

## **Anionic ring opening polymerization of 3,4-benzo-1,1-dimethyl-1-silacyclopentene**

### **Properties of poly(3,4-benzo-1,1-dimethyl-1-silapentene)**

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### **SUMMARY**

Treatment of 3,4-benzo-1,1-dimethyl-1-silacyclopentene with a catalytic amount of *n*-butyllithium and HMPA in THF yields poly(3,4-benzo-1,1-dimethyl-1-silapentene). This polymer has the highest melting temperature, glass transition temperature and thermal stability of any poly(1-silapent-3-ene) yet prepared.

### **INTRODUCTION**

There is considerable interest in ring opening polymerizations.<sup>1</sup> High melting temperature and thermal stability are necessary polymer properties for many applications.<sup>2</sup> Anionic ring opening polymerization of silacyclopent-3-enes is a new reaction which provides access to poly(1-silapent-3-enes).<sup>3</sup> poly(3,4-Benzo-1,1-dimethyl-1-silapentene) is the most thermally stable member of this series of unsaturated silyl substituted polymer yet prepared.

### **EXPERIMENTAL**

<sup>1</sup>H, <sup>13</sup>C and <sup>29</sup>Si NMR spectra were obtained on an IBM-Brucker 270-SY spectrometer operating in the Fourier transform mode. <sup>13</sup>C NMR spectra were run with broad band proton decoupling. A DEPT pulse sequence was used to obtain <sup>29</sup>Si NMR spectra. This was effective since all the silicon atoms have at least two methyl group bonded to them.<sup>4</sup> Identical <sup>29</sup>Si spectra could be obtained by use of a heteronuclear gated decoupling pulse sequence with a pulse delay of 30 sec (NONOE).<sup>5</sup> Ten to fifteen percent solutions in CDCl<sub>3</sub> were used to obtain <sup>13</sup>C and <sup>29</sup>Si spectra. Five percent solutions were used to obtain <sup>1</sup>H NMR spectra. Chloroform or benzene were utilized as an internal standard for <sup>1</sup>H and <sup>13</sup>C NMR spectra. <sup>29</sup>Si NMR spectra were externally referenced to TMS. IR spectra were recorded on a Perkin Elmer PE-281 spectrometer. UV spectra were recorded on a Shimadzu UV-260 UV visible spectrometer. Spectra quality cyclohexane was used to prepare solutions for UV spectroscopy.

Gel permeation chromatographic (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

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pump, a R401 differential refractometer and a Maxima 820 data station. A 7.8 mm x 30 cm Waters Ultrastaygel 10  $\mu\text{m}$  particle size mixed pore size crosslinked polystyrene gel column maintained at 70°C was used for the analysis. The eluting solvent was HPLC grade toluene at a flow rate of 1.0 mL/min. The retention times were calibrated against known monodisperse polystyrene standards:  $M_p$  179,300; 110,000; 20,400 and 1,350 whose  $M_w/M_n$  are less than 1.09.

Thermogravimetric analysis (TGA) of the polymer was carried out on a Perkin-Elmer TGS-2 instrument at a nitrogen flow rate of 40  $\text{cm}^3/\text{min}$ . The temperature program for the analysis was 50°C for 10 min followed by an increase of 5°C/min to 650°C. The glass transition temperature ( $T_g$ ) and the melting point ( $T_m$ ) were determined by differential scanning calorimetry (DSC) on a Perkin Elmer DSC-4 system. The initial temperature for this analysis was 30°C. This was increased at a rate of 20°C/min to 200°C. The melting point was also determined on a Electrothermal melting point apparatus and is uncorrected.

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° molecular sieves. Hexane was distilled from  $\text{LiAlH}_4$ . *n*-Butyl lithium in hexane (2.5 M) and potassium *t*-butoxide were used as received from Aldrich. Dimethyldichlorosilane and hexamethyldisilazane were obtained from Petrarch System. They were purified by fractional distillation.

Preparative GLPC was carried out on a Gow-Mac 550 GC equipped with a 1/4" x 10' stainless steel column packed with 10% SE-30 on Chromosorb W NAW 60/80 mesh. The column was deactivated immediately prior to use by injection of 50  $\mu\text{L}$  of hexamethyldisilazane.

All glassware was dried overnight in an oven at 120°C and was flame dried immediately prior to use. All reactions were conducted under an atmosphere of prepurified argon.

### 3.4-Benzo-1,1-dimethyl-1-silacyclopentene (I)<sup>6</sup>

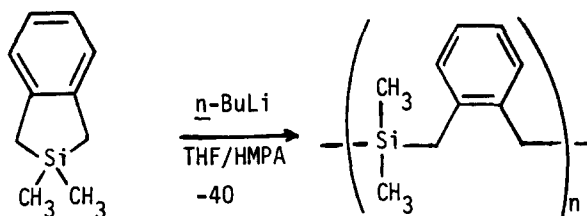
In a 500 mL rb flask equipped with a reflux condenser and a Teflon covered magnetic stirring bar was placed potassium *t*-butoxide (18 g, 0.16 mol), *o*-xylene (8.5 mL, 70 mmol) and 350 mL of hexane. To this mixture was added *n*-butyllithium (63 mL, 0.16 mol). The suspension was refluxed under argon for 1 h and was then allowed to cool to room temperature. The dianion of *o*-xylene was filtered and washed with an additional aliquot of hexane. The red colored dianion was suspended in a 500 mL rb flask containing 400 mL of hexane. Dichlorodimethylsilane (12 mL, 0.09 mol) was added via a syringe to the well stirred suspension. After the color of the dianion had disappeared, the solution was washed with water, dried over anhydrous magnesium sulfate, filtered and the volatile solvents removed by evaporation under reduced pressure. The product was fractionally distilled through a 15 cm vacuum jacketed Vigreux column. A fraction bp 74-75°C/0.4 mm was collected, 7.4 g, 65% yield. Finally purification was by preparative GLPC. <sup>1</sup>H NMR  $\delta$ : 0.19(s,6H), 2.03(s,4H), 7.04(d of d,2H, J = 5.7 and 3.5 Hz) and 7.18(d,2H, J = 5.8 Hz). <sup>13</sup>C NMR  $\delta$ : -2.31, 21.25, 125.54, 129.22, 142.28. <sup>29</sup>Si NMR  $\delta$ : 18.31. IR (neat NaCl plates)  $\nu$ : 3060, 3010, 2950, 2880, 1470, 1450, 1250, 1120, 1070, 830, 740  $\text{cm}^{-1}$ . UV  $\lambda_{\text{max}}$  nm ( $\epsilon$ ): 204(8,600); 214(6,900); 269(890); 276(990).

**poly(3,4-Benzo-1,1-dimethyl-1-silapentene (II))**

In a 100 mL Schlenk flask equipped with a Teflon covered magnetic stirring bar was placed I (1.0 g, 6.2 mmol), THF (15 mL) and five drops of HMPA. The flask was sealed with a rubber septum and was cooled to  $-78^{\circ}\text{C}$ . *n*-Butyllithium (0.5 mL, 1.25 mmol) was slowly added via a syringe. The mixture was stirred at  $-78^{\circ}\text{C}$  for 3 h. The mixture was then allowed to warm to room temperature and 10 mL of saturated aq.  $\text{NH}_4\text{Cl}$  and 50 mL of THF were added. The polymer, suspended in the organic layer, was washed with water. After separation of the layers, the organic solvents were removed by evaporation under reduced pressure. The polymer was washed with ether. In this way, 0.95 g of white crystalline polymer mp  $163\text{--}165^{\circ}\text{C}$  was obtained. By DSC:  $T_m$  was  $167^{\circ}\text{C}$  and  $T_g$  was  $75^{\circ}\text{C}$ . The polymer did not dissolve in THF or ether, but was soluble in warm benzene or warm toluene.  $M_w/M_n = 122,000/35,400$ .  $^1\text{H NMR}$   $\delta$ : 0.011(s,6H), 2.07(s,4H), 6.98(s,4H).  $^{13}\text{C NMR}$   $\delta$ : -2.49, 23.33, 124.92, 129.65, 137.03.  $^{29}\text{Si NMR}$   $\delta$ : 2.78. IR (KBr pellet)  $\nu$ : 3060, 3000, 2950, 2890, 1590, 1470, 1450, 1250, 1210, 1180, 1150, 1050, 850, 830,  $750\text{ cm}^{-1}$ . UV  $\lambda_{\text{max}}$  nm ( $\epsilon$ ) 208(20,000); 230(7,600); 275(1,100); 283(1,100). Elemental Anal. Calcd. for  $\text{C}_{10}\text{H}_{14}\text{Si}$ : C, 74.00; H, 8.69. Found: C, 73.91; H, 8.55.

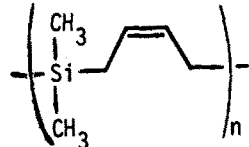
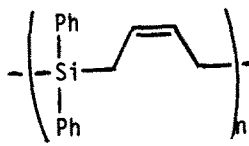
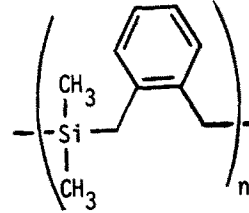
**RESULTS AND DISCUSSION**

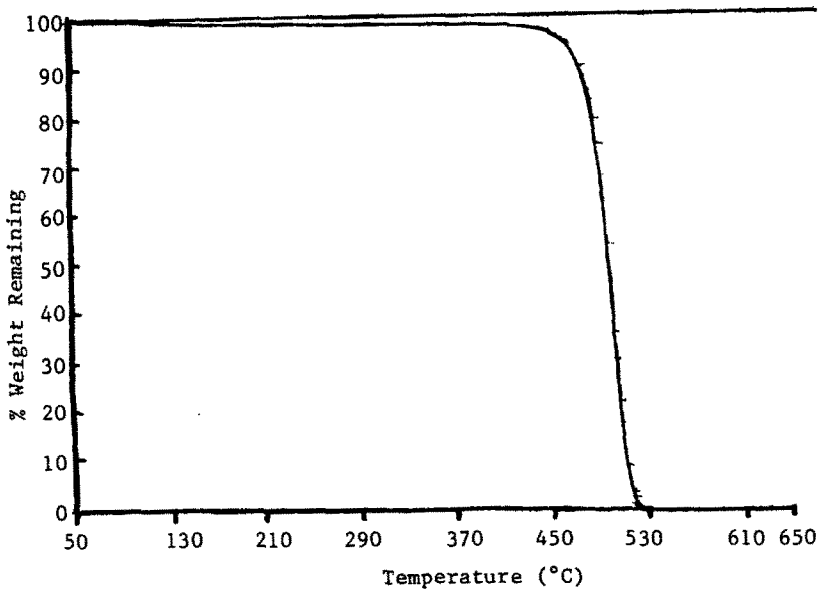
3,4-Benzo-1,1-dimethyl-1-silacyclopentene (I) undergoes anionic ring opening polymerization on treatment with a catalytic amount of *n*-butyllithium and HMPA in THF to yield poly(3,4-dibenzo-1,1-dimethyl-1-silapentene) (II).



Similar anionic ring opening polymerizations of sila- and germa cyclopent-3-enes have been reported.<sup>3</sup> Treatment of I with a potassium mirror in THF at  $-100^{\circ}\text{C}$  results in polymerization by an anion radical process. The structure of this polymer has been assigned on the basis of infrared spectroscopy.<sup>7</sup>  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectroscopy as well as IR, UV, GPC and elemental analysis have been utilized to characterize II. The IR spectra of II and the previously reported polymer are similar.<sup>7</sup> Of importance, the molecular weight of II is reasonably high  $M_w/M_n = 122,000/35,400$ . Further, the  $T_m$  and  $T_g$  of II are the highest so far found for any poly(1-sila-pent-3-ene) (Table 1). In addition, TGA indicates that II is significantly more thermally stable than other poly(1-sila-pent-3-enes). Thus, between  $50$  and  $430^{\circ}\text{C}$  II loses only two percent of its initial weight. Above  $450^{\circ}$  rapid weight loss occurs. By  $520^{\circ}\text{C}$  total weight loss has occurred (Figure 1). By comparison, poly(1,1-diphenyl-1-sila-*cis*-pent-3-ene) undergoes rapid weight loss above  $300^{\circ}\text{C}$  while poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene) undergoes weight loss above  $350^{\circ}\text{C}$ .<sup>3</sup> The relationship of these properties and polymer microstructure is under active investigation.

**Table 1.** Comparison of  $T_m$  and  $T_g$  of poly(1-silyl-pent-3-enes).

	$T_m$	$T_g$
	25°	-64°
	130-136°	18°
	163-165°	75°



**Figure 1.** TGA of Polymer II.

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## **REFERENCES**

1. McGrath, J. E.; "Ring-Opening Polymerization Kinetics, Mechanisms, and Synthesis" ACS Symposium 286, ACS, Washington, D.C. 1985.
2. Jellinek, H. H. G.; "Aspects of Degradation and Stabilization of Polymers," Elsevier Scientific Publishing Inc. Amsterdam, The Netherlands, 1978, p. 573-604.
3. Zhang, X.; Zhou, Q.; Weber, W. P.; Horvath, R. F.; Chan, T.H.; Manuel, G. *Macromolecules*, 1988, 21, 1563.
4. Pegg, D.T.; Doddrell, D. M.; Bendall, M. R. *J. Chem. Phys.*, 1982, 77, 2745.
5. Freeman, R; Hill, H. D. W.; Kaptein, R. *J. Magn. Reson.*, 1972, 7, 327.
6. Bates, R. B.; Ogle, C. A. *J. Org. Chem.*, 1982, 47, 3949.
7. Nametkin, N. S.; Vdovin, V. M.; Finkel'shtein, E. Sh.; Konobeevskii, K.S.; Oppengeim, V. D. *Dokl. Akad. Nauk SSSR*, 1965, 162, 585
8. Zhou, Q.; Weber, W.P.; Manuel, G. *Macromolecules*, in press 1989.

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