Polymer Bulletin 23, 583–587 (1990)

Polymer Bulletin

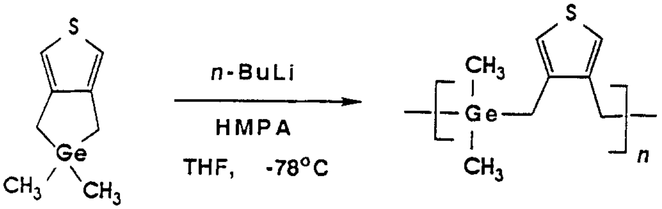
Synthesis and anionic ring opening polymerization of 1-germa-1,1-dimethyl[3,4,*c*]thienocyclopentane

Stephen Q. Zhou[1], William P. Weber[1,*], Pierre Mazerolles[2], and C. Laurent[2]

[1]D.P. and K.B. Loker Hydrocarbon Research Institute, Department of Chemistry,
University of Southern California, Los Angeles, CA 90089-1661, USA
[2]Laboratoire des Organométalliques, U.A. 477, Université Paul Sabatier, 118 route des Narbonne,
F-31062 Toulouse Cedex, France

SUMMARY

1-Germa-1,1-dimethyl[3,4,*c*]thienocyclopentane (I) has been prepared from 3-germa-3,3-dimethyl-7-thiabicyclo[3,3,0]oct-1-ene (II) [1] by oxidation with dichorodicyanoquinone (DDQ). Treatment of I with a catalytic amount of *n*-butyllithium and HMPA in THF yields poly(1-germa-1,1-dimethyl[3,4,*c*]thienopentane) (III).



INTRODUCTION

While there has been extensive work on several types of polymers having silicon in the main chain due to their scientific and industrial importance, [2-5] few studies on polymers containing germanium in the backbone have been reported. Despite this limited research, polygermanes have been observed to have interesting properties. For example, they have been found to be photoactive. They undergo photobleaching [6] as well as to have thermochromic properties. [7] Most recently, germylenes, stable divalent germanium species, have been found to undergo a novel oxidation-reduction copolymerization with benzoquinones. [8] Anionic ring opening polymerization of I yields III, a carbogermanium polymer in which both carbon and germanium atoms make up the polymer backbone. [9]

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were obtained on a Brucker AM-360 spectrometer operating in the Fourier Transform mode. ^{13}C NMR

---

*To whom offprint requests should be sent spectra were run with broad band proton decoupling. Ten to fifteen percent solutions in chloroform-d were used to obtain ^{13}C NMR spectra. Five percent solutions were used to obtain ^{1}H NMR spectra. Chloroform was utilized as an internal standard for ^{1}H and ^{13}C NMR spectra. IR spectra were recorded on a Perkin-Elmer PE-281 spectrometer. Spectra were taken on neat films on NaCl plates. UV spectra were recorded on a Shimadzu UV-260 UV visible spectrometer. Spectra quality cyclohexane or THF was used to prepare solutions for UV spectroscopy. Low resolution mass spectra were taken on a Finnegan MAT Incos 50 GCMS instrument at an ionizing voltage of 70 eV. A 0.25 mm x 30 m fused silica DB-5 capillary column was used as the gas chromatographic inlet of the mass spectrometer. High resolution mass spectra were obtained at the University of California Riverside on a VG-7070 E mass spectrometer. Exact masses were determined by peak matching against known masses of perfluoro kerosene.

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 pump, a R401 differential refractometer and a Maxima 820 data station. A 7.8 mm x 30 cm Waters Ultrastyragel 10 μm particle size mixed pore size crosslinked polystyrene gel column maintained at 25°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 179,000; 110,000; 20,400 and 4,800 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 cm^3/min. The temperature program for the analysis was 50°C for 10 min followed by an increase of 4°C/min to 850°C.

The glass transition temperature (T_g) was determined by differential scanning calorimetry (DSC) on a Perkin-Elmer DSC-7 instrument. Indium and cyclohexane (spectroquality) were used for temperature calibration. The initial temperature for this analysis was -100°C. The temperature was then increased at a rate of 20°C/min to 100°C. An additional run was performed by quenching the sample to -100°C and repeating the temperature scan.

The melting point was determined on an 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 4 A° molecular sieves.

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.

1-Germa-1,1-dimethyl[3,4,*c*]thienocyclopentane (I)

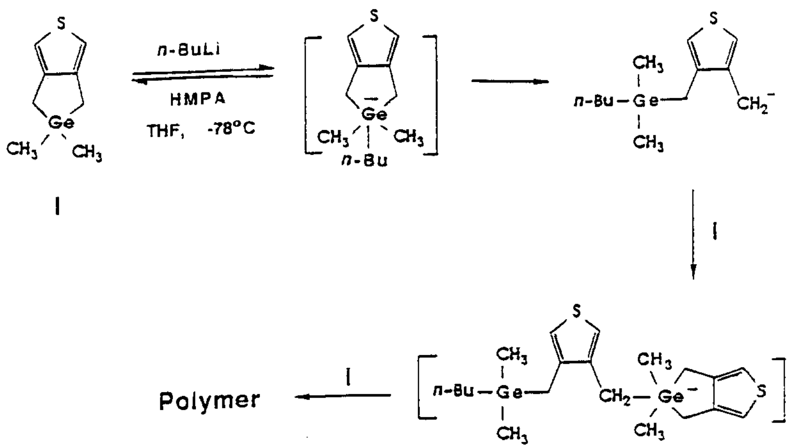
In a two neck 25 mL rb flask equipped with a Teflon covered magnetic stirring bar, a reflux condenser and a rubber septum was placed DDQ (1.51 g, 6.65 mmol) and 10 mL of *p*-dioxane. To this was added dropwise a solution of II (1.43 g, 6.65 mmol) in 2 mL of *p*-dioxane via a syringe. An exothermic reaction occurs which leads to a dark mixture whose color gradually fades to give a pink precipitate. The reaction was heated to reflux for 1 h. It was cooled and pentane (100 mL) was added. The mixture was filtered and the filtrate was washed with water (5 x 100 mL). The organic layer was dried over anhydrous sodium sulfate, filtered and the solvents removed by evaporation under reduced pressure. The residue was distilled. A fraction bp 47°C/0.2 mm, 1.03 g 73% yield was obtained. I has the following properties.: n_D^{20} = 1.5683. ^{1}H NMR δ: 0.46(s,6H), 2.02(s,4H), 6.87(s,2H). ^{13}C NMR δ: -1.27, 15.73, 117.74, 145.99. IR ν: 3090, 2975, 2900, 1405, 1340, 1235, 1160, 1110, 1080, 850, 830, 800(s) cm^{-1}. UV λ_{max} nm (ε) (hexane): 242.5(8,670), 250.8(9700), 258.0(6,900). GC/MS m/e (rel. intensity): 217(2.0), 216(18.0), 215(10.0), 214(79.0), 213(27.0), 212(57.0), 211(4.0), 210(40.0) ($M^{+\cdot}$), 202(2.0), 201(23.0), 200(10.0), 199(84.0), 198(22.0), 197(61.0), 196(4.0), 195(50.0) (M-15$^+$), 173(3.0), 171(12.0), 170(3.0), 169(8.0), 167(4.0), 112(4.0), 111(11.0), 110(39.0), 109(15.0), 93(100.0). High resolution MS m/e calcd. for $^{12}C_8{}^1H_{12}{}^{32}S^{74}Ge$ ($M^{+\cdot}$) 213.98715; found 213.9875. Elemental Anal. Calcd. for $C_8H_{12}SGe$: C, 45.15; H, 5.68. Found: 45.01; H, 5.69.

poly(1-Germa-1,1-dimethyl[3,4,*c*]thienopentane)(III)

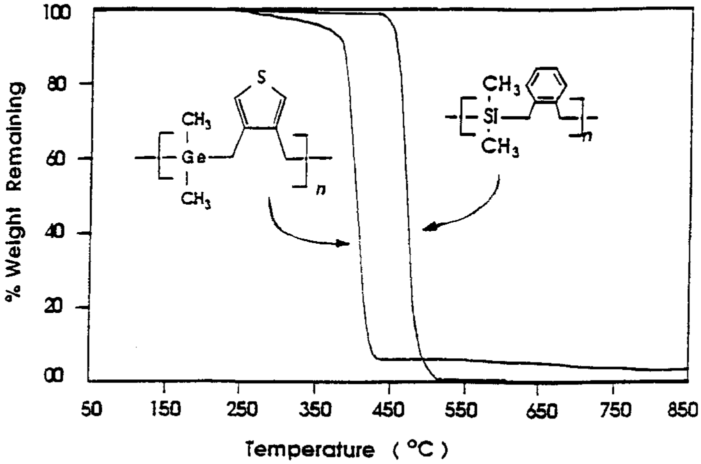
The polymerization of I was carried out in a flame dried 100 mL Schlenk flask equipped with a Teflon covered magnetic stirring bar. I (0.5 g, 2.3 mmol), 10 µL of HMPA and 5 mL of THF were placed in the flask which was cooled to -78°C. To this mixture was added 80 L of 2.5 M *n*-butyllithium in hexane. The mixture became viscous and turned orange color immediately. The mixture was stirred at -78°C for 2 h. Water (10 mL) and ether (50 mL) were added at -78°C to quench the reaction. The polymer is only partially soluble in ether. The polymer, suspended in ether, was washed repeatedly with water. The ether solvent was reduced to 5 mL by evaporation. The polymer was removed by filtration. It was washed several times with cold ether. In this way, 0.48 g, 96% yield of III was obtained. III is a white solid mp 105-107°C. III is soluble in $CHCl_3$ and THF. M_w/M_n = 96,500/47,500. ^{1}H NMR δ: 0.02(s,6H), 1.98(s,4H), 6.57(s,2H). ^{13}C NMR δ: -3.34, 17.19, 117.56, 138.72. IR ν: 3080, 2950, 2900, 1525, 1435, 1400, 1375, 1235, 1140, 1065, 865, 805(s), 780(s) cm^{-1}. UV λ_{max} (ε) (THF): 236.2(3,200), 261.8(4,600), 269.0(3,500), 284.0(1,000). Elemental Anal. Calcd. for $C_8H_{12}SGe$: C, 45.15; H, 5.69. Found: C, 45.12; H, 5.62.

Results and Discussion

I undergoes anionic ring opening polymerization on treatment with a catalytic amount of *n*-butyllithium and HMPA in THF at low temperature to yield III. While we have previously reported the anionic ring opening polymerization of 3,4-benzo-1,1-dimethyl-1-silacyclopentene (IV),[10] the polymerization of I is unexpected. This is due to well known tendency of thiophene rings to undergo hydrogen-metal exchange (metallation) reactions at the carbons adjacent to the sulfur atom.[11] We believe that the polymerization of I proceeds by a similar mechanism to that proposed for the polymerization of IV. The observation of a most probable molecular weight distribution for III, M_w/M_n = 96,500/47,500 = 2.03, is consistent with this proposal.



The melting point (mp 105-107°C) and glass transition temperature (-11.0°C) of III are lower than those of poly(3,4-benzo-1,1-dimethyl-1-silapentene) (IV) (mp 163-165°C, T_g 75°C).[10] Likewise, the thermal stability of III as determined by TGA is lower than that of IV (See Figure). In an inert atmosphere, III is thermally stable to 260°C. Between 260 and 375°C III loses ten percent of its initial weight. Above 375°C rapid weight loss occurs. By 425°C less than eight percent of the initial sample weight remains. Between 450 and 850°C an additional four percent of the initial weight is lost. A black residue amounting to four percent remains.



The ultraviolet spectrum of III is particularly interesting. In addition to an absorption at 261.8 nm which is similar to the long wavelength band of the monomer I at 258.0 nm, a long wavelength shoulder at 269.0 nm is observed. These are strongly suggestive of π-π interactions through space between neighboring nonconjugated thiophene rings. There has been considerable interest in conjugated polythiophene which can be converted to highly conducting materials by treatment with oxidative dopants.[12-16] The nature of this through space electronic interaction and the special properties arising from it are under active investigation.

Acknowledgement: This work was supported by the Air Force Office of Scientific Research 89-0007 and the Office of Naval Research.

REFERENCES

1. Mazerolles, P.; Laurent, C. *J. Organometal. Chem.,* 1990 in press.
2. For a recent review of Silicones: Stark, F. O.; Falender, J. R.; Wright, A. P. Silicones. in *Comprehensive Organometallic Chemistry;* Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds. Pergamon Press: Oxford, 1982, Vol. 2, pp. 305-363.
3. For a recent review of Polysilanes: West, R. Organopolysilanes. in *Comprehensive Organometallic Chemistry;* Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds. Pergamon Press: Oxford, 1982, Vol. 2, pp. 365-397.
4. *Inorganic and Organometallic Polymers* ; Zeldin, M., Wynne, K. J., Allcock, H. R., Eds. American Chemical Society: Washington, DC, 1988.
5. *Silicon Based Polymer Science;* Zeigler, J. M.; Fearon, G. F. W., Eds. Advances in Chemistry Series 224, American Chemical Society: Washington, DC, 1990.
6. Trefonas, P.; West, R. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 2099.
7. Miller, R. D.; Sooriyakurmaran, R. *J. Polym. Sci., Polym. Chem. Ed.* **1987** *25*, 111.
8. Koyayahi, S. Iwata, S. Abe, M. Shoda, S. I. *J. Am. Chem. Soc.,* **1990**, *112*, 1625.
9. Zhang, X.; Zhou, Q.; Weber, W. P.; Horvath, R. F.; Chan, T. H.; Manuel, G. *Macromolecules* **1988**, *21*, 1563.
10. Park, Y. T.; Zhou, Q.; Weber, W. P. *Polymer Bull.* **1989**, *22*, 349.
11. For a recent example of this reaction see: Berlin, A.; Pagani, G. A.; Sannicolo, F. *J. Chem. Soc., Chem. Commun.,* **1986**, 1663.
12. Sato, M.; Tilanak. S.; Kaeriyama, K. *J. Chem. Soc., Chem. Commun.,* **1985**, 713.
13. Cunningham, D. D.; Laguren-Davidson. L.; Mark. H. B. Jr.; Pham, C. V.; Zimmer, H. *J. Chem. Soc., Chem. Commun.,* **1987**, 1021.
14. Wudl, F. Kobayashi, M.; Heeger, A. J. *J. Org. Chem.,* **1984**, *49*, 3382.
15. Aizawa, M.; Watanabe, S.; Shinohara, H.; Shirakawa, H. *J. Chem. Soc., Chem. Commun.,* **1985**, 264.
16. Kobayashi, M.; Chen, J.; Moraes, T. C.; Heeger, A. J.; Wudl, F. *Synth. Metals,* **1984**, *9*, 77.

Accepted April 12, 1990 K