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Synthesis and microstructure of poly(1-phenyl-1-sila-*cis*-pent-3-ene)

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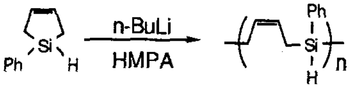
SUMMARY

poly(1-Phenyl-1-sila-*cis*-pent-3-ene) (I) has been prepared by the anionic ring opening polymerization of 1-phenyl-1-sila-cyclopent-3-ene (II). This reaction is co-catalyzed by *n*-butyl-lithium and HMPA in THF at low temperature. I has been characterized by ^{1}H, ^{13}C and ^{29}Si NMR, IR, UV, GPC and TGA. The low molecular weight of I permits end group analysis. Pyrolysis of I gives significant char yields.

INTRODUCTION

Silicon-hydrogen bonds are reactive functional groups. The addition of Si-H bonds across C-C double bonds, often catalyzed by chloroplatinic acid, constitutes the hydrosilation reaction.[1] Silicon-hydrogen bonds can also be oxidized to Si-OH [2,3] or converted to Si-Cl bonds [4] which can be easily hydrolyzed to Si-OH bonds. Condensation of silanols results in formation of siloxanes. These reactions permit the facile chemical modification of polymers which contain Si-H bonds. For example, hydrosilation reactions have been utilized to modify commercially available polymethylhydrosiloxanes.[5,6] On the other hand, polycarbosilanes which possess reactive Si-H bonds are much less common. The proposal that poly[(methylsilylene)methylene] $[\text{-CH}_3\text{SiH-CH}_2\text{-}]_n$ is an intermediate in the conversion of poly(dimethylsilane) $[\text{-(CH}_3)_2\text{Si-}]_n$ fibers to silicon carbide fibers has increased interest in these systems.[7-9] poly(1-Phenyl-1-sila-*cis*-pent-3-ene) (I) is an orthogonal difunctional polymer which contains both reactive Si-H and C-C doulbe bonds. Intra and inter-polymer chain hydrosilation reactions can be catalyzed by chloroplatinic acid leading to crosslinked materials.



EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were obtained on a Bruker AM-360 spectrometer operating in the Fourier Transform mode (FT). ^{29}Si NMR spectra were run on an IBM-Bruker 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.[20]

IR spectra of neat films on NaCl plates were obtained on an IBM-FT-IR spectrometer. UV spectra were recorded on a Shimadzu UV-260 spectrometer of THF or hexane solutions.

GPC analysis was performed with a Waters system comprised of a U6K injector, 510 HPLC sol-

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*To whom offprint requests should be sent vent 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 particles 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: 612,000; 114,200; 47,500; 18,700; 5,120 whose M_w/M_n are less than 1.09.

TGA was carried out on a Perkin Elmer TGS-2 instrument at a nitrogen or air flow rate of 40 cc/min. The initial temperature for the analysis was 50°C followed by an increase of 4°C/min to 750°C.

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

All reactions were conducted in flame dried glassware under an atmosphere of purified nitrogen or argon. 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 A° molecular sieves prior to use. Phenyldichlorosilane (PCR) was redistilled.

In the case of known compounds, we have reported spectral data if this is not available.

1,1-Dichloro-1-silacyclopent-3-ene (V)

V was prepared in two steps from *cis*-1,4-dichloro-2-butene and trichlorosilane following literature procedures.[17]

1-Allyl-1-phenyl-1-silacyclopent-3-ene (VII)

VII was prepared by a dissolving metal (magnesium) reaction of phenylallyldichlorosilane (Petrarch) with 1,3-butadiene according to literature procedures.[21]

1-Chloro-1-phenyl-1-silacyclopent-3-ene (VI) by Reaction of Phenylmagnesium Chloride with V

In a 200 mL rb three neck flask equipped with a pressure equalizing addition funnel, a Teflon covered magnetic stirring bar and a rubber septum were placed V (9.8 g, 60 mmol) and 20 mL of THF. The reaction mixture was cooled to -78°C. A solution of phenylmagnesium chloride in THF (2M, 30 mL, 60 mmol) was placed in the addition funnel and was added dropwise to the reaction mixture. The reaction was stirred at -78°C for 4 h. The solvent was removed by distillation at atmospheric pressure. The residue was distilled through a 10 cm vacuum jacketed Vigreux column. A fraction bp 75°C/0.1 mm, 7.3 g, 62% yield, was isolated. ^{1}H NMR δ: 1.80(s,4H), 5.98(s,2H), 7.37(m,3H), 7.64(m,2H). ^{13}C NMR δ: 19.17, 128.13, 130.00, 130.61, 133.52, 133.60. ^{29}Si NMR δ: 32.59. IR ν: 3072, 3052, 3025, 2923, 1606, 1591, 1429, 1399, 1206, 1176, 1119, 1100, 1062, 1027, 997, 945, 808, 739, 723, 697, 639 cm^{-1}.

1-Chloro-1-phenyl-1-silacyclopent-3-ene (VI) by Reaction of 1-Allyl-1-phenyl-1-silacyclopent-3-ene (VII) with Mercuric Chloride

In 200 mL rb flask equipped with a Teflon covered magnetic stirring bar and a reflux condenser was placed VII (4.0 g, 20 mmol), mercuric chloride (5.9 g, 22 mmol) and 50 mL of THF. The reaction mixture was heated to 50°C overnight. Pentane was added to precipitate excess mercuric chloride. The combined organic solution was filtered through a sintered glass funnel and the volatile solvents were removed by evaporation under reduced pressure. The residue was purified by fractional distillation through a 15 cm vacuum jacketed Vigreux column. A fraction bp 96°C/0.7 mm, 2.08 g, 53% yield was obtained. It had spectral properties identical with IV prepared by the procedures above.

1-Phenyl-1-silacyclopent-3-ene (II) by $LiAlH_4$ Reduction of VI

In a 100 mL three neck rb flask equipped with a reflux condenser, a Teflon covered magnetic stirring bar and two rubber septa was placed $LiAlH_4$ (1 g, 28.3 mmol) and 30 mL of ether. VI (5.5 g, 28.3 mmol) was slowly added to the well stirred reaction via a syringe. The reaction was stirred for 3 h at 0°C and then was refluxed for 1 h. Ice water (10 mL) was added dropwise and the organic layer was separated. The aqueous layer was extracted with ether (3 x 30 mL). The combined organic layer was washed with water, dried over anhydrous magnesium sulfate, filtered and the volatile solvents removed by evaporation under reduced pressure. The residue was distilled through a 10 cm vacuum jacketed Vigreux column. A central fraction bp 62-62.5°C/1.6 mm, 3.63 g, 80% yield, was collected. ^{1}H NMR δ : 1.61(d,m,2H, J = 18 Hz), 1.79(d,m,2H, 18 Hz), 4.76(q,1H, J = 3Hz), 6.02(s,2H), 7.37(m,3H), 7.60(m,2H). ^{13}C NMR δ: 15.30, 127.93, 129.57, 130.99, 134.34, 135.17. ^{29}Si NMR δ: -3.59. IR ν: 3069, 3052, 3021, 2892, 2135 (s), 1609, 1429, 1398, 1304, 1202, 1171, 1153, 1100, 1046, 1028, 998, 945, 912, 858, 841, 761, 729, 697, 680, 663, 640 cm^{-1}. UV λ_{max} nm (ε): 237.0(489), 254.0(463), 260.2(519), 265.0(509), 271.2(397). Elemental Anal. Calcd for $C_{10}H_{12}Si$: C, 74.93; H, 7.55. Found: C, 75.19; H, 7.82.

1-Phenyl-1-silacyclopent-3-ene (II) by Dissolving Metal Reduction

In a 500 mL two neck rb flask equipped with a reflux condenser, a Teflon covered magnetic stirring bar and a rubber septum was placed magnesium powder (9.6 g, 0.4 mol), phenyldichlorosilane (35.4 g, 0.2 mol) and THF (300 mL). The reflux condenser was connected to a refrigeration unit. Ethylene glycol cooled to -20°C was circulated through the reflux condenser. 1,3-Butadiene (15.1 g, 0.28 mol) was condensed at -78°C into a volumetric flask which was sealed with a rubber septum. The 1,3-butadiene was transferred into the reaction via a cannula. The reaction mixture was stirred at rt for 24 h. Ether (2 x 100 mL) was added. The organic solution was decanted from the magnesium chloride salts. These were transferred to a sintered glass funnel and were washed with ether (100 mL). The combined organic solution was washed with water (2 x 50 mL), dried over anhydrous magnesium sulfate, filtered and the volatile solvents removed by evaporation under reduced pressure. The residue was purified by distillation through a 10 cm vacuum jacketed Vigreux column. A fraction, bp 87°/5 mm, 6.0 g, 19% yield, was collected. It had spectral properties which were identical with those reported for II above.

poly(1-Phenyl-1-sila-*cis*-pent-3-ene) (I)

In a 100 mL rb flask equipped with a Teflon covered magnetic stirring bar and a rubber septum was placed II (2.1 g, 13 mmol), THF (50 mL) and HMPA (80μL). The mixture was cooled to -78°C and a hexane solution of *n*-butyllithium (0.2 mL, 2.5 M, 0.5 mmol) was added via a syringe. The reaction mixture was stirred at -78°C for 1 h. It was allowed to warm to -20°C over 20 min. A saturated solution of aqueous ammonium chloride (20 mL) was added. The organic layer was separated, washed with water (20 mL), dried over anhydrous magnesium sulfate, filtered and the volatile solvents removed by evaporation under reduced pressure. The residue was dissolved in a minimum amount of THF and I was precipitated from methanol. This process was repeated twice. I was dried under vacuum. In this way, 1.1 g, 52% yield of I, M_w/M_n = 2,000/1,800 was obtained. ^{1}H NMR δ: 0.96(br.s, 0.26 H), 1.44(br.s, 0.21 H), 1.62(s, 0.07 H), 1.80(br.s, 1.69 H), 1.92(br.s, 3.18 H), 4.32(br.s, 0.08 H), 4.55(br.s, 0.33 H), 5.43(br.s, 2.35 H), 6.02(s, 0.02 H), 7.46(br.s, 3.0 H), 7.65(br.s, 2.0 H). ^{29}Si NMR δ : 11.59, -3.84, -5.09, -11.69, -14.34, -15.57, -15.67, -15.72. IR ν: 3087, 3068, 3048, 3007, 2955, 2927, 2872, 2776, 2115 (s), 1637, 1609, 1589, 1568, 1486, 1334, 1300, 1262, 1065, 1031, 1004, 998, 964, 935 cm^{-1}. UV λ_{max} nm (ε) (hexane): 267.5(807), 263.0(1280), 258.0(1660), 227.4 (28,300). Elemental Anal. Calcd. for $C_{10}H_{12}Si$: C, 74.93; H, 7.55. Found: C, 72.71; H, 7.56.

Phenyltriallylsilane

Phenyltriallylsilane was prepared by the reaction of phenyltrichlorosilane with allylmagnesium chloride in THF in 75% yield.[22] ^{13}C NMR δ: 19.49, 114.27, 127.69, 129.28, 133.74, 134.15, 135.14. ^{29}Si NMR δ : -7.83.

Phenyldi-*n*-butylsilane

Phenyldi-*n*-butylsilane was prepared by the addition of *n*-butyllithium to phenyldichlorosilane.[23] ^{13}C NMR δ : 11.69, 13.75, 26.28, 26.75, 127.78, 129.07, 134.63, 136.09. ^{29}Si NMR δ : -9.10.

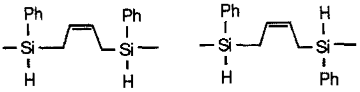
Phenyldiallylmethylsilane

Phenyldiallylmethylsilane was prepared by the reaction of allylmagnesium chloride with phenylmethyldichlorosilane.[24] ^{13}C NMR δ: -5.87, 21.55, 113.82, 127.72, 129.15, 133.89, 134.13, 136.83. ^{29}Si NMR δ : -5.74.

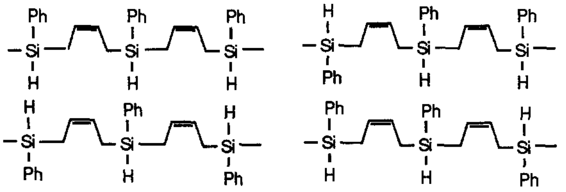
RESULTS AND DISCUSSION

1-Phenyl-1-silacyclopent-3-ene (II) [10] undergoes stereoregular anionic ring opening polymerization on treatment with catalytic amounts of *n*-butyllithium and HMPA in THF at -78^{o}C to give I. Similar results have been obtained with *n*-butyllithium and TMEDA as co-catalysts. While 1-methyl-1-phenyl-1-silacyclopent-3-ene (III) undergoes polymerization under similar conditions to yield poly(1-methyl-1-phenyl-1-sila-*cis*-pent-3-ene) (IV), [11,12] the formation of I is unexpected since II 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 does not interfere with the polymerization. [13,14]

The microstructure of I has been determined by ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy. The following resonances have been assigned to 1-phenyl-1-sila-*cis*-pent-3-ene units: ^{1}H NMR : 1.92 (br.s, 3.2 H), 4.55(br.s, 0.33 H), 5.43(s, 2.35 H), 7.46(br.s, 3.0 H), 7.65(br.s, 2.0 H). It should be noted that the integration of the ^{1}H NMR signal at 4.55 ppm due to the Si-H is low. This point will be discussed later. Due to the low molecular weight of I the ^{13}C NMR is complicated. Resonances at 123.37 and 122.52 are assigned to the vinyl carbons of 1-phenyl-1-sila-*cis*-pent-3-ene units. The stereochemical relationship of the adjacent phenylsilylene units apparently affects the chemical shift of these carbons.



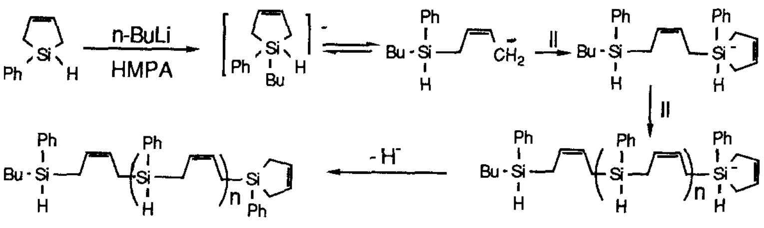
Signals at 12.51, 11.84, and 11.75 maybe assigned to the allylic carbons of these units. These assignments are consistent with those of II, III and IV (See Table 1). ^{29}Si NMR : -15.57, -15.67, -15.72 ppm in a 2:1:1. These maybe explained by a triad analysis.



We believe this polymerization process is initiated by coordination of *n*-butyllithium to the silyl center of II 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 II 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. [15]

Of particular interest, the low molecular weight of I permits end group analysis. In addition to the resonances discussed above, a number of signals are observed which may be assigned to the 1-*n*-butyl-1-phenyl-1-sila-*cis*-pent-3-ene group formed in the initiation process. Among these are ^{1}H NMR signals at 0.96(br.s, 0.26H), 1.44(br.s, 0.21H), and 4.32(br.s, 0.08H) ppm, ^{13}C NMR signals at 26.60, 26.15, 13.75, and 11.69 ppm due the *n*-butyl group as well as ^{29}Si NMR signals at -11.60 ppm. These assignments are consistent with the chemical shifts observed for phenyldi-*n*-butylsilane.

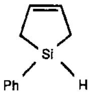
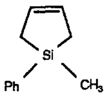
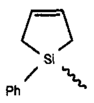
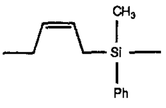
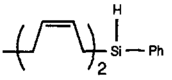
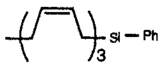
A number of NMR resonances are observed which are consistent with the presence of 1-phenyl-1-silacyclopent-3-ene rings. The existence of such rings is most easily explained if these are end groups. These are probably formed by loss of hydride from the chain propagating pentacoordinate silicone intermediate. This process is apparently competitive with ring opening to a *cis*-allyl anion. Signals assigned to such rings are observed in the ^{1}H, ^{13}C and ^{29}Si NMR. Among these are ^{1}H NMR signals at 6.02 ppm due to vinyl hydrogens as well as a signal at 1.62 ppm due to allyl hydrogens; ^{13}C NMR signals at 131.00 ppm due to vinyl carbons as well as a ^{29}Si NMR signal at 11.59 ppm. These assignments are based on comparison with the spectra of 1-methyl-1-phenyl-1-silacyclopent-3-ene and II (See Table 1).

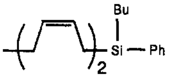
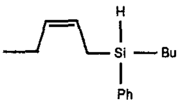
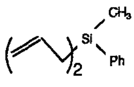
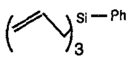


Polymerization of 1-Phenyl-1-silacyclopent-3-ene (II)

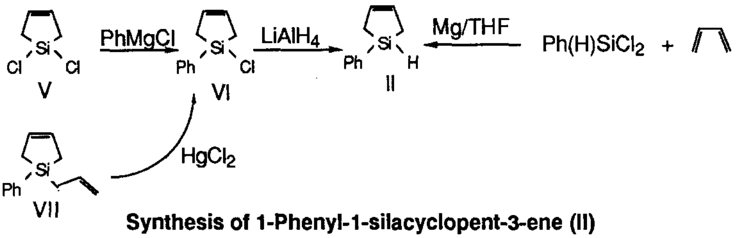
Finally, it appears that I contains numerous branch points. These can be formed by nucleophilic attack of a propagating *cis*-allyl anion on one of the silyl centers of the polymer chain with loss of hydride. ^{29}Si NMR signals are observed at -3.84 and -5.09 ppm. These may be assigned to branch points. Phenyltriallylsilane and phenyldiallylmethylsilane may be suitable model compounds for such branch points. (See Table 1). The presence of branch points accounts for the low integration of the ^{1}H NMR signals at 4.54 ppm due to hydrogens bonded to silicon previously mentioned. It should be noted that most other poly(1-sila-*cis*-pent-3-enes) which have been prepared have been characterized as linear polymers.[11,12] 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.[16]

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

						
$^1H_{allyl}$	1.74	1.62	1.69	1.62	1.91	1.79
$^1H_{vinyl}$	6.03	6.02	6.02	5.31	5.43	5.43
$^{13}C_{allyl}$	15.29	17.58	15.65	15.23		
$^{13}C_{vinyl}$	131.02	131.07	131.00	123.24	122.52	123.20
^{29}Si	-3.59	11.46	11.59	-4.33	-15.74	-5.09

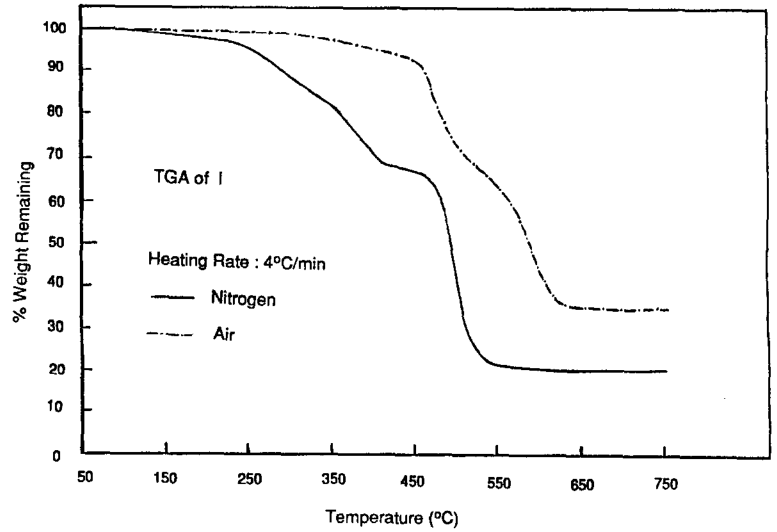
			Ph(H)SiBu$_2$		
$^1H_{allyl}$	1.94	1.82		1.89	1.97
$^1H_{vinyl}$	5.43	5.43			
$^{13}C_{allyl}$				21.55	19.49
$^{13}C_{vinyl}$	123.10	123.12		113.82/134.13	114.27/134.15
^{29}Si	-3.84	-11.73	-9.11	-5.74	-7.83

1-Phenyl-1-silacyclopent-3-ene (II) has been prepared by two synthetic routes and has been fully characterized. Thus phenylmagnesium bromide reacts selective with only one of the two Si-Cl bonds of 1,1-dichloro-1-silacyclopent-3-ene (V) [17] at -78°C to yield 1-chloro-1-phenyl-1-silacyclopent-3-ene (VI). Alternatively, VI has been prepared by electrophilic cleavage of the allyl group from 1-allyl-1-phenyl-1-silacyclopent-3-ene (VII) by mercuric chloride. Reduction of VI with lithium aluminum hydride in THF yields II. The recent preparation of V starting from commercially available *cis*-1,4-dichloro-2-butene and trichlorosilane makes this synthetic route feasible. Alternatively, II can be prepared by the dissolving metal reaction of 1,3-butadiene, magnesium with phenyldichlorosilane in THF.



Synthesis of 1-Phenyl-1-silacyclopent-3-ene (II)

The thermal stability of I has been determined in both an inert (nitrogen atmosphere) as well as in air. In nitrogen, I is stable to 100°C. Between 100 and 200°C, I loses three percent of its initial weight. An additional thirty percent weight loss is observed between 200 and 350°C. Virtually no further weight is lost between 350 and 400°C. Above 400°C rapid weight loss occurs. By 470°C only twenty percent of the initial weight of I remains. Virtually no further weight loss occurs on heating the black colored residue to 750°C. In air, I is thermally stable to 200°C. Between 200 and 400°C approximately six percent of the initial weight of I is lost. Above 400°C rapid weight loss occurs. By 575°C thirty-five percent of the initial sample weight remains. No further weight is lost on heating the light tan residue to 750°C. This is close to the theoretical yield of silicon dioxide. The formation of high char yields on thermolysis of I despite its low molecular weight may reflect the branched nature of I as well as the presence of reactive Si-H and C-C double bonds in I which may undergo crosslinking via inter-chain hydrosilation reactions during the (4°C./min) heat treatment. [9,18,19]



TGA of poly(1-phenyl-1-sila-*cis*-pent-3-ene)

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