

## Partial and complete hydrogenation of poly(1-methyl-1-phenyl-1-sila-*cis*-pent-3-ene)

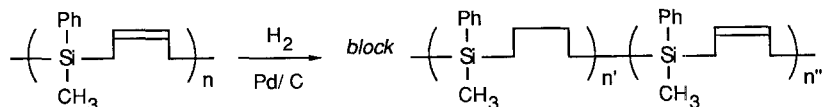
### Synthesis and characterization of poly(1-methyl-1-phenyl-1-silapentane) and *block* copoly(1-methyl-1-phenyl-1-sila-*cis*-pent-3-ene/1-methyl-1-phenyl-1-silapentane)

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#### Summary

Poly(1-methyl-1-phenyl-1-silapentane)(II), and *block* copoly(1-methyl-1-phenyl-1-sila-*cis*-pent-3-ene/1-methyl-1-phenyl-1-silapentane)(*block*-III) have been prepared by catalytic hydrogenation of poly(1-methyl-1-phenyl-1-sila-*cis*-pent-3-ene)(I) over 5% palladium on carbon. These polymers have been characterized by  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR as well as IR spectroscopy. Molecular weight distributions have been evaluated by gel permeation chromatography (GPC). Thermal stabilities have been measured by thermogravimetric analysis (TGA). Glass transition temperatures ( $T_g$ 's) have been determined by differential scanning calorimetry (DSC).



#### Introduction

There is considerable interest in chemical modification of intact polymers (1-4). Such reactions are often utilized to prepare polymers which can not be prepared directly. There are numerous examples of modification of unsaturated polymers, such as poly(1,4-butadiene), by catalytic hydrogenation over heterogeneous catalysts (5,6). High molecular weight I can be prepared by anionic ring opening polymerization of 1-methyl-1-phenyl-1-silacyclopent-3-ene (7,8). In this paper, we report our results on the heterogeneous catalytic hydrogenation of I over palladium on carbon.

#### Experimental

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were run on a Bruker AM-250 spectrometer operating in the Fourier transform (FT) mode.  $^{29}\text{Si}$  NMR spectra were recorded on a Bruker 270 spectrometer.  $^{13}\text{C}$  NMR spectra were run with broad band proton decoupling.  $^{29}\text{Si}$  NMR spectra were obtained by use of a heteronuclear gated decoupling pulse sequence (INVGATE) with a pulse delay of 15-20 s (9).  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectra were obtained in fifteen percent solution of chloroform-*d*.  $^1\text{H}$  NMR spectra were obtained in five percent solution of chloroform-*d*. Chloroform was utilized as an internal standard for  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra.  $^{29}\text{Si}$  NMR spectra were externally referenced to TMS. IR spectra of neat films on sodium chloride plates were recorded on an IBM FT-IR/30S, DTGS/CSI spectrometer.

The molecular weight distribution of these polymers was determined by gel permeation chromatography on a Waters systems comprised of a U6K injector, a 510 HPLC solvent delivery system, a R401 differential refractometer and a Maxima 820 control system. A Water 7.8 mm x 30 cm Ultrastaygel linear column packed with < 10  $\mu\text{m}$  particles of mixed pore size crosslinked styrene-divinylbenzene copolymer was utilized for analysis. The column was maintained at rt. The eluting solvent was

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HPLC grade THF at a flow rate 0.7 mL/min. The retention times were calibrated against known monodisperse polystyrene standards: 612,000 114,200 47,500 18,700 5,120 and 2,200 whose  $M_w/M_n$  values are < 1.09.

TGA was carried out on a Perkin-Elmer TGS-2 instrument with a nitrogen flow rate of 40 cc/min. The temperature program for this analysis was 50° for 2 min. The temperature was then increased at a rate of 4°C/min to 750°C. The  $T_g$  of these polymers were determined by DSC on a Perkin Elmer DSC-7 instrument. The melting point of indium and spectral grade *n*-hexane were utilized to calibrate the DSC.

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

Tetrahydrofuran was distilled immediately prior to use from a deep blue solution of sodium benzophenone ketyl. Palladium on carbon (Pd/C 10%) and Raney nickel were purchased from Aldrich. All reactions were conducted in flame-dried glassware under an atmosphere of argon.

**Poly(1-methyl-1-phenyl-1-sila-cis-pent-3-ene)(I)**,  $M_w/M_n = 126,400/62,400$ , was synthesized by the anionic ring opening polymerization of 1-methyl-1-phenyl-1-silacyclopent-3-ene (7,8). It was stored in a refrigerator.

**Poly(1-methyl-1-phenyl-1-silapentane)(II)** was prepared by hydrogenation of I (0.5 g) in THF (35 mL) over Pd/C (0.37 g) in a Parr pressure reactor (600 cc) equipped with a mechanical stirrer. The mixture was stirred for 72 h under 800 psi of hydrogen. The catalyst was removed by filtration through a pad of Celite and the solvent was evaporated under reduced pressure. The polymer was dissolved in a minimum amount of THF and was precipitated by addition of methanol. The process was repeated twice. The polymer was dried under vacuum for 24 h at 80°C. In this way, 0.475 g, 95% yield of II,  $M_w/M_n = 14,100/8,400$ ,  $T_g = -10.4$  °C, was obtained. This polymer has spectral properties which are identical to those of II previously prepared by reduction of I with diimide (10).  $^1\text{H NMR}\delta$ : 0.212(s, 3H), 0.72(br.s, 4H), 1.29(br.s, 4H), 7.34(br.s, 3H), 7.49(br.s, 2H).  $^{13}\text{C NMR}\delta$ : -5.09, 14.05, 28.10, 127.63, 128.62, 133.79, 138.92.  $^{29}\text{Si NMR}\delta$ : -2.14. Anal. Calcd. for  $\text{C}_{11}\text{H}_{16}\text{Si}$ : C, 74.45; H, 9.75. Found: C, 73.72; H, 9.74.

**Block-copoly(1-methyl-1-phenyl-1-sila-cis-pent-3-ene/1-methyl-1-phenyl-silapentane) (60:40) (Block-III-60:40)** was prepared by reaction of I (0.5 g) and Pd/C (0.17 g) in THF (35 mL) under 800 psi of hydrogen for 72 h. After work-up, 0.47 g, 93% yield of polymer,  $M_w/M_n = 65,900/38,200$ ,  $T_g = -11.2$  °C was obtained.  $^1\text{H NMR}\delta$ : 0.21(s, 1.2H), 0.24(s, 1.8H), 0.72(br.m, 1.6H), 1.30(br.m, 1.6H), 1.62(br.m, 2.4H), 5.31(br.m, 1.2H), 7.34(br.m, 3H), 7.47(br.m, 2H).  $^{13}\text{C NMR}\delta$ : -5.40, -5.15, 14.02, 15.35, 27.85, 123.36, 127.65, 128.64, 128.97, 133.82, 133.89, 137.93, 138.96.  $^{29}\text{Si NMR}\delta$ : -4.34, -3.14, -2.25.

**Block-III-40:60** was prepared by the reaction of I (0.5 g) and Pd/C (0.17 g) in THF (35 mL) under 800 psi of hydrogen for 96 h as above. After work-up, 0.47 g, 93% yield of polymer,  $M_w/M_n = 59,700/20,100$  was obtained.  $^1\text{H NMR}\delta$ : 0.20 (s, 1.8H), 0.23(s, 1.2H), 0.71(br.m, 2.4H), 1.29(br.m, 2.4H), 1.60(br.m, 1.6H), 5.30(br.m, 0.8H), 7.32(br.m, 3H), 7.45(br.m, 2H).  $^{13}\text{C NMR}\delta$ : -5.38, -5.26, -5.13, 14.04, 15.37, 27.84, 123.38, 127.63, 128.62, 128.96, 133.77, 133.81, 137.91, 138.95.  $^{29}\text{Si NMR}\delta$ : -4.29, -3.14, -2.21.

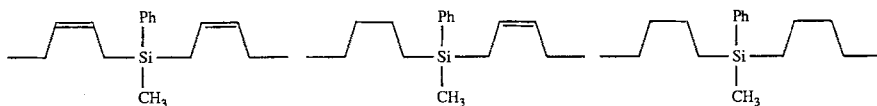
**Block-III-90:10** was prepared by the reaction of I (0.5 g) and Pd/C (57 mg) in THF (35 mL) under 800 psi of hydrogen for 72 h as above. After work-up, 0.48 g, 94% yield of polymer,  $M_w/M_n = 90,200/58,900$  was obtained.  $^1\text{H NMR}\delta$ : 0.22 (s, 0.3H), 0.25(s, 2.7H), 0.74(br.m, 0.4H), 1.32(br.m, 0.4H), 1.64(br.m, 3.6H), 5.32(br.m, 1.8H), 7.35 (br.m, 3H), 7.50(br.m, 2H).  $^{13}\text{C NMR}\delta$ : -5.30, -5.08, 14.14, 15.47, 27.86, 123.47, 127.68, 128.64, 128.97, 133.53, 133.84, 138.01, 139.03.  $^{29}\text{Si NMR}\delta$ : -4.29, -2.21.

**Random-copoly(1-methyl-1-phenyl-1-sila-cis-pent-3-ene/1-methyl-1-phenyl-1-**

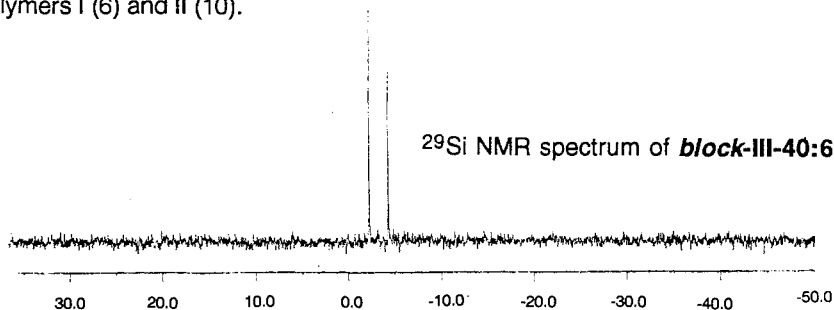
**silapentane/1-cyclohexyl-1-methyl-1-sila-*cis*-pent-3-ene/1-cyclohexyl-1-methyl-1-silapentane) (*Random-IV*)** was prepared by the reaction of I (0.5 g) and Raney Ni (0.17 g) in THF (35 mL) under 1400 psi of hydrogen for 72 h as above. After work-up, 0.45 g, 91% yield of polymer,  $M_w/M_n = 101,500/70,700$ , was obtained. The final copolymer had thirty-six percent saturated units.  $^1\text{H NMR}_\delta$ : -0.13(br.m, 0.6H), 0.17-0.23(br.m, 2.4H), 0.47(br.m, 1.0H), 0.67(br.m, 1.3H), 1.20-1.27(br.m, 3.1H), 1.53-1.70(br.m, 4.6H), 5.26(br.m, 1.3H), 7.27-7.46(br.m, 3.9H).  $^{13}\text{C NMR}_\delta$ : -6.86, -5.30, -5.19, -5.08, 9.79, 12.37, 13.92, 14.14, 15.10, 15.46, 15.69, 25.23, 27.21, 27.88, 27.96, 28.17, 28.42, 123.20, 123.47, 123.73, 127.69, 128.65, 128.82, 128.98, 133.85, 133.93, 138.02, 138.50, 139.04.  $^{29}\text{Si NMR}_\delta$ : -4.29, -3.14, -2.21, 3.21, 7.32.

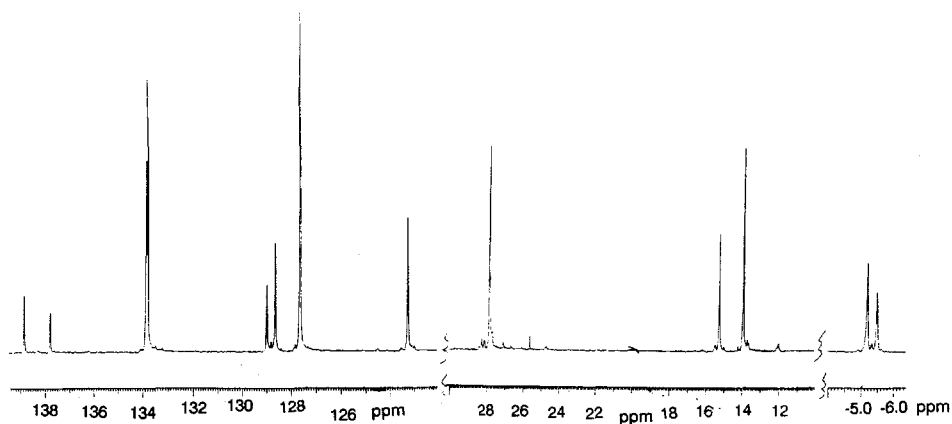
### Results and Discussion

Our interest in the catalytic hydrogen of I was stimulated by our observation that I undergoes rapid degradation in the presence of strong acids. This probably occurs by cleavage of the allylic Si-C bonds of I. The Si-C bonds of monomeric allylsilanes are well known to be susceptible to cleavage by Brønsted acids (11). We hopes that the reduction of the C-C double bonds of I would improve the stability of I towards acids. This approach to increase unsaturated polymer stability has been previously utilized. For example, partially (90%) hydrogenated polybutadiene has increased resistance to ozone (6). Unfortunately, attempts to hydrogenate I over Pt/C or Pd/BaSO<sub>4</sub> resulted in extensive polymer degradation. We believe this results from the acidic nature of the platinum catalysts. Hydrogenation of I over 10% Pd/C gave low molecular weight II. Polymer degradation during catalytic hydrogenation has been previously observed (5). Attempts to catalytically hydrogenate I to II while minimizing polymer degradation by use of less catalyst were unsuccessful. Rather partially hydrogenation of I over 5% or 2% Pd/C gave *block-III*. The block nature of this material is shown by  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectra. Thus only two intense  $^{13}\text{C}$  NMR signals due to methyl carbons are observed. The one at -5.40 ppm is due to methylphenylsilylene units which have 1,4-*cis*-but-2-enylene units (unsaturated units on either side, while the one at -5.15 ppm is due to methylphenylsilylene units which have 1,4-butanylene units (saturated units) on either side. Only a very small peak at -5.26 ppm due to methylphenylsilylene units with an unsaturated units on one side and a saturated unit on the other side is detected.



Similarly, only two intense  $^{29}\text{Si}$  NMR signals are observed. The peak at -4.34 ppm is due to methylphenylsilylene units with unsaturated units on either side, while the signal at -2.25 ppm is due to methylphenylsilylene units with saturated units on either side. Only a very small peak at -3.14 ppm due to methylphenylsilylene units which have an unsaturated unit on one side and a saturated unit on the other side is observed. These NMR assignments are consistent with the NMR spectra of homopolymers I (6) and II (10).





$^{13}\text{C}$  NMR spectrum of **block-III-40:60**.

On the other hand, hydrogenation of I over Raney-Ni at 1400 psi results in random partial (35%) hydrogenation of the C-C double bonds of I. Unfortunately, reduction of the phenyl groups of I is competitive with reduction of the C-C double bonds of I. The  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectra of *random-IV* are sensitive to dyad microstructures. Four signals due to methyl carbons are observed. The one at -6.86 ppm is due to methylcyclohexylsilylene units. The signals at -5.38, -5.26 and -5.13 ppm are assigned to methylphenylsilylene units as above. Similarly, three signals due to methylphenylsilylene units are detected in the  $^{29}\text{Si}$  NMR at -4.29, -3.14 and -2.21 ppm. These are also assigned on the basis of the dyad analysis above.

There is one previous closely related report on partial hydrogenation of *cis*-polyisoprene over Pd/C to yield *block*-copoly(2-methyl-1,4-butanylene/*cis*-2-methylbut-2-enylene) (12).

We believe that this type of selective partial hydrogenation over Pd/C results from adsorption of a C-C double bond of I onto an active catalyst site. This is followed by reduction of the C-C double bond. As the saturated unit is desorbed, an adjacent C-C double is apparently adsorbed onto the active site. This process serves to move the active catalyst site down the unsaturated polymer backbone in one direction. When the active site of the catalyst reaches the end of the polymer chain the *block* copolymer is desorbed.

Block copolymers can have two different  $T_g$ 's. However, only a single  $T_g$  is observed for *block-III-60:40* at -11.2° C is observed. This is intermediate between the  $T_g$ 's of I (-14.9° C) and II (-10.5° C). The TGA of II is similar to that of high molecular weight I (8). It is thermally stable to 250° C. Between 250 and 350° C a three percent weight loss occurs. By 450° C catastrophic decomposition occurs.

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