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Anionic ring opening polymerization of 1-silacyclopent-3-ene

Characterization of poly(1-sila-*cis*-pent-3-ene) by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy

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SUMMARY

1-Silacyclopent-3-ene (I) undergoes anionic ring opening polymerization catalyzed by methyllithium/HMPA to yield poly(1-sila-*cis*-pent-3-ene) (II). II was characterized by ^1H, ^{13}C, and ^{29}Si NMR, GPC, TGA and elemental analysis. The low molecular weight of II permits end group analysis. Pyrolysis of II gives high char yields. These have been characterized by EDS.

INTRODUCTION

While polymethylhydrosiloxanes are well known,[1] other polymers which possess reactive Si-H bonds such as polycarbosilanes are less common. The proposal that poly[(methylsilylene)methylene] $[-CH_3SiH-CH_2-]_n$ is an intermediate in the conversion of poly(dimethylsilane) $[-(CH_3)_2Si-]_n$ fibers to silicon carbide fibers has increased interest in these systems.[2,3]

EXPERIMENTAL

^1H and ^{13}C NMR spectra were obtained on a Brucker AM-360 spectrometer while ^{29}Si NMR spectra were run on an IBM Brucker WP-270-SY spectrometer. ^{13}C NMR spectra were run with broad band proton decoupling. A heteronuclear gated decoupling pulse sequence (NONOE) with a delay of 20 sec was used to obtain ^{29}Si NMR spectra.[4] GPC analysis was performed with a Waters system comprised of a U6K injector, 510 HPLC solvent delivery system, R401 differential refractive index detector and a model 820 Maxima Control System. A Waters 7.8 mm x 30 cm Ultrastyragel linear gel column packed with less than 10 μm particle of mixed pore size crosslinked styrene divinyl benzene copolymer was maintained at 20°C. The eluting solvent was HPLC grade THF at a flow rate of 0.6 mL/min. Retention times were calibrated against known monodisperse polystyrene standards: 110,00; 20,400; 4,800 and 1,530 whose M_w/M_n 1.09. TGA was carried out on a Perkin Elmer TGS-2 instrument at a gas flow rate of 80 cc/min. The initial temperature for the analysis was 50°C followed by an increase of 3°C/min to 850°C. Energy dispersive spectra (EDS) were run on a Link AN-10,000 at the University of Southern California Electron Microanalysis Center. Elemental analysis was performed by Galbraith Laboratories, Knoxville, TN.

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THF was distilled from a deep blue solution of sodium benzophenone ketyl immediately prior to use. Hexamethylphosphoramide (HMPA) was distilled from calci um hydride and was stored over activated 4 A^0 molecular sieves. All glassware was dried in an oven overnight at 120^{o}C and was flame dried immediately prior to use. All reactions were conducted under an atmosphere of prepurified nitrogen.

Preparation of 1-Silacyclopent-3-ene (I)

I was prepared by the $LiAlH_4$ reduction of 1,1-dichloro-1-silacyclopent-3-ene.[5]

Polymerization of 1-Silacyclopent-3-ene

In a dry 75 mL Schlenk flask equipped with a Teflon covered magnetic stirring bar under N_2 was placed I (1.2 g, 14 mmol) and dry THF (20 mL). The flask and its contents were cooled to -78^{o}C. Methyllithium (1 mL, 1.4 mmol) was added. The reaction was stirred for 1.5 h. Aqueous NH_4Cl and ether were added. The organic layer was washed with aq. NH_4Cl, H_2O, dried over anhydrous $CaCl_2$, filtered and the solvents removed by evaporation under reduced pressure. The viscous oil was dissolved in THF. II was precipitated from methanol and was dried under high vacuum for 12 h. One g, 83% yield of II was obtained. M_w/M_n = 2000/1650. IR ν: 3000, 2920, 2880, 2120 (s), 1635, 1405, 1370, 1150, 1095, 1020, 935, 870 (s) cm^{-1}. Elemental anal.: Calcd. for C_4H_8Si: C, 57.07; H, 9.59. Found: C, 57.89; H, 9.50.

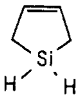
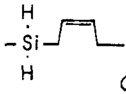
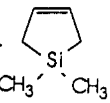
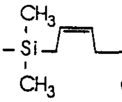
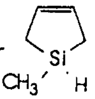
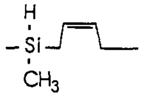
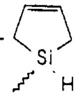
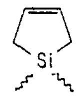
RESULTS AND DISCUSSION

We have found that 1-silacyclopent-3-ene (I) undergoes stereoregular anionic ring opening polymerization on treatment with catalytic amounts of methyllithium and HMPA in THF at -78^{o}C to give poly(1-sila-*cis*-pent-3-ene)(II). Similar results have been obtained with *n*-butyllithium/HMPA as co-catalysts. 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),[6] the formation of II is unexpected since I possesses reactive Si-H bonds. Apparently, the well known ability of hydride to function as a leaving group in nucleophilic substitution reactions at silyl centers [7,8] does not interfere with polymerization.

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-sila-*cis*-pent-3-ene units, ^{1}H NMR δ: 1.61(m,4H), 3.70(m,1.3H), 5.39(m,2H); ^{13}C NMR δ: 10.30, 123.64; ^{29}Si NMR δ: -33.10. It should be noted that the integration of the ^{1}H NMR signal at 3.70 ppm due to the Si-H is low. This point will be discussed later. These assignments are consistent with those of I, III, IV, 1-methyl-1-silacyclopent-3-ene (V) and poly(1-methyl-1-sila-*cis*-pent-3-ene) (VI) (see Table 1).

We believe this polymerization process is initiated by coordination of methyllithium to the silyl center of I to form a pentacoordinate cyclic siliconate intermediate. Ring opening of this intermediate leads to a *cis*-allyl anion which reacts rapidly with another molecule of I to form a new anionic siliconate species. This chain propagation process must occur faster than conversion of the *cis*-allyl anion to a *trans*-allyl anion by rotation about the partial C-C double bonds (see Figure 1).[9]

Table 1. ^{1}H, ^{13}C, ^{29}Si NMR Chemical Shifts in ppm

	 I	 II	 III	 IV	 V	 VI	 VII	 VIII
$^{1}H_{vinyl}$	5.92	5.39	5.73	5.29	5.78	5.35	5.88	5.83
$^{1}H_{allyl}$	1.53	1.61	1.25	1.41	1.44; 1.16	1.55	1.47; 1.36	1.29
$^{13}C_{vinyl}$	130.92	123.64	130.74	123.22	130.83	123.33	130.90	130.93
$^{13}C_{allyl}$	11.53	10.30	17.80	16.47	15.36	13.91		
$^{13}C_{methyl}$			-2.30	-3.41	-5.01	-6.36		
^{29}Si	-27.70	-33.10	16.50	2.17	-3.19	-12.70	-1.90	17.60

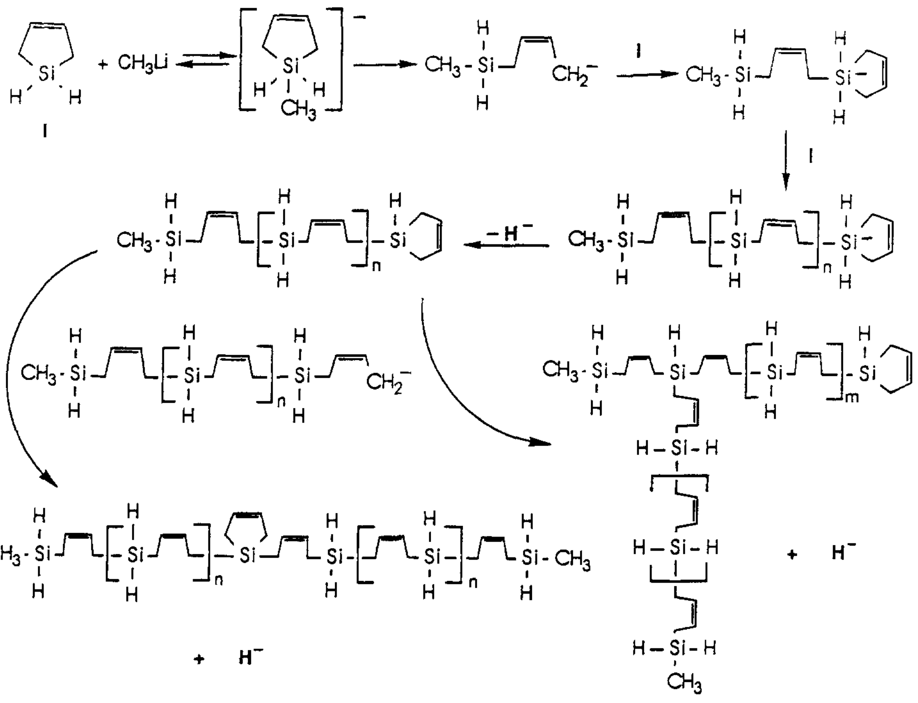


Figure 1. Polymerization of 1-silacyclopent-3-ene

Of particular interest, the low molecular weight of II, permits end group analysis. In addition to the resonances discussed above, a number of signals are observed which may be assigned to the 1-methyl-1-sila-*cis*-pent-3-ene group formed in the initiation process. Among these are ^{1}H NMR signals at 0.15(t,3H, J = 2.9 Hz) and 3.52(q,2H, J = 2.8 Hz) ppm due to the CH_3-SiH_2- group. A ^{13}C NMR signal at -8.54 ppm and ^{29}Si NMR signal at -34.90 ppm are also due to this group.

A number of signals are observed which are consistent with the presence of 1-silacyclopent-3- ene rings (VII and VIII). Specifically, ^{1}H NMR resonances are observed at 5.83 and 5.88 ppm which can be assigned to the vinyl hydrogens of VIII and VII respectively. For comparison, the vinyl hydrogens of I give rise to a signal at 5.92 ppm while those of III produce a resonance at 5.73 ppm. In addition, a multiplet centered at 4.15 ppm is observed in the ^{1}H NMR. This may be assigned to the Si-H bond of VII. By comparison, the Si-H bond of V is found at 4.14 ppm. In agreement with these assignments, the integrated ratio of the signal at 5.88 ppm to that at 4.15 ppm is 2:1. The diastereotopic allylic hydrogens of VII give rise to two signals at 1.47 and 1.35 ppm. These can be compared to the chemical shifts of the allylic hydrogens of V which are found at 1.44 and 1.16 ppm. Further, a signal observed at 1.29 ppm may be assigned to the allylic hydrogens of VIII. The allylic hydrogens of III are also found at 1.29 ppm. Consistent with these assignments, the integration ratio of the signal at 5.83 to that at 1.29 ppm is 1:2.

Likewise, ^{13}C NMR and ^{29}Si NMR signals are observed which can be assigned to VII and VIII. Among these are ^{13}C signals at 130.90 and 130.93 ppm which have been assigned to the vinyl carbons of VII and VIII. These chemical shifts are similar to those of the vinyl carbon resonances of I, III and V which come respectively at 130.92, 130.74 and 130.83 ppm. Finally, silicon signals are observed at 17.60 and -1.92 ppm. The first is consistent with the ^{29}Si NMR chemical shift observed for III (16.50 ppm), while the latter is close to the value found for V (-3.19 ppm).

The presence of groups VII is most easily explained if these are end groups. The formation of VII probably results by loss of hydride from the chain propagating pentacoordinate silicon intermediate rather than ring opening to a *cis*-allyl anion. On the other hand, VIII is probably formed by attack of a propagating *cis*-allyl anion on VII rather than I followed by loss of hydride from the silyl center of this new anionic pentacoordinate silicon species. This process results in a 1-silacyclopent-3-ene ring in the middle of the polymer chain rather than at the end.

Finally, it appears that II contains numerous branch points. These can be formed by nucleophilic attack of a propagating *cis*-allyl anion on one of the silyl centers in the polymer chain with loss of hydride. The ^{29}Si NMR signals which are observed at -10.66 and -11.87 ppm may be assigned to such branch points. These chemical shifts are consistent with those found for silicon atoms which are substituted by three allyl groups and one hydrogen. Thus, the ^{29}Si NMR resonance of poly(1-methyl-1-sila-*cis*-pent-3-ene) comes at -12.70 ppm.[12] Additional signals in the ^{1}H and ^{13}C NMR spectra have been assigned to branch points microstructures. Among these are ^{13}C signals at 123.37 assigned to vinyl carbons adjacent to branch points as well as numerous signals assigned to allylic carbons proximate to branch centers. In the ^{1}H NMR, multiplets centered at 3.82 and 3.72 ppm have been assigned to Si-H bonds at branch points.

The presence of branch points accounts for the low integration of the ^{1}H NMR signal at 3.70 ppm for the hydrogens bonded to silicon previously mentioned. It should be noted that all other poly(1-sila-*cis*-pent-3-enes) which have been prepared have been characterized as linear polymers. Apparently, the presence of reactive Si-H bonds which can undergo nucleophilic displacement by chain propagating *cis*-allyl anions provides a facile mechanism for formation of a branched polymer.[7,8]

The TGA of II is particularly unusual. II is stable in an Argon to 100°C. When II is heated above this temperature, weight loss occurs in two stages. Between 100 and 300°C twelve percent of the initial weight of the sample is lost. No further weight loss occurs until 420°C. Between 420 and 600°C an additional thirty percent weight is lost. No further weight loss occurs, even when the sample is held at 850°C for several hours. After this treatment, a black residue is found which amounts to fifty-seven percent of the initial weight of the polymer. The presence of this high char yield is striking since all previous poly(1-sila-*cis*-pent-3-enes) undergo almost complete weight loss above 450°C.[6,12,13] This char has been analyzed by EDS. It is composed of silicon and carbon. Reheating this sample in air for 7 h at 850°C results in little further weight loss (7%). This material has a white coating over a black interior. On the other hand, when II is heated in air, no weight loss is observed until 320°C. Between 340 and 550°C a forty percent weight loss occurs. No further weight loss occurs when the sample is heated to 850°C (Figure 2). The residue in this case is a white porous material which has been analyzed as containing silicon and oxygen by EDS. The formation of high char yields on thermolysis of II may reflect the branched nature of II,[3,10,11] as well as the presence of reactive Si-H and C-C double bonds in II which may undergo crosslinking during the (3°C/min) heat treatment.

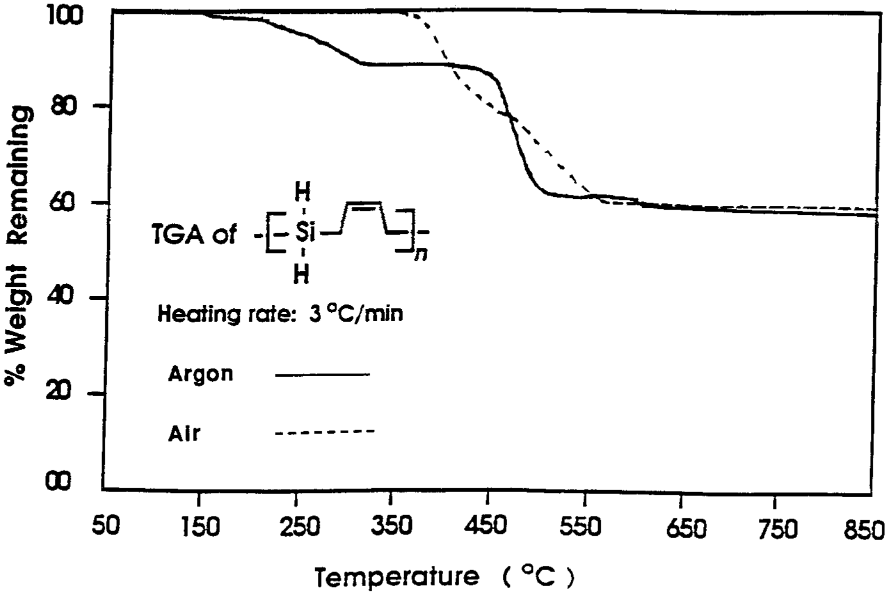


Figure 2. TGA of poly(1-sila-*cis*-pent-3-ene).

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