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Synthesis and characterization of poly([3,4,*c*]furano-1-germa-1,1-dimethylcyclopentane)

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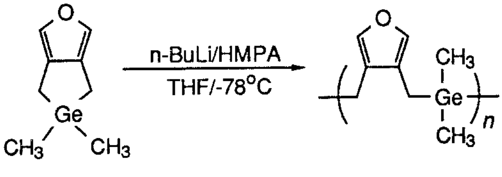
SUMMARY

Poly([3,4, *c*]furano-1-germa-1,1-dimethylcyclopentane) (I) has been prepared by the anionic ring opening polymerization of 3-oxa-7,7-dimethyl-7-germabicyclo[3.3.0]- octa-1,4-diene (II) co-catalyzed by *n*-butyllithium and HMPA in THF. I has been characterized by ^1H, ^{13}C NMR, IR and UV spectroscopy as well as by elemental analysis. The molecular weight distribution of I has been determined by gel permeation chromatography (GPC), its thermal stability established by thermogravimetric analysis (TGA) and its glass transition temperature (T_g) measured by differential scanning calorimetry (DSC).



II I

INTRODUCTION

While there has been extensive work on silicone polymers, polysilanes and polycarbosilanes, few studies have been reported on polygermoxanes, polygermanes and polycarbogermanes. Despite this limited research, interesting properties and novel synthetic routes to these germanium containing polymers have been reported. For example, polygermanes absorb light in the ultraviolet, are thermochromic and undergo photobleaching (1,2). Polygermoxanes have been prepared by hydrolysis of dialkyldichlorogermanes (3) while ring opening polymerization of octamethylcyclotetragermoxane with dimethyldichlorogermane yields α, ω-dichloro poly(dimethylgermoxanes) (4). Recently, novel polymers with Ge-O backbones have been formed by oxidation-reduction copolymerization of divalent germylenes with benzoquinones (5). Saturated polycarbogermanes have been prepared by the thermal or chloroplatinic acid catalyzed ring opening polymerization of dialkylgermacyclobutanes (6,7), as

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well as by the hydrogermylation reaction of dibutylgermane with diethyldivinylgermane catalyzed by benzoyl peroxide (8). Unsaturated polycarbogermanes have recently been prepared by the anionic ring opening polymerization of 1,1-dimethyl-1-germacyclopent-3-ene (9) and 1-germa-1,1-dimethyl[3,4,*c*]thienocyclopentane (III) (10).

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-360 spectrometer. Five percent weight/volume solutions of the polymer in chloroform-*d* were used to determine ^{1}H and ^{13}C NMR spectra. ^{13}C NMR spectra were run with broad band proton decoupling. Chloroform was used as an internal reference for ^{1}H and ^{13}C NMR spectra. IR spectra were recorded on an IBM FT-IR spectrometer of neat films on NaCl plates. UV spectra were recorded on a Shimadzu UV-260 ultraviolet visible spectrometer of solutions prepared in diethyl ether. GPC analysis of the molecular weight distribution of the polymer was performed on a Waters system. This was comprised of a U6K injector, a 510 pump, a R401 differential refractometer detector and a Maxima 820 controller. A 7.8 mm x 30 cm Waters Ultrastyragel 10 m particle size, mixed pore size, crosslinked polystyrene gel column maintained at room temperature was used for the separation. The eluting solvent was reagent THF at a flow rate of 0.6 mL/min. The retention times were calibrated against known monodisperse polystyrene standards: M_p 612,000; 114,000; 47,500; 18,700 and 5,120 whose M_w/M_n are less than 1.09.

TGA of I was determined 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 system. Indium (mp 165°C) and spectral quality *n*-hexane (mp -95°C) were used to calibrate the DSC. The initial temperature for the analysis was -70°C. After two min at -70°C, the temperature was increased at a rate of 20°C/min to 150°C. The melting point of I was determined on an Electrothermal melting point apparatus.

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

Tetrahydrofuran (THF) was distilled immediately prior to use from sodium benzophenone ketyl. Hexamethylphosphoramide (HMPA) was distilled from calcium hydride and stored over 4A$^{\circ}$ molecular sieves. All reactions were carried out under an atmosphere of argon in flame dried glassware.

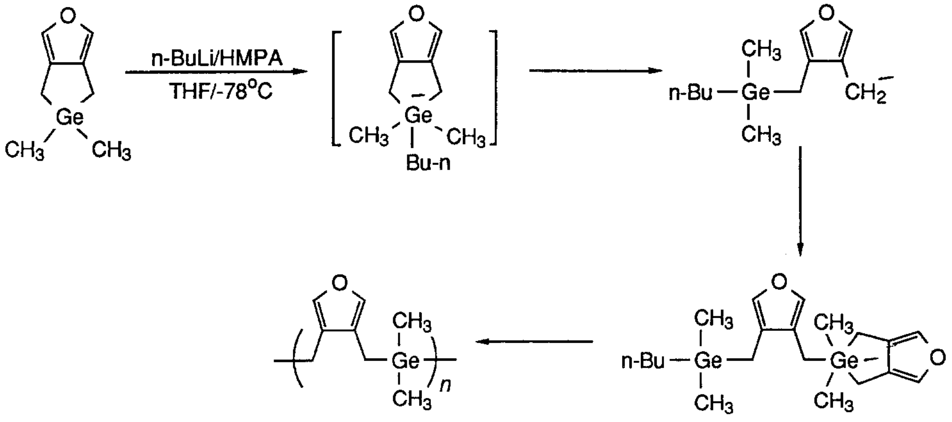
3-Oxa-7,7-dimethyl-7-germabicyclo[3.3.0]octa-1,4-diene (II) was prepared by the oxidation of 3-oxa-7,7-dimethyl-7-germabicyclo-[3.3.0]oct-1(5)-ene with 2,3-dichloro-5,6-dicyanoquinone (DDQ) following the method of Mazerolles (11). Final purification was carried out by column chromatography on silica gel with pentane. II is a clear liquid. ^{13}C NMR δ: -1.28, 9.75, 129.61, 136.55. IR ν: 2918, 1411, 1266, 1253, 1148, 1091, 1041, 1028, 800, 590, 578 cm^{-1}. UV λ_{max} nm (ε) 225.0 (3480), 256.0(451).

Synthesis of Poly([3,4, *c*]furano-1-germa-1,1-dimethylpentane) (I)

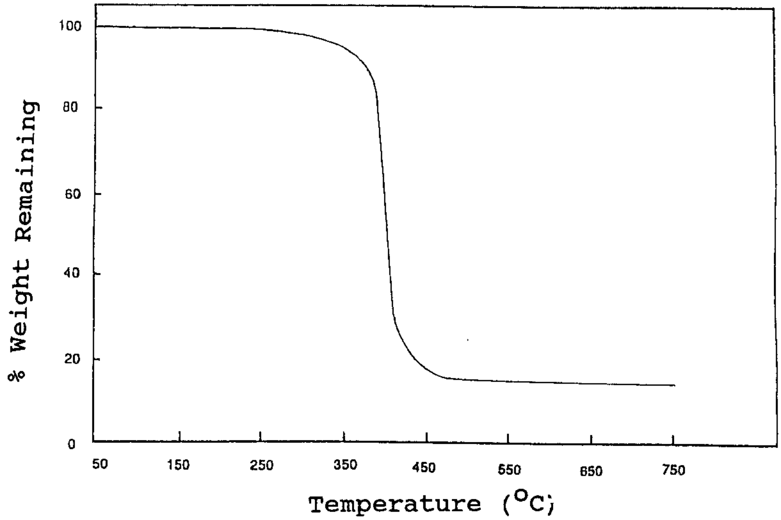
In a 100 mL round bottom flask equipped with a Teflon covered magnetic stirring bar and a rubber septum was placed freshly purified II (300 mg, 1.53 mmol), THF (25mL) and HMPA(10 L). The mixture was cooled to -78°C and a hexane solution of *n*-butyllithium (0.05 mL, 2.5 M, 0.125 mmol) was added via a syringe. The reaction mixture was stirred at -78°C for 30 min. A saturated solution of aqueous ammonium chloride (10 mL) was added. The organic layer was separated, washed with water (2x10 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, 250 mg, 83% yield of I, mp 68-70°C, M_w/M_n = 14,300/8,100 was obtained. ^{1}H NMR δ : 0.08(s,6H), 1.74(s,4H), 6.99(s,2H). ^{13}C NMR δ : -3.64, 9.73, 122.28, 137.60. IR ν : 3134, 2972, 2908, 1759, 1661, 1597, 1407, 1370, 1282, 1237, 1187, 1152, 1094, 1047, 879, 810, 778, 660, 602, 589 cm^{-1}. UV λ_{max} nm (ε): 223.6 (3,841). Elemental Anal. Calcd. for $C_8H_{12}GeO$: C, 48.61; H, 6.15. Found: C, 47.02; H, 6.00.

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. A significant problem in the preparation of I, is that II is not very stable. For this reason, II must be purified by column chromatography immediately prior to polymerization. While we have previously reported the anionic ring opening polymerization of 3,4-benzo-1,1-dimethyl-1-silacyclopentane (IV) (12), the polymerization of II is unexpected due to the well known tendency of furans to undergo hydrogen-metal exchange (metallation) at the carbons adjacent to the oxygen atom (12,13). We believe that the polymerization of II proceeds by a similar mechanism to that proposed for the polymerization of IV. The observation that the molecular weight distribution for I, M_w/M_n = 14,300/8,100 = 1.8, is approximately that expected for a most probable distribution is consistent with this proposal.



The melting point (mp 68-70°C) and glass transition temperature (-28°C) of I are lower than those of either poly(3,4-benzo-1,1,-dimethyl-1-silapentane) (V) mp 163-165°C, T_g 75°C (12) or III mp 105-107°C, T_g -11.0°C (10). The thermal stability of I has been determined by TGA (Figure 1). I is thermally stable to 370°C. Thus, I is more thermally stable than III (10) but less stable than V (12). Finally, the ultraviolet spectrum of I and II are quite similar. Apparently, there is no strong interaction of neighboring aromatic furan rings through space as was observed for thiophene rings in III (10).



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