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Synthesis and characterization of poly(1-methyl-1-silabutane), poly(1-phenyl-1-silabutane) and poly(1-silabutane)

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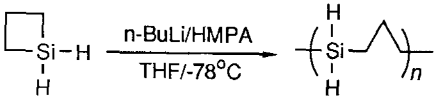
Summary:

Anionic ring opening polymerization of 1-methyl-1-silacyclobutane, 1-phenyl-1-silacyclobutane and 1-silacyclobutane co-catalyzed by *n*-butyllithium and hexamethylphosphoramide (HMPA) in THF at -78°C yields poly(1-methyl-1-silabutane), poly(1-phenyl-1-silabutane) and poly(1-silabutane) respectively. These saturated carbosilane polymers possess reactive Si-H bonds. They have been characterized by ^{1}H, ^{13}C and ^{29}Si NMR as well as FT-IR and UV spectroscopy. Their molecular weight distributions have been determined by gel permeation chromatography (GPC), thermal stabilities by thermogravimetric analysis (TGA) and glass transition temperatures (T_g) by differential scanning calorimetry (DSC).

Introduction

While polymethylhydrosiloxanes are well known commercial products (1), polycarbosilanes which possess reactive Si-H bonds have only recently attracted significant attention. The proposal by Yajima that poly(1-methyl-1-silaethane) $(\text{-CH}_3\text{-SiH-CH}_2\text{-})_n$ is an intermediate in the pyrolytic conversion of poly(dimethylsilane) fibers into silicon carbide fibers (2,3) stimulated interest in such systems (4,5). Oligo(1-silapropane) has been prepared by hydrosilation polymerization of vinyldichlorosilane to yield poly(1,1-dichloro-1-silapropane) followed by reduction of the Si-Cl bonds with lithium aluminum hydride (6,7). Low molecular weight poly(1-methyl-1-sila-*cis*-pent-3-ene) and poly(1-sila-*cis*-pent-3-ene), carbosilane polymers which contain both reactive Si-H and carbon-carbon double bonds have been prepared by anionic ring opening polymerization of 1-methyl-1-silacyclopent-3-ene and 1-silacyclopent-3-ene respectively (8,9).



Experimental

^{1}H and ^{13}C NMR spectra were obtained on a Bruker AM-360 spectrometer operating in the Fourier Transform mode (FT). ^{29}Si NMR spectra were recorded on an IBM-Bruker WP-270-SY spectrometer. Five to ten percent weight/volume solutions of polymer in chloroform-*d* were used for ^{1}H NMR spectra, whereas fifteen to twenty percent solutions were utilized for ^{13}C and ^{29}Si NMR spectra. ^{13}C NMR spectra were run with broad band proton decoupling. A heteronuclear gated decoupling pulse sequence (NONOE) with a 20 sec delay was used to acquire ^{29}Si NMR spectra (10).

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These were externally referenced to TMS. Chloroform was used as an internal standard for ^{1}H and ^{13}C NMR spectra. IR spectra of neat films on NaCl plates were recorded on an IBM FT-IR spectrometer. UV spectra of solutions in diethyl ether were acquired on a Shimadzu UV-260 ultraviolet visible spectrometer.

Gel permeation chromatographic (GPC) analysis of the molecular weight distribution of these polymers were performed on a Waters system comprised of a U6K injector, a 510 HPLC solvent delivery system, a R401 refractive index detector and a Model 820 Maxima control system. A Water 7.8 mm x 30 cm Ultrastyragel linear column packed with less than 10 m particles of mixed pore size crosslinked styrene divinylbenzene copolymer 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. The retention times were calibrated against those of known monodisperse polystyrene standards: M_p 612,000; 114,000; 47,500; 18,700 and 5,120 whose M_w/M_n are less than 1.09.

Thermogravimetric analysis (TGA) of the polymers was carried out on a Perkin-Elmer TGS-2 instrument with a nitrogen flow rate of 40 cm^3/min. The temperature program for the analysis was 50°C for 10 min followed by an increase of 4°C.min to 750°C. The glass transition temperatures (T_g's) of the polymers were determined by differential scanning calorimetry (DSC) on a Perkin-Elmer DSC-7 instrument. The melting points of indium (mp 165°C) and spectra quality *n*-hexane (mp -95°C) were used to calibrate the DSC. The program for the analysis was -100°C for 10 min followed by an increase in temperature of 20°C/min to 150°C.

Elemental analysis was performed by Galbraith Laboratories, Knoxville TN.

Methyldichlorosilane, phenyldichlorosilane, trichlorosilane and platinum-divinyltetramethyldisiloxane complex were obtained from Huls America.

All reactions were carried out under an atmosphere of argon in flame dried glassware. THF was dried by distillation from a deep blue solution of sodium/benzophenone ketyl immediately prior to use. HMPA was distilled from calcium hydride and stored over activated 4 A° molecular sieves.

1-Methyl-1-silacyclobutane (I)

I was prepared in three steps following literature procedures (11). Thus chloroplatinic acid catalyzed hydrosilation of allyl chloride with methyldichlorosilane gives 3-chloropropylmethyldichlorosilane (12,13). Treatment of this with magnesium yields 1-methyl-1-chloro-1-silacyclobutane (11). The Si-Cl bond of this is converted to a Si-H bond by reduction with lithium aluminum hydride. ^{1}H NMR δ: 0.27(d,3H, J = 3.6 Hz), 0.86(m,2H), 1.02(m,2H), 2.04(m,2H), 4.61(m,1H). ^{13}C NMR δ: -2.37, 12.63, 19.69. ^{29}Si NMR δ: 0.11.

1-Phenyl-1-silacyclobutane (II)

II was prepared as above from allyl chloride and phenyldichlorosilane following literature procedures (11). ^{1}H NMR δ: 1.39(m,4H), 2.31(m,2H), 5.25(m,1H), 7.46(m, 3H), 7.70(m,2H). ^{13}C NMR δ: 12.71, 19.67, 127.98, 129.88, 134.35, 135.19. ^{29}Si NMR δ: -1.80.

1-Silacyclobutane (III)

III was prepared from trichlorosilane and allyl chloride as above following literature procedures (11). ^{1}H NMR δ: 1.13(m,4H), 2.23(m,2H), 4.56(m,2H). ^{13}C δ: 9.14, 22.18. ^{29}Si NMR δ: -23.66.

Poly(1-methyl-1-silabutane) (IV)

In a 100 mL round bottom flask equipped with a Teflon covered magnetic stirring bar and a rubber septum was placed I (1.00 g, 11.6 mmol), THF (40 mL) and HMPA (200 L). The mixture was cooled to -78°C and a hexane solution of *n*-butyllithium (80 L, 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, filtered and the volatile solvents were removed by evaporation under reduced pressure. The residue was dissolved in a minimum amount of THF and IV was precipitated from methanol. This process was repeated twice. IV was dried under vacuum. In this way, 0.65 g, 65% yield of IV with M_w/M_n = 12,200/ 6,100 and T_g = -89°C was obtained. ^{1}H NMR δ: 0.20(d,3H, J =3.5 Hz), 0.65(m,4H), 1.42(m,2H, J = 8.1 Hz), 3.75(m,1H, J = 3.5 Hz). ^{13}C NMR δ: -6.23, 16.90, 19.76. ^{29}Si NMR δ: -11.46. IR ν: 2957, 2914, 2877, 2853, 2974, 2105 (s), 1450, 1410, 1335, 1251, 1215, 1142, 1081, 1025, 985, 946, 877, 832, 721 cm^{-1}. Anal. Calcd for $C_4H_{10}Si$: C, 55.78; H, 11.70. Found: C, 56.28; H, 11.57.

Poly(1-phenyl-1-silabutane) (V)

The polymerization of II (1 g, 6.8 mmol) was carried out as above except that 300 L of HMPA and only 50 L of *n*-butyllithium were utilized. In this way, 0.15 g, 15% yield of V with M_w/M_n = 730,000/ 390,000 was obtained. Removal of methanol gave a 40% yield of oligomer M_w/M_n = 900/800. The oligomer was not further characterized. ^{1}H NMR δ: 0.77(m,4H), 1.35(pentet,2H, J = 8.3 Hz), 4.11(t,1H, J = 3.3 Hz), 7.23(m,3H), 7.32(m,2H). ^{13}C NMR δ: 15.84, 15.79, 19.72, 127.77, 129.07, 134.59, 135.63. ^{29}Si NMR δ: -11.24, -11.30, -11.37. IR ν: 3068, 3049, 3012, 2999, 2955, 2917, 2896, 2792, 2109 (s), 1486, 1456, 1428, 1409, 1335, 1234, 1214, 1140, 1113, 1082, 1067, 1028, 998, 983, 944, 191, 810, 734, 699 cm^{-1}. Anal. Calcd for $C_9H_{12}Si$: C, 72.94; H, 8.16. Found: C, 72.59; H, 8.45.

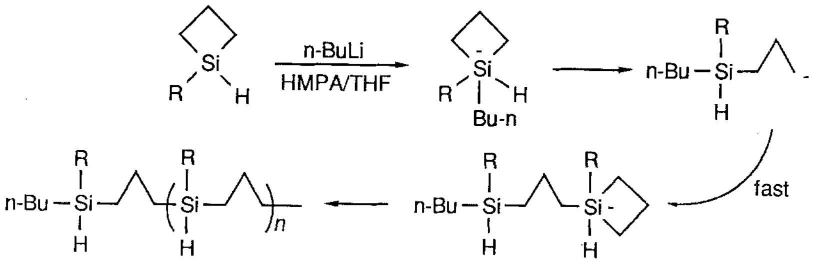
Poly(1-silabutane)(VI)

The polymerization of III (1 g, 13.9 mmol) was carried out as above. In this way, 0.70 g, 70% yield, of VI, M_w/M_n = 84,400/23,900 was obtained. ^{1}H NMR δ: 0.76(m,4H), 1.49(m,2H), 3.62(m,2H, J = 3.6 Hz). ^{13}C NMR δ: 12.77, 21.64. ^{29}Si NMR δ: -30.38. IR ν: 2914, 2885, 2853, 2793, 2120 (s), 1451, 1404, 1336, 1342, 1214, 1144, 1083, 944, 926, 841, 769, 708, 699 cm^{-1}.

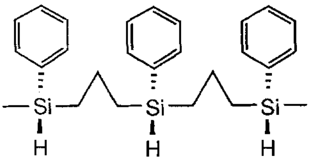
Results and discussion

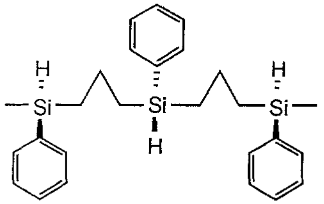
We should like to report the preparation and characterization of poly(1-methyl-1-silabutane), poly(1-phenyl-1-silabutane) and poly(1-silabutane) by the anionic ring opening polymerization of 1-methyl-1-silacyclobutane, 1-phenyl-1-silacyclobutane and 1-silacyclobutane respectively. While anionic (14), platinum catalyzed (15,16) and thermal (17) polymerization of 1,1-dimethyl-1-silacyclobutane and related systems is well known, neither anionic nor platinum catalyzed polymerization of silacyclobutanes with reactive Si-H bonds has been previously reported. The thermal polymerization of 1-methyl-1-silacyclobutane has been described in a patent (18).

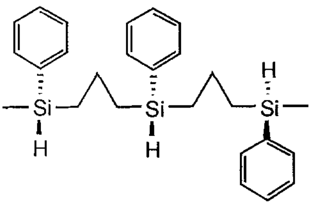
We believe that the anionic ring opening polymerization of silacyclobutanes proceeds by nucleophilic attack at the silyl center with formation of a pentacoodinate siliconate anion intermediate. Ring opening of the silacyclobutane ring results in relief of ring strain (26 kcal/mol) (19) and formation of a primary carbanion which attacks the silyl center of another molecule of silacyclobutane to yield a new hypervalent siliconate intermediate as outlined blow. This mechanism is similar to that which has been proposed for the anionic ring opening polymerization of 1,1-dimethyl-1-silacyclobutane (20,21). Such anionic polymerization is unexpected since hydride can serve as a leaving group in nucleophilic substitution reactions at silyl centers (22,23).

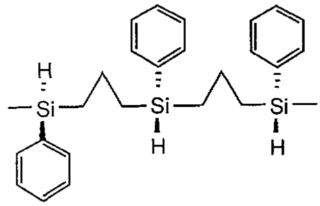


The silyl centers of both poly(1-methyl-1-silabutane) and poly(1-phenyl-1-silabutane) are chiral. However, no affect of chirality on microstructure is detected in either the ^{13}C or ^{29}Si NMR spectra of poly(1-methyl-1-silabutane). On the other hand, the chiral of adjacent silyl centers affect both the ^{13}C and ^{29}Si NMR of poly(1-phenyl-1-silabutane). Thus three ^{29}Si resonances in a 1:2:1 intensity ratio are observed. These can be accounted for in terms of a triad analysis.

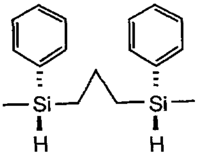


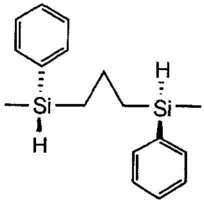




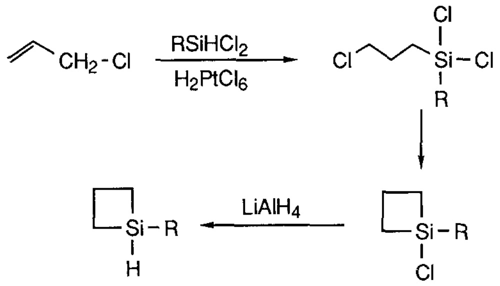


In addition, two signals of equal intensity are observed for the methylene groups adjacent to the silyl center. These can be accounted for in terms of the stereochemistry of the adjacent chiral silyl centers.

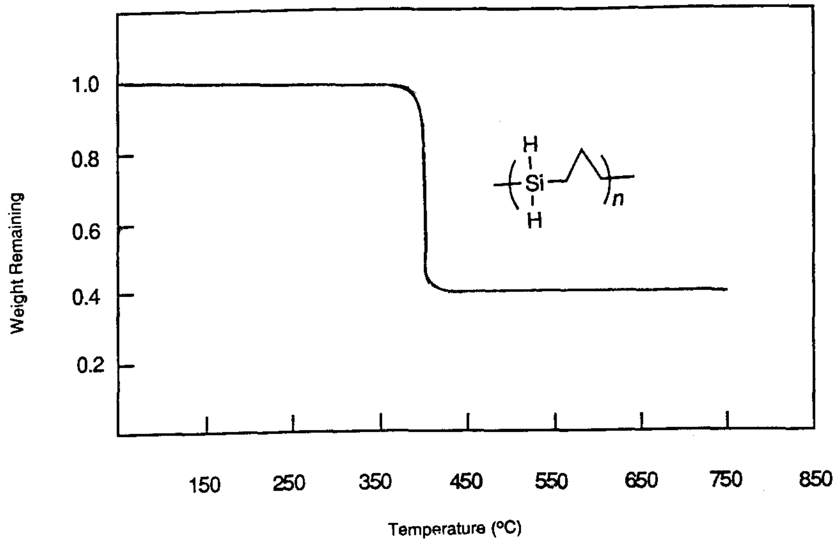




1-Methyl-2-silacyclobutane, 1-phenyl-1-silacyclobutane have been prepared in three steps starting from methyldichlorosilane and phenyldichlorosilane respectively. Thus chloroplatinic acid catalyzed hydrosilation of allyl chloride with methyldichlorosilane gives 3-chloropropylmethyldichlorosilane (12,13). Similar reaction with phenyldichlorosilane gives 3-chloropropylphenyldichlorosilane. Treatment of these with magnesium results in generation of a Grignard reagent and cyclization to yield respectively 1-chloro-1-methyl-1-silacyclobutane and 1-chloro-1-phenyl-1-silacyclobutane (11). Treatment of these with lithium aluminum hydride gives 1-methyl-1-silacyclobutane and 1-phenyl-1-silacyclobutane. 1-Silacyclobutane can be prepared in a similar manner starting from trichlorosilane and allyl chloride. However, 1,1-dichloro-1-silacyclobutane is commercially available (Huls). Lithium aluminum hydride reduction of 1,1-dichloro-1-silacyclobutane yields 1-silacyclobutane (11).



The thermal stability of these polymers has been determined in nitrogen. Poly(1-methyl-1-silabutane) is stable to 240°C. Above 240°C, sudden weight loss occurs. At 475°C, nine percent of the initial sample weight remains. Poly(1-phenyl-1-silabutane) is stable to 230°C. Above this temperature weigh loss is rapid. At 500°C, an eleven percent residue is found. Poly(1-silabutane) is stable to 400°C. Above this temperature weight loss is fast. By 500°C sixty percent weight loss has occurred. No further weight loss occurs on heating these samples to 750°C. Thus poly(1-silabutane) gives a forty percent char yield. The conversion of organometallic polymers to ceramic char usually depends on the occurrence of crosslinking reaction leading to network structures. The nature of the crosslinking reaction which occur on pyrolysis of poly(1-silabutane) in an inert atmosphere are under active investigation.



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