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Dimerization and Polymerization of 2,3-Benzo-5-silaspiro[4.4]nona-2,7-diene

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ABSTRACT: Treatment of 2,3-benzo-5-silaspiro[4.4]nona-2,7-diene (I) with catalytic amounts of *n*-butyllithium and hexamethylphosphoramide (HMPA) in THF results in dimerization of I to give 2,3:12,13-dibenzo-5,10-disiladispiro[4.4.4.4]octadeca-2,7,12,16-tetraene (II). On the other hand, ring-opening metathesis polymerization (ROMP) of I cocatalyzed by tungsten hexachloride and tetraphenyltin gives poly[(3,4-benzo-1-silacyclopent-3-en-1-ylene)-*cis*- and -*trans*-but-2-en-1,4-ylene] (*cis*- and *trans*-III).

Introduction

We have been interested in the ring-opening polymerization of 1-silacyclopent-3-enes. These reactions generally lead to poly(1-sila-*cis*-pent-3-enes).[1] Recently, we studied the anionic polymerization of several 5-silaspiro[4.4]nona-2,7-diene systems and found that dimerization competes with polymerization in some of these cases.[2,3] In an attempt to better understand the factors controlling this competition, we studied both the anionic and ring-opening metathesis polymerization of 2,3-benzo-5-silaspiro[4.4]-nona-2,7-diene (I).

Results and Discussion

2,3-Benzo-5-silaspiro[4.4]nona-2,7-diene (I) was prepared from benzyl(chloromethyl)dichlorosilane (IV) (Figure 1). Thus aluminum chloride catalyzed intramolecular Friedel–Crafts cyclization of IV gives 1,1-dichloro-3,4-benzo-1-silacyclopent-3-ene (V),[4] which reacts with 1,3-butadiene and magnesium in THF to yield I.

Treatment of I with catalytic amounts of *n*-butyllithium and HMPA did not result in anionic ring-opening polymerization and formation of poly[(3,4-benzo-1-silacyclopent-3-en-1-ylene)-*cis*-but-2-en-1,4-ylene] (*cis*-III) but rather in formation of a dimer 2,3:12,13-dibenzo-5,10-disiladispiro[4.4.4.4]octadeca-2,7,12,16-tetraene (II) (Figure 2). By comparison, both 1,1-dimethyl-1-silacyclopent-3-ene and 1,1-dimethyl-3,4-benzo-1-silacyclopentene undergo anionic ring-opening polymerization to yield respectively poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene)[1] and poly(1,1-dimethyl-3,4-benzo-1-silapentene).[5]

The anionic dimerization of I to yield II may be related to the dimerization of 2,3-dimethyl-5-silaspiro[4.4]nona-2,7-diene (VI) which gives 2,3:12,13-tetramethyl-5,10-disiladispiro[4.4.4.4]octadeca-2,7,12,16-tetraene (VII), whose structure has been rigorously established by X-ray crystallography.[3] The molecular weight of II was determined by mass spectrometry while its structure was established by ^{1}H, ^{13}C, and ^{29}Si NMR as well as by IR and UV spectroscopy. In particular, the ^{29}Si NMR resonance for I is found at 33.51 ppm while that for II is observed at 19.12 ppm, an upfield shift of 14.4 ppm. This is similar to the 13.7 ppm upfield shift that is observed when the ^{29}Si NMR resonance for VI (25.54 ppm) is compared to that of VII (11.87 ppm). In addition, the chemical shifts of the vinyl protons and carbons are consistent with structure II. In particular, the vinyl protons of I are observed at 6.08 ppm while those for II are found at 5.39 ppm. By comparison, the ^{1}H NMR signals for the vinyl protons of VI are found at 5.91 ppm while those of VII are observed at 5.30 ppm. Likewise, the allyl, benzyl and vinyl ^{13}C NMR signals of I and II can be compared to those of VI and VII (Table I). The nature of the factors which favor dimerization of I and VI under anionic catalysis is not fully understood.

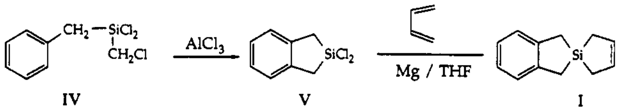

Figure 1. Synthesis of 2,3-benzo-5-silaspiro[4.4]nona-2,7-diene (I).

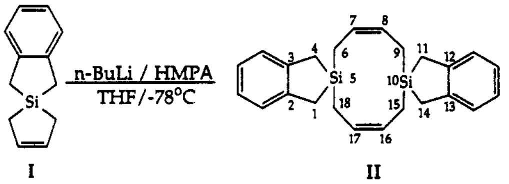

Figure 2. Treatment of I with *n*-butyllithium. Synthesis of 2,3:12,13-dibenzo-5,10-disiladispiro[4.4.4.4]octadeca-2,7,12,16-tetraene (II).

On the other hand, ring-opening metathesis polymerization of I cocatalyzed by tungsten hexachloride and tetraphenyltin with activation by cyclopentene is successful and results in *cis*- and *trans*-III (Figure 3). Ring-opening metathesis polymerization reactions are often stereoselective but not stereospecific.[6] Tungsten hexachloride and tetraphenyltin have been frequently utilized as catalysts for ROMP. Cyclopentene has been previously utilized to activate such ROMP catalyst systems.[7]

The stereochemical composition of III can be determined by integration of the allyl and vinyl hydrogen resonances. Specifically the ^{1}H NMR signal at 1.94 ppm is assigned to the allylic hydrogens of *trans*-III units, while the resonance at 1.97 ppm is assigned to *cis*-III units. Likewise, the ^{1}H NMR signal at 5.20 ppm is assigned to the vinyl hydrogens of *trans*-III units while that at 5.25 ppm results from the *cis*-III units. Integration of these is consistent with a polymer composed of 16% *trans*-III units and 84% *cis*-III units.

The ^{13}C and ^{29}Si NMR of the 3,4-benzo-1-silacyclopent-3-en-1-ylene (VIII) units are sensitive to microenvironment (Figure 4). Three ^{29}Si NMR signals are observed. These can be accounted for on the basis that the but-2-en-1,4-ylene (IX) units on either side of VIII units can be both *cis*-IX, one *cis*-IX and one *trans*-IX, or both *trans*-IX. The microenvironment for VIII with *cis*-IX on either side is most probable while that with *trans*-IX units on either side is least probable. The ^{29}Si NMR

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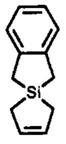
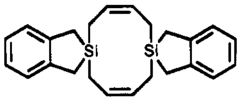
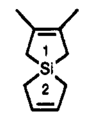
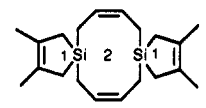
Table I
^{13}C NMR Chemical Shifts (ppm) of I, II, VI, and VII

	 I	 II	 VI	 VII
vinyl	131.03	122.84	130.87, 131.16	130.58 (1), 122.92 (2)
allyl	16.06	13.59	19.18 (1), 16.54 (2)	19.34 (1), 14.06 (2)
benzyl	19.61	18.76		

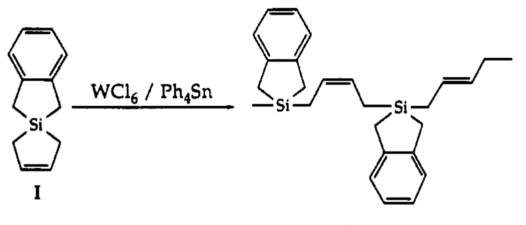


Figure 3. Ring-opening metathesis polymerization of I.

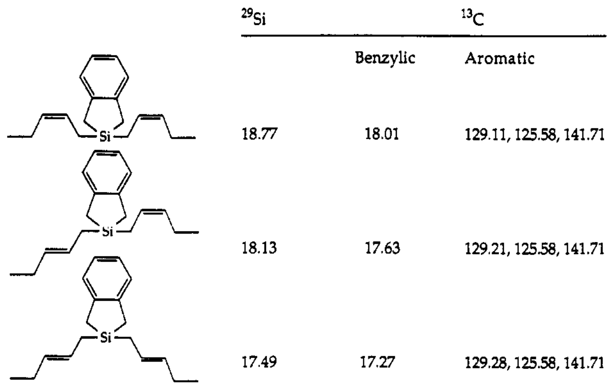


Figure 4. Assignment of ^{29}Si and ^{13}C NMR chemical shifts (ppm) to microenvironments of 3,4-benzo-1-silacyclopent-3-en-1-ylene units (VIII).

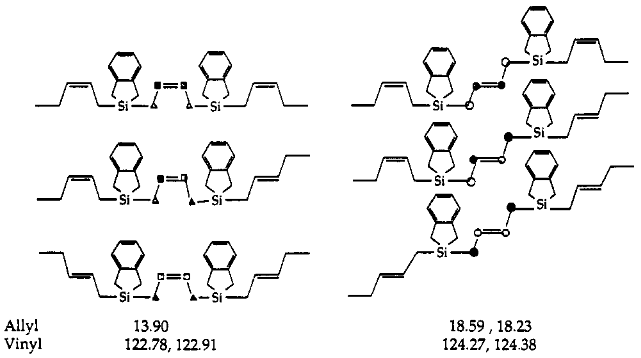


Figure 5. Assignment of ^{13}C NMR chemical shifts (ppm) to microenvironments of cis-but-2-en-1,4-ylene (*cis*-IX) and *trans*-but-2-en-1,4-ylene (*trans*-IX) units.

resonances have been assigned to specific microenvironments on this basis. Similarly, three resonances are observed in the ^{13}C NMR for the benzylic carbons of VIII. On the other hand, only one of the aromatic carbons of VIII is sensitive to microstructure.

The ^{13}C NMR of the *cis*-but-2-en-1,4-ylene (*cis*-IX) and *trans*-but-2-en-1,4-ylene (*trans*-IX) units can be rationalized on the basis that only the stereochemistry of nearest-neighbor IX groups affects microenvironments (Figure 5). Thus *trans*-IX units exist in three microenvironments: one of these has *cis*-IX units on either side of the central *trans*-IX unit, another has a *cis*-IX unit on one side and a *trans*-IX unit on the other, and finally one has *trans*-IX units on both sides. Two signals due to *trans*-allyl carbons (18.59 and 18.23 ppm) and two due to *trans*-vinyl carbons (124.27 and 124.38 ppm) are observed. Apparently, the allyl and vinyl carbons of the central *trans*-IX unit are only sensitive to the stereochemistry of the nearest-neighbor IX unit which can either be cis or trans. Likewise, *cis*-IX units exist in three microenvironments. However, only two *cis*-vinyl carbons (122.78 and 122.91 ppm) and a single *cis*-allyl carbon at 13.90 ppm are observed. Apparently, the *cis*-vinyl carbons are sensitive to the stereochemistry of the nearest-neighbor IX unit which can either be cis or trans, while the *cis*-allyl carbons are *not* sensitive to microstructure.

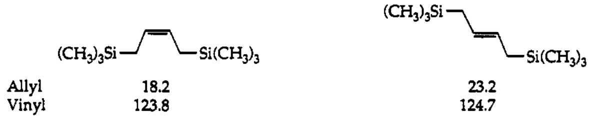


Figure 6. ^{13}C NMR chemical shifts (ppm) of 1,4-bis(trimethylsilyl)-*cis*-but-2-ene and 1,4-bis(trimethylsilyl)-*trans*-but-2-ene.

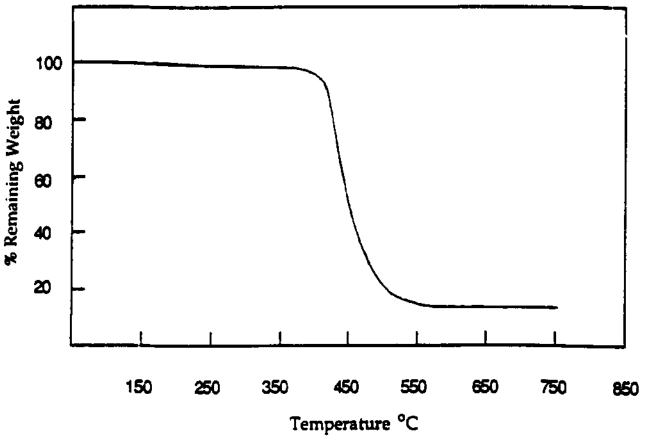


Figure 7. TGA of *cis*- and *trans*-III.

The differences in the chemical shifts of *cis*- and *trans*-allyl (4.5 ppm) and -vinyl carbons (1.4 ppm) in IX units are consistent with those observed for model compounds 1,4-bis(trimethylsilyl)-*cis*-but-2-ene and 1,4-bis(trimethylsilyl)-*trans*-but-2-ene (Figure 6).[8]

The thermal stability of *cis*- and *trans*-III was determined by TGA (Figure 7). The polymer is stable to 150 °C. Between 150 and 350 °C the polymer loses 3% of its initial weight. Above 400 °C rapid weight loss occurs. By 550 °C only 14% of the initial polymer weight remains. No further weight loss occurs above this temperature.

The formation of a residue on thermal decomposition of *cis*- and *trans*-III is unusual. For comparison, poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene) undergoes catastrophic decomposition above 400 °C in nitrogen and leaves no residue.[9] The formation of a ceramic char suggests that cross-linking occurs during the thermal decomposition. This may occur by loss of benzocyclobutene and formation of a reactive silylene or silene intermediate in

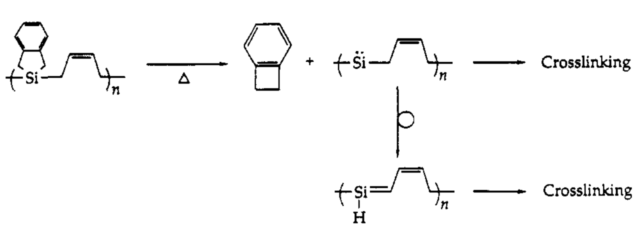


Figure 8. Formation and cross-linking of reactive silylene and silene intermediates.

the polymer chain (Figure 8).[2]

Experimental Section

^{1}H and ^{13}C NMR spectra were run on a Bruker AM-360 spectrometer operating in the Fourier transform (FT) mode. ^{29}Si NMR spectra were recorded on an IBM-Bruker 270-SY spectrometer. ^{13}C NMR spectra were run with broad-band proton decoupling. ^{29}Si NMR spectra were obtained by use of a heteronuclear gated decoupling pulse sequence (NONOE) with a pulse delay of 15 s.[10] ^{13}C and ^{29}Si NMR were obtained on 10% solutions in chloroform-*d*. ^{1}H NMR spectra were obtained on 5% solutions. Chloroform was utilized as an internal standard for ^{1}H and ^{13}C NMR spectra. ^{29}Si NMR spectra were externally referenced to TMS. IR spectra were recorded on an IBM FTIR/30S, DTGS/CSI spectrometer. Spectra were taken of neat films on NaCl plates. UV spectra were recorded on a Shimadzu UV-vis 260 spectrometer of THF solutions.

The molecular weight distribution of *cis*- and *trans*-III was determined by gel permeation chromatography on a Waters system. This was comprised of 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 was utilized for the analysis. The column 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: 929 000, 114 200, 47 500, 13 700, 5120, and 2200 whose M_w/M_n values are <1.09.

Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer TGS-2 instrument. The temperature program for the analysis was 50 °C for 2 min. The temperature was then increased at a rate of 4 °C/min to 100 °C. The temperature was held at 100 °C for 10 min. This was followed by an increase of 4 °C/min to 750 °C. These runs were conducted with a nitrogen 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 instrument. The melting points of indium (mp 156 °C) and spectral-grade *n*-hexane (mp -95 °C) were used to calibrate the DSC. After equilibration at -100 °C for 20 min scans were conducted by increasing the temperature at a rate of 20 °C/min to 150 °C.

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.

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

Tetrahydrofuran (THF) was distilled immediately prior to use from a deep blue solution of sodium benzophenone ketyl.

All glassware was dried overnight in an oven at 120 °C. It was assembled and flame-dried under an atmosphere of purified argon. All reactions and transfers were conducted under an atmosphere of purified argon.

1,1-Dichloro-3,4-benzo-1-silacyclopent-3-ene (V). V was prepared by the reaction of benzyl(chloromethyl)dichlorosilane (IV) with aluminum chloride in benzene. It was purified by fractional distillation through a 15-cm vacuum-jacketed Vigreux column. A fraction [bp 80-82 °C (4 mm) [lit.[4] bp 82-84 °C (4 mm)]] was obtained in 67% yield. ^{1}H NMR: δ 2.55 (s, 4 H), 7.14 (m, 2 H), 7.19 (m, 2 H). ^{13}C NMR: δ 25.14, 126.94, 129.01, 137.02. ^{29}Si NMR: δ 38.31.

2,3-Benzo-5-silaspiro[4.4]nona-2,7-diene (I). In a 250-mL three-neck round-bottomed flask equipped with a Teflon-covered magnetic stirring bar and an efficient reflux condenser was placed magnesium powder (1.7 g, 73 mmol), V (10 g, 49 mmol), and THF (20 mL). The other two necks of the flask were sealed with rubber septa. The reflux condenser was connected to a refrigeration unit. Isopropyl alcohol, cooled to -25 °C, was circulated through the reflux condenser. 1,3-Butadiene (20 mL, 12.5 g, 0.23 mol) was condensed at -78 °C into a volumetric flask which was sealed with a rubber septum. The 1,3-butadiene was transferred to the reaction flask via a cannula. The reaction was stirred for 48 h. Excess 1,3-butadiene was allowed to evaporate. Ether (100 mL) was added, and 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 × 50 mL), dried over anhydrous magnesium sulfate, and filtered, and the volatile solvents were removed by evaporation under reduced pressure. The residue was purified by fractional distillation through a vacuum-jacketed Vigreux column. A central fraction [bp 130-132 °C (3.5 mm), 5.0 g, 54% yield] was obtained. ^{1}H NMR: δ 1.66 (d, 4 H, *J* = 1 Hz), 2.39 (s, 4 H), 6.08 (t, 2 H, *J* = 1 Hz), 7.20 (dd, 2 H, *J* = 5.5 and 4 Hz), 7.38 (dd, 2 H, *J* = 5.5 and 4 Hz). ^{13}C NMR: δ 16.06, 19.61, 125.73, 129.11, 131.03, 141.84. ^{29}Si NMR: δ 33.51. IR (ν): 3058, 3016, 2883, 2774, 1607, 1570, 1477, 1451, 1394, 1210, 1170, 1125, 1100, 1031, 944, 847, 827, 761 cm^{-1}. UV [λ_{max}, nm (ε, M^{-1} cm^{-1})]: 276.4 (1198), 269.2 (1145), 262.4 (907). Anal. Calcd for $C_{12}H_{14}Si$: C, 77.35; H, 7.57. Found: C, 77.07; H, 7.71.

2,3:12,13-Dibenzo-5,10-disiladispiro[4.4.4.4]octadeca-2,7,12,16-tetraene (II). In a 50-mL round-bottomed flask equipped with a Teflon-covered magnetic stirring bar and a rubber septum was placed I (0.52 g, 2.8 mmol), THF (8 mL), and 50 L of HMPA. The flask and its contents were cooled to -30 °C in a methanol/dry ice bath. *n*-Butyllithium (0.1 mL, 2.5 M in hexane) was added dropwise via a syringe. The solution became red. After stirring for 2.5 h at -30 °C, the reaction was quenched by addition of saturated aqueous ammonium chloride. Ether was added, the organic layer was washed with water (3 × 30 mL), dried over anhydrous magnesium sulfate, and filtered, and the volatile solvents were removed by evaporation under reduced pressure. A sticky white solid (0.52 g) was obtained. This was recrystallized from 9 mL of a 1:2 mixture of THF and methanol. In this way 0.26 g, 50% yield, of a white solid which melted with decomposition at 330 °C was obtained. Analysis of the supernant revealed a mixture of I and II. ^{1}H NMR: δ 1.67 (d, 8 H, *J* = 5.9 Hz), 2.16 (s, 8 H), 5.39 (t, 4 H, *J* = 5.9 Hz), 7.08 (dd, 4 H, *J* = 5.3 and 3.5 Hz), 7.25 (dd, 4 H, *J* = 4.7 and 3.5 Hz). ^{13}C NMR: δ 13.59, 18.76, 122.84, 125.75, 129.44, 141.64. ^{29}Si NMR: δ 19.12. IR (KBr, ν): 3051, 3001, 2938, 2865, 2771, 1694, 1632, 1595, 1568, 1467, 1450, 1391, 1374, 1283, 1260, 1204, 1155, 1124, 1110, 1093, 1070, 1023, 961, 941, 931, 868, 830, 773, 751, 729, 681 cm^{-1}. UV [λ_{max}, nm (ε, M^{-1} cm^{-1})]: 282.4 (4018), 276.4 (6875), 269.6 (5938), 262.4 (4524). MS (relative intensity): *m/e* 374 (11), 373 (36), 372 (100, M$^{\cdot+}$), 344 (8), 319 (4), 318 (10), 317 (16), 268 (5), 267 (17), 237 (3), 236 (10), 188 (7), 187 (22), 186 (81), 160 (4), 159 (8), 158 (13), 146 (3), 145 (10), 144 (18), 134 (3), 133 (14), 132 (58). High-resolution MS (M$^{\cdot+}$) calcd for $C_{24}H_{28}Si_2$: 372.1730. Found: 372.1736.

Poly[(3,4-benzo-1-silacyclopent-3-en-1-ylene)-*cis*- and -*trans*-but-2-en-1,4-ylene] (*cis*- and *trans*-III). Tungsten hexachloride (25.9 mg, 0.065 mmol) and tetraphenyltin (33.2 mg, 0.078 mmol) were weighted into a dry 25-mL round-bottomed flask containing a Teflon-covered magnetic stirring bar in a Vacuum Atmospheres drybox. The flask and its contents were sealed with a rubber septum. Cyclopentene (12 μL) was added via syringe, and the catalyst system was stirred for 5 min at room temperature before I (0.8 g, 4.3 mmol) was added. The reaction mixture became black immediately and highly viscous in 2 h. The mixture was allowed to stand at room temperature for 16 h. The polymer was dissolved in THF (2 mL), and the reaction mixture was centrifuged. The supernant THF solution was removed, and the polymer was precipitated by addition of methanol. The polymer was separated by centrifugation. The supernatant liquid was discarded, and the polymer was redissolved in a minimum amount of THF and reprecipitated by addition of methanol. This process was repeated twice. The polymer was dried under vacuum. In this way, a white solid (0.68 g, 60% yield, M_w/M_n = 144 000/54 000 = 2.7, T_g = −3.6 °C) was obtained. ^{1}H NMR: δ 1.54 (d, 4 H, J = 6.3 Hz), 1.94 (br s, 0.65 H), 1.97 (br s, 3.35 H), 5.20 (s, 0.34 H), 5.25 (t, 1.66 H, J = 5.5 Hz), 7.00 (dd, 2 H, J = 5.4 and 3.5 Hz), 7.12 (dd, 2 H, J = 5.4 and 3.5 Hz). ^{13}C NMR: δ 13.90, 17.27, 17.63, 18.01, 18.24, 18.58, 122.78, 122.91, 124.27, 124.38, 125.58, 129.11, 129.21, 129.28, 141.71. ^{29}Si NMR: δ 18.77, 18.13, 17.49. IR (ν): 3058, 3010, 2924, 2878, 1477, 1452, 1390, 1375, 1208, 1151, 1125, 1021, 938, 847, 830, 747, 611 cm^{-1}. UV [λ_{max}, nm (ε, M^{-1} cm^{-1})]: 277.0 (804), 270.0 (998), 263.4 (702), 236.8 (849). Anal. Calcd for $C_{12}H_{14}Si$: C, 77.35; H, 7.57. Found: C, 75.15; H, 7.71.

A solution of tungsten hexachloride in chlorobenzene was prepared in a drybox. This solution (0.65 mL, 0.1 M) was utilized to prepare the ROMP catalyst. Except for this difference, the ROMP was conducted as above. Under these conditions, the polymer was formed in 50% yield and had identical spectral properties but lower molecular weight M_w/M_n = 83 100/46 600 = 1.78.

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