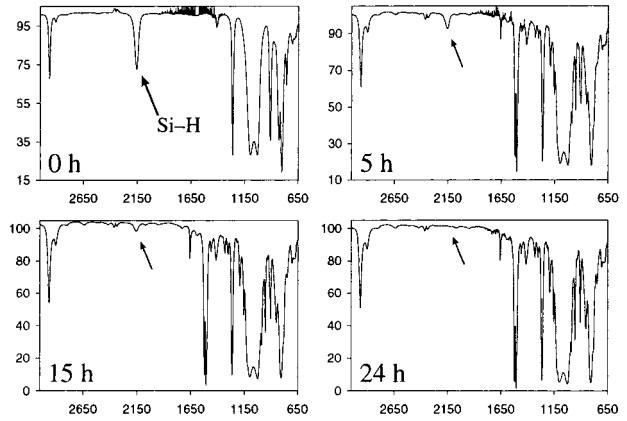

Figure 6. IR spectra (% T/ν [cm^{-1}]) of Karstedt-catalyzed hydrosilylation reaction of **I** and pentafluorostyrene initially and after 5, 15, and 24 h.

slower and incomplete (~95%) despite the use of excess pentafluorostyrene. The presence of 5% unreacted D^H units complicates the microstructure of **IV**. In addition to an intense resonance in the ^{29}Si NMR at −24.54 ppm due to DD*F*DD (F = 2-pentafluorophenylethyl-SiCH_3) units, resonances due to DD*D*^{H}DD at −36.3 ppm (5%) and to D^HDD*F*DDF at −24.50 ppm are detected. Similarly, in addition to an intense signal at −20.95 due to FD*D*FD units, additional low-intensity resonances at −20.81 and −20.33 ppm due to D units are detected.

The progress of the Karstedt-catalyzed hydrosilylation reaction has been followed by monitoring the disappearance of the Si−H bond of **II** by FT-IR (Figure 6).

Experimental Section

^{1}H, ^{13}C, and ^{29}Si NMR spectra were obtained on a Bruker AMX-500 MHz spectrometer. ^{1}H and ^{13}C NMR spectra were run on 5% w/v acetone-d_6 solutions. Twenty-five percent w/v solutions were used to obtain ^{29}Si NMR spectra. ^{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. Si−H coupling constants were with the ^{1}H decoupler turned off. All spectra were referenced to an internal TMS standard. IR spectra of neat films on KCl plates were recorded on a Perkin-Elmer Spectrum 2000 FT-IR spectrometer. UV spectra of cyclohexane solutions were run on a Shimadzu UV-260 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 0.6 mL/min. The retention times were calibrated against known monodisperse polystyrene standards: 929 000, 114 200, 13 700, 794. The T_g and T_m of the polymers were determined on a Perkin-Elmer DSC-7 instrument. The DSC was calibrated from the

heat of transition (−87.06 °C)[23] and mp (6.54 °C) of cyclohexane as well as from the T_g (−125 °C)[24] of poly(dimethylsiloxane). The analysis was begun by equilibration at −150 °C for 20 min, followed by an increase in temperature of 10 °C/min to 30 °C. Low-resolution mass spectra were obtained by GC/MS on a Hewlett-Packard 5890 series II GC with a Hewlett-Packard 5971 series mass selective detector. The gas chromatograph was equipped with a 30 m capillary column from J&W, part no. 1225032. Elemental analysis was carried out by Oneida Research Services Inc., Whitesboro, NY.

Diphenyldisilanediol, methyldichlorosilane, dimethyldichlorosilane, trimethylchlorosilane hexamethyldisiloxane, and Karstedt catalyst were obtained from Gelest. Pentafluorostyrene was purchased from Oakwood Products, Inc. Solvents were dried prior use.[25] Reactions were conducted in flame-dried glassware under argon.

Tetramethyldisiloxane-1,3-diol was prepared by hydrolysis of dimethyldichlorosilane.[26]

Initiator. Dilithium diphenylsilanediolate was prepared by treatment of diphenylsilanediol with *n*-butyllithium in THF. Styrene was used as an indicator.[27]

Dihydridocarbonyltris(triphenylphosphine)ruthenium (Ru catalyst) was prepared from ruthenium trichloride hydrate.[28]

1,3,3,5,5-Pentamethylcyclotrisiloxane (I).[29] A solution of Et_3N (56.3 mL, 402 mmol) and 200 mL of Et_2O was placed in a 500 mL three-neck, round-bottom flask equipped with two 100 mL pressure equalizing addition funnels and a Tru-bore mechanical stirrer fitted with a Teflon paddle. A solution of methyldichlorosilane (21.7 g, 189 mmol) and 25 mL of Et_2O was placed in one addition funnel. A solution of tetramethyldisiloxane-1,3-diol[30] (31.4 g, 189 mmol) and 50 mL of Et_2O was placed in the other. The two solutions were added simultaneously dropwise over 1 h at room temperature to the well-stirred solution of Et_2O and Et_3N. Stirring was continued for 1 h. The solution was then washed three times with saturated aqueous KH_2PO_4. It was then dried over anhydrous $MgSO_4$ and filtered. Distillation gave a fraction, bp 43 °C/30 mm, 20.0 g, 51% yield. The ^{1}H NMR and IR of **I** have been reported.[29] On the other hand, neither the ^{13}C, ^{29}Si NMR, nor its GC/MS has been described. ^{1}H NMR δ: 0.15 (s, 12H), 0.19 (d, 3H, $J = 1$ Hz), 4.80 (q, 1H, $J = 1$ Hz). ^{13}C NMR δ: 0.60, 0.98, 1.39. ^{29}Si NMR δ: −24.63 (d, 1Si, $J_{Si-H} = 244$ Hz), −7.92 (s, 2Si). IR ν: 2966, 2906, 2165(Si−H), 1260, 1019, 923, 907, 844, 808, 763, 611 cm^{-1}. GC/MS M/Z (relative intensity): 207 $(M - 1)^+$ (8.3), 193 $(M - 15)^+$ (100), 177 (6.8), 163 (4.5), 147 (2.9), 133 (8.3), 119 (3.6), 103 (2.3).

Poly(1-hydrido-1,3,3,5,5-pentamethyltrisiloxane) (II). I (2.1 g, 10.1 mmol) and 2 mL of THF were cooled to −78 °C. Dilithium diphenylsilanediolate (49 μL, 14.1 μmol) was added. After 3 h, trimethylchlorosilane (15 μL, 118 μmol) and Et_3N (15 μL, 108 μmol) were added to quench the reaction. After warming to room temperature over 5 h, the polymer was precipitated three times from Et_2O/MeOH and vacuum-dried overnight. In this way, 1.91 g, 96% yield, M_w/M_n = 84 620/53 170, T_g = −129 °C, and T_m = −61 °C were obtained. ^{1}H NMR δ: 0.13 (s, 12H), 0.17 (s, 3H) 4.73 (s, 1H). ^{13}C NMR δ: 0.99, 1.08, 1.50. ^{29}Si NMR δ: −37.55 (d, 1Si, $J_{Si-H} = 239$ Hz), −20.29 (s, 2Si). IR ν: 2965, 2906, 2156 (Si−H), 1261, 1095, 1030, 911, 829, 802, 759, 705 cm^{-1}. Elemental Anal. Calcd for $C_5H_{16}O_3Si_3$: C, 28.81%; H, 7.74%. Found: C, 28.96%; H, 7.08%.

Poly(1-diphenylmethoxy-1,3,3,5,5-pentamethyltrisiloxane) (III). II (0.575 g, 2.76 mmol), benzophenone (1.0 g, 5.49 mmol), and 2 mL of toluene were placed into a 20 mL Ace-pressure tube equipped with a Teflon-covered magnetic stir bar and a Teflon-threaded stopper. Ru catalyst (in toluene, 50 μL, 5.4 μmol), which had been previously activated with a stoichiometric amount of styrene,[31] was injected into the solution. The tube was sealed and placed in oil bath (135 °C) for 6 h. After cooling to room temperature, the tube was opened and the polymer was precipitated three times from Et_2O/MeOH and vacuum-dried overnight. In this way, 0.92 g, 86% yield, M_w/M_n = 120 500/64 290, T_g = − 52 °C, and T_m = − 46 °C were obtained. ^{1}H NMR δ: 0.03 (s, 6H), 0.06 (s, 9H) 6.05 (s, 1H), 7.15 (t, 2H, $J = 7.5$ Hz), 7.24 (t, 4H, $J = 7.5$ Hz), 7.40 (d, 4H, $J = 7.5$ Hz). ^{13}C NMR δ: −2.94, 1.06, 1.11, 76.56, 126.90, 127.58, 128.69, 145.23. ^{29}Si NMR δ: −59.03 (s, 1Si), −20.80 (s, 2Si). IR ν: 3089, 3065, 3030, 2963, 2905, 1494, 1455, 1262, 1084, 1065, 1043, 1026, 888, 843, 802, 743, 701, 604 cm^{-1}. UV λ_{max} nm (ϵ): 258.6 (913). Elemental Anal. Calcd for $C_{18}H_{26}O_4Si_3$: C, 55.34%; H, 6.71%. Found: C, 54.51%; H, 6.37%.

Poly[1-(2′-pentafluorophenylethyl)-1,3,3,5,5-pentamethyltrisiloxane] (IV). II (1.04 g, 5.0 mmol, M_w/M_n = 67 170/45 480), pentafluorostyrene (1.3 g, 6.7 mmol), toluene (4 mL), and Pt complex of divinyltetramethyldisiloxane (Karstedt catalyst, 150 μL), previously treated with a stoichiometric amount of tetramethyldisiloxane, were placed into an Ace pressure tube as above and were allowed to react at 100 °C for 24 h. More pentafluorostyrene (2 × 250 μL) was added during the reaction. The progress of the reaction was monitored by IR from the disappearance of the Si−H resonance of **II** at 2156 cm^{-1}. This was done by removal of small aliquots from the reaction. Toluene solvent and other volatiles were removed under vacuum prior to obtaining IR spectra. Poly(pentafluorostyrene) was formed as a side product. Both polymers were precipitated twice with MeOH/Et_2O. **IV** was soluble in hexamethyldisiloxane (HMDS) whereas poly(pentafluorostyrene) was not, allowing separation of poly(pentafluorostyrene) from the HMDS solution of **IV** by centrifugation. **IV** was precipitated from HMDS with MeOH and dried in high vacuum for 24 h. In this way, 1.83 g, 91%, M_w/M_n = 121 040/62 220, and T_g = −81 °C were obtained. ^{1}H NMR δ: 0.19 (s, 12H), 0.21 (s, 3H) 0.92 (m, 1.75H), 2.82 (m, 1.74H). ^{13}C NMR δ: −0.44, 1.28, 1.31, 16.85, 18.55, 119.00 (t, $J = 18$ Hz), 128.29 (dm, $J = 249$ Hz), 140.22 (dm, $J = 236$ Hz), 145.68 (dm, $J = 247$ Hz). ^{19}F NMR δ: −164.28 (td, 2F, $J = 21$ and 8 Hz), 160.20 (t, 1F, $J = 20$ Hz), 145.67 (dd, 2F, $J = 21$ and 8 Hz). ^{29}Si NMR δ: −36.32 (s, 0.05Si), −24.54 (s, 0.85Si), −24.50 (s, 0.1Si), −20.95 (s, 1.8Si), −20.81 (s, 0.1Si), −20.33 (s, 0.1Si). IR ν: 2964, 2903, 1656, 1521, 1504, 1414, 1263, 1190, 1154, 1099, 1023, 986, 953, 903, 851, 806, 749, 703, 608 cm^{-1}. UV λ_{max} nm (ϵ): 219.0 (3011), 250.2 (1574). Elemental Anal. Calcd for $C_{18}H_{26}O_4Si_3$: C, 38.79%; H, 4.76%, F, 23.60%. Found: C, 38.99%; H, 4.37%, F, 23.32%.

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