Macromolecules 1993, *26*, 869–871 869

Polygermynes: Synthesis and Properties of Germanium–Germanium Bonded Network Polymers

Walter J. Szymanski, Glenn T. Visscher, and Patricia A. Bianconi*

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

Received September 9, 1992
Revised Manuscript Received December 3, 1992

The synthesis and properties of a new class of silicon-backbone polymers, the poly(*n*-alkylsilynes) ($[RSi]_n$), were recently reported.[1,2] These polymers adopt a σ-bonded network structure unprecedented in carbon-based polymers. Chemical and spectroscopic analyses indicated that they are constructed primarily of sp^3-hybridized monoalkylsilyne moieties assembled into rigid but irregular networks via Si–Si σ-bonds. The continuous random network backbone, analogous to that postulated for bulk amorphous silicon,[3] confers unusual properties on the polysilynes, such as extensive σ-conjugation and delocalization. As a whole, the polysilynes' properties approach those of a soluble form of amorphous silicon.[3]

In the area of germanium–germanium bonded polymers, fewer examples are reported. The polygermanes, linear germanium polymers which are the germanium analogues of polyolefins, exhibit properties similar to those of the polysilanes.[4] Due to their σ-delocalization, they readily undergo photoscission and display intense UV absorption maxima which are 20–40 nm red-shifted from those of their polysilane analogues. However, germanium-backbone network polymers ($[GeR]_n$) are not known. We report here the synthesis of the first examples of such polymers, the polygermynes, and their copolymers with polysilynes.

The polygermynes were synthesized by reductive condensation of *n*-butylgermanium trichloride (12.63 mL, 100 mmol) or phenylgermanium trichloride (16.2 mL, 100 mmol) monomers with an ultrasonically-generated NaK alloy emulsion (8.85 g, 285 mequiv) in THF under an inert atmosphere, in a procedure similar to those reported for poly(alkylsilynes)[1] (eq 1). After reductive condensation,

$$\underset{\text{R = n-butyl, phenyl}}{\text{RGeCl}_3} + 2.85\ \text{NaK} \xrightarrow[\text{pentane, THF}]{\text{375W, 20kHz ultrasound}} [\text{RGe}]_n + 2.85\ \text{Na(K)Cl} \qquad (1)$$

alkylating agents (phenylmagnesium chloride, 2.0 M in THF, 1.5 mL; or *n*-butyllithium, 2.5 M in hexanes, 2.0 mL) were added to the reaction mixture in order to "cap" any residual Ge–Cl bonds with hydrocarbyl groups. After purification by precipitation from THF with alcohols, the polygermynes were isolated as dark-brown powders. Poly(phenylgermyne) (**1**) and poly(*n*-butylgermyne) (**2**) were collected in 41% and 11% yields, respectively.[5,6] Colloidal germanium was also collected in both syntheses in yields of 30% and 38% for **1** and **2**. This side product arises from reduction of the monomers' Ge–R bonds, demonstrating, since colloidal silicon is never formed in analogous polysilyne syntheses, the relative weakness of Ge–R bonds to their Si–R analogues. The mean molecular weights $\bar{M}_w$ of **1** and **2** (determined by GPC, reported vs polystyrene standards) were found to be 3160 and 7040, respectively. In both cases, however, the actual molecular weight of the polymer is probably several times higher than that found by GPC, as is seen both in linear polysilanes[7] and in network polysilynes.[1,2]

The polygermynes appear to adopt a random network structure identical to that of the polysilynes. This is deduced from ^1H and ^{13}C NMR data, physical properties, UV/visible spectra, and crystal structures of related germyne oligomers. The ^1H and ^{13}C NMR spectra of **1** and **2** are identical to the spectra of their polysilyne analogues.[1] They show similar broadening of the NMR peaks, indicating that the germanium backbone is both randomly constructed and very rigid, consistent with network structures. The physical properties of the polygermynes include ready solubility in organic solvents, good film-forming properties, lack of any peaks in X-ray diffraction spectra, and lack of any discrete melting points. These properties all tend to indicate an amorphous, random morphology and were also seen in the polysilynes.[1,2] The UV/visible spectra of **1** and **2** show broad and intense absorption bands identical in shape to those of the polysilynes,[1,2] except that they tail into the visible to approximately 800 nm, accounting for the polygermynes' deep-brown color. Such intense absorption band indicate extended conjugation in three dimensions over the germanium backbone, consistent with the network structure. Finally, crystallographic structure determinations reported for two oligogermynes, $[(Me_3Si)_2CHGe]_6$[8] and $[t\text{-BuGe}]_8Br_2$,[9] show that these hexa- and octagermynes exist as tetrahedral sp^3-hybridized GeR units assembled via germanium–germanium single bonds into polyhedral shapes. These model compounds therefore adopt the same structure as that indicated by our spectral data for the polygermyne network backbone.

On the basis of these spectra and physical properties and the structure of the oligomeric germyne compounds, we conclude that continuous random network backbones, analogous to those seen in the polysilynes, are also present in polygermynes. The difference in electronic properties displayed by the silicon and germanium backbones further supports the analogy of inorganic network polymers to solubilized semiconductor clusters. Thus, although the UV/visible spectra of the silynes and germynes are qualitatively similar, they display some important quantitative differences. While linear polygermanes ($[R_1R_2Ge]_n$) show only a 20–40-nm red shift in UV absorption compared to their polysilane congeners,[4] the polygermynes show an extraordinarily large red shift in their band edge (onset of absorption at approximately 800 nm, compared to 450 nm for the polysilynes[1]). In this absorption behavior the polymers are acting as clusters of solubilized germanium: since elemental germanium has a much smaller bandgap than elemental silicon, a solubilized "cluster" of germanium should display a greatly red-shifted UV absorption compared to its silicon analogue.

Polygermynes share at least one important reaction with polysilynes,[1,2] again evidencing a similarity of structure. Both classes of polymers undergo photooxidation, to give in the case of polygermynes cross-linked networks of germanoxanes ($[RGeO_{1.5}]_n$; eq 2). A band at 846 cm^{-1},

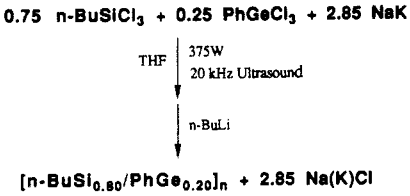
$$\underset{\text{R = n-butyl, phenyl}}{[\text{RGe}]_n} \xrightarrow[\text{O}_2]{h\nu} [\text{RGeO}_{1.5}]_n \qquad (2)$$

arising from Ge–O–Ge stretching, appears in IR spectra of the polygermynes when films of the polymers are irradiated in the presence of oxygen. This band grows in intensity as the irradiation time increases. The analogous photooxidative insertion of oxygen into the Si–Si bonded network is the reaction which confers photopatterning properties on polysilynes and has led to their development

0024-9297/93/2226-0869$04.00/0

as waveguides[10] and photoresists.[11] Similar photopatterning may be possible with the polygermynes.

Copolymers of silyne/germyne units have also been synthesized (eq 3). Reduction of 0.75 equiv of *n*-butyl-



$$\begin{array}{c} 0.75\ \text{n-BuSiCl}_3 + 0.25\ \text{PhGeCl}_3 + 2.85\ \text{NaK} \\ \text{THF}\ \Big\downarrow\ \begin{array}{l}\text{375W} \\ \text{20 kHz Ultrasound}\end{array} \\ \Big\downarrow\ \text{n-BuLi} \\ [\text{n-BuSi}_{0.80}/\text{PhGe}_{0.20}]_n + 2.85\ \text{Na(K)Cl} \end{array} \qquad (3)$$

trichlorosilane and 0.25 equiv of phenyltrichlorogermane with a preformed NaK alloy/THF emulsion, capping with a Grignard or lithium reagent, and purification by precipitation with alcohols gave an 18% yield of a light-brown powder of $\bar{M}_w = 15\,940$ (GPC), with no significant colloidal germanium being collected.[12] The copolymer's composition, as determined by ^{1}H NMR integration was $[(n\text{-BuSi})_{0.80}(\text{PhGe})_{0.20}]_n$ (**3**). The copolymer shows the spectral properties characteristic of the network backbone structure,[1,2] and it is completely soluble in pentane, proving that it does not merely consist of a mixture of the separate homopolymers $[n\text{-BuSi}]_n$ and $[\text{PhGe}]_n$. Since butyl-substituted network polymers are pentane-soluble but phenyl-substituted network polymers are not,[1,13] extraction with pentane separates butylsilyne and phenylgermyne components if they are merely physically mixed. Since **3** is completely pentane-soluble, its silyne and germyne components must be covalently bonded in the network backbone.

The electronic properties of **3** are intermediate between those of the two parent homopolymers and vary with the relative amount of each inorganic component. The UV/visible absorption of $[(n\text{-BuSi})_{0.80}(\text{PhGe})_{0.20}]_n$, for example, has an onset at ca. 650 nm and a moderately high extinction coefficient, and the polymer is light brown. The electronic properties of the network polymers can therefore be "tuned" by incorporating the correct amount of various inorganic species into the backbone.

In conclusion, a new class of inorganic polymers, $[\text{RGe}]_n$, and their copolymers with polysilynes, $[(\text{RSi})_{1-x}(\text{RGe})_x]_n$, have been synthesized. These new polymers appear to adopt random network structures analogous to their polysilyne congeners. This structure may be a general one for inorganic monosubstituted polymers, rather than the linear structure adopted by polyacetylenes. It appears to convey some characteristic properties and reactivity on the polymers which persist in spite of changes in the elemental composition of the backbone, suggesting that polymers of many differing backbone elements could be synthesized in the network structure which would still display its characteristic properties. Conversely, other characteristics of the backbone, such as its electronic properties, can be tuned by choice of backbone elemental composition. Finally, the properties of these new polymers support the analogy of soluble inorganic network materials to semiconductor clusters.

Acknowledgment. We acknowledge the National Science Foundation, Division of Materials Research, for support of this research under Grant DMR-8919049. We also thank Dr. Timothy Weidman, of AT&T Bell Laboratories, for helpful discussions.

References and Notes

(1) Bianconi, P. A.; Weidman, T. W. *J. Am. Chem. Soc.* **1988**, *110*, 2342.

(2) (a) Bianconi, P. A.; Schilling, F. C.; Weidman, T. W. *Macromolecules* **1989**, *22*, 1697. (b) Weidman, T. W.; Bianconi, P. A.; Kwock, E. W. *Ultrasonics* **1990**, *28*, 310.

(3) (a) Zachariasen, W. H. *J. Am. Chem. Soc.* **1932**, *54*, 3841. (b) Zallen, R. *The Physics of Amorphous Solids*; John Wiley and Sons: New York, 1983. (c) Mott, N. F. *Conduction in noncrystalline materials*; Clarendon Press and Oxford Press: Oxford and New York, 1987; pp 71–76.

(4) (a) West, R.; Trefonas, P. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 2099. (b) Miller, R. D.; Sooriyakumaran, R. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *28*, 111.

(5) 1: In an inert atmosphere drybox, NaK alloy (8.85 g, 285 mequiv) in 250 mL of THF was ultrasonically irradiated at full power for 2 min, forming a cloudy blue emulsion. Phenylgermanium trichloride (16.2 mL, 100 mmol) was added dropwise to the solution over a 7-min period. After the addition was completed, ultrasonic irradiation was continued for an additional 5 min. Phenylmagnesium chloride (2.0 M in THF) was added (approximately 1.5 mL) until a hydrolyzed aliquot of the reaction mixture tested at neutral pH. The resulting dark-green solution was removed from the drybox, and 200 mL of distilled water was carefully added. The brown solid was removed from the aqueous layer, redissolved in THF, and separated from the colloidal germanium (5.66 g, 38%) by filtration. The polymer was then sequentially precipitated from THF solution with methanol and ethanol, which gave 6.1 g (41%) of poly(phenylgermyne) ($[\text{PhGe}]_n$) 1 as a soluble dark-brown solid. Spectral data for 1: ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C): δ 7.1 (br, C$_6$*H*$_5$Ge). ^{13}C{^{1}H} NMR (200 MHz, CDCl$_3$, 25 °C): δ 132.2, 130.1, 128.2 (br, *C*$_6$H$_5$Ge). IR (neat film on KBr, cm^{-1}): 3050 (vs), 2970 (s), 1625 (vs), 1500 (vs), 1475 (vs), 1325 (vs), 1200 (vs), 1105 (s), 1050 (s), 900 (m), 752 (vs), 701 (vs), 450 (vs). UV/visible (cyclohexane): onset at 800 nm, increasing gradually in intensity with decreasing wavelength to 200 nm. Anal. Calcd: C, 48.32; H, 3.36; Ge, 48.32. Found: C, 48.45; H, 3.61; Ge, 48.35. GPC (THF vs polystyrene standard): $\bar{M}_w = 3160$.

(6) 2: In an inert atmosphere drybox, a solution of *n*-butylgermanium trichloride (12.63 mL, 100 mmol) in 200 mL of pentane was ultrasonically irradiated as NaK alloy (8.85 g, 285 mequiv) was added dropwise over 5 min. Sonication was continued for 10 min after the last addition of NaK. *n*-Butyllithium (2.5 M in hexanes, approximately 2 mL) was added (approximately 3.0 mL) until a hydrolized aliquot of the reaction mixture tested at a neutral pH. Purification of the polymer was carried out as described for 1. Colloidal germanium (3.87 g, 30%) was removed by filtration. This procedure gave 1.6 g (11%) of poly(*n*-butylgermyne) (**2**) as a dark-brown solid. Spectral data for 2: ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C): δ 1.65 (br, CH$_3$(C*H*$_2$)$_3$Ge), 1.05 (br, C*H*$_3$(CH$_2$)$_3$Ge). ^{13}C{^{1}H} NMR (200 MHz, CDCl$_3$, 25 °C): δ 14.01 (CH$_3$), 27.8 (C$_3$), 32.96 (C$_2$), C$_1$ broad and undefined. IR (neat film on KBr, cm^{-1}): 2955 (s), 2930 (s), 2870 (s), 1502 (vs), 1475 (s), 1400 (vs), 1336 (s), 1260 (s), 1245 (s), 1195 (m), 1120 (vs), 1090 (m), 1000 (vs), 850 (w), 790 (w), 700 (s), 650 (s), 500 (w). UV/visible (cyclohexane): onset at 750 nm, increasing gradually in intensity with decreasing wavelength to 200 nm. GPC (THF vs polystyrene standards): $\bar{M}_w = 7040$.

(7) West, R. *J. Organomet. Chem.* **1986**, *300*, 327.

(8) Sekiguchi, A.; Kabuto, C.; Sakuri, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 55.

(9) Weidenbrunch, M.; Grimm, F.; Pohl, S.; Saak, W. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 198.

(10) (a) Hornak, L. A.; Weidman, T. W.; Kwock, E. W. *J. Appl. Phys.* **1990**, *67*, 2235. (b) Weidman, T. W.; Kwock, E. W.; Wilson, W. L.; Hornak, L. A. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1990**, *31*, 250.

(11) (a) Kunz, R. R.; Horn, M. W.; Goodman, R. B.; Bianconi, P. A.; Smith, D. A.; Freed, C. A. *J. Vac. Sci. Technol.* **1990**, *B88*, 1820. (b) Kunz, R. R.; Horn, M. W.; Bianconi, P. A.; Smith, D. A.; Freed, C. A. *J. Vac. Sci. Technol.* **1991**, *A9* (3), 1447. (c) Kunz, R. R.; Bianconi, P. A.; Horn, M. W.; Paladugu, R. R.; Shaver, D. C.; Smith, D. A.; Freed, C. A. *SPIE Adv. Resist. Technol. Proc. II* **1991**, 21.

(12) 3: In an inert atmosphere drybox, *n*-butylsilicon trichloride (12.15 mL, 75 mmol) and phenylgermanium trichloride (3.8 mL, 25 mmol) were simultaneously added dropwise over a 5-min period to a sonicated solution of NaK alloy (8.85 g, 285 mequiv) in 250 mL of THF. After the final addition of the monomers, the reaction mixture was sonicated for an additional 5 min. *n*-Butyllithium (2.5 M in hexanes, approximately 2 mL) was added (approximately 3.0 mL) until a hydrolized aliquot of the reaction mixture tested at a neutral pH and the copolymer was purified as described for 1. No colloidal germanium was collected. This procedure gave 1.8 g (18%) of $[(n\text{-BuSi})_{0.80}(\text{PheGe})_{0.20}]_n$ (**3**) as a light-brown powder. Spectral data for 3: ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C): δ 1.10 (br,

CH_3), 1.63 (br, CH_2), 7.2 (br, C_6H_5). IR (neat film on KBr, cm^{-1}): 3070 (m), 2950 (vs), 2871 (vs), 2800 (s), 1503 (s), 1310 (vs), 1250 (w), 1127 (vs), 1021 (m), 1000 (s), 926 (m), 750 (w). UV/visible (cyclohexane): onset at 650 nm, increasing gradually in intensity with decreasing wavelength to 200 nm. GPC (THF vs polystyrene standards): $\bar{M}_w$ = 15 940.

(13) Bianconi, P. A.; Weidman, T. W.; Kwock, E. W. Design, Synthesis, and Characterization of New Polysilynes Oligomers for Waveguide Applications. In *Polymers For Lightwave and Integrated Optics: Technology and Applications*; Hornak, L., Ed.; Optical Engineering Series; Marcel Decker: New York, 1991; pp 195–207.