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A New Type of Inorganic Polymer with Ordered SiSiGe Sequences

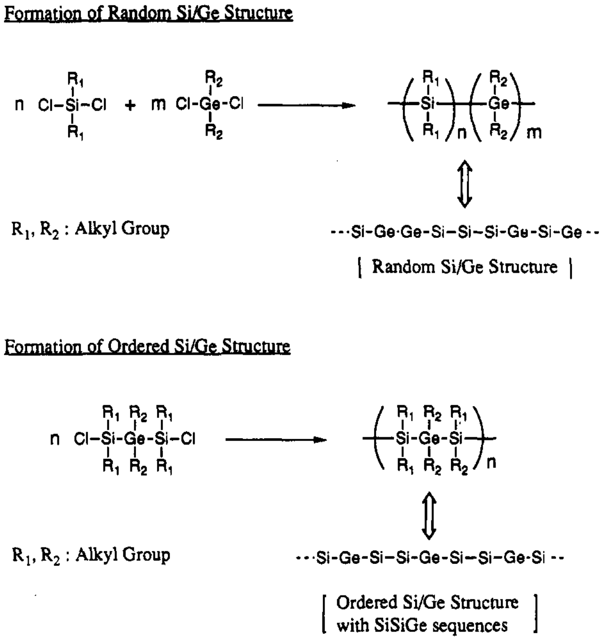
Polysilanes and polygermanes are a new class of inorganic polymers based on linear backbones of catenated silicon atoms and germanium atoms, respectively. These polymers show remarkable properties such as photoconductivity,[1-3] highly efficient photoluminescence,[4] conductivity induced by chemical doping,[5] and third-order nonlinear effects.[6,7] Recently, a theoretical approach suggested that Si/Ge copolymers with ordered sequences corresponded to one-dimensional superlattice structures.[8] A one-dimensional superlattice would be of great scientific interest. However, a Wurtz type reaction of a mixture of organodichlorosilane and organodichlorogermane gives a random Si/Ge copolymer.[9,10] In this paper, we present a new idea that catenation of monomers with an SiGeSi sequence generates a periodic structure of SiSiGe sequences along a chain (Scheme I). This is the first report of the synthesis of a new type of inorganic polymer with ordered Si/Ge sequences.

The new polymer was synthesized in a three-step process.[11] First, 10 g of sodium/potassium alloy (1:1 weight ratio) was dispersed in 300 mL of THF solution and refluxed. The mixture of 10.0 g (39 mmol) of di-*n*-butyldichlorogermane (Bu_2GeCl_2) and 16.9 g (150 mmol) of trimethylchlorosilane (Me_3SiCl) was added dropwise to the solution. After 3 h of reflux, the reaction mixture was filtered and the filtrate was distilled under reduced pressure. A total of 2.43 g (7.3 mmol) of bis(trimethylsilyl)di-*n*-butylgermane ($(Me_3Si)_2GeBu_2$) was obtained [yield: 18.9%, bp: 69 °C (0.3 mmHg)]. Second, 4 h of stirring of the mixture of 2.43 g of $(Me_3Si)_2GeBu_2$, 10 g of Me_3SiCl, and anhydrous aluminum chloride as a catalyst at 48 °C gave 530 mg (1.4 mmol) of bis(dimethylchlorosilyl)di-*n*-butylgermane ($(Me_2ClSi)_2GeBu_2$) [yield: 19.2%, bp: 93 °C (0.5 mmHg)]. Third, 100 mg of sodium was dispersed in 10 mL of refluxed toluene. A total of 530 mg of $(Me_2ClSi)_2GeBu_2$ was added dropwise to the suspension and stirred for 3 h. The reaction mixture was filtered, and the filtrate was poured dropwise into excess ethanol. A total of 110 mg of polymer 1 was obtained (overall yield based on Bu_2GeCl_2: 0.94%).

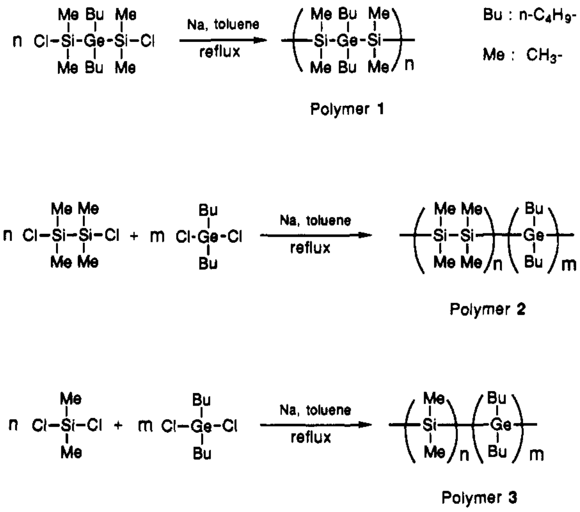
For the characterization of polymer 1, two random copolymers consisting of Si and Ge were also prepared by the ordinary method (Scheme II). The mixture of 7.26 g (39 mmol) of 1,1,2,2-tetramethyl-1,2-dichlorodisilane ($ClMe_2SiSiMe_2Cl$) and 10.0 g (39 mmol) of Bu_2GeCl_2 and added dropwise to 150 mL of toluene including 4.3 g (197 mmol) of sodium dispersion. After 6 h of reflux, the reaction mixture was filtered and the filtrate was poured dropwise into excess ethanol. A total of 384 mg of poly(tetramethyldisilane-*ran*-di-*n*-butylgermane) (polymer 2) was obtained. Poly(dimethylsilane-*ran*-di-*n*-butylgermane) (polymer 3) was synthesized by a similar method using 10 g (77 mmol) of dimethyldichlorosilane (Me_2SiCl_2), 10 g of Bu_2GeCl_2, and 6.0 g of sodium dispersion. A total of 390 mg of polymer 3 was obtained.

The resulting polymers were characterized by GPC, X-ray fluorescence analysis (XFA),[12] UV absorption, ^1H NMR (200 MHz), and ^{29}Si NMR (39 MHz). All NMR spectra were measured in tetrahydrofuran-d_8 at 20 °C. Table I shows the results of these analyses, and Figure 1 shows the ^{29}Si NMR spectra. The atomic ratios (Si/Ge) of polymers 2 and 3 are quite different from the nominal compositions. In contrast, the atomic ratio (Si/Ge) of polymer 1 is 2.00, as expected from the procedure.

Scheme I



Scheme II



In the ^{29}Si NMR spectra, polymer 2 has two major multiple peaks near −38 and −29 ppm and polymer 3 has three near −37, −29, and −20 ppm. Two triad configurational sequences are predicted for polymer 2 (SiSi*Si and SiSi*Ge) and three for copolymer 3 (SiSi*Si, SiSi*Ge, and GeSi*Ge). The results of ^{29}Si NMR are consistent with this prediction. Since ^{29}Si NMR chemical shifts for catenated silicon atoms with methyl substituents can be observed in the range of −36 to −40 ppm,[13] the peaks observed near −36 ppm in polymers 2 and 3 are assigned to Si* with a SiSi*Si triad configurational sequence. The peaks near −29 ppm and near −20 ppm are assigned to Si* with SiSi*Ge and GeSi*Ge triad configurational sequences, respectively, because a germanium atom causes the signals of a nearby silicon atom to be shifted downfield. The ^1H NMR spectra of polymers 2 and 3 also reflect the number of triad configurational sequences. Polymer 2 has two peaks that are assigned to $SiCH^*_3$, and polymer 3 has three. In addition, the multiplicity of the ^{29}Si peaks shown in polymers 2 and 3 is attributed to several pentad configurational sequences such as SiGeSi*SiGe and SiGeSi*SiSi. These results mean that polymers 2 and 3 have random Si/Ge chain structures.

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Table I

polymer[a]	nominal composn of Si/Ge (atomic ratio)	yields of polymer, %	mol wts (weight-averaged)[c]	atomic ratio of Si/Ge[d]	λ_{max},[e] nm	^{1}H NMR chemical shifts of SiCH$^*_3$,[f] ppm from TMS
1	2.0[b]	25.6	6 000	2.00	298.6	0.391
2	2.0	3.2	11 000	1.16	308.5	0.278 (1.0), 0.396 (0.8)
3	2.0	7.9	13 000	0.35	312.0	0.263 (1.0), 0.385 (0.8), 0.487 (0.8)

[a] All polymers were purified twice by reprecipitation with a toluene–ethanol system. Toluene-soluble fractions of polymers 2 and 3 were used in measurements. [b] Atomic ratio of the monomer. [c] Molecular weights were determined by GPC based on a polystyrene standard. [d] Compositional ratios were determined by XFA analysis. [e] UV spectra were measured in hexane at 25 °C. [f] TMS: tetramethylsilane. Values in parentheses are relative intensities.

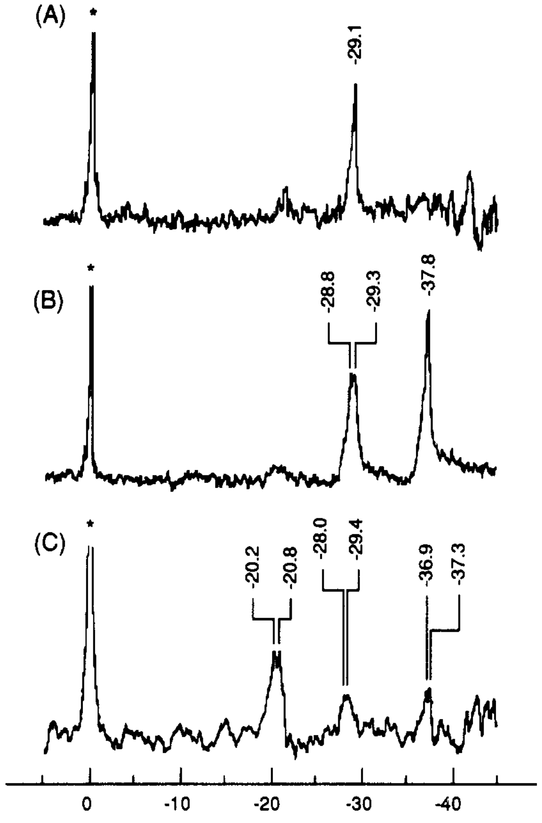

Figure 1. ^{29}Si NMR spectra (39 MHz) in tetrahydrofuran-d_8 at 20 °C of (a) polymer 1, (b) polymer 2, and (c) polymer 3. Asterisks indicate the tetramethylsilane internal signals.

In contrast, polymer 1 has one peak assigned to SiCH$^*_3$ at 0.391 ppm in the ^{1}H NMR spectrum and only one peak at −29.1 ppm in the ^{29}Si NMR spectrum. This peak in the ^{29}Si NMR is assigned to Si* with an SiSi*Ge triad configurational sequence because of the similar chemical shift to the peaks observed in polymers 2 and 3. The singularity of the ^{29}Si signal means that polymer 1 has only one type of pentad configurational sequence. Therefore, polymer 1 consists of ordered SiSiGe sequences.

In summary, the present study shows that polymer 1 is in a periodic SiSiGe one-dimensional structure. Polymer 1 is the first example of a soluble one-dimensional superlattice. We are currently measuring the properties of these polymers, and they will be reported elsewhere.

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References and Notes

(1) Kepler, R. G.; Zeigler, J. M.; Harrah, L. A.; Kurtz, S. R. *Phys. Rev. B* **1987**, *35*, 2818.
(2) Fujino, M. *Chem. Phys. Lett.* **1987**, *136*, 451.
(3) Abkowitz, M.; Stolka, M. *J. Non-Cryst. Solids* **1989**, *114*, 342.
(4) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359.
(5) West, R. *J. Organomet. Chem.* **1986**, *300*, 327.
(6) Kajzar, F.; Messier, J.; Rosilio, C. *J. Appl. Phys.* **1986**, *60*, 3040.
(7) Baumert, J. C.; Bjorklund, G. C.; Jundt, D. H.; Jurich, M. C.; Looser, H.; Miller, R. D.; Rabolt, J.; Sooriyakumaran, R.; Swalen, J. D.; Twieg, R. J. *Appl. Phys. Lett.* **1988**, *53*, 1147.
(8) Takeda, K.; Shiraishi, K.; Matsumoto, N. *J. Am. Chem. Soc.* **1990**, *112*, 5043.
(9) Trefonas, P.; West, R. *J. Polym. Chem., Polym. Chem. Ed.* **1985**, *23*, 2099.
(10) Miller, R. D.; Sooriyakumaran, R. *J. Polym. Sci., Part A: Polym. Chem.* **1987**, *25*, 111.
(11) This procedure is a modification of a previously reported method: Fujino, M.; Matsumoto, N.; Ban, H.; Sukegawa, K. *J. Polym. Sci., Part C: Polym. Lett.* **1988**, *26*, 109.
(12) Samples and a reference standard (Si/Ge = 1/1 weight ratio) were prepared by casting on acrylic resin substrates. Characteristic X-rays used in the analysis are Ge Kα, Ge Lβ, and Si Kα. Si/Ge atomic ratios were converted from intensity ratios of Ge Kα/Si Kα and Ge Lβ/Si Kα.
(13) Ishikawa, M.; Iyoda, J.; Ikeda, H.; Kotake, K.; Hashimoto, T.; Kumada, M. *J. Am. Chem. Soc.* **1981**, *103*, 4845.

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