Anionic Dimerization and Ring-Opening Polymerization of 1,1-Divinyl-1-silacyclopent-3-ene

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ABSTRACT: Anionic ring-opening polymerization of 1,1-divinyl-1-silacyclopent-3-ene (I) cocatalyzed by *n*-butyllithium and hexamethylphosphoramide (HMPA) in THF at low temperature (−78 °C) leads to a mixture of 1,1,6,6-tetravinyl-1,6-disilacyclodeca-3,8-diene (dimer) and poly(1,1-divinyl-1-sila-*cis*-pent-3-ene) (polymer). These have been separated and characterized by ^{1}H, ^{13}C, and ^{29}Si NMR, IR, and UV spectroscopy and elemental analysis. The molecular weight of the dimer has been determined by mass spectroscopy, while the molecular weight distribution of the polymer has been measured by gel permeation chromatography (GPC). Thermogravimetric analysis (TGA) of the polymer in nitrogen gave a 62% char yield. The glass transition temperature (T_g) −65 °C of the polymer was determined by differential scanning calorimetry (DSC). The mechanism of this reaction has been studied.

Introduction

The proposal by Yajima that poly(1-methyl-1-silaethane) $[CH_3SiHCH_2]_n$ is a key intermediate in the conversion of poly(dimethylsilane) into β silicon carbide has stimulated considerable interest in the chemistry of polycarbosilanes.[1] Saturated polycarbosilanes such as poly(1,1-dimethyl-1-silabutane) and poly(1,1-dimethyl-1-silaethane) have been prepared by anionic,[2–4] platinum-catalyzed,[5] and thermal[6–9] ring-opening polymerization of 1,1-dimethyl-1-silacyclobutane and 1,1,3,3-tetramethyl-1,3-disilacyclobutane, respectively. We have been interested in the preparation of stereoregular unsaturated polycarbosilane such as poly(1-sila-*cis*-pent-3-enes).[10–12] These have been prepared by the anionic ring-opening polymerization of 1-silacyclopent-3-enes. Studies designed to elucidate the mechanism of these polymerization reactions have shown a number of unusual features. For example, 1,1,3,4-tetramethyl-1-silacyclopent-3-ene undergoes exchange of alkyl groups bonded to silicon rather than polymerization on treatment with *n*-butyllithium and hexamethylphosphoramide (HMPA) in tetrahydrofuran (THF) at low temperature.[11] This observation as well as the presence of 1-methyl-1-silacyclopent-3-ene end groups in poly(1-methyl-1-sila-*cis*-pent-3-ene)[13,14] has been interpreted in terms of the importance of anionic hypervalent siliconate intermediates in these polymerization reactions (see Figure 1).

In this paper, we report that anionic ring-opening polymerization of 1,1-divinyl-1-silacyclopent-3-ene yields poly(1,1-divinyl-1-silacyclopent-3-ene) (polymer) as expected. This carbosilane polymer has a very high degree of unsaturation and is converted on thermal decomposition to a high char yield. However, of greater mechanistic interest, significant amounts of 1,1,6,6-tetravinyl-1,6-disila-3,8-cyclodecadiene (dimer) are isolated along with the polymer. Experiments on the effect of monomer concentration and temperature on the ratio of dimer to polymer provide additional understanding of the mechanism of this reaction. The observation that pure polymer can be equilibrated to a mixture of dimer and polymer under polymerization reaction conditions is particularly significant (see Figure 2).
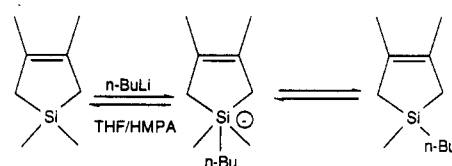

Figure 1. Equilibration of 1-silacyclopent-3-enes via siliconate intermediates.
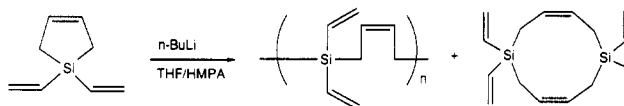

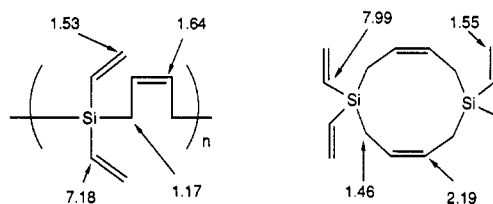**Figure 2.** Anionic dimerization–ring-opening polymerization of I.

Figure 3. ^{13}C NMR T_1 values in seconds for polymer and dimer.

Experimental Section

^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Bruker AM-360 spectrometer operating in the Fourier transform mode. ^{29}Si NMR spectra were obtained by use of heteronuclear gated decoupling pulse sequence (NONOE) with a pulse delay of 20 s.[15] Five percent weight/volume solutions in chloroform-*d* were used to measure ^{1}H and ^{13}C NMR spectra, whereas 15% solutions were utilized to obtain ^{29}Si NMR spectra.

The ratio of dimer to polymer was determined by integration of quantitative ^{13}C NMR spectra. ^{13}C T_1 values for dimer and polymer were determined using the inversion recovery method[16] (Figure 3). Samples of polymer and of mixtures of dimer and polymer dissolved in chloroform-*d* were placed in 5-mm NMR tubes. These solutions were degassed by bubbling UHP argon through them for 2 h. The NMR tubes were then sealed. The spectra were obtained at 30 °C on a Bruker SY-270 FT spectrometer using a π pulse of 12.4 μs and a $\pi/2$ pulse of 6.2 μs. Fifty-six scans were accumulated with relaxation delays of 0.01, 0.1, 0.5, 1.0, 5.0, 10.0, 20.0, 40.0, 80.0, and 120.0 seconds. Analysis of these data gives the ^{13}C T_1 values for both the dimer and the polymer.

This information permits determination of the conditions necessary for quantitative ^{13}C NMR spectroscopy. These were obtained of the crude polymerization reaction using the inverse gated decoupler pulse sequence (Invgate) with a delay of 40 s. This is 5 times the T_1 value of the slowest relaxing carbon in the system. The ^{13}C FIDs were multiplied by a suitable line-broadening value, and the relative amounts of polymer and dimer were obtained from the integration. To account for the symmetry of dimer, the areas of resonances due to polymer were multiplied by a factor of 2. For typical spectra the ratio of the areas of the allyl and vinyl carbons were nearly identical. The maximum difference observed was ±3%. For consistency, the ratios of the allyl carbons are reported in all cases since these signals have the greatest difference in chemical shift and are therefore the best resolved.

IR spectra were recorded on a Perkin-Elmer PE-281 spectrometer. Spectra were taken of neat films on NaCl plates. UV spectra of *n*-hexane solutions were taken on a Shimadzu UV–vis 260 spectrometer.

The molecular weight distribution of polymer was determined by GPC on a Waters system. This comprised 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 cross-linked styrene–divinylbenzene copolymer maintained at 20 °C was used for the analysis. The eluting solvent was HPLC grade THF at a flow rate of 0.8 mL/min. Retention times were calibrated both before and after sample runs against known monodisperse polystyrene standards.

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 850 °C. These runs were conducted with a nitrogen or air flow rate of 40 cm^3/min.

The glass transition temperature (T_g) was determined by differential scanning calorimetry (DSC) on a Perkin-Elmer DSC-7 system. Indium (mp 156 °C) and spectral quality *n*-hexane (mp –95 °C) were used to calibrate the DSC. After equilibration at –140 °C for 5 min, the temperature was increased at a rate of 20 °C/min to 0 °C.

Low-resolution mass spectra were obtained on a Finnigan MAT Incos 50 GCMS instrument at an ionizing voltage of 70 eV. A 0.25 mm × 30 m fused silica DB-5 capillary column was used in the gas chromatographic inlet of the mass spectrometer. 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.

THF and ether were freshly distilled from dark blue solutions of sodium benzophenone ketyl under nitrogen. *n*-Butyllithium (2.5 M in hexane) was purchased from Aldrich. All reactions were conducted in flame-dried glassware under an atmosphere of purified argon.

1,1-Divinyl-1-silacyclopent-3-ene. In a 1-L three-neck flask equipped with a Teflon-covered magnetic stirring bar, reflux condenser, and a pressure-equalizing addition funnel was placed vinyl magnesium bromide (0.5 mol) in THF (350 mL). The flask and its contents were cooled to 0 °C in an ice–water bath. 1,1-Dichloro-1-silacyclopent-3-ene (11 g, 72 mmol)[17] dissolved in THF (20 mL) was added dropwise to the reaction mixture. The reaction was allowed to slowly warm to room temperature over 6 h and was then poured into an ice-cold solution of saturated aqueous ammonium chloride. Ether (200 mL) was added, and the organic layer was washed with 3 equal volumes of water. The organic layer was dried over anhydrous calcium chloride and filtered, and the volatile organic solvents were removed by distillation through a 15-cm vacuum-jacketed Vigreux column at atmosphere pressure. The product was distilled under reduced pressure. A fraction bp 43–45 °C/16 mmHg, 9.4 g, 95% yield was obtained: ^{1}H NMR δ 1.44 (d, 4 H, J = 1 Hz), 5.87 (t, 2 H, J = 1 Hz), 5.81 (dd, 2 H, J = 20 and 3.9 Hz), 6.06 (dd, 2 H, J = 14.5 and 3.9 Hz), 6.22 (dd, 2 H, J = 20 and 14.5 Hz); ^{13}C NMR δ 15.46, 130.71, 134.00, 135.02; ^{29}Si NMR δ 1.56; IR ν 3040, 3020, 2940, 2885, 1605, 1400, 1200, 1095, 1000, 950, 943, 815, 795, 725, 690 cm^{-1}; UV λ (ε) 207 nm (2.5 × 10^3); GC/MS *m/e* (rel intensity) 138 (1.3), 137

(4.0), 136 (26.6) M$^{\bullet+}$, 135 (3.4), 123 (0.4), 122 (1.2), 121 (8.3) (M – 15)$^+$, 110 (6.2), 109 (26.2), 108 (100.0), 107 (36.3), 106 (17.6), 105 (4.8), 95 (18.0), 94 (7.0), 93 (10.15), 84 (4.1), 83 (20.9), 82 (65.7), 81 (33.3), 80 (17.5), 67 (39.5). Anal. Calcd for C$_8$H$_{12}$Si: C, 70.51; H, 8.88. Found: C, 70.96; H, 9.06.

Anionic Dimerization and Ring-Opening Polymerization of 1,1-Divinyl-1-silacyclopent-3-ene. In a 70-mL Schlenk flask equipped with a Teflon-covered magnetic stirring bar were placed 1,1-divinyl-1-silacyclopent-3-ene (1.5 g, 11 mmol), THF (25 mL), and HMPA (0.1 mL). The flask and its contents were cooled to –78 °C. *n*-Butyllithium (0.2 mL, 0.5 mmol) was added to the well-stirred solution. The reaction became deep red in color. The reaction was stirred and maintained at –78 °C for 6.5 h. It was quenched by addition of saturated aqueous ammonium chloride. Ether was added, and the organic layer was washed with saturated aqueous ammonium chloride and water, dried over anhydrous calcium chloride, and filtered; the ether was removed by evaporation under pressure. The residue (1.3 g), 87% yield, was found to be a mixture of dimer and polymer.

The dimer was separated from the polymer by selective precipitation of the polymer. Thus, 0.2 g of the mixture was dissolved in 0.5 mL of THF and was reprecipitated from 12 mL of methanol overnight. The precipitate, 0.12 g (60%), was 98% polymer by GPC. Pentane was added to the clear supernatant liquid. The combined organic phase was washed with water, dried over anhydrous calcium chloride, and filtered and the pentane removed by evaporation under reduced pressure. The residue, 0.08 g (40%), was 95% dimer by NMR. This process is repeated once on each fraction. In this way, pure dimer and polymer are obtained.

Polymer: M_w/M_n = 19 700/9400; T_g = –65 °C; ^{1}H NMR δ 1.58 (d, 4 H, J = 6.4 Hz), 5.35 (t, 2 H, J = 5.4 Hz), 5.76 (dd, 2 H, J = 18.4 and 5.8 Hz), 6.02 (dd, 2 H, J = 14.5 and 5.8 Hz), 6.13 (dd, 2 H, J = 18.4 and 14.5 Hz); ^{13}C NMR δ 13.82, 123.03, 133.98, 134.98; ^{29}Si NMR δ –15.36; IR ν 3040, 3000, 2920, 1635, 1590, 1400, 1375, 1150, 1000, 945, 820 cm^{-1}; UV λ (ε) 204 nm (9 × 10^3). Anal. Calcd for C$_8$H$_{12}$Si: C, 70.51; H, 8.88. Found: C, 70.47; H, 8.66.

Dimer: ^{1}H NMR δ 1.61 (d, 8 H, J = 6.5 Hz), 5.30 (t, 4 H, J = 5.6 Hz), 5.78 (dd, 4 H, J = 18.4 and 5.6 Hz), 6.07 (dd, 4 H, J = 14.5 and 5.6 Hz), 6.17 (dd, 4 H, J = 18.4 and 14.5 Hz); ^{13}C NMR δ 12.60, 122.69, 134.04, 135.17; ^{29}Si NMR δ –13.65; IR ν 3045, 3000, 2950, 2930, 2875, 1635, 1590, 1405, 1375, 1155, 1005, 950, 825, 735, 680 cm^{-1}; UV λ (ε) 207 nm (1.8 × 10^4); GC/MS *m/e* (rel intensity) 274 (2.6), 273 (7.1), 272 (26.2) M$^{\bullet+}$, 217 (8.0), 216 (6.0), 203 (7.3), 191 (4.7), 190 (18.6), 189 (5.2), 177 (13.3), 164 (10.9), 163 (8.9), 162 (10.1), 137 (7.0), 136 (27.5), 135 (10.2), 134 (5.3), 111 (5.2), 110 (13.3), 109 (70.9), 108 (100.0), 107 (36.8), 106 (17.1), 95 (22.5), 93 (35.3), 83 (57.5), 82 (72.5), 81 (48.1), 80 (11.1). High-resolution MS *m/e* calcd for C$_{16}$H$_{24}$Si$_2$: 272.1416. Found: 272.1408.

Effect of Temperature on the Ratio of Polymer to Dimer. In a 25-mL round-bottom flask equipped with a Teflon-covered magnetic stirring bar were placed THF (1.6 mL), HMPA (0.1 mL), and 1,1-divinyl-1-silacyclopent-3-ene (0.5 g, 3.7 mmol). The flask and its contents were sealed with a rubber septum and immersed in either a dry ice/acetone (–78 °C), chloroform/dry ice (–64 °C), chlorobenzene/dry ice (–45 °C), or carbon tetrachloride/dry ice bath (–23 °C). After temperature equilibration for 10 min, *n*-butyllithium (90 μL, 0.23 mmol) was slowly added to the vigorously stirred reaction mixture. The solution turns a deep red color. This color fades over 3 h. After 4 h, the reaction is quenched by addition of 6 mL of saturated aqueous ammonium chloride. The experiment carried out at –23 °C resulted in gelation. In the other cases, the mixture was extracted with ether (2 × 40 mL) and the organic layer was washed with water (3 × 20 mL), dried over anhydrous calcium chloride, and filtered; the volatile solvents were removed by evaporation under reduced pressure. The residue was dissolved in chloroform-*d* and was transferred to an NMR tube. The ^{13}C Invgate spectrum of this material was run under conditions (40-s delay) which permit the quantitative analysis of the ratio of polymer to dimer. The solution was then transferred to a round-bottom flask, and the chloroform-*d* was removed by evaporation under reduced pressure. The residue was dissolved in THF (1 mL) and analyzed by gel permeation chromatography (GPC). The polymer was

Table I
Anionic Dimerization and Ring-Opening Polymerization
of I

expt	[monomer], M	solvent	temp, °C	ratio of polymer/dimer	M_w/M_n
A	0.24	THF	−78	52/48	7169/5086
B	0.25	THF	−64	50/50	5614/4615
C	0.23	THF	−45	54/46	5843/3709
D	0.30	THF	−23	gel	gel
E	1.55	THF	−78	69/31	25955/17041
F	1.90	ether	−23	81/19	405136/11948

precipitated with methanol (8 mL). This process was repeated and resulted in a pure polymer sample whose molecular weight distribution was determined by GPC. GPC analyses before and after polymer purification were virtually identical (see Table I).

Monomer-Catalyzed Anionic Equilibration of Polymer. Polymer (150 mg, 1.1 mequiv; M_w/M_n = 5600/4600) was placed in a 25-mL round-bottom flask equipped with a Teflon-covered magnetic stirring bar. The flask and its contents were evacuated at 0.3 Torr for 24 h. The flask was filled with argon and sealed with a rubber septum. THF (4 mL), HMPA (0.1 mL), and monomer (20 µL, 0.13 mmol) were added via a syringe. The flask and its contents were cooled to −78 °C in a dry ice/acetone bath. n-Butyllithium (40 µL) was slowly added to the vigorously stirred reaction mixture. The reaction became dark red in color. Over 2 h, the intensity of the color faded slightly. The reaction was continued for an additional 1.5 h, at which time it was terminated at −78 °C by the dropwise addition of 2 mL of 1:1 water/methanol. All volatile solvents were removed by evaporation under reduced pressure. The residue was dissolved (3 × 0.3 mL) in chloroform-d. The solution was transferred to an NMR tube, and half the chloroform was removed under a stream of argon. A quantitative ^{13}C Invgate spectrum was run with a relaxation delay of 40 s. Integration of this spectrum shows a mixture of 39% dimer and 61% polymer.

Attempted Anionic Equilibration of Polymer. The reaction was carried out as above, except that no monomer was added. n-Butyllithium (100 µL) was added. No obvious reaction occurred. The solution viscosity did not increase, and no change in color was noted. Additional n-butyllithium (50 µL) was added. This caused the solution to completely gel within 1 min. The gel was insoluble in THF and other common organic solvents.

Results and Discussion

Anionic ring-opening polymerization of 1-silacyclopent-3-enes generally yields linear high polymers—poly-(1-sila-*cis*-pent-3-ene)s.[10-12] Anionic dimerization has only been previously observed in the case of 5-silaspiro[nona-2,7-dienes].[18,19] In this regard, the anionic polymerization of 1,1-divinyl-1-silacyclopent-3-ene is unique in that it yields both dimer and polymer. We have carried out a number of experiments in the hope of understanding the factors which affect the ratio of dimerization to polymerization and more generally the mechanism of this reaction.

The observation of only a single ^{29}Si NMR signal and one allyl and three vinyl ^{13}C NMR resonances for poly-(1,1-divinyl-1-sila-*cis*-pent-3-ene) indicates that the polymer is stereoregular within the limitation of detection by NMR spectroscopy. The cis stereochemical assignment is based on similarity of the ^{13}C NMR chemical shifts for the allyl carbon of poly(1,1-divinyl-1-sila-*cis*-pent-3-ene) which is found at 13.82 ppm and that of poly(1,1-diphenyl-1-sila-*cis*-pent-3-ene) which has been observed at 13.67 ppm.[10]

Increasing the concentration of monomer leads to an increase in the ratio of polymer to dimer and to an increase in the molecular weight of the polymer (Table I, experiments A and E).

On the other hand, varying the temperature of the reaction from −78 to −45 °C did not affect the ratio of
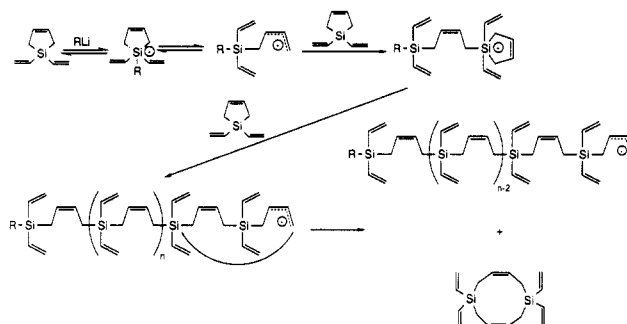
Figure 4. Proposed pathway for formation of polymer and dimer.
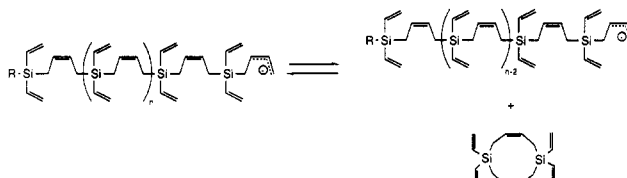
Figure 5. Equilibration of polymer and dimer.

polymer to dimer, nor did it appreciably change the molecular weight distribution of the polymer (Table I, experiments A–C).

The mechanism of anionic ring-opening polymerization of 1-silacyclopent-3-enes has been previously proposed to involve the formation of hypervalent pentacoordinate silicon species (Figure 4). Specifically, propagation occurs by attack of a *cis*-allyl anion formed by ring opening of a hypervalent siliconate anion on another molecule of 1-silacyclopent-3-ene. Propagation thus involves formation of a hypervalent siliconate intermediate. Similarly, dimer formation may result from attack of a terminal allyl anion on an adjacent silyl center of the polymer with formation of a hypervalent silicon intermediate which fragments with formation of dimer and an allyl anion. Thus, the transition states for both propagation and dimer formation may involve hypervalent siliconate species. While it is tempting to ascribe the red color observed in these reactions to siliconate intermediates, no experimental evidence supporting such an assignment exists.[20] These two processes apparently have similar energies of activation, since a change in temperature has little or no effect on the ratio of dimer to polymer. This explanation rests on an assumption that the reaction is under kinetic control.

An alternative explanation is that the polymerization is a living anionic system. Such an active polymer (D_p = n) could be in equilibrium with dimer and a polymer (D_p = n − 2) (see Figure 5). This would be analogous to the situation found in the anionic polymerization of octamethylcyclotetrasiloxane (D_4) in which poly(dimethylsiloxane) anion is in equilibrium with D_4 and other cyclics.[21-33] The lack of temperature dependence on the distribution of polymer and dimer in this system implies that the enthalpy for the process is small. This is reasonable if there is little or no ring strain associated with the 10-membered dimer.[18]

To distinguish between these two possibilities, experiments to demonstrate the existence of an equilibrium between polymer and dimer were carried out. Specifically, treatment of pure polymer with a catalytic amount of monomer, n-butyllithium, and HMPA in THF at −78 °C resulted in formation of significant amounts of dimer as well as polymer. The ratio of dimer to polymer, however, is somewhat lower than that found in the polymerization/dimerization of monomer. The reasons for this difference are not known. We believe that the function of monomer
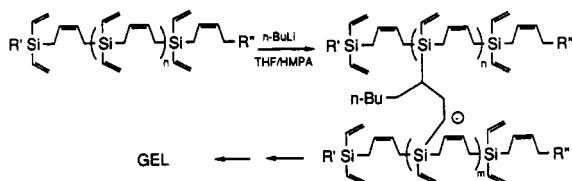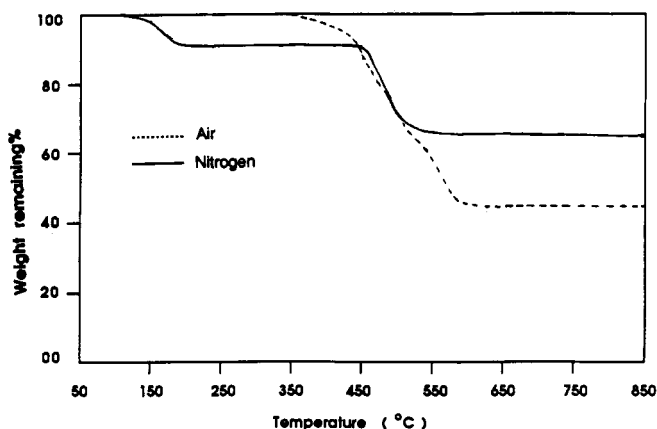
Figure 6. Possible cross-linking mechanism.

Figure 7. TGA of polymer.

Figure 8. DSC of polymer.

in this system is to convert the n-butyllithium into a hypervalent siliconate intermediate which can catalyze the equilibration.

On the other hand, when pure polymer was subjected to treatment with n-butyllithium and HMPA in THF at −78 °C, gelation occurred. Gelation on treatment of polymer with n-butyllithium and HMPA may result from addition of alkyllithium reagent to the pendant vinyl groups of the polymer. Addition of alkyllithium reagents to the carbon double bonds of vinylsilanes to yield carbanions α to silicon is well-known.[24-26] However, due to the lack of solubility of the gel, we were unable to obtain spectroscopic evidence for this by NMR.

In this regard, the anionic polymerization of 1,1-divinyl-1-silacyclopent-3-ene is rather remarkable. Apparently anionic addition to the silyl center of monomer to form a hypervalent siliconate species is faster than anion addition to the pendant carbon–carbon double bonds of the polymer. On the other hand, anion attack at the unstrained silyl centers of the polymer must be slow relative to addition to the carbon–carbon double bonds of the pendant vinyl groups.

Gelation also occurs on attempted polymerization of 1,1-divinyl-1-silacyclopent-3-ene at −23 °C in THF (Table I, experiment D). Polymerization at −23 °C in ether results in dimer and polymer (19:81) with M_w/M_n = 405 000/11 950. We believe that the high molecular weight and polydispersity in this case is the result of cross-linking (see Figure 6). Thus, at −23 °C in either THF or ether anionic addition to the pendant vinyl groups competes with anionic dimerization and ring-opening polymerization which proceeds by hypervalent siliconate intermediates. Low temperature is critical to the success of the polymerization.

The thermal stability of poly(1,1-divinyl-1-sila-cis-pent-3-ene) was determined by thermogravimetric analysis (see Figure 7). The polymer is stable to 100 °C in nitrogen. Between 100 and 200 °C a 9% weight loss occurs. No further weight loss occurs until 450 °C. Between 450 and 550 °C a rapid 25% weight loss occurs. Between 550 and 650 °C a further loss of 3% occurs. After 650 °C, no further weight loss is seen. A black residue amounting to 62% of the original sample weight is formed. Thermal decom-

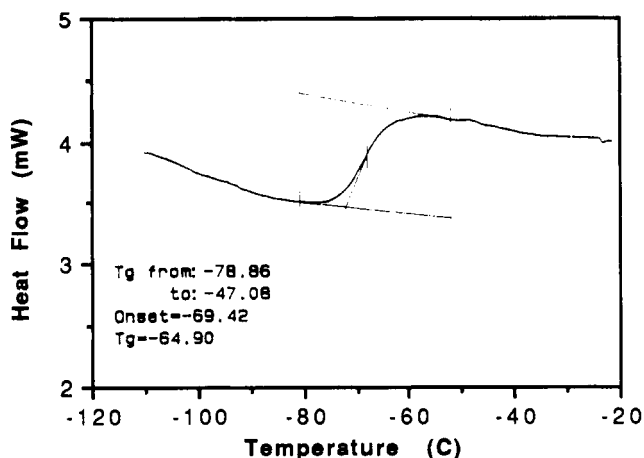position in an air atmosphere is different. The polymer loses no weight until 350 °C. Between 350 and 580 °C a 56% weight loss occurs. After 600 °C, no further weight loss is observed. A white residue of silicon dioxide amounting to 43% of the initial sample weight is found. The theoretical yield of silicon dioxide, 44%, is in remarkable agreement.

The formation of a high char yield is unexpected. Thus, in a nitrogen atmosphere both poly(1,1-dimethyl-1-sila-cis-pent-3-ene) and poly(1-methyl-1-phenyl-1-sila-cis-pent-3-ene) undergo catastrophic decomposition. No residue is left. Linear polymers give high chars when a mechanism to cross-link them to a network structure exists.[27,28] The mechanism of such a cross-linking process in this case is not obvious at present. Studies to determine the mechanism for thermal cross-linking in this case are in progress.

The glass transition temperature for the polymer, M_w/M_n = 19 700/9400, T_g = −65 °C, is almost identical to that for poly(1,1-dimethyl-1-sila-cis-pent-3-ene), T_g = −64 °C[12] (see Figure 8).

In summary, anionic ring opening of 1,1-divinyl-1-silacyclopent-3-ene at low temperature leads to a mixture of polymer and dimer in high yield. The ratio of polymer to dimer is insensitive to temperature (−78 to −45 °C) but dependent upon monomer concentration. Treatment of polymer with catalytic initiator results in gelation. Alternatively, catalytic initiator and monomer lead to equilibration of polymer to a mixture of polymer and dimer. These observations have been accounted for in terms of a mechanism involving anionic hypervalent silicon species.

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Registry No. 1,1-Divinyl-1-silacyclopent-3-ene (homopolymer), 140658-43-1; 1,1,6,6-tetravinyl-1,6-disila-3,8-cyclodecadiene, 140658-41-9; 1,1-divinyl-1-silacyclopent-3-ene, 140658-42-0; vinyl magnesium bromide, 1826-67-1; 1,1-dichloro-1-silacyclopent-3-ene, 872-46-8.