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Anionic Ring-Opening Polymerization of 2,3-Benzo-1-silacyclobutenes. Characterization of Poly(2,3-benzo-1-silabutenes)

Marcus Theurig, Steven J. Sargeant, Georges Manuel, and William P. Weber*

Katherine B. and Donald P. Loker Hydrocarbon Research Institute, Department of Chemistry, University of Southern California, Los Angeles, California 90089-1661

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ABSTRACT: Anionic ring-opening polymerization of 2,3-benzo-1,1-dimethyl-1-silacyclobutene (I), 2,3-benzo-1-methyl-1-phenyl-1-silacyclobutene (II), and 2,3-benzo-1,1-diphenyl-1-silacyclobutene (III) catalyzed by *n*-butyllithium and hexamethylphosphoramide (HMPA) in THF at low temperature (−78 °C) yields respectively poly(2,3-benzo-1,1-dimethyl-1-silabutene) (IV), poly(2,3-benzo-1-methyl-1-phenyl-1-silabutene) (V), and poly(2,3-benzo-1,1-diphenyl-1-silabutene) (VI). These polymers have been characterized by ^{1}H, ^{13}C, and ^{29}Si NMR as well as by IR and UV–visible spectroscopy. Their molecular compositions have been determined by elemental analysis. The molecular weight distributions of these polymers have been measured by gel permeation chromatography (GPC), their thermal stabilities by thermogravimetric analysis (TGA), and their glass transition temperatures (T_g) by differential scanning calorimetry (DSC).

Introduction

While there has been considerable work done on the ring-opening polymerization of silacyclobutanes, the polymerization of 2,3-benzo-1-silacyclobutene systems has been less thoroughly studied. This paper reports the synthesis and characterization of poly(2,3-benzo-1,1-dimethyl-1-silabutene) (IV), poly(2,3-benzo-1-methyl-1-phenyl-1-silabutene) (V), and poly(2,3-benzo-1,1-diphenyl-1-silabutene) (VI). These polymers were prepared by the anionic ring-opening polymerization of 2,3-benzo-1,1-dimethyl-1-silacyclobutene (I), 2,3-benzo-1-methyl-1-phenyl-1-silacyclobutene (II), and 2,3-benzo-1,1-diphenyl-1-silacyclobutene (III), respectively.

Experimental Section

^{1}H, ^{13}C, and ^{29}Si NMR spectra were obtained on an IBM-Bruker 270-SY spectrometer operating in the Fourier transform mode. ^{13}C NMR spectra were run with broad-band proton decoupling. Ten to fifteen percent solutions in chloroform-*d* were used to obtain ^{13}C and ^{29}Si NMR spectra. Five percent solutions were used to obtain ^{1}H NMR spectra. Chloroform or TMS were utilized as an internal standard for ^{1}H and ^{13}C NMR spectra. A heteronuclear gated decoupling pulse sequence (NONOE) with a delay of 20 s was used to obtain ^{29}Si NMR spectra which were externally referenced to TMS.[1]

IR spectra were recorded on a Perkin-Elmer PE-281 spectrometer of neat liquid samples on sodium chloride plates or as potassium bromide pellets for solids. UV spectra were recorded on a Shimadzu UV-260 UV–visible spectrometer. Spectra-quality THF was used to prepare solutions of polymers, and spectra-quality hexane was used to prepare solutions of monomers for UV spectroscopy.

Gel permeation chromatographic (GPC) analysis of the molecular weight distribution of the polymers was performed on a Waters system. This was comprised of a U6K injector, a 510 solvent delivery system, a R401 differential refractometer, and a Maxima 820 data station. A 7.8 mm × 30 cm Waters Ultrastyragel linear column packed with <10-μm particles of mixed pore size, cross-linked styrene–divinylbenzene copolymer was used for the analysis. The eluant was HPLC-grade THF at a flow rate of 0.8 mL/min. Retention times were calibrated against known monodisperse polystyrene standards M_p 179 000, 110 000, 20 400, and 1350 whose M_w/M_n are less than 1.09.

Preparative GLPC was carried out on a Gow Mac 550 GC equipped with a 1/4 in. × 10 ft stainless steel column packed with 10% SE-30 on Chromosorb W NAW 60/80 mesh. The column was deactivated immediately prior to use by injection of 50 μL of hexamethyldisilazane.

Thermogravimetric analysis (TGA) of the polymers was carried out on a Perkin-Elmer TGS-2 instrument at a nitrogen flow rate of 40 cm^3/min. The temperature program for these analyses was 50 °C for 10 min followed by an increase of 5 °C/min to 100 °C. After 10 min at 100 °C the temperature was increased at a rate of 5 °C/min to 750 °C. The glass transition temperature (T_g) and the melting point (T_m) were determined by differential scanning calorimetry (DSC) on a Perkin-Elmer DSC-4 system. The inital temperature for the analysis was 30 °C. This was increased at a rate of 20 °C/min to 200 °C. The melting points of the polymers were also measured on an Electrothermal melting point apparatus and are uncorrected.

High-resolution mass spectra were obtained at the University of California Riverside Mass Spectrometry Facility on a VG-7070 EHF mass spectrometer at an ionizing voltage of 20 eV. Exact masses were determined by peak matching against known masses of perfluorokerosene.

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

Tetrahydrofuran (THF) was distilled immediately prior to use from sodium benzophenone ketyl. Hexamethylphosphoramide (HMPA) was distilled from calcium hydride and was stored over 4-Å molecular sieves. Hexane was distilled from lithium aluminum hydride. *n*-Butyllithium in hexane (2.5 M) and 2-bromobenzyl bromide (Aldrich) were used as received. Dimethyldichlorosilane, methylphenyldichlorosilane, and diphenyldichlorosilane were obtained from Hüls. They were purified by fractional distillation.

All glassware was dried overnight in an oven at 120 °C and was flame dried prior to use. All reactions were conducted under an atmosphere of purified argon.

2,3-Benzo-1,1-dimethyl-1-silacyclobutene (I).[2] I was prepared by the reaction of 2-bromobenzyl bromide and dimethyldichlorosilane with magnesium powder in ether following literature procedures. The product was purified by fractional distillation through a 15-cm vacuum-jacketed Vigreux column. A fraction [bp 106/107 °C/60 mm (lit.[2] 73 °C/17 mm)] of 17 g (44% yield) was isolated. ^{1}H NMR δ 0.36 (s, 6 H), 2.06 (s, 2 H), 7.03 (m, 2 H), 7.18 (m, 2 H). ^{13}C NMR: δ −0.45, 20.13, 126.18, 126.91, 130.38, 130.46, 145.94, 150.55. ^{29}Si NMR: δ 9.41. IR: ν 3056, 2960, 2909, 1586, 1450, 1436, 1282, 1247, 1043, 849, 823, 786, 718 cm^{-1}. UV: λ_{max} nm (ϵ) 219 (5300), 262 (1200), 269 (1700), 276 (1550).

2,3-Benzo-1-methyl-1-phenyl-1-silacyclobutene (II). In a 500-mL three-necked round-bottom flask equipped with a reflux condenser, a pressure equalizing addition funnel, and a Teflon-covered magnetic stirring bar was placed magnesium powder (9.7 g, 0.4 mol) and ether (30 mL). A mixture of 2-bromobenzyl bromide (33 g, 0.13 mol) and methylphenyldichlorosilane (26.8 g, 0.4 mol) in ether (150 mL) was placed in the addition funnel

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and was slowly added to the vigorously stirred refluxing reaction mixture. The reaction was stirred for 24 h and was then treated with 50 mL of aqueous ammonium chloride. The ether layer was separated, dried over anhydrous magnesium sulfate, and filtered, and the volatile solvents were removed by evaporation under reduced pressure. The residue was transferred to a 50-mL round-bottom flask. The product was purified by fractional distillation through a 15-cm vacuum-jacketed Vigreux column. A fraction (bp 116 °C/0.8 mm) of 11.3 g (39% yield) was isolated. ^{1}H NMR: δ 0.76 (s, 3 H), 2.35 (s, 2 H), 7.20 (m, 2 H), 7.35 (br s, 5 H), 7.57 (m, 2 H). ^{13}C NMR: δ −2.76, 20.65, 126.57, 126.94, 127.97, 128.30, 129.97, 130.85, 133.98, 136.32, 144.39, 151.88. ^{29}Si NMR: δ −0.61. IR: ν 3054, 2959, 2909, 1584, 1450, 1436, 1428, 1283, 1250, 1112, 1042, 818, 781, 735, 698 cm^{-1}. UV: λ_{max} nm (ϵ) 211 (12 600), 263 (850), 269 (1050), 276 (900). MS: *m/e* (rel intens) 213 (1.0), 212 (5.0), 211 (17.0), 210 (86.0) [M$^{\bullet+}$], 209 (41), 208 (7.0), 207 (1.0), 197 (5.0), 196 (19.0), 195 (100) [M − 15$^+$], 194 (9.0), 193 (32), 165 (37.0). High resolution MS: calcd for $C_{14}H_{14}Si$, *m/e* M$^{\bullet+}$ 210.0865; found, 210.08648.

2,3-Benzo-1,1-diphenyl-1-silacyclobutene (III).[3] III was prepared by reaction of 2-bromobenzyl bromide with diphenyldichlorosilane and magnesium powder in ether following literature procedures. III was purified by chromatography on a silica gel column (1.5 cm × 30 cm) with pentane. In this way, 15.7 g (42% yield) of III, mp 73 °C (lit. mp 73–75 °C), was obtained. ^{1}H NMR: δ 2.63 (s, 2 H), 7.30 (m, 3 H), 7.41 (m, 6 H), 7.54 (m, 1 H), 7.68 (m, 4 H). ^{13}C NMR: δ 20.38, 126.86, 127.07, 128.03, 130.07, 130.98, 131.06, 134.23, 143.38, 151.89. ^{29}Si NMR: δ −3.91. IR: ν 3047, 1820, 1727, 1584, 1450, 1281, 1118, 1041, 786, 725, 698 cm^{-1}. UV: λ_{max} nm (ϵ) 222 (23 000), 263 (2400), 270 (2900), 277 (2200).

Poly(2,3-benzo-1,1-dimethyl-1-silabutene) (IV). I (1.0 g, 6.7 mmol), THF (20 mL), and 5 drops of HMPA were placed in a 100-mL Schlenk tube equipped with a Teflon-covered magnetic stirring bar. The flask was sealed with a rubber septum and was cooled to −78 °C in a dry-ice/acetone bath. *n*-Butyllithium (134 μL, 0.33 mmol) was added as rapidly as possible via a syringe to the well-stirred reaction mixture. The reaction mixture immediately became red in color and then turned yellow after a few seconds. The reaction was stirred and maintained at −78 °C for 1 h. It was then allowed to warm to room temperature and was quenched by addition of 10 mL of saturated aqueous ammonium chloride. THF (50 mL) was added. The organic layer was washed with water, separated, dried over anhydrous magnesium sulfate, and filtered, and the organic solvents were removed by evaporation under reduced pressure. The residue was triturated with a minimum amount of ether. The residue was then dissolved in a minimum amount of THF, and the polymer was precipitated from methanol. In this way, 0.93 g (93% yield) of a white crystalline polymer (mp 201–203 °C) was obtained. By DSC, T_m = 204 °C and T_g = 48 °C. The polymer did not dissolve in cold THF or ether but was soluble in warm THF or benzene. M_w/M_n = 33 900/17 200. ^{1}H NMR: δ 0.16 (br s, 6 H), 2.41 (br s, 2 H), 6.82 (d, 1 H, J = 7.5 Hz), 6.99 (t, 1 H, J = 7.25 Hz), 7.07 (t, 1 H, J = 7.25 Hz), 7.31 (d, 1 H, J = 7.0 Hz). ^{13}C NMR: δ −0.35, 26.43, 123.75, 128.80, 129.05, 135.21, 136.16, 146.13. ^{29}Si NMR: δ −4.07. IR: ν 3053, 2955, 2897, 1586, 1467, 1433, 1258, 1248, 1195, 1109, 871, 791 cm^{-1}. UV: λ_{max} nm (ϵ) 239 (23 000), 274 (5000), 289 (3200). Elem anal. Calcd for $C_9H_{12}Si$: C, 72.9; H, 8.16. Found: C, 71.62; H, 8.25.

Poly(2,3-benzo-1-methyl-1-phenyl-1-silabutene) (V). The polymerization of II was carried out essentially as above. *n*-Butyllithium (134 μL, 0.333 mmol) was added to a mixture of II (1.41 g, 6.7 mmol), THF (30 mL), and HMPA (200 L) at −78 °C as above. After 2 h, the reaction was quenched at −78 °C by the dropwise addition of 10 mL of saturated aqueous ammonium chloride. After workup, the polymer was purified by precipitation from methanol twice. In this way, 1.2 g (85% yield) of a white crystalline polymer, M_w/M_n = 25 600/14 400, was obtained. On heating, V became glassy above 140 °C and melted as 215–216 °C. By DSC, T_g was 93.8 °C; T_m was not observed. ^{1}H NMR: δ −0.03 (s, 3 H), 2.43 (s, 2 H), 6.67 (br s, 1 H), 7.00 (br s, 2 H), 7.10 (s, 4 H), 7.21 (br s, 2 H). ^{13}C NMR: δ −2.69, 23.60, 123.92, 127.71, 128.86, 129.25, 134.32, 135.37, 135.95, 138.19, 145.77, 154.83. ^{29}Si NMR: δ −9.37. IR: ν 3050, 3000, 2962, 1587, 1562, 1468, 1427, 1260, 1195, 1108, 1067, 806, 725, 699 cm^{-1}. UV: λ_{max} nm (ϵ) 238 (44 000), 268 (9150). Elem anal. Calcd for $C_{14}H_{14}Si$: C, 79.94; H, 6.71. Found: C, 78.10; H, 6.82.

Poly(2,3-benzo-1,1-diphenyl-1-silabutene) (VI). The polymerization of III (1.82 g, 6.7 mmol) in THF (40 mL) and HMPA (200 μL) catalyzed by *n*-butyllithium (134 L, 0.33 mmol) was carried out as above. VI was purified by precipitation from methanol twice. In this way, 1.75 g (96% yield) of a white crystalline polymer, M_w/M_n = 96 100/60 200, was obtained. On heating VI became glassy above 155 °C and melted at 239–240 °C. By DSC, T_g = 122 °C; no T_m was observed. ^{1}H NMR: δ 2.55 (s, 2 H), 6.76 (m, 5 H), 6.87 (m, 6 H), 7.24 (m, 3 H). ^{13}C NMR: δ 24.18, 124.29, 127.59, 128.90, 129.38, 130.13, 134.63, 135.33, 135.63, 137.60, 145.62. ^{29}Si NMR: δ −14.01. IR: ν 3068, 3049, 2998, 1588, 1486, 1427, 1261, 1195, 1108, 805, 776, 740, 699 cm^{-1}. UV: λ_{max} nm (ϵ) 238 (31 000), 270 (4300), 273 (5800). Elem anal. Calcd for $C_{19}H_{16}Si$: C, 83.77; H, 5.92. Found: C, 80.42; H, 5.55.

Results and Discussion

There is considerable interest in ring-opening polymerization reactions.[4–6] The polymerization of three- and four-membered heterocyclic compounds generally proceeds to yield high molecular weight polymers. The relief of ring strain in these systems provides a significant thermodynamic driving force for their polymerization. Specifically, the enthalpy of such polymerizations generally has a large negative value which ensures that the free energy of the polymerization has a significant negative value.[7] Hartree–Fock SCF calculations have recently been carried out on silacyclobutene. The calculated strain energy determined by these techniques is 28 kcal/mol.[8] The calculated strain energy for silacyclobutene is approximately equal to that of silacyclobutane (26 kcal/mol) which has been determined from the enthalpy of combustion.[9,10] This suggests that silacyclobutenes would have a thermodynamic driving force for polymerization approximately equal to that of silacyclobutanes. Nevertheless, while considerable work has been done on the ring-opening polymerization of silacyclobutanes under anionic,[11] thermal,[12] and platinum catalysis,[13] no work has been done on the polymerization of silacyclobutenes. This is probably due to the synthetic difficulty in their preparation.[14–18]

There are, nevertheless, three reports on the polymerization of the synthetically more accessible benzosilacyclobutenes. The polymerization of 2,3-benzo-1,1-dimethyl-1-silacyclobutene (I) under anionic, thermal, and free-radical conditions was reported 20 years ago. Characterization of poly(2,3-benzo-1,1-dimethyl-1-silabutene) (IV) was limited to its ^{1}H NMR spectrum, elemental analysis, and intrinsic viscosity.[19] An earlier paper describes the thermal, potassium metal, and anionic polymerization of I and the IR spectrum of IV.[20] The platinum-catalyzed polymerization of 2,3-benzo-1,1-diphenyl-1-silacyclobutene (III) has also been reported.[21] The disappearance of an IR band characteristic of the monomer and the formation of a polymer "gum" were described.

The *fragmentary nature* of these previous reports justifies, in our opinion, a thorough study of the anionic polymerization of 2,3-benzo-1-silacyclobutenes. In this paper we report the anionic ring-opening polymerization of 2,3-benzo-1,1-dimethyl-1-silacyclobutene (I), 2,3-benzo-1-methyl-1-phenyl-1-silacyclobutene (II), and 2,3-benzo-1,1-diphenyl-1-silacyclobutene (III). We anticipated that such benzo polymers might have high thermal stabilities and relatively high glass transition temperatures and melting behavior. These properties might make these polymers suitable for a variety of practical applications.

The T_gs for IV–VI are found at 47, 95, and 121 °C (see Figures 1–4). For comparison, the T_g of poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene) (VII) is −64 °C,[22] while that for poly-

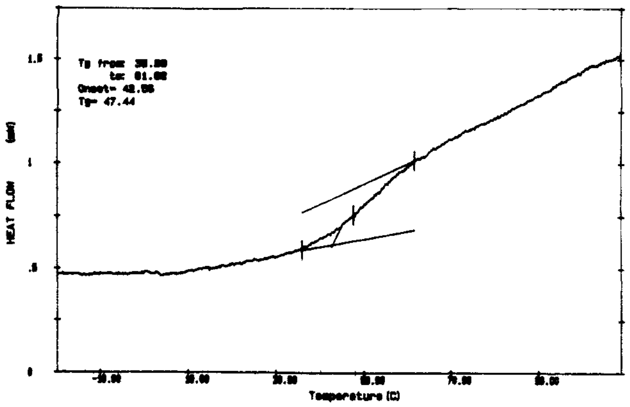


Figure 1. DSC of poly(2,3-benzo-1,1-dimethyl-1-silabutene) T_g.

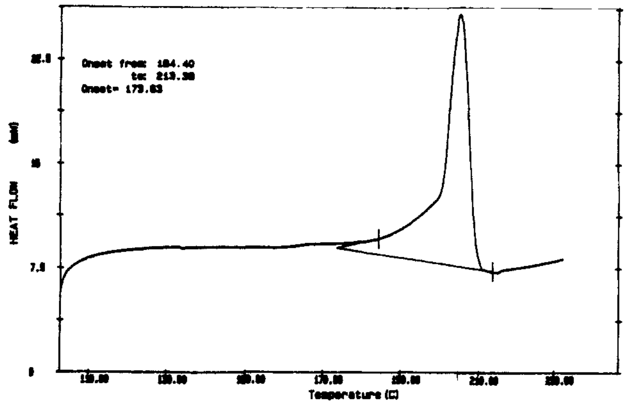


Figure 2. DSC of poly(2,3-benzo-1,1-dimethyl-1-silabutene) T_m.

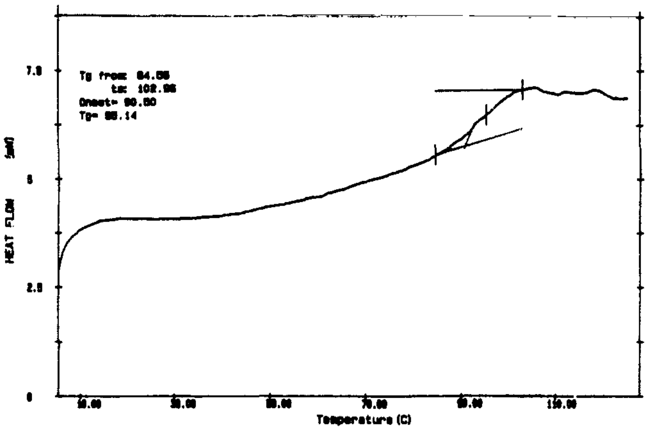


Figure 3. DSC of poly(2,3-benzo-1-methyl-1-phenyl-1-silabutene) T_g.

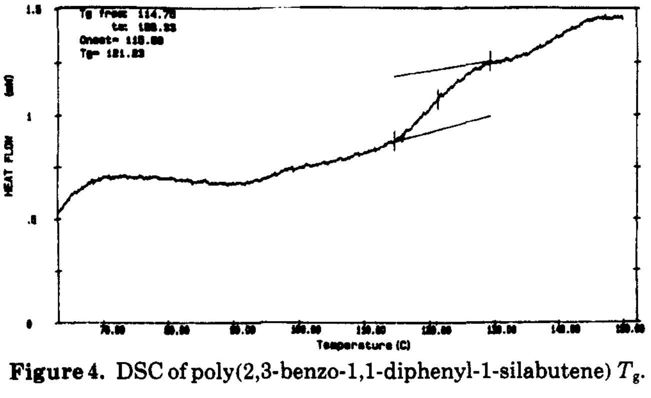


Figure 4. DSC of poly(2,3-benzo-1,1-diphenyl-1-silabutene) T_g.

(1,1-diphenyl-1-sila-*cis*-pent-3-ene) (VIII) is 35 °C[23] and that for poly(3,4-benzo-1,1-dimethyl-1-silapentene) (IX) is 75 °C.[22] Based on the comparison of the T_gs of IV and VI with those of VII and VIII, it is evident that replacement of the methyl groups on silicon by phenyl groups results in increased T_g. In addition, it is evident from the comparison of the T_gs of VII and IX that replacement of a carbon–carbon double bond with a benzo unit in the polymer backbone also increases the T_g of the polymers.

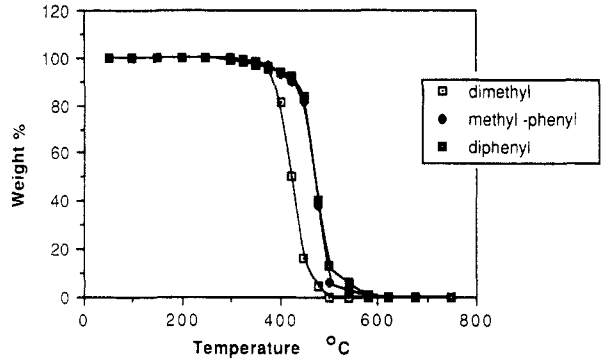


Figure 5. TGA of IV–VI in nitrogen.

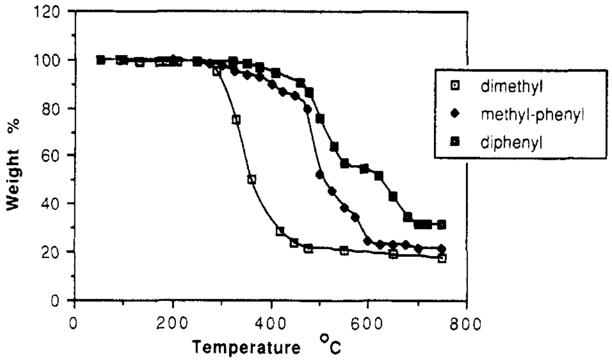


Figure 6. TGA of IV–VI in air.

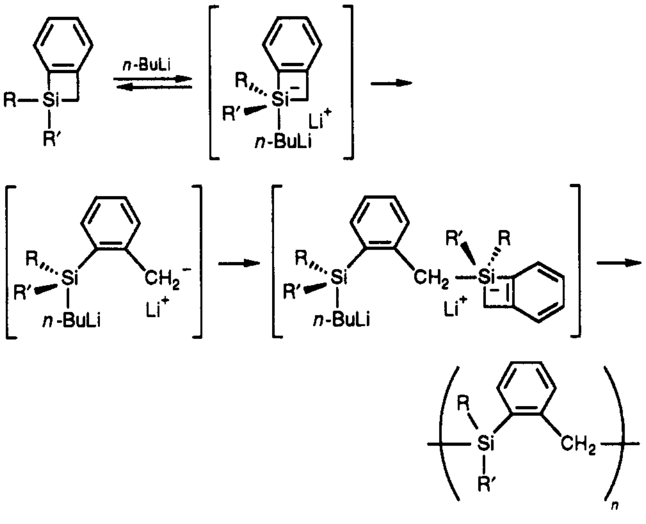
The thermal stabilities of IV–VI have been determined by thermogravimetric analysis (TGA). In nitrogen IV is thermally stable to 300 °C. Above 360 °C rapid catastrophic decomposition occurs. V is also thermally stable to 300 °C. Between 320 and 400 °C, 5% of the initial sample weight is lost. Above 425 °C catastrophic decomposition occurs. The thermal stability of VI is similar to that of V (see Figure 5). Surprisingly, none of these poly(2,3-benzo-1-silabutenes) is as thermally stable as IX which is thermally stable to almost 450 °C in nitrogen.

In air, IV is thermally stable to 250 °C (Figure 6). Above this temperature rapid decomposition occurs. Above 450 °C a 20% residue is observed. In air V is thermally stable to 250 °C. Between 250 and 450 °C 15% of the initial sample weight is lost. Above 475 °C rapid decomposition occurs. Above 600 °C a 22% residue is found. VI is thermally stable in air to 300 °C. Between 300 and 475 °C an 11% weight loss is observed. Between 475 and 550 °C 33% of the initial sample weight is rapidly lost. Between 550 and 625 °C only a few percent of the sample weight is lost. A final 20% weight loss occurs between 625 and 700 °C.

We believe that the mechanism of this anionic ring-opening polymerization of benzosilacyclobutenes proceeds by nucleophilic attack at the silyl center to form a pentacoordinate anionic silicon intermediate (Scheme I). Ring opening of this intermediate leads to a benzylic anion which reacts rapidly with another molecule of benzosilacyclobutene to form a new hypervalent siliconate intermediate. This mechanism is similar to that previously proposed for the anionic ring-opening polymerization of 1,1-dimethyl-1-silacyclobutane[24] and 1-silacyclopent-3-enes.[25,26]

Nevertheless, there are several facts which are difficult to explain at present. The ratio of 2,3-benzo-1-silacy-

Scheme I
Mechanism of Anionic Ring-Opening Polymerization of 2,3-Benzo-1-silacyclobutenes[a]



[a] I: $R = R' = CH_3$. II: $R = CH_3$; $R' = C_6H_5$. III: $R = R' = C_6H_5$.

clobutene monomer (I, II, or III) to *n*-butyllithium initiator was 20:1 in each case. In normal anionic living polymerization the molecular weight of the polymer depends inversely on the concentration of the initiator. On this basis, we might expect M_n for the polymers IV–VI to be equal. Further, we would anticipate that their molecular weights would be significantly lower than those observed. The molecular weight distributions observed for IV–VI are close to 2. This is not consistent with the narrow molecular weight distributions usually observed in carefully controlled living anionic polymerizations. These observations may be consistent with the presence of equilibria between 2,3-benzosilacyclobutenes and alkyllithium reagents on the one hand and pentacoordinate siliconate intermediates on the other. Alternatively these differences may result from experimental inconsistencies. Further work to clarify these questions is in progress.

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Registry No. I, 26710-06-5; I (homopolymer), 17158-47-3; I (SRU), 26970-34-3; II, 141848-37-5; II (homopolymer), 141848-38-6; II (SRU), 141848-41-1; III, 733-87-9; III (homopolymer), 141848-39-7; III (SRU), 141848-42-2; HMPA, 680-31-9; BrC_6H_4-*o*-CH_2Br, 3433-80-5; $MePhSiCl_2$, 149-74-6; BuLi, 109-72-8.