

Synthesis of poly(1-methyl-1-phenyl-1-silapentane) by chemical reduction of poly(1-methyl-1-phenyl-1-sila-*cis*-pent-3-ene with diimide

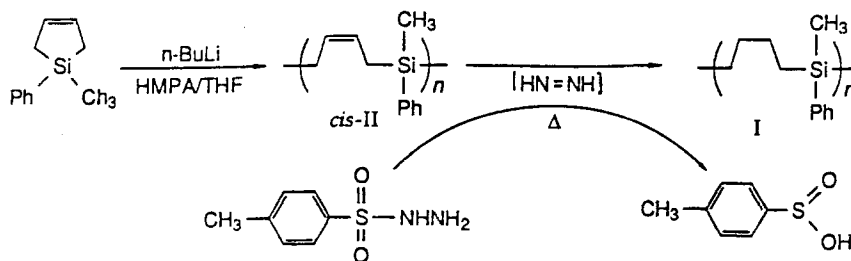
Characterization and chemical modification of poly(1-methyl-1-phenyl-1-silapentane)

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SUMMARY

Poly(1-methyl-1-phenyl-1-silapentane) (I) has been prepared by the chemical reduction of the carbon-carbon double bonds of poly(1-methyl-1-phenyl-1-sila-*cis*-pent-3-ene (*cis*-II) with diimide, which was generated *in-situ* by the thermal decomposition of *p*-toluenesulfonhydrazide in refluxing toluene. At lower temperature (100°C), *cis*-II is isomerized by *p*-toluenesulfonic acid to lower molecular weight poly(1-methyl-1-phenyl-1-sila-*cis* and *trans*-pent-3-ene) (*cis/trans*-II). Protodesilylation of I with trifluoromethanesulfonic acid yields poly(1-methyl-1-trifluoromethanesulfonyl-1-silapentane) (III). The structures of I and *cis/trans*-II have been characterized by ¹H, ¹³C and ²⁹Si NMR, GPC, TGA and elemental analysis. The structure of I has been characterized spectroscopically by ¹H, ¹³C, ¹⁹F and ²⁹Si NMR.



INTRODUCTION

There is considerable interest in chemical modification of polymers.¹⁻⁴ Such reactions often permit the synthesis of polymers which cannot be prepared directly. For example, while 1,1-dimethyl-1-silacyclopent-3-ene undergoes anionic ring opening polymerization to yield high molecular weight poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene),^{5,6} we have been unable to polymerize 1,1-dimethyl-1-silacyclopentane.⁶ Reduction of the carbon-carbon double bonds of *cis*-II by catalytic hydrogenation would produce I. While there are numerous examples of modification of unsaturated polymers by catalytic hydrogenation,^{1,7,8} attempts to catalytic hydrogenation of *cis*-II over a variety of heterogeneous and homogeneous catalysts [Pt/C, Pd/C, Pd/BaSO₄, Raney Ni and (Ph₃P)₃RhCl] gave only very low molecular weight I.

Our interest in this reaction originated from our observations that *cis*-II undergoes rapid degradation in the presence of strong acids. This probably occurs by cleavage of the allylic Si-C bonds

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of *cis*-II. In this regard, the Si-C bonds of monomeric allyl silanes are known to be susceptible to cleavage by Bronsted acids.⁹ On this basis, reduction of the carbon-carbon double bonds of *cis*-II should improve the stability of *cis*-II to acid. Saturated derivatives of II have been prepared by addition of both dichlorocarbene¹⁰ and difluorocarbene¹¹ to the carbon-carbon double bonds of II.

We were also interested in I due to our expectation that it could be further chemically modified by protodesilylation reactions to yield carbosilane polymers with reactive silyl functional groups and benzene. For example, the phenyl group of phenyltrimethylsilane can be cleaved by trifluoromethanesulfonic acid to yield benzene and trimethylsilyl triflate,^{12,13} a most reactive silylating agents¹⁴ as well as a strong electrophilic catalyst.^{15,16}

EXPERIMENTAL

¹H and ¹³C NMR spectra were obtained on a Bruker AM-360 spectrometer while ²⁹Si NMR spectra were run on an IBM Bruker WP-270-SY spectrometer operating in the Fourier transform mode. ¹³C NMR spectra were run with broad band proton decoupling. Five to ten percent (W/V) solutions in chloroform-*d* were used to obtain ¹H NMR spectra, whereas, fifteen to twenty percent solutions were utilized for ¹³C, ¹⁹F and ²⁹Si NMR spectra. ¹³C NMR spectra were run with broad band proton decoupling. Chloroform was used as an internal standard for ¹H and ¹³C NMR spectra. ¹⁹F NMR spectra were externally referenced to CCl₃F. A heteronuclear gated decoupling pulse sequence (NONOE) with a pulse delay of 15 sec was utilized to obtain ²⁹Si NMR spectra.¹⁷ These were externally referenced to TMS. IR spectra of neat films on NaCl plates were recorded on an IBM FT-IR spectrometer.

GPC analysis of the molecular weight distribution of the polymers was performed on 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 Ultrastaygel linear gel column packed with less than 10_μm particles of mixed pore size crosslinked styrene divinyl benzene copolymer, maintained at 20°C was utilized for the analysis. 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; 114,000; 47,500; 18,700 and 5,120, whose M_w/M_n are less than 1.09.

TGA analysis of the polymers was carried out on a Perkin-Elmer TGS-2 instrument at a nitrogen flow rate of 40 cc/min. The temperature program for the analysis was 50°C for 10 min followed by an increase in temperature of 4°C/min to 750°C.

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

Toluene was distilled from a deep blue solution of sodium benzophenone ketyl immediately prior to use. All reactions were carried out under an atmosphere of nitrogen in flame dried glassware.

1-Methyl-1-phenyl-1-silacyclopent-3-ene (IV)

IV was prepared by the dissolving metal reaction of 1,3-butadiene, methylphenyldichlorosilane and magnesium in THF. It had properties in agreement with literature values.¹⁸

Poly(1-methyl-1-phenyl-1-sila-*cis*-pent-3-ene) (*cis*-II)

II ($M_w/M_n = 229,000/115,000$) was prepared by the anionic ring opening polymerization of IV.^{5,6} It was stored at 0°C under argon.

Poly(1-methyl-1-phenyl-1-silapentane)(I)

In a 250 mL rb flask equipped with a reflux condenser and a Teflon covered magnetic stirring bar were placed toluene (50 mL), *cis*-II (0.87 g, 5 mmol) and *p*-toluenesulfonhydrazide (4.65 g, 25 mmol). The stirred mixture was heated to reflux 12 h. After cooling to rt, ether (50 mL) was added. The combined organic layer was washed with water (2 x 30 mL), dried over anhydrous sodium sulfate, filtered. The solvents were removed by evaporation under reduced pressure. The residue was dissolved in a minimum amount of THF and the polymer was purified by precipitation from methanol. This procedure was repeated. The polymer was dried under vacuum. In this way, 0.74 g, 85% yield of I with

$M_w/M_n = 82,000/48,700$ was obtained. $^1\text{H NMR}$: 0.186(s,3H), 0.69(br.s,4H), 1.275(br.s,4H), 7.32-(br.s,3H), 7.44(br.s,2H). $^{13}\text{C NMR}$: -5.24, 14.06, 27.82, 127.58, 128.61, 133.76, 138.83. $^{29}\text{Si NMR}$: -2.14. Elemental anal. calcd. for $\text{C}_{11}\text{H}_{16}\text{Si}$: C, 74.45; H, 9.75. Found: C, 73.73; H, 9.74.

Copoly(1-methyl-1-phenyl-1-sila-*cis* and *trans*-pent-3-ene)(*cis/trans*-II)

This isomerization was carried out as above, expect that the reaction mixture was only heated to 100°C for 2 h. After work-up, 0.80 g, 92% yield of polymer with $M_w/M_n = 77,000/30,100$ was obtained. $^1\text{H NMR}$: 0.128(s,0.8H), 0.191(s,2.2H), 1.58(br.s,4H), 5.176(br.s,0.5H), 5.264(br.s,1.5H), 7.30-(br.s,3H), 7.43(br.s,2H). $^{13}\text{C NMR}$: -5.66, -5.52, 15.21, 19.91, 123.00, 123.22, 124.47, 127.60, 127.77, 128.88, 128.94, 133.81, 137.59, 137.74. $^{29}\text{Si NMR}$: -5.35, -4.76, -4.24. IR: 3060, 2950, 2918, 2880, 1628, 1430, 1376, 1248, 1145, 1112, 1022, 870, 810, 730, 700 cm^{-1} .

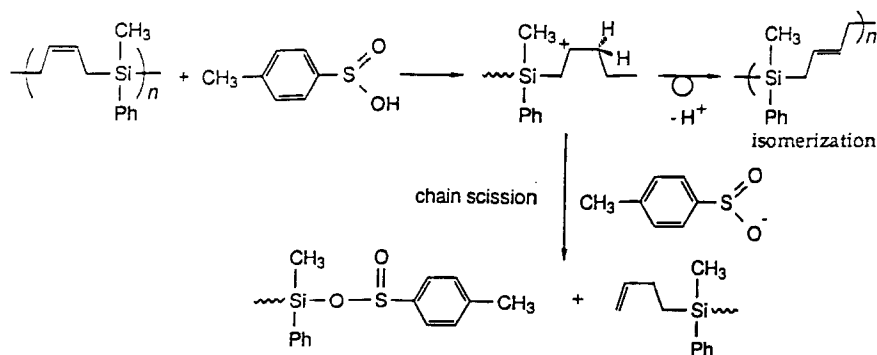
Poly(1-methyl-1-trifluoromethanesulfonyl-1-silapentane)(III)

I (400 mg, 2.3 mmol) and methylene chloride (50 mL) were placed in a 100 mL three neck round bottom flask equipped with a Teflon covered magnetic stirring bar. The flask and its contents were cooled to -25°C and trifluoromethanesulfonic acid (540 mg, 3.4 mmol) was added dropwise over 5 min. The reaction mixture was stirred for 2 h at rt. The solvent was removed by evaporation under a stream of nitrogen. $^1\text{H NMR}$: 0.46(s,3H), 0.91(br.s,4H), 1.45 (br.s,4H). $^{13}\text{C NMR}$: -3.41, 14.37, 25.19, 118.26 (q, $J = 315.4$ Hz) $^{29}\text{Si NMR}$: 45.42. $^{19}\text{F NMR}$: -77.36.

Results and Discussion

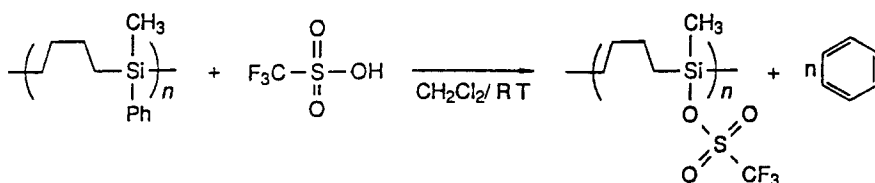
We should like to report the chemical reduction of *cis*-II by diimide, generated by pyrolysis of *p*-toluenesulfonylhydrazide in refluxing toluene, to yield I. Diimide must be generated *in-situ* due to its facile disproportionation to nitrogen and hydrazine. Diimide has been generated by oxidation of hydrazine,^{20,21} pyrolysis of *p*-toluenesulfonylhydrazide,²² decomposition of azodicarboxylic acid²³ or thermolysis of the Diels-Alder adduct of diimide and anthracene.²⁴ Attempts to achieve diimide reduction of *cis*-II by *in-situ* oxidation of hydrazine failed. This is probably due to the low solubility of hydrazine in solvents in which *cis*-II is soluble.

The *cis/trans* isomerization of *cis*-II which is observed on treatment with *p*-toluenesulfonylhydrazide at 100°C is probably results from small amounts of *p*-toluenesulfonic acid formed by the thermolysis of *p*-toluenesulfonylhydrazide. The decrease in molecular weight of *cis/trans*-II results from heterolytic cleavage of allylic Si-C bonds which competes with acid catalyzed *cis/trans* isomerization. One mole of *p*-toluenesulfonic acid is consumed each time the polymer chain is broken.



Finally we have carried out the protodesilylation of I with trifluoromethanesulfonic acid to yield

III. Protodesilylation reactions using trifluoromethanesulfonic acid have been previously utilized to remove phenyl groups from the silyl centers of poly(methylphenylsilane).^{25,26} Trimethylsilyl trifluoromethanesulfonate has been shown to be a useful initiator with appropriate promoters for cationic polymerization of heterocycles such as THF.²⁷



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