85 (11.63), 83 (16.96), 71 (8.36), 69 (10.31), 67 (8.13), 59 (40.98). High-resolution MS. Calcd for $C_{11}H_{22}Si$ ($M^{\bullet +}$): *m/e* 182.1491. Found: *m/e* 182.1494.

(2,3-Dimethylbut-2-enyl)-*n*-butyldimethylsilane (VIII). ^1H NMR: δ −0.053 (s, 6 H), 0.46 (t, 2 H, J = 7.1 Hz), 0.86 (t, 3 H, J = 7.0 Hz), 1.27 (m, 4 H), 1.49 (s, 2 H), 1.56 (s, 3 H), 1.59 (s, 3 H), 1.61 (s, 3 H). GC/MS (relative intensity): *m/e* 200 (0.36), 199 (1.31), 198 (7.06; $M^{\bullet +}$), 183 (0.17; $M - 15^+$), 141 (1.01; $M - 57^+$), 125 (1.38), 117 (0.95), 116 (2.98), 115 (25.40; $M - 83^+$), 99 (4.51), 75 (1.74), 74 (4.10), 73 (48.17), 61 (3.52), 60 (7.53), 59 (100.00). High-resolution MS. Calcd for $C_{12}H_{26}Si$ ($M^{\bullet +}$): *m/e* 198.1804. Found: *m/e* 198.1815.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research (Grant 89-0007) and the Office of Naval Research.

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Registry No. I (homopolymer), 34056-65-0; I, 3528-14-1; (*Z*)-IV, 16054-36-7; (*E*)-IV, 16109-36-7; VI, 16109-39-0; VII, 125541-30-2; VIII, 125541-31-3.

Anionic Polymerization of 1-Methyl-1-silacyclopent-3-ene. Characterization of Poly(1-methyl-1-sila-*cis*-pent-3-ene) by ^1H, ^{13}C, and ^{29}Si NMR Spectroscopy and Mechanism of Polymerization

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Received August 8, 1989; Revised Manuscript Received October 11, 1989

ABSTRACT: 1-Methyl-1-silacyclopent-3-ene (I) undergoes anionic ring opening polymerization on treatment with *n*-butyllithium and HMPA as cocatalysts in THF to yield poly(1-methyl-1-sila-*cis*-pent-3-ene) (II). II has been characterized by IR and ^1H, ^{13}C, and ^{29}Si NMR spectroscopy as well as by GPC, TGA, and elemental analysis. Due to the low molecular weight of II, ^1H, ^{13}C, and ^{29}Si NMR spectroscopy affords detailed information that permits characterization of microstructures involved in initiation and termination. End groups have been identified as substituted 1-methyl-1-silacyclopent-3-enes. The mechanism of this polymerization is discussed.

While poly(methylhydrosiloxanes) are well-known,[1] other polymers that possess reactive Si–H bonds such as carbosilane polymers are less common. The proposal by Yajima that poly[(methylsilylene)methylene] is an intermediate in the pyrolytic conversion of poly(dimethylsilane) fibers to silicon carbide fibers has stimulated considerable interest in such systems.[2,3] We should like to report that 1-methyl-1-silacyclopent-3-ene (I) undergoes stereospecific anionic ring opening polymerization on treatment with catalytic amounts of *n*-butyllithium and hexamethylphosphoramide (HMPA) in THF at low temperature to give poly(1-methyl-1-sila-*cis*-pent-3-ene) (II). While 1,1-dimethyl-1-silacyclopent-3-ene (III) undergoes polymerization under similar conditions to yield poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene) (IV),[4] formation of II is unexpected since I possesses a reactive Si–H bond. This might be expected to interfere with polymerization since it is well-known that hydride can function as a leaving group in nucleophilic substitution reactions at silyl centers.[5,6] Thus reaction of I with *n*-butyllithium might be anticipated to yield 1-*n*-butyl-1-methyl-1-silacyclopent-3-ene. This potential problem cannot be avoided if the polymerizations of I and III occur by similar mechanistic pathways, since the polymerization of III involves coordination of a carbanion to the silyl center of III to form anionic pentacoordinate silicon intermediates. Anionic polymerization of 4-(dimethylsilyl)styrene is one of the few previous examples of successful anionic polymerization of a monomer containing a Si–H group.[7] In this latter case, nucleophilic attack at silicon is not an essential step in the polymerization mechanism.

The microstructure of II has been determined by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy. The following resonances have been assigned to 1-methyl-1-sila-*cis*-pent-3-ene (V) units: ^1H NMR δ 0.037–0.076 (m, 3 H), 1.53–1.59 (m, 4 H), 3.78 (m, 1 H), 5.31–5.35 (m, 2 H); ^{13}C NMR δ −6.36, 13.91, 123.33; ^{29}Si NMR δ −12.70. These assignments are consistent with the ^1H, ^{13}C, and ^{29}Si NMR spectra of I, III, and IV (see Table I). An upfield shift is observed when one compares the ^{29}Si NMR absorption of I at −3.19 ppm to that of II at −12.70 ppm. A similar upfield shift is observed when one examines the

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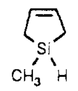
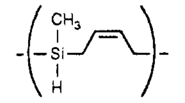
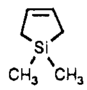
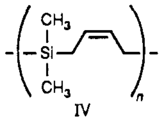
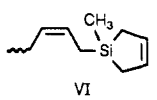
Table I
^{1}H, ^{13}C, and ^{29}Si NMR Chemical Shifts of I, II, III, IV, and VI

	 I	 II	 III	 IV	 VI
^{1}H vinyl	5.78	5.35	5.73	5.29	5.83
^{13}C vinyl	130.83	123.33	130.74	123.22	130.91
^{13}C allyl	15.36	13.91	17.80	16.47	16.46, 15.85
^{13}C methyl	-5.01	-6.36	-2.30	-3.41	-3.76
^{29}Si	-3.19	-12.70	16.5	2.17	17.17

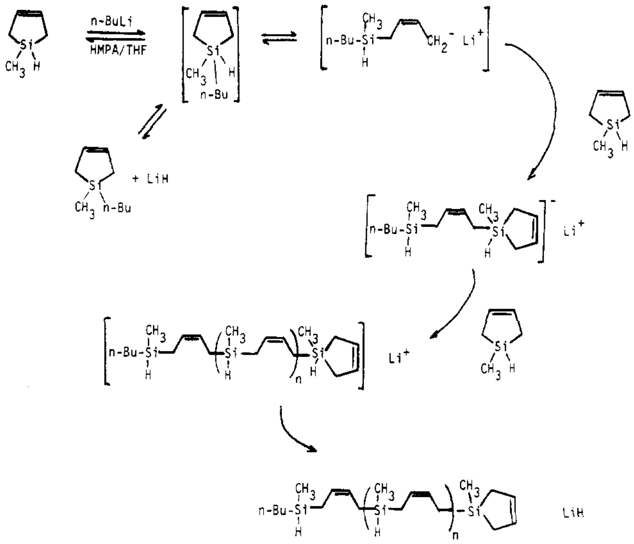


Figure 1. Polymerization of I by n-butyllithium.

^{29}Si NMR of III and IV.

We believe that this process is initiated by nucleophilic addition of n-butyllithium to the silyl center of I to form a cyclic pentacoordinate anionic silicon intermediate. Ring opening of this intermediate leads to a cis allylic anion that reacts rapidly with another molecule of I. This chain growth process leads to a new cyclic pentacoordinate anionic silicon species. This reaction must occur faster than conversion of the cis allylic anion into a trans allylic anion by rotation about the partial carbon–carbon double bond to account for the cis stereochemistry observed in II (see Figure 1).

Of particular interest, the low molecular weight of II, M_w/M_n = 1900/1600 (-78 °C), permits end group analysis. By comparison, we have been unable to determine the nature of the polymer end groups in IV due to its high molecular weight. In addition to the resonances discussed above, a number of signals are observed that are consistent with the presence of 1-methyl-1-silacyclopent-3-ene rings (VI) in II. Specifically, a resonance is observed at 5.83 ppm in the ^{1}H NMR of II. This can be assigned to the vinyl hydrogens of VI. For comparison, the vinyl hydrogens of I give rise to a signal at 5.78 ppm while the vinyl hydrogens of III produce a resonance at 5.73 ppm. Likewise, a ^{13}C NMR signal is observed at 130.91 ppm. This chemical shift is similar to those of the vinyl carbon resonances of I and III which are respectively at 130.83 and 130.74 ppm. Finally a silicon resonance is observed at 17.17 ppm. This is consistent with that expected for VI since the ^{29}Si NMR signal for III is at 16.50 ppm. The presence of VI groups in II is most easily explained if these are end groups. The intensities of the vinyl ^{1}H NMR signals assigned to V units compared to those due to VI groups is 18:1. Likewise, the integration of the ^{29}Si NMR signal at -12.70 compared to that at 17.17 ppm is 18:1. This is consistent with the number of end groups expected in an oligomer of this molecular weight as determined by gel permeation chromatography (GPC).

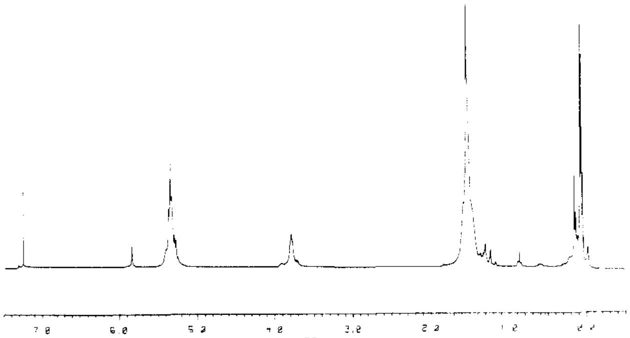


Figure 2. ^{1}H NMR spectrum of II.

The formation VI end groups can be accounted for by loss of a hydride from chain-propagating anionic pentacoordinate silicon intermediates (Figure 1). If this novel termination mechanism is operating in the polymerization of both I and III, the greater ease of displacement of a hydride from a silyl center compared to that of a methyl anion may account for the lower molecular weight of II (M_w/M_n = 1900/1600) compared to that of IV (M_w/M_n = 158 000/59 000).[4] It should be noted that a similar ratio of initiator to monomer was utilized in both the polymerizations of I and III. Termination by loss of hydride is analogous to the previously observed exchange of alkyl groups bonded to silicon, which have been proposed to proceed via anionic pentacoordinate silicon intermediates.[8,9]

Additional ^{1}H, ^{13}C, and ^{29}Si NMR signals are observed that may be assigned to the 1-n-butyl-1-methyl-1-sila-*cis*-pent-3-ene (VII) group formed in the initiation step. Among these is a small ^{29}Si NMR signal at -13.47 ppm as well as ^{13}C NMR signals at -6.28, 12.41, 13.09, 26.14, and 26.70 ppm. These resonances were assigned on the basis of comparison with the ^{13}C NMR signal of allyl-n-butyldimethylsilane. It should be noted that the intensities of the ^{29}Si NMR signals at -13.47 and 17.17 ppm associated respectively with initiation and termination are almost equal.

Finally signals are observed that may result from 1-n-butyl-1-methyl-1-sila-*cis*-pent-3-ene units. These may be formed either by copolymerization of small amounts of 1-n-butyl-1-methyl-1-silacyclopent-3-ene, formed by nucleophilic displacement of a hydride from the silyl center of I by n-butyllithium, or by nucleophilic displacement of a hydride from the silyl centers of II. Among these are ^{29}Si NMR signals at 2.92 and 2.57 ppm. Such ^{29}Si NMR signals are associated with silyl centers substituted with four alkyl groups (Figures 2–4 for ^{1}H, ^{13}C, and ^{29}Si NMR spectra of II).

The thermal stability of II was determined by thermogravimetric analysis (TGA). II is stable to 150 °C in a

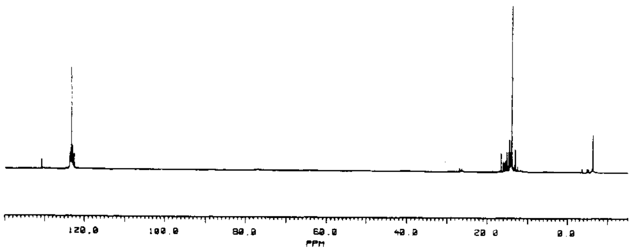


Figure 3. ^{13}C NMR spectrum of II.

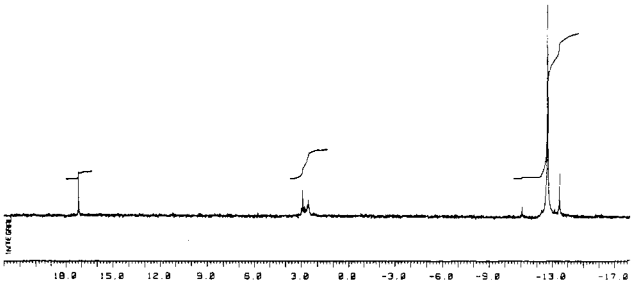


Figure 4. ^{29}Si NMR spectrum of II.

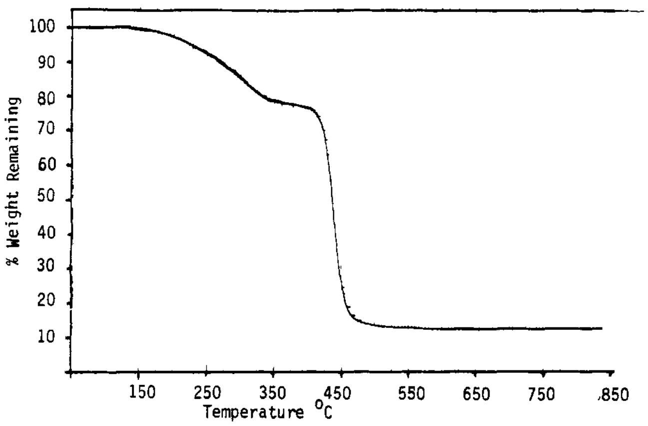


Figure 5. TGA of II.

nitrogen atmosphere. This stability is surprising considering the low molecular weight of II. Weight loss occurs in two stages. Between 150 and 350 °C samples of II lose 22% of their initial weight. Between 350 and 400 °C no further weight loss is observed. Between 400 and 475 °C rapid weight loss occurs. A black residue amounting to 12% of the initial sample weight remains and is stable to at least 850 °C (Figure 5).

Experimental Section

^{1}H, ^{13}C, and ^{29}Si NMR spectra were obtained on an IBM Brucker WP-270-SY spectrometer operating in the FT mode. ^{13}C NMR spectra were run with broad-band proton decoupling. Solutions (10–15%) in chloroform-*d* were used to obtain ^{13}C and ^{29}Si NMR spectra, whereas 5% solutions were used for ^{1}H NMR spectra. Chloroform was utilized as an internal standard for ^{1}H and ^{13}C NMR spectra. All chemical shifts reported were externally referenced to TMS. A heteronuclear gated decoupling pulse sequence with a pulse decay of 20 s (NONOE) was used to obtain ^{29}Si NMR spectra.[10]

GPC analysis of the molecular weight distribution of the polymer was 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 Waters 7.8 mm × 30 cm Ultrastyragel linear gel column packed with less than 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 0.6 mL/min. The retention times were calibrated against known monodisperse polystyrene standards: M_p 170 000, 110 000, 20 400, 4800, and 1350 whose M_w/M_n are less than 1.09.

TGA of II was carried out on a Perkin-Elmer TGS-2 instrument at a nitrogen or Argon flow rate of 80 cm^3/min. The temperature program for the analysis was 50 °C for 10 min followed by an increase of 4 °C/min to 850 °C.

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

All reactions were conducted in flame-dried glassware under an atmosphere of purified nitrogen. Both THF and ether were purified by distillation from sodium benzophenone ketyl immediately prior to use. HMPA was distilled from calcium hydride and was stored over 4-Å molecular sieves prior to use.

1-Methyl-1-silacyclopent-3-ene was prepared by the reaction of methyldichlorosilane, 1,3-butadiene, and magnesium in ether at room temperature following procedures previously used to prepare III.[11] I has previously been prepared by the reaction of methylsilylene with 1,3-butadiene.[12,13] I was purified by fractional distillation through a 20-cm vacuum-jacketed Vigreux column, bp 89–90 °C. It had the following spectral properties. ^{1}H NMR: δ 0.116 (d, 3 H, J = 3.4 Hz), 1.16 (d, 1 H, J = 17.8 Hz), 1.44 (d, 1 H, J = 17.8 Hz), 4.145 (q, 1 H, J = 3.4 Hz), 5.78 (s, 2 H). ^{13}C NMR: δ -5.01, 15.36, 130.83. These ^{13}C NMR data are in agreement with literature values.[10] ^{29}Si NMR: δ -3.19.

Polymerization of 1-Methyl-1-silacyclopent-3-ene. In a 75-mL Schlenk flask equipped with a Teflon-covered magnetic stirring bar was placed I (1.2 g, 12 mmol), THF (30 mL), and HMPA (20 μL). The flask and its contents were cooled to −78 °C. *n*-Butyllithium (0.5 mL, 1.2 mmol) was slowly introduced via a syringe. The reaction mixture immediately became yellow. The mixture was stirred at −78 °C for 2 h. Saturated aqueous ammonium chloride (20 mL) was added. The mixture was extracted with three 50-mL aliquots of ether. The combined organic layer was washed with water, dried over activated 4-Å molecular sieves, and filtered, and the solvents were removed by evaporation under reduced pressure. The product polymer was purified twice by precipitation from methanol. In this way, 0.8 g (75% yield) of the polymer was obtained. IR: ν 3000, 2940, 2915, 2860, 2100 (s), 1645, 1400, 1370, 1250, 1150, 1020, 870, 830 cm^{-1}. Anal. Calcd: C, 61.14; H, 10.26. Found: C, 60.07; H, 10.02.

Allyl-*n*-butyldimethylsilane was prepared by addition of *n*-butyllithium to allyldimethylchlorosilane (Aldrich) in THF. It had properties in agreement with literature values.[14] ^{13}C NMR: δ -3.77, 13.70, 14.63, 23.36, 26.07, 26.55, 112.57, 135.16.

Acknowledgment. This work was supported by the Office of Naval Research.

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Registry No. I, 55544-25-7; I (homopolymer), 125440-21-3; I (SRU), 125440-20-2; HMPA, 680-31-9; $CH_2{=}CHCH{=}CH_2$, 106-99-0; methyldichlorosilane, 75-54-7; *n*-butyllithium, 109-72-8.