1639

Synthesis and Characterization of Poly(1-methyl-1-vinyl-1-silabutane), Poly(1-phenyl-1-vinyl-1-silabutane), and Poly(1,1-divinyl-1-silabutane)

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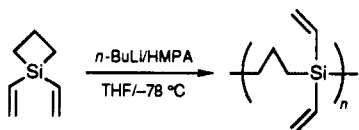
ABSTRACT: Poly(1-methyl-1-vinyl-1-silabutane), poly(1-phenyl-1-vinyl-1-silabutane), and poly(1,1-divinyl-1-silabutane) have been prepared by anonic ring-opening polymerization, cocatalyzed by *n*-butyllithium and hexamethylphosphoramide (HMPA) in THF at −78 °C, of 1-methyl-1-vinyl-1-silacyclobutane, 1-phenyl-1-vinyl-1-silacyclobutane, and 1,1-divinyl-1-silacyclobutane, respectively. These polymers have been characterized by ^{1}H, ^{13}C, and ^{29}Si NMR as well as FT-IR and UV spectroscopy. Their molecular weight distribution has been determined by gel permeation chromatography (GPC), their thermal stability by thermogravimetric analysis (TGA), and their glass transition temperatures (T_g) by differential scanning calorimetry (DSC). Thermal degradation of poly(1,1-divinyl-1-silabutane) in an inert atmosphere gives a 45% char yield.

Introduction

While there has been considerable work on siloxane polymers over the last 50 years,[1] there has been much less work done on carbosilane polymers. Yajima's proposal that poly[(methylsilylene)methylene], $[-CH_3SiHCH_2-]_n$, is a key intermediate in the conversion of poly(dimethylsilane) into silicon carbide has stimulated considerable interest in the chemistry of poly(carbosilanes).[2] Siloxane polymers which have reactive pendant or terminal Si–vinyl groups such as dimethylsiloxane–vinylmethylsiloxane copolymers and dimethylsiloxane polymers which are terminated by vinyldimethylsilyl groups are commercially available (Huls). By comparison, there are only two reports of poly(carbosilanes) substituted with terminal Si–vinyl groups. Thus, the thermal ring-opening polymerization of 1-methyl-1-vinyl-1-silacyclobutane has been reported to yield an insoluble (cross-linked) polymer which has not been further characterized.[3] Oligo(carbosilanes), such as poly(1,1-dichloro-1-silapropane), which possess terminal Si–vinyl groups have been prepared by chloroplatinic acid catalyzed hydrosilation copolymerization of vinyldichlorosilane with small amounts of divinyldichlorosilane.[4,5] Several recent patents report the preparation of preceramic poly(silacyclobutasilazanes).[6-9]

We report the preparation of poly(carbosilanes) which are regularly substituted with reactive pendant Si–vinyl groups. These can be prepared by the anionic ring-opening polymerization of 1-vinyl-1-silacyclobutanes such as 1-methyl-1-vinyl-1-silacyclobutane, 1-phenyl-1-vinyl-1-silacyclobutane, and 1,1-divinyl-1-silacyclobutane.

Experimental Section

^{1}H and ^{13}C NMR spectra were obtained on a Bruker AM-360 spectrometer operating in the Fourier transform mode. ^{13}C NMR spectra were run with broad-band proton decoupling. ^{29}Si NMR spectra were recorded on an IBM–Bruker WP-270-SY spectrometer. Solutions of 5–10% (w/v) of polymer in chloroform-*d* were used to determine ^{1}H NMR spectra, whereas 15–20% solutions were utilized to obtain ^{13}C and ^{29}Si NMR spectra. A

heteronuclear gated decoupling pulse sequence (NONOE) with a delay of 20 s was used to obtain ^{29}Si NMR spectra.[10] Chloroform was used as an internal standard for ^{1}H and ^{13}C NMR spectra. ^{29}Si NMR spectra were externally referenced to TMS. IR spectra were recorded on an IBM FT-IR spectrometer of neat films on NaCl plates. UV spectra were recorded on a Shimadzu UV–vis 260 spectrometer of diethyl ether solutions.

The molecular weight distribution of polymers was determined by gel permeation chromatography on a Waters system. This was comprised of a U6K injector, a 510 HPLC solvent delivery system, an R401 differential refractometer, and a Maxima 820 control system. A Waters 7.8 mm × 30 cm Ultrastyragel linear column packed with <10-μm particles of mixed pore size maintained at 20 °C was used for the analysis. The eluting solvent was HPLC-grade THF at a flow rate of 0.6 mL/min. Retention times were calibrated against known monodisperse polystyrene standards: 612 000, 114 000, 47 500, 18 700, and 5120 whose M_w/M_n are less than 1.09.

Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer TGS-2 instrument. The temperature program for the analysis was 50 °C for 10 min followed by an increase of 4 °C/min to 750 °C. These runs were conducted with a nitrogen flow of 40 cm³/min. The glass transition temperature (T_g) was determined by differential scanning calorimetry on a Perkin-Elmer DCS-7 system. Indium (mp 156 °C) and spectral quality *n*-hexane (mp −95 °C) were used to calibrate the DSC. After equilibration at −110 °C for 20 min, the temperature was increased at a rate of 20 °C/min to 150 °C.

Elemental analysis was performed by Galbraith Laboratories, Knoxville, TN.

All reactions were carried out under an atmosphere of argon in flame-dried glassware. Tetrahydrofuran (THF) was distilled immediately prior to use from a deep blue solution of sodium benzophenone ketyl. Hexamethylphosphoramide (HMPA) was distilled from calcium hydride and was stored over activated 4-Å molecular sieves.

1-Methyl-1-vinyl-1-silacyclobutane was prepared from methyldichlorosilane and allyl chloride following literature procedures.[11,12] ^{1}H NMR: δ 0.33 (s, 3 H), 1.03 (m, 4 H), 2.05 (m, 2 H), 5.82 (dd, 1 H, *J* = 20.0 and 4.0 Hz), 6.04 (dd, 1 H, *J* = 14.6 and 4.0 Hz), 6.31 (dd, 1 H, *J* = 14.6 and 20.0 Hz). ^{13}C NMR: δ −2.12, 13.92, 18.09, 132.56, 138.19. ^{29}Si NMR: δ 9.69.

1-Phenyl-1-vinyl-1-silacyclobutane was prepared from phenyldichlorosilane and allyl chloride following literature procedures.[12] ^{1}H NMR: δ 1.35 (t, 4 H, *J* = 7.7 Hz), 2.22 (m, 2 H, *J* = 7.7 Hz), 5.96 (dd, 1 H, *J* = 20.4 and 3.8 Hz), 6.22 (dd, 1 H, *J* = 14.6 and 3.8 Hz), 6.48 (dd, 1 H, *J* = 20.4 and 14.6 Hz), 7.42 (m,

3 H), 7.65 (m, 2 H). ^{13}C NMR: δ 13.39, 18.19, 127.93, 129.57, 134.05, 134.78, 135.68, 136.54. ^{29}Si NMR: δ 4.18.

1,1-Divinyl-1-silacyclobutane was prepared by addition of vinylmagnesium bromide to 1,1-dichloro-1-silacyclobutane.[12] ^{1}H NMR: δ 1.04 (t, 4 H, J = 8.2 Hz), 1.96 (m, 2 H, J = 8.2 Hz), 5.77 (dd, 1 H, J = 19.8 and 4.1 Hz), 6.01 (dd, 1 H, J = 14.6 and 4.1 Hz), 6.21 (dd, 1 H, J = 19.8 and 14.6 Hz). ^{13}C NMR: δ 13.09, 18.09, 134.11, 135.85. ^{29}Si NMR: δ 1.40.

Poly(1-methyl-1-vinyl-1-silabutane). In a 100-mL round-bottomed flask equipped with a Teflon-covered magnetic stirring bar and a rubber septum was placed 1-methyl-1-vinyl-1-silacyclobutane (1.00 g, 8.9 mmol) THF (40 mL), and HMPA (40 μL). The mixture was cooled to -78 °C, and a hexane solution of *n*-butyllithium (80 μL, 2.5 M, 0.2 mmol) was added via a syringe. The reaction mixture was stirred at -78 °C for 1 h. A saturated solution of aqueous ammonium chloride (15 mL) was added. The organic layer was separated, washed with water (20 mL), dried over anhydrous magnesium sulfate, and filtered, and the volatile solvents were removed by evaporation under reduced pressure. The residue was dissolved in a minimum amount of THF, and the polymer was precipitated from methanol. This process was repeated twice. The polymer was dried under vacuum. In this way, 0.65 g, 65 % yield of poly(1-methyl-1-vinyl-1-silabutane) was obtained. M_w/M_n = 8200/6000, was obtained. T_g = -41.0 °C. ^{1}H NMR: δ 0.01 (s, 3 H), 0.61 (t, 4 H, J = 7.9 Hz), 1.32 (m, 2 H), 5.63 (dd, 1 H, J = 19.8 and 3.8 Hz), 5.93 (dd, 1 H, J = 14.8 and 3.8 Hz), 6.10 (dd, 1 H, J = 14.8 and 19.8 Hz). ^{13}C NMR: δ -5.27, 18.28, 18.69, 131.63, 138.48. ^{29}Si NMR: δ -6.03. IR: ν 3047, 3009, 2957, 2915, 2875, 2793, 1592, 1454, 1404, 1335, 1252, 1215, 1141, 1081, 1009, 949, 907, 787, 698 cm^{-1}. UV: λ_{max} 221 nm (ϵ 1110). Anal. Calcd for C$_6$H$_{12}$Si: C, 64.25; H, 10.78. Found: C, 63.76; H, 10.76.

Poly(1-phenyl-1-vinyl-1-silabutane). The polymerization of 1-phenyl-1-vinyl-1-silacyclobutane (1.0 g, 5.7 mmol) was carried out as above. In this way 0.63 g, 63% yield, of polymer was obtained. M_w/M_n = 15 800/11 300 was obtained. T_g = -18 °C. ^{1}H NMR: δ 0.85 (m, 4 H), 1.37 (m, 2 H), 5.85 (m, 1 H), 6.01 (m, 1 H), 6.15 (m, 1 H), 7.30 (m, 3 H), 7.38 (m, 2 H). ^{13}C NMR: δ 17.16, 18.15, 127.64, 128.82, 133.76, 134.37, 135.76, 136.60. ^{29}Si NMR: δ -10.86. IR: ν 3135, 3068, 3048, 3009, 2919, 2875, 2793, 1653, 1591, 1487, 1456, 1427, 1403, 1336, 1302, 1261, 1235, 1216, 1191, 1140, 1110, 952, 900, 790, 699 cm^{-1}. UV: λ_{max} 271 nm (ϵ 913), 266 (1680), 260 (1933), 254 (1267), 230 (9667). Anal. Calcd for C$_{11}$H$_{14}$Si: C, 75.68; H, 8.28. Found: C, 75.83; H, 8.10.
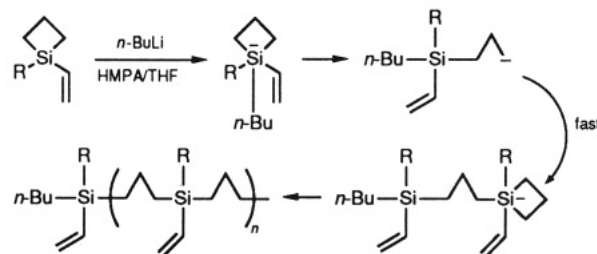
Poly(1,1-divinyl-1-silabutane). The polymerization of 1,1-divinyl-1-silacyclobutane (1.0 g, 8.1 mmol) was carried out as above. In this way 0.88 g, 88% yield of polymer was obtained. M_w/M_n = 34 200/11 100 was obtained. ^{1}H NMR: δ 0.70 (t, 4 H, J = 8.0 Hz), 1.38 (m, 2 H), 5.68 (dd, 1 H, J = 18.6 and 5.4 Hz), 6.06 (m, 2 H, J = 18.6, 14.7, and 5.4 Hz). ^{13}C NMR: δ 17.20, 18.14, 133.16, 136.01. ^{29}Si NMR: δ -13.43. IR: ν 3048, 3007, 2919, 2794, 1592, 1454, 1403, 1334, 1235, 1215, 1141, 1081, 1009, 951, 791, 712 cm^{-1}. UV: λ_{max} 227 nm (ϵ 2000). Anal. Calcd for C$_7$H$_{12}$Si: C, 67.71; H, 9.74. Found: C, 67.29; H, 9.90
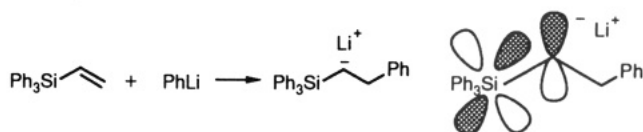
Results and Discussion

We have been interested in the preparation of unsaturated poly(carbosilanes). In this regard, we have prepared poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene) and related systems by the anionic ring-opening polymerization of 1,1-dimethyl-1-silacyclopent-3-ene and similar 1-silacyclopent-3-enes.[13-15] In these polymers, the carbon-carbon double bond is an integral part of the polymer chain. The allylic relationship of the carbon-carbon double bonds to the silyl centers in these polymers makes them susceptible to acid-catalyzed degradation. Electrophilic cleavage of allylic carbon-silicon bonds is well-known in monomeric compounds.[16,17] Poly(1-methyl-1-vinyl-1-silabutane), poly-(1-phenyl-1-vinyl-1-silabutane), and poly(1,1-divinyl-1-silabutane) reported herein are expected to be much more stable to acid. While they contain a carbon-carbon double bond in each unit of the polymer, it is a pendant group rather than part of the polymer backbone. In this sense,

these polymers are analogous to poly(1,2-butadiene). The relationship of the carbon-carbon double bonds to the silyl centers of these polymers is vinylic rather than allylic. While monomeric vinyl silanes are well-known to undergo electrophilic desilation substitution reactions, they are significantly less susceptible to electrophilic cleavage than allylic silicon-carbon bonds.[18-20]

We believe that the anionic ring-opening polymerization of these vinyl-substituted silacyclobutanes proceeds primarily by nucleophilic attack at the silyl center with formation of a pentacoordinate siliconate anion. Ring opening of the silacyclobutane ring results in relief of ring strain and formation of a primary carbanion which attacks the silyl center of another molecule of silacyclobutane to yield a new hypervalent siliconate intermediate as outlined below. This mechanism is similar to that which has been proposed for the anionic ring-opening polymerization of 1,1-dimethyl-1-silacyclobutane.[21,22]

Such anionic polymerizations are novel and unexpected since it is well-known that alkyllithium reagents as well as Grignard reagents readily add to the carbon-carbon double bond of vinylsilanes to yield carbanions adjacent to the silyl center. Such α-silyl anions may be stabilized by delocalization of the extra electron density centered in a 2p orbital on carbon into an empty σ^* orbital on the adjacent silicon.[23-27] In fact, trimethylvinylsilane undergoes anionic polymerization catalyzed by *s*-butyllithium.[28,29] Apparently nucleophilic attack at the silyl center of these 1-vinyl-1-silacyclobutanes proceeds more rapidly than nucleophilic addition to the carbon-carbon double bond resulting in linear polymer. However, the observation that the M_w/M_n for poly(1,1-divinyl-1-silabutane) is 3 suggests that a small amount of cross-linking has, in fact, in this case occurred by nucleophilic addition across the carbon-carbon double bonds of the pendant Si-vinyl groups. By comparison, the molecular weight distributions for poly(1-phenyl-1-vinyl-1-silabutane) and poly(1-methyl-1-vinyl-1-silabutane) are significantly smaller. Anionic ring-opening polymerization of strained silacyclobutanes is expected to give a narrow molecular weight distribution if a linear polymer is formed which has no cross-linking.

The starting monomers 1-methyl-1-vinyl-1-silacyclobutane, 1-phenyl-1-vinyl-1-silacyclobutane, and 1,1-divinyl-1-silacyclobutane are known compounds. They have been prepared by reaction of vinylmagnesium bromide with 1-chloro-1-methyl-1-silacyclobutane, 1-chloro-1-phenyl-1-silacyclobutane, and 1,1-dichloro-1-silacyclobutane, respectively.[11,12] While 1,1-dichloro-1-silacyclobutane is commercially available, 1-chloro-1-methyl-1-silacyclobutane and 1-chloro-1-phenyl-1-silacyclobutane are not. These have been prepared by an intramolecular
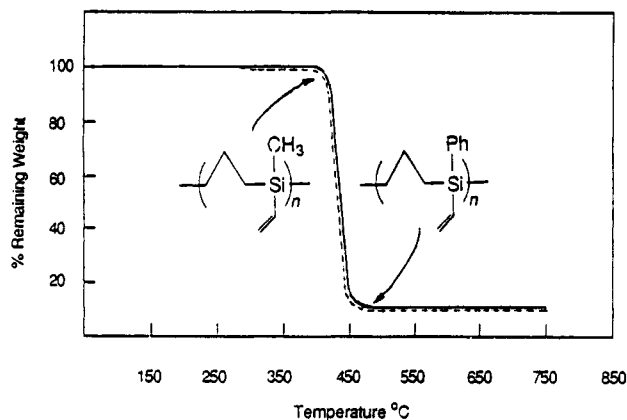
Figure 1. TGA of poly(1-methyl-1-vinyl-1-silabutane) and poly-(1-phenyl-1-vinyl-1-silabutane).
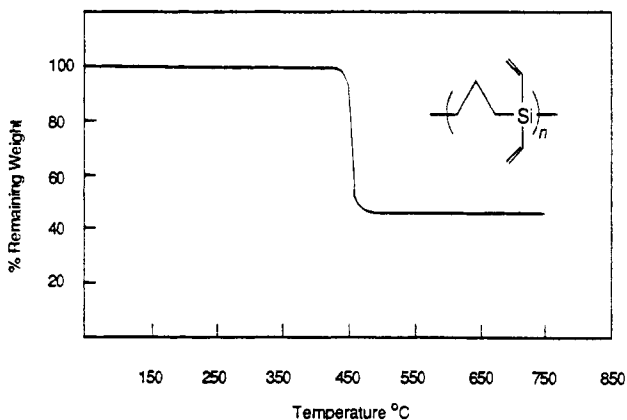

Figure 2. TGA of poly(1,1-divinyl-1-silabutane).

Grignard cyclization. For example, 1-chloro-1-methyl-1-silacyclobutane results from treatment of 3-(chloropropyl)-methyldichlorosilane with magnesium powder in ether.[12] 3-(Chloropropyl)methyldichlorosilane and 3-(chloropropyl)phenyldichlorosilane have been prepared by the chloroplatinic acid catalyzed hydrosilation of allyl chloride with methyldichlorosilane and phenyldichlorosilane, respectively.[30-32]

The thermal stability of these 1-vinyl-1-silabutane polymers has been determined by thermogravimetric analysis in a nitrogen atmosphere. Both poly(1-methyl-1-vinyl-1-silabutane) and poly(1-phenyl-1-vinyl-1-silabutane) are thermally stable to 400 °C. Between 400 and 450 °C both undergo almost complete decomposition. Less than 12% residue is found (Figure 1). On the other hand, poly(1,1-divinyl-1-silabutane) is thermally stable to almost 450 °C. Between 450 and 500 °C 55% of the original sample weight is lost. However, no further weight loss occurs up to 750 °C (Figure 2). The formation of such a high char yield is unanticipated. Cross-linking is usually an essential requirement for the high-yield conversion of organometallic polymers to ceramic materials.[33,34] In this regard, we have found that unsaturated carbosilane polymers which contain reactive Si–H bonds form high char yields.[35,36] The mechanism of cross-linking which is operable in the case of poly(1,1-divinyl-1-silabutane) is not understood at present and is the subject of further study.

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Registry No. MeSi(CH=CH₂)(CH₂)₃ (SRU), 138754-17-3; PhSi(CH=CH₂)(CH₂)₃ (SRU), 138754-18-4; Si(CH=CH₂)₂-(CH₂)₃ (SRU), 138754-19-5; MeSi(CH=CH₂)(CH₂)₃ (homopolymer), 129515-69-1; PhSi(CH=CH₂)(CH₂)₃ (homopolymer), 138877-15-3; Si(CH=CH₂)₂(CH₂)₃ (homopolymer), 138877-16-4.