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Anionic Ring-Opening Polymerization of 1,1,3-Trimethyl-1-silacyclopent-3-ene. Effect of Temperature on Poly(1,1,3-trimethyl-1-sila-*cis*-pent-3-ene) Microstructure

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ABSTRACT: 1,1,3-Trimethyl-1-silacyclopent-3-ene (I) undergoes anionic ring-opening polymerization on treatment with *n*-butyllithium and HMPA cocatalysts in THF to yield poly(1,1,3-trimethyl-1-sila-*cis*-pent-3-ene) (II). Comparison of ^{1}H, ^{13}C, and ^{29}Si NMR spectra of II with those of model compounds, (*Z*)- and (*E*)-2-methyl-1,4-bis(trimethylsilyl)-2-butene (IV), permits assignment of polymer II microstructures. When the polymerization of I is conducted at −42 °C, the NMR spectra of II are consistent with a polymer in which *cis*-1,4-isoprene units are joined to dimethylsilylene units. A 1:2:1 distribution of head-to-head, head-to-tail, and tail-to-tail arrangements of adjacent *cis*-1,4-isoprene units is found. On the other hand, when the polymerization is conducted at −78 °C, the microstructure of II is predominantly head-to-tail. The mechanism of polymerization, which may account for the observed regioselectivity, is discussed.

We have previously reported that anionic ring-opening polymerization of 1,1,3-trimethyl-1-silacyclopent-3-ene (I) catalyzed by *n*-butyllithium/hexamethylphosphoramide (HMPA) or methyllithium/tetramethylethylenediamine (TMEDA) in THF solvent at −40 °C leads to poly(1,1,3-trimethyl-1-sila-*cis*-pent-3-ene) (II).[1] While the microstructure of the closely related system, poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene) (III) was assigned on the basis of comparison of ^{13}C NMR chemical shifts with model compouunds,[2] the assignment of the microstructure of II was made on the basis of less firm evidence. Several experiments have led us to more thoroughly study this system. Chief among these was the observation that when we conducted the polymerization at different temperatures, the intensity ratio of the ^{1}H and ^{13}C NMR signals assigned to the methyl groups bonded to silicon changed (Figures 1 and 2).

To clarify this situation, we have prepared both (*Z*)- and (*E*)-2-methyl-1,4-bis(trimethylsilyl)-2-butene [(*Z*)-IV and (*E*)-IV]. While these model compounds are known,[3] neither high-field ^{1}H, ^{13}C, nor ^{29}Si NMR spectra of them have been reported. The assignment of ^{13}C NMR chemical shifts was done on the basis of ^{1}H-coupled ^{13}C NMR spectra. The significant difference in the ^{13}C chemical shift of the methyl and the proximate methylene carbons bonded to a cis carbon–carbon double bond compared to those bonded to a trans carbon–carbon double bond should be noted (Figures 3–5).

Of great significance, we have found that when I is treated with *n*-butyllithium/HMPA cocatalysts in THF

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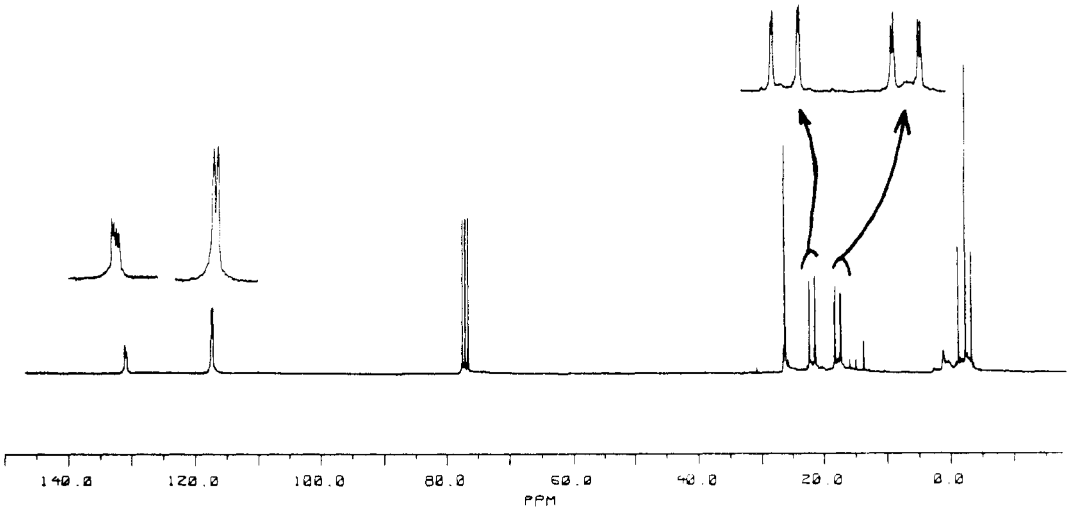

Figure 1. ^{13}C NMR spectrum of II (−42 °C).

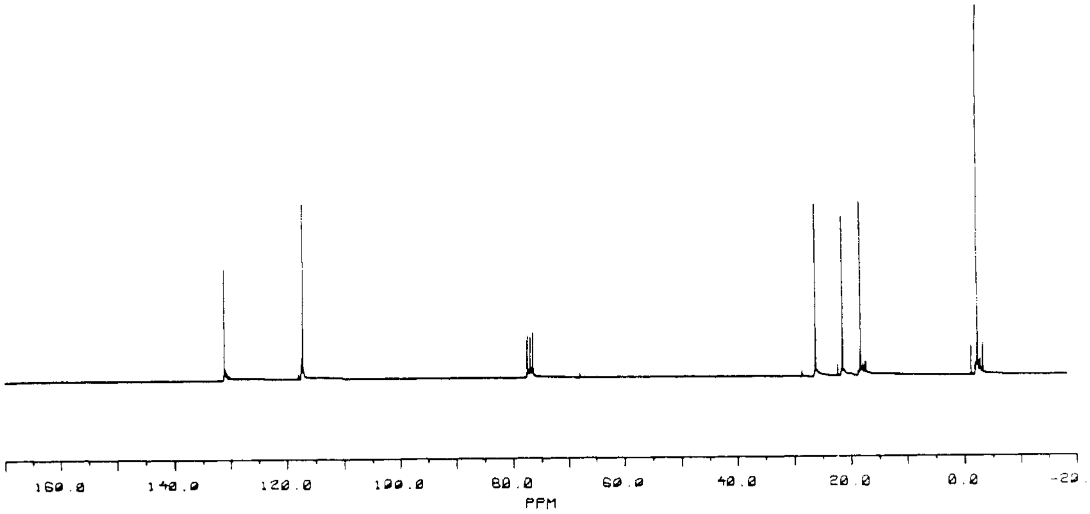

Figure 2. ^{13}C NMR spectrum of II (−78 °C).

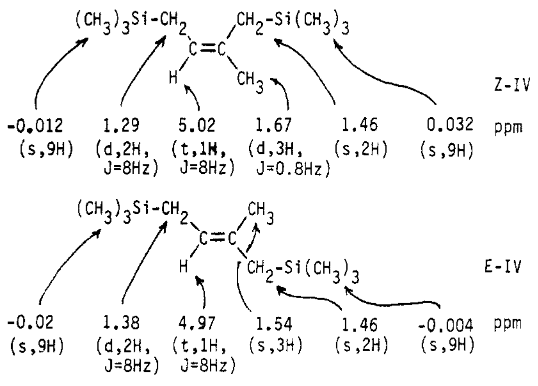

Figure 3. Assignment of ^{1}H NMR chemical shifts of (*Z*)- and (*E*)-IV.

at −78 °C for 3 h, regioselective polymerization occurs. Thus the NMR spectra of II produced in this way is consistent with a polymer microstructure in which 1,4-isoprene units are preferentially joined to dimethylsilane groups in a head-to-tail manner. The methyl groups bonded to silicon give rise to three resonances in both the ^{1}H and ^{13}C NMR spectra (2:27:2). This is expected if a single microenvironment is dominant. Comparison of the peak heights of these ^{13}C NMR signals indicates that the head-to-tail microstructure is favored over the head-to-head plus tail-to-tail microstructures by approximately 7:1. Further, the ^{1}H and ^{13}C NMR chemical shifts of the most intense resonances assigned to II are virtually identical with those of (*Z*)-IV (Figure 6).

This information has permitted us to fully analyze the ^{1}H, ^{13}C, and ^{29}Si NMR spectra of II produced at −42 °C. The methyl groups bonded to silicon give rise to three ^{1}H and three ^{13}C resonances. Both of these sets have a 1:2:1 intensity ratio. These may be interpreted in terms of diad microstructures in which 1,4-isoprene units are bonded to dimethylsilyl groups in head-to-head, head-to-tail, and tail-to-tail arrangements (1:2:1) (Figure 7). On the other hand, the ^{1}H and ^{13}C NMR resonances due to the 1,4-isoprene units can be accounted for by triad analysis. This leads to a prediction of eight unique methylene signals, as well as eight distinct vinyl and four methyl resonances, in the ^{13}C NMR. These have in fact been observed (Figure 8). Of particular importance, no ^{13}C NMR signal is observed near 30 ppm. A signal in this region would be expected for one of the methylene carbons if *trans*-1,4-isoprene units were present. Apparently, ring-opening polymerization of I occurs in a stereoregular cis manner at both −42 and −78 °C.

We have previously proposed a mechanism for the anionic ring-opening polymerization 1,1-dimethyl-1-silacyclopent-3-ene (V) that involves hypervalent pentacoordinate siliconate intermediates. Chain growth occurs by ring opening of these anionic species to yield an allylic anion, which reacts rapidly with another molecule of V. To account for the cis stereospecificity observed, this reac-

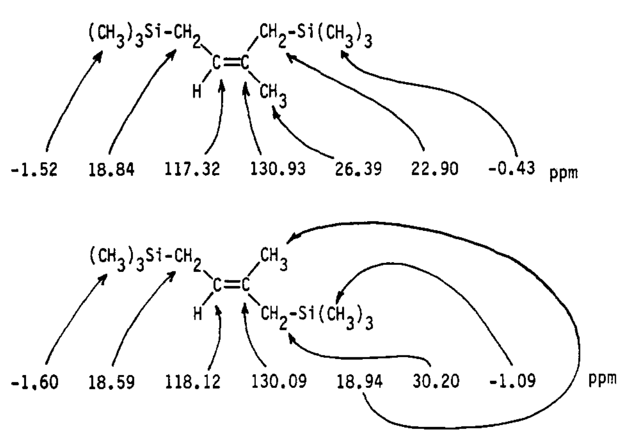

Figure 4. Assignment of ^{13}C NMR chemical shifts of (*Z*)- and (*E*)-IV.

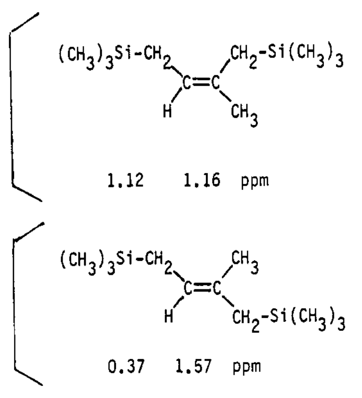

Figure 5. ^{29}Si NMR chemical shifts of (*Z*)- and (*E*)-IV.

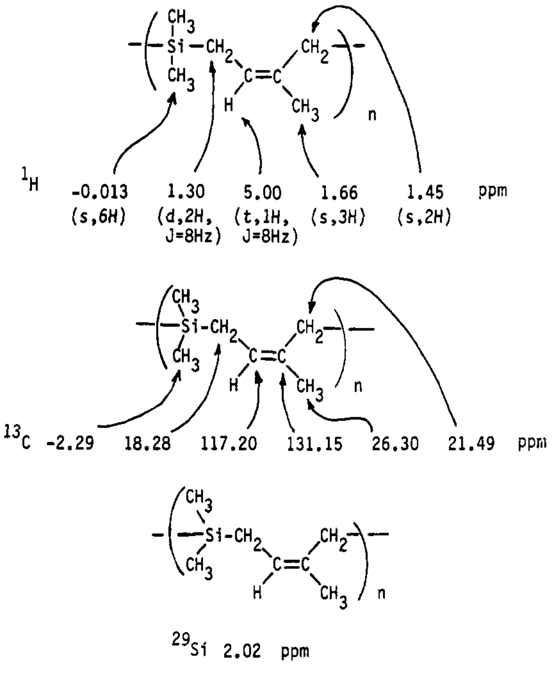

Figure 6. Assignment of ^{1}H, ^{13}C, and ^{29}Si NMR chemical shifts of II (−78 °C).

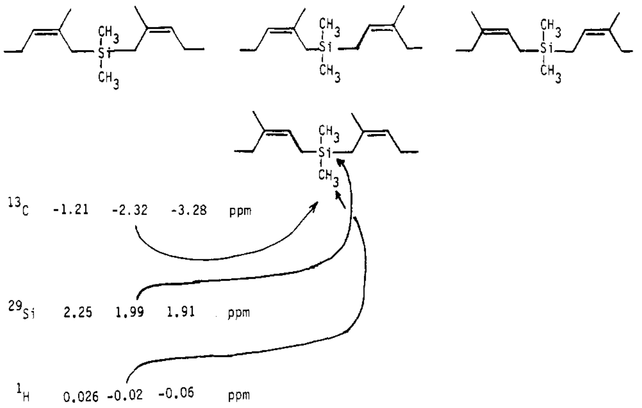

Figure 7. Diad microstructures and ^{1}H, ^{13}C, and ^{29}Si NMR chemical shifts of dimethylsilylene units of II (−42 °C).

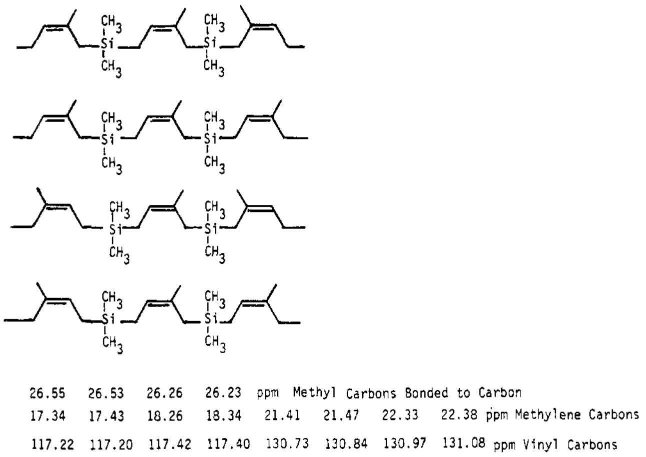

Figure 8. Triad microstructures and ^{13}C NMR chemical shifts of *cis*-1,4-isoprene units of II (−42 °C).

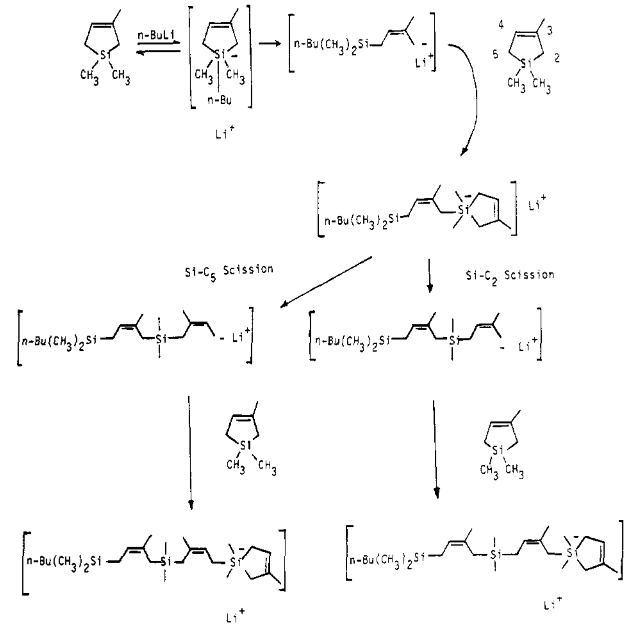

Figure 9. Mechanism of anionic ring-opening polymerization of II.

tion must occur faster than isomerization of the *cis*-allyl anion into a *trans*-allyl anion by rotation about the partial carbon–carbon double bond. In the case of anionic polymerization of I, a further constraint must apply at −78 °C. Specifically, the pentacoordinate siliconate intermediates must undergo preferential ring opening by scission of only one of the two distinct allylic silicon–carbon single bonds (Si–C_2) to yield a unique allylic anion. This is necessary to account for the regioselective formation of a polymer with predominant microstructure in which adjacent isoprene units are all in a head-to-tail relationship. If, on the other hand, scission of both allylic Si–C_2 and Si–C_5 bonds occurs, a microstructure with head-to-head, head-to-tail, and tail-to-tail arrangements of adjacent isoprene units will be observed (Figure 9).

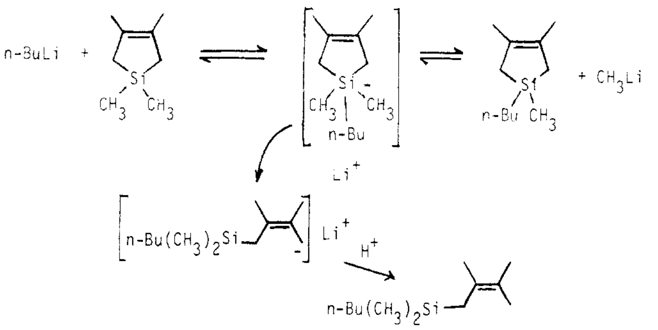

Figure 10. Reaction of VI with *n*-butyllithium.

This selectivity may result from the fact that scission of the Si–C_2 bond results in an allylic anion in which the negative charge is delocalized by resonance on both primary and secondary carbon atoms, while cleavage of the Si–C_5 bond results in an allylic anion in which the negative charge is delocalized on both primary and tertiary carbon atoms. It is well-known that tertiary carbanions are less stable than secondary, which in turn are less stable than primary.[4] We conclude that anionic polymerization of I at −78 °C occurs predominantly by ring opening of pentacoordinate siliconate intermediates to yield the more stable allylic anion. Apparently, the ring opening of the intermediates involved in the polymerization of I is much less selective at −42 °C. This would result in a polymer that would have microstructures in which adjacent isoprene units would have a statistical distribution of head-to-head, head-to-tail, and tail-to-tail arrangements.

An additional anomalous observation may also be explained by our proposal. Specifically, we have found that 1,1,3,4-tetramethyl-1-silacyclopent-3-ene (VI) does not undergo anionic polymerization on treatment with *n*-butyllithium/HMPA cocatalysts in THF. Rather, 1-*n*-butyl-1,3,4-trimethyl-1-silacyclopent-3-ene (VII) and (2,3-dimethylbut-2-enyl)-*n*-butyldimethylsilane (VIII) as well as low molecular weight oligomers of VI have been isolated (Figure 10). This is consistent with the view that ring opening to an allylic anion in which the charge is delocalized on both primary and tertiary carbon atoms is not favored. Formation of VII may be accounted for if the initial nucleophilic addition of *n*-butyllithium to the silyl center of VI is reversible. Similarly, previous workers have found that treatment of 1,1-dimethyl-1-silacyclopentane with methyl-d_3-lithium results in exchange of methyl groups bonded to the silyl center for deuterium-labeled ones[5] and that the methyl groups of 1,1,3,4-tetramethyl-1-silacyclopentadiene undergo exchange on treatment with other alkyllithium reagents.[6]

Experimental Section

^{1}H, ^{13}C and ^{29}Si NMR spectra were recorded on an IBM Brucker WP-270-SY spectrometer operating in the Fourier transform mode. ^{13}C NMR spectra were run with broad-band proton decoupling. Solutions (5–10%) in chloroform-*d* were used to obtain these spectra. Chloroform was used as an internal standard for ^{1}H and ^{13}C NMR. All chemical shifts reported were externally referenced to TMS. A DEPT pulse sequence was used to obtain ^{29}Si NMR spectra. This was effective since all the silicon atoms have at least two methyl groups bonded to them.[7] Identical ^{29}Si NMR spectra could be obtained by use of heteronuclear gated decoupling pulse sequence with a pulse delay of 30 s (NONOE).[8] IR spectra were recorded on a Perkin-Elmer PE-281 spectrometer. Spectra were taken on neat films on NaCl plates. Low-resolution mass spectra were recorded 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, CA, on a VG-7070E mass spectrometer. Exact masses were determined by peak matching against known masses of perfluorokerosene.

GPC analysis of the molecular weight distribution of polymers was performed on a Waters system comprised of a U6K injector, 510 HPLC solvent delivery system, R401 refractive index detector, and a Model 820 Control System. A Waters 7.8 mm × 30 cm Ultrastyragel 10-μm particle size mixed pore size cross-linked polystyrene gel column maintained at 20 °C was used for the analysis. The retention times were calibrated against known monodisperse polystyrene standards: M_p 1 850 000, 170 900, 110 000, 20 400, and 1350 whose M_w/M_n are less than 1.09.

Volatile products were purified by preparative GLPC on a GOW-MAC 500 GC. A 1/4 in. × 10 ft stainless steel column packed with 10% SE-30 on Chromosorb W NAW 60/80 mesh was employed. The column was deactivated immediately prior to use by silation with hexamethyldisilazane.

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.

All reactions were conducted under an atmosphere of prepurified nitrogen.

(*E*)-2-Methyl-1,4-bis(trimethylsilyl)-2-butene [(*E*)-IV] was prepared following literature procedures by reaction of isoprene, trimethylchlorosilane, and lithium in THF.[3] Final purification was by preparative GLPC.

(*Z*)-2-Methyl-1,4-bis(trimethylsilyl)-2-butene [(*Z*)-IV] was prepared by reaction of isoprene, trimethylchlorosilane, and sodium in THF.[3] Final purification was by preparative GLPC.

1,1,3-Trimethyl-1-silacyclopent-3-ene (I) was prepared as previously reported.[1]

Poly(1,1,3-trimethyl-1-sila-*cis*-pent-3-ene) (II) was prepared as previously reported.[1] M_w/M_n = 52 300/29 870 when the polymerization was carried out at −78 °C.

1,1,3,4-Tetramethyl-1-silacyclopent-3-ene (VI) was prepared by the reaction of dimethyldichlorosilane with 2,3-dimethyl-1,3-butadiene (Aldrich) and magnesium in THF/HMPA. ^{13}C NMR: δ −1.89, 19.22, 25.67, 130.56. ^{29}Si NMR: δ 9.88. ^{1}H, IR and GCMS data was in complete agreement with literature values.[9]

Reaction of VI with *n*-Butyllithium. In a flame-dried 50-mL round-bottom flask equipped with a Teflon-covered magnetic stirring bar was placed VI (1.7 g, 12.1 mmol), THF (15 mL), and 5 drops of HMPA. The flask was sealed with a rubber septum and was cooled to either −42 °C in a dry ice/diethyl ketone bath or −78 °C in a dry ice/acetone bath. To the well-stirred reaction mixture was slowly added *n*-butyllithium (1.5 mL, 2.4 mmol) via a syringe. The reaction was allowed to stir for 3 h. The reaction was then quenched by addition of saturated aqueous ammonium chloride. Ether was added, and the solution was extracted with water, dried over anhydrous magnesium sulafte, and filtered, and the volatile solvents were removed by evaporation under reduced pressure. The residue was taken up in THF. Addition of methanol resulted in no precipitation. The solvents were removed by evaporation, and the residue was subjected to bulb-to-bulb distillation under high vacuum. The volatile mixture was analyzed by preparative GLPC. In a reaction conducted at −78 °C, the following products were obtained: recovered starting material, VI (0.92 g, 54%), VII (0.31 g, 14%), and VIII (42 mg, 1.8%). The nonvolatile residue (84 mg) was analyzed by GPC; M_w/M_n = 524/372. This data is consistent with low oligomers of VI.

1-*n*-Butyl-1,3,4-tri-1-silacyclopent-3-ene (VII). ^{1}H NMR: δ 0.079 (s, 3 H), 0.62 (t, 2 H, *J* = 5.4 Hz), 0.87 (t, 3 H, *J* = 6.6 Hz), 1.30 (s, 4 H), 1.19–1.37 (m, 4 H), 1.67 (s, 6 H). ^{13}C NMR: δ −3.56, 13.69, 14.55, 19.18, 24.41, 26.28, 26.43, 130.65. ^{29}Si NMR: δ 11.52. IR: ν 2960, 2920, 2880, 1600 (w), 1460, 1450, 1400, 1380, 1250, 1180, 880, 835, 780 cm^{-1}. GC/MS (relative intensity): *m/e* 184 (1.44), 183 (4.90), 182 (28.82; $M^{\bullet+}$), 167 (2.34; M − 15^+), 140 (2.49), 127 (6.46), 126 (20.84), 125 (100.00; M − 57^+), 124 (5.72), 123 (18.12), 113 (1.25), 112 (3.93), 111 (30.56), 110 (3.19), 109 (13.85), 99 (3.12), 98 (3.19), 97 (15.75), 96 (1.79), 95 (9.03), 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). ^{1}H 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.

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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 ^{1}H, ^{13}C, and ^{29}Si NMR Spectroscopy and Mechanism of Polymerization

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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 ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy as well as by GPC, TGA, and elemental analysis. Due to the low molecular weight of II, ^{1}H, ^{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 ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy. The following resonances have been assigned to 1-methyl-1-sila-*cis*-pent-3-ene (V) units: ^{1}H 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 ^{1}H, ^{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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