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Anionic ring opening polymerization of 1-phenyl-1-vinyl-1-silacyclopent-3-ene

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

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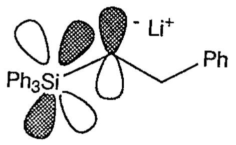
SUMMARY

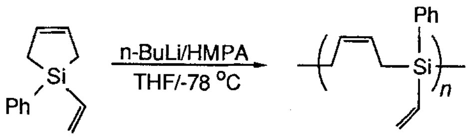
Poly(1-phenyl-1-vinyl-1-sila-*cis*-pent-3-ene) (I) has been prepared by the anionic ring opening polymerization of 1-phenyl-1-vinyl-1-silacyclopent-3-ene (II) co-catalyzed by *n*-butyllithium and hexamethylphosphoramide (HMPA) in THF at -78°C. I has been characterized by ^1H, ^{13}C and ^{29}Si NMR as well as by IR and UV spectroscopy. The molecular weight distribution of I has been determined by gel permeation chromatography (GPC), its thermal stability by thermogravimetric analysis (TGA) and its glass transition temperature (T_g) by differential scanning calorimetry (DSC). Thermal degradation of I in an inert atmosphere gives a twenty-seven percent char yield.

INTRODUCTION

While 1-methyl-1-phenyl-1-silacyclopent-3-ene has been reported to under go anionic ring opening polymerization to yield poly(1-methyl-1-phenyl-1-sila-*cis*-pent-3-ene) (1,2), similar anionic ring opening polymerization of II to yield I was unanticipated. The reason for this is that alkyllithium reagents as well as Grignard reagents are well known to add to the carbon-carbon double bonds of vinyl silanes to yield carbanions adjacent to the silyl center (3-7). Such *alpha* silyl anions may be stabilized by delocalization of the extra electron density centered in a 2p orbital on carbon into an empty 3d orbital on the adjacent silicon. In fact, trimethylvinylsilane undergoes anionic polymerization catalyzed by *s*-butyllithium (8,9).



Nevertheless, anionic ring opening polymerization of II co-catalyzed by *n*-butyllithium and HMPA proceeds smoothly at -78°C in THF to yield I. I is a particularly interesting since it has three different types of unsaturated functionality in each repeating unit of the polymer: allyl, terminal vinyl as well as aryl silane groups. The terminal vinyl groups in particular are expected to be quite reactive toward addition reactions such as hydrosilation.



II I

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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 recorded on an IBM-Bruker WP-270-SY spectrometer. Five to ten percent weight/volume (w/v) solutions of polymer in chloroform-*d* were used to measure ^{1}H NMR spectra, whereas fifteen to twenty percent solutions were utilized to run ^{13}C and ^{29}Si NMR spectra. ^{13}C NMR spectra were run with broad band proton decoupling. A heteronuclear gated decoupling pulse sequence (NONOE) with a delay of 15 sec was used to obtain ^{29}Si NMR spectra (10). Chloroform was used as an internal reference standard for ^{1}H and ^{13}C NMR spectra. ^{29}Si NMR spectra were externally referenced to TMS. IR spectra were taken of neat films between NaCl plates using an IBM FT IR/30S spectrometer. UV spectra of ether solutions of I or II were recorded on a Shimadzu UV-260 ultraviolet visible spectrometer.

GPC analysis of the molecular weight distribution of I was performed on a Water systems comprised of a U6K injector system, a 510 solvent pump, a R401 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 m particles of mixed pore size crosslinked styrene-divinylbenzene copolymers maintained at 20°C was used for the analysis. The eluting solvent was HPLC grade THF at a flow rate of 0.6 mL/min. The retention times were calibrated against known monodisperse polystyrene standards: M_p 612,000; 114,200; 47,500; 18,700 and 5,120 having M_w/M_n less than 1.09.

TGA of I 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 of 4°C/min to 750°C. The T_g of I was determined by 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.

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

All reactions were conducted in flame dried glassware under an atmosphere of argon. THF was purified by distillation from sodium benzophenone ketyl immediately prior to use. HMPA was distilled from calcium hydride and was stored over 4A° molecular sieves prior to use.

1-Phenyl-1-vinyl-1-silacyclopent-3-ene (II)

II was prepared by the reaction of phenylvinyldichlorosilane (Petrarch Systems Inc), 1,3-butadiene and magnesium in THF. It had spectral properties in agreement with literature values (11,12). ^{1}H NMRδ: 1.70 (s, 4H), 5.92 (dd, 1H, J = 20 and 3.8 Hz), 6.02 (s, 2H), 6.17 (dd, 1H, J = 14.7 and 3.8 Hz), 6.46 (dd, 1H, J = 20 and 14.7 Hz), 7.40 (m, 3H), 7.62 (m, 2H). ^{13}C NMRδ : 16.09, 127.87, 129.38, 130.84, 134.26, 134.62, 134.75, 136.00. ^{29}Si NMRδ: 4.69.

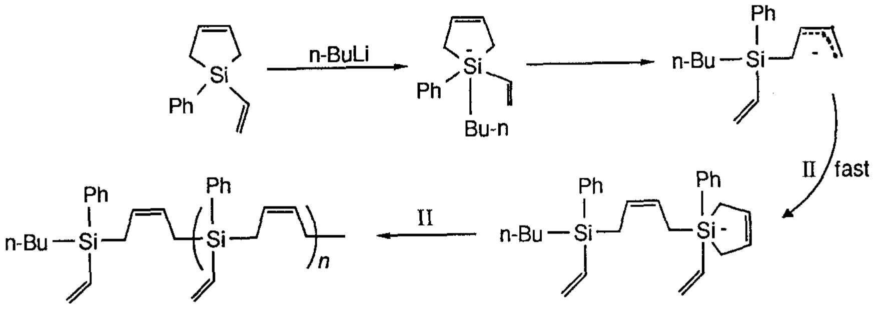
Poly(1-phenyl-1-vinyl-1-sila-*cis*-pent-3-ene) (I)

In a 100 mL round bottom flask equipped with a Teflon covered magnetic stirring bar and a rubber septum was placed II (1.00 g, 5.4 mmol), THF (40 mL) and HMPA (40 µL). The mixture was cooled to -78°C and a hexane solution of *n*-butyllithium (80 µL, 2.5 M, 0.2 mmol) was added via a syringe. The reaction mixture was stirred -78°C for 1 h. A saturated solution of aqueous ammonium chloride (15 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, 0.80 g, 80% yield of I, M_w/M_n = 10,400/6,800 was obtained. T_g = -19.2°C. ^{1}H NMRδ: 0.89 (br.s, 0.16H), 1.34 (br.s, 0.16H), 1.51 (br.s, 0.15H), 1.66 (d, 4H, J = 5.9 Hz), 5.30 (t, 2H, J = 5.5 Hz), 5.71 (dd, 1H, J = 20 and 4.5 Hz), 6.04 (dd, 1H, J = 14.7 Hz and 4.7 Hz), 6.19(dd, 1 H, J = 20 and 14.7 Hz), 7.34 (m, 3H), 7.46 (m, 2H). ^{13}C NMRδ: 13.78, 122.84, 123.27, 127.64, 129.16, 134.50, 134.57, 134.80, 136.08. ^{29}Si NMRδ: -11.05, -11.07, -13.24. IRν: 3069, 3051, 3020, 2968, 2945, 2916, 2890, 1609, 1592, 1429, 1404, 1235, 1204, 1172, 1115, 1100, 1007, 956, 945, 878, 817, 802, 726, 698, 638, 618 cm^{-1}. UV λ_{max} nm (ε) : 216 (18,500). Elemental Anal. Calcd. for $C_{12}H_{14}Si$: C, 77.39; H, 7.58. Found: C, 76.53; H, 7.83.

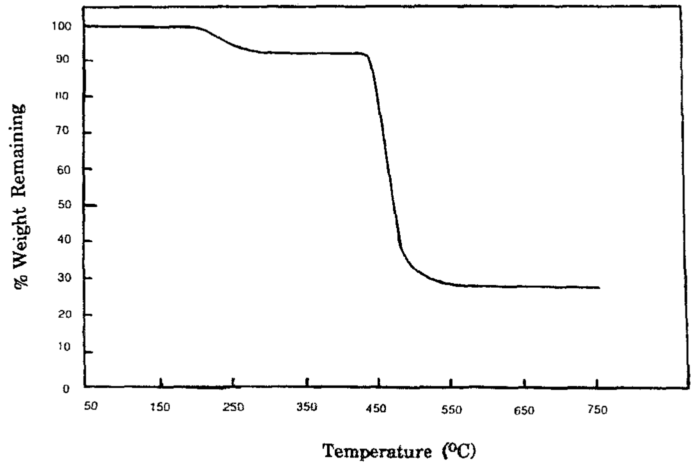
RESULTS AND DISCUSSION

II undergoes anionic ring opening polymerization on treatment with a catalytic amount of *n*-butyllithium and HMPA in THF at low temperature to yield I. The molecular weight of I is much lower than that of poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene) M_w/M_n = 1,120,000/744,000 or poly(1-methyl-1-phenyl-1-sila-*cis*-pent-3-ene) M_w/M_n = 349,000/171,00 but comparable to the molecular weight observed for poly(1,1-diphenyl-1-sila-*cis*-pent-3-ene) (1,2). It may be that low molecular weight polymers are observed when two of the Si-C bonds of the silacyclopent-3-ene ring involve sp^2 hybridized carbons atoms. Experiments to increase the molecular weight of I are currently in progress.

The polymerization of II to yield I is unexpected due to the well known ability of alkyllithium reagents to add to carbon-carbon double bonds of vinyl silanes to yield *alpha* silyl carbanions as discussed in the introduction. We believe that the polymerization of II proceeds by a mechanism analogous to that previously proposed for the anionic ring opening polymerization of 1,1-dimethyl-1-silacyclopent-3-ene and related systems. Apparently, nucleophilic attack of the organolithium reagent at the silyl center of II to yield a pentacoordinate anion is more favorable than nucleophilic addition across the vinyl silane carbon-carbon double bond. The presence of *n*-butyl groups associated with initiation is observed in the ^{1}H and ^{13}C NMR as small peaks.



The thermal stability of I in an inert atmosphere has been determined by TGA. I is thermally stable to 200°C. Between 200 and 250°C and eight percent weight loss is observed. No further weight loss occurs until 440°C. Between 440 and 500°C an additional sixty-five percent weight loss rapidly occurs. No further weight loss up to 750°C. A black residue amounting to twenty-seven percent of the initial sample weight is found.



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