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)

Xugao Liao and William P. Weber*

D. P. and K. B. Loker, Hydrocarbon Research Institute, Department of Chemistry, University of Southern California, Los Angeles, CA 90089-1661, USA

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-toluenesulfonylhydrazide 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). Protodesilation of I with trifluoromethanesulfonic acid yields poly(1-methyl-1-trifluoromethanesulfonyl-t-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-silacyclopetane. \(^6\) 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/BaSO\(_4\), Raney Ni and (Ph\(_3\)P)\(_3\)RhCl] 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

*To whom offprint requests should be sent
of cis-II. In this regard, the Si-C bonds of monomeric allyl silanes are known to be susceptible to cleavage by Bronsted acids. 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 dichlorocarbene and difluorocarbene 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 protodesilation reactions to yield carbosilane polymers with reactive silyl functional groups and benzene. For example, the phenyl group of phenyltrimethylsilane can be cleaved by trifluoromethane-sulfonic acid to yield benzene and trimethylsilyl triflate, a most reactive silylating agents as well as a strong electrophilic catalyst.

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. 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 Ultrastyragel linear gel column packed with less than 10μm 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 Mw/Mn 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, methylphenyl dichlorosilane and magnesium in THF. It had properties in agreement with literature values.

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

II (Mw/Mn = 229,000/115,000) was prepared by the anionic ring opening polymerization of IV.

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-toluenesulfonylhydrazide (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