

Photodegradation of thin films of polygermanes

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Abstract

Upon ultraviolet irradiation of thin films of linear polygermanes in air, the germanium–germanium bond in thin films of polygermanes changed into digermoxane chains. The laser flash photolysis of the linear polygermane films showed the formation of polygermyl radicals generated by germanium–germanium bond homolysis as reactive intermediates during photodegradation. © 1997 Elsevier Science S.A.

Keywords: Polygermane; Photodegradation; Laser flash photolysis; Homolysis

1. Introduction

Group 14 element (silicon, germanium, tin) backbone polymers have been subject of considerable interest in recent years as a new class of soluble, film-forming polymers due to both their unique chemical, physical, and optical properties and their potential technological utility [1–7]. Among them, linear organopolygermanes strongly absorb light in the ultraviolet (UV) and near-UV regions, owing to σ delocalization along the linear Ge–Ge polymer backbone [8–19]. Bleaching of the absorption band is caused by a photodegradation of the Ge–Ge bond under UV irradiation. These polygermanes are very photoactive with photoscission processes and have an attractive possibility to be used as mid- and deep-UV photoresists, as sensitive photoinitiators for olefin polymerizations, and other applications.

Previously, we have reported on photochemical reactions of polygermanes in solutions by chemical trapping experiments and laser flash photolysis [16,20]. Photolysis of polygermanes involves both Ge–Ge bond homolysis to give polygermyl radicals and extrusion of germynes. However, there have been few reports on photodecomposition of thin films of polygermanes [9,18]. It is thus necessary to make clear photodegrada-

tion processes of polygermane films because of the development of their technological utility.

We describe herein the studies on the mechanism of photodegradation of polygermane films in view of the unique properties of polygermane films and the current interest in the photoactivity of these polymer films.

2. Results and discussion

Synthesis of polygermanes was done by Wurtz-coupling reactions of alkyl- and phenyl-substituted dichlorogermanes with sodium metal [8,9,16]. Thus, polygermanes, poly(dihexylgermylene), (n-Hex₂Ge)_n (1), poly(hexylmethylgermylene), (n-HexMeGe)_n (2), poly(c-hexylmethylgermylene), (c-HexMeGe)_n (3), and poly(methylphenylgermylene), (PhMeGe)_n (4) were prepared by condensation of the corresponding dichlorogermanes with sodium metal in toluene. The polygermanes were fractionated by precipitation from toluene with 2-propanol. Molecular weights and distributions of the polygermanes 1–4 were determined by gel permeation chromatography (GPC) analysis using polystyrene samples for calibration. The polygermanes prepared by Wurtz coupling reactions had a narrow molecular weight distribution, but were in relatively low yields (10–30%). Fig. 1 shows absorption spectra of films of the polygermanes 1–4. The polygermane films

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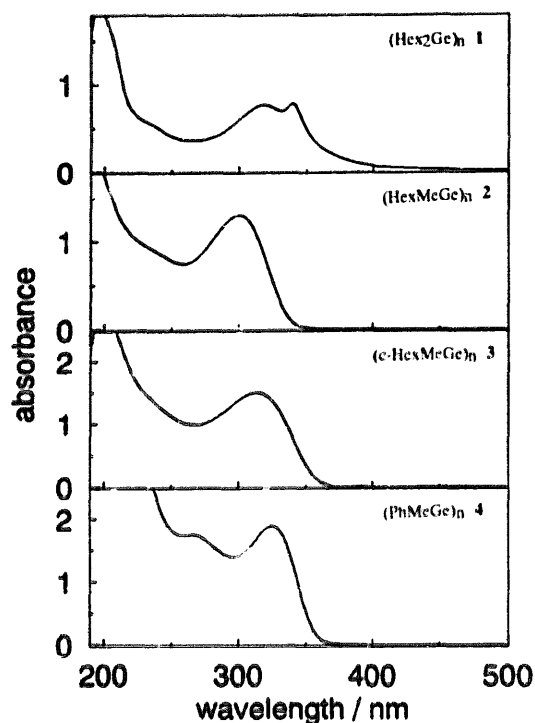


Fig. 1. Absorption spectra of films of polygermananes 1–4.

1–4 have characteristic electronic absorption bands at 301–325 nm. The poly(dihexylgermylene) 1 shows two absorption peaks at 317 and 339 nm, as shown in Fig. 1. The molecular weight (\bar{M}_w) and absorption maxima (λ_{max}) of the polygermane films together with those in solutions are summarized in Table 1.

From the study of thermochromic behavior of polysilanes [6,21] and polygermanes [8,9,22], it is clearly that absorption bands at 301–317 nm for alkyl-substituted polygermane films 1–3 reflect helical-*gauche* conformation of the germanium backbone. Absorption bands at 339 nm for 1 and at 325 nm for 4 reflect all-*trans* conformations.

Thin films of polygermanes were prepared by spin-coating from a 5–10% tetrahydrofuran (THF) solution. The film was deposited on quartz plates ($10 \times 30 \times 1$ mm) and dried under vacuum (10^{-4} mmHg, 1 mmHg = 133.322 Pa) at room temperature. They were homo-

Table 1
Properties of polygermanes 1–4

Polymer	\bar{M}_w^a	\bar{M}_n	\bar{M}_w/\bar{M}_n	λ_{max} (nm)	
				film	solution ^b
(Hex ₂ Ge) _n 1	9100	5500	1.7	339, 317	327
(HexMeGe) _n 2	14700	7600	1.9	301	307
(c-HexMeGe) _n 3	4400	2800	1.7	312	315
(PhMeGe) _n 4	5400	3900	1.4	325	329

^a Molecular weights are relative to polystyrene standards.

^b In THF.

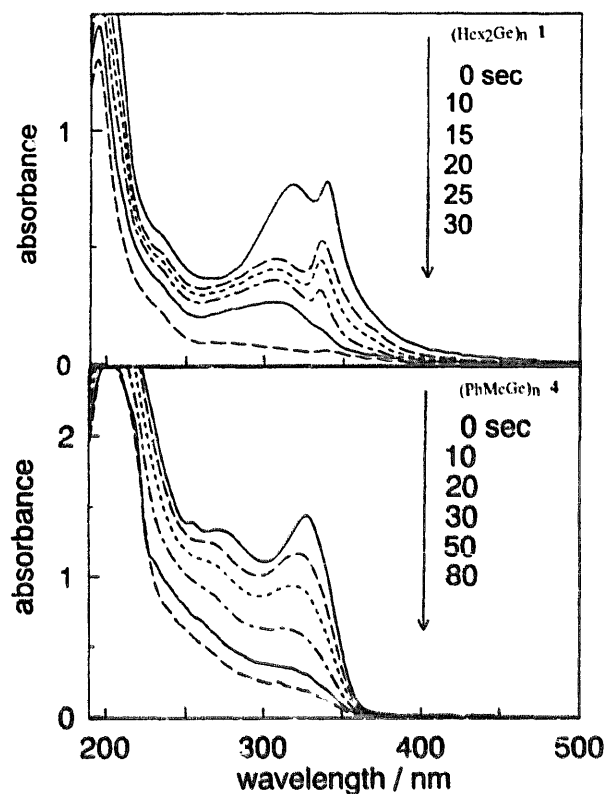


Fig. 2. UV spectra of films of polygermanes 1, 4 with successive UV irradiation.

geneous and transparent in the visible range. The film thickness of polygermanes, which were determined by UV-vis spectrometry, was 0.4–0.7 μm [23].

As expected, polygermane films are quite UV light sensitive. As typical examples, Fig. 2 shows the bleaching of films of 1 as alkyl-substituted polygermanes and 4 as phenyl-substituted polygermanes by irradiation with an 110-W low pressure Hg arc lamp ($\lambda = 254$ nm) at room temperature in air. Similarly, as reported for a solution of polygermanes [9,18], a blue shift of their absorption maxima and decrease of their absorbance are caused by a Ge–Ge chain scission, which products lower molecular weight chain fragments. After UV irradiation for 1 min, the polygermane films were dissolved in THF and their molecular weights and distributions were determined by GPC analysis. GPC spectra showed a large decrease of \bar{M}_w for 1–4. For example, molecular weight and distribution ($\bar{M}_w = 5.4 \times 10^4$, $\bar{M}_w/\bar{M}_n = 1.4$) of 4 changed to $\bar{M}_w = 2.9 \times 10^4$, $\bar{M}_w/\bar{M}_n > 3.0$.

The solid-state quantum yield for the polygermane films 1–4 was measured at 290 nm by potassium tris(oxalato)ferrate (III) actinometer [24]. $\ln(e^{-2.303OD} - 1)$, when plotted against t , must give a straight line. O.D. is the optical density for an polygermane film. The inclination determined from the straight line corresponds to $2.303\Phi I_0 \epsilon \times 10^3$. Φ is the quantum yield, I_0

the light intensity, and ϵ the molar extinction coefficient of a polygermane film. Using a chemical actinometer, the quantum yield (Φ) for **1** was calculated to be $380 \times \epsilon^{-1}$. The value of Φ for poly(dihexylgermylene) film **1** was determined to be 0.038, assuming a value of ca. 10^4 at 290 nm for ϵ . Similarly, the values of Φ for **2–4** were determined to be 0.026, 0.009, and 0.007, respectively. The quantum efficiencies (0.007–0.038) for these photodegradation in films were very low, and dependent upon the nature of the organic substituent. The quantum yields for polygermanes in solutions have not yet been reported. The quantum yields of polysilanes in solid states have been reported to be quite lower ($(1-50) \times 10^{-2}$ times) than those in solutions [6,25].

In addition to UV observations, the process of photodegradation of the polygermane films was observed by X-ray photoelectron spectroscopy (XPS) spectra [26]. Fig. 3 shows XPS spectra of the Ge 3d region for the polygermane films **1** and **4** observed before and after UV irradiation at 254 nm. The XPS spectra before UV irradiation shows a peak at 29.8 eV for **1** and **4**, and a shoulder near 32.0 eV for **1**, as shown in Fig. 3. The peak at 29.8 eV is attributed to the Ge–Ge structure of the polygermane and that at 32.0 eV is the Ge–O–Ge structure, which is incorporated by the replacement of the remaining chlorine atom at the end of the poly-

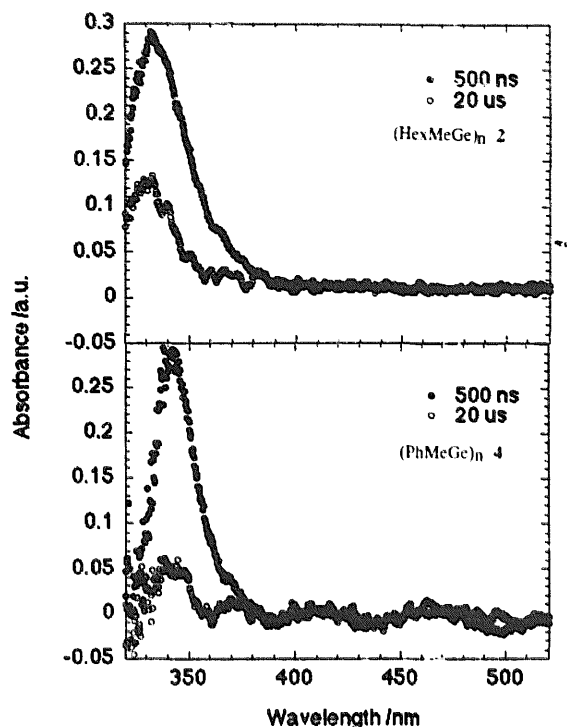


Fig. 4. Transient absorption spectra obtained by laser flash photolysis of polygermane films **2**, **4** in the air after excitation at 500 nm and 20 μ s.

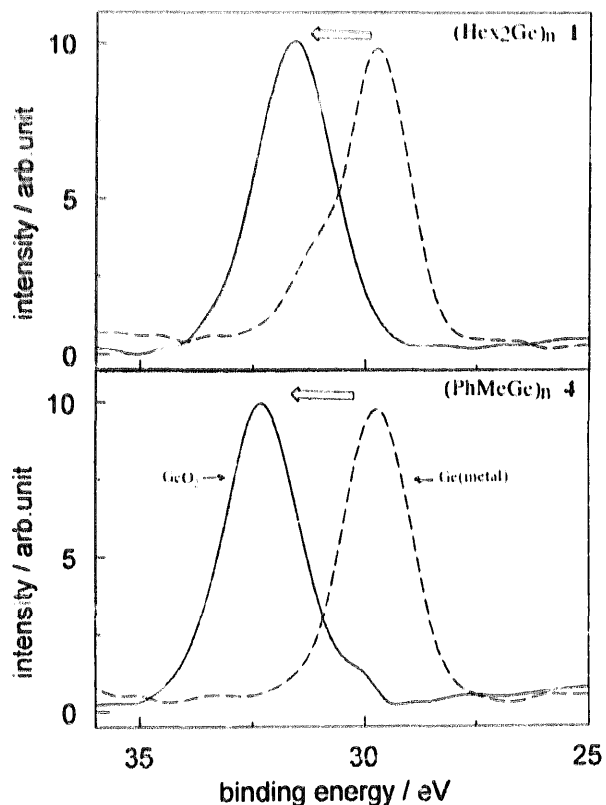
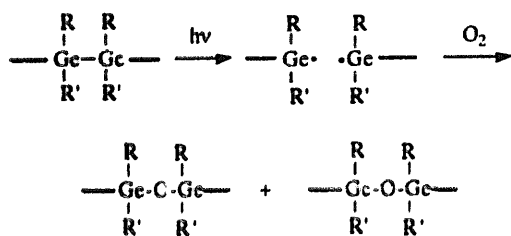


Fig. 3. XPS spectra of films of polygermanes **1**, **4** before UV irradiation (—) and after UV irradiation (---) in the air.

merization. After UV irradiation of **1** for 10 min in air, the peak of Ge–Ge disappeared, and the peak of the Ge–O–Ge structure increased, as shown in Fig. 3. However, for **4** a shoulder peak at 29.8 eV due to Ge–Ge structure was remained. These results of XPS spectra showed that the Ge–Ge bonds in films of polygermanes almost changed into Ge–O–Ge chains after UV irradiation.

To obtain information about reactive intermediates in the photodegradation of polygermane films, laser flash photolysis ($\lambda = 266$ nm, pulse width 5 ns, power 10 mJ/pulse) of the polymer films was carried out in air. To avoid the thermal and photodegradation of the polygermane film induced by the intense pulsed laser light, measuring spot on the film was shifted after each excitation. The laser flash photolysis of the polygermane films **2** and **4** at 293 K gave transient absorption bands at 332 and 340 nm, respectively, after excitation at 500 ns and 20 μ s, as shown in Fig. 4. On the other hand, laser flash photolysis of the polygermane films **1** and **3** did not give transient absorption bands, but bleaching spectra due to their intense absorption bands at λ_{\max} . The transient signals show rapid rise and subsequent decay. The transient peaks at ca. 330–340 nm may be assigned to those of the polygermyl radicals from comparison of their spectral characteristics with those of similar previously reported [16,20]. No transient peaks assigned to germylenes were observed. Thus, the key intermediate is polygermyl radicals generated

by a Ge–Ge bond scission in the photodegradation of the polygermane films in air. The oxygenation of polygermyl radicals in air afforded Ge–O–Ge backbone polymers.



These results are sharply contrast to those of polygermanes in solutions [16,20]. Photolysis of solutions of polygermanes involves both Ge–Ge bond homolysis to give polygermyl radicals and extrusion of germylenes. The formation of germylenes through a concerted process and photodecomposition of polygermyl radical is a complicated problem [27–29]. However, if germylenes may be produced from the polygermyl radicals generated by the Ge–Ge bond homolysis in solution, polygermyl radicals generated in the polymer films in air quickly are oxidized to give digermoxane frameworks with no extrusion of germylenes.

3. Experimental details

^1H spectra were recorded with a Varian Unity-Inova 400 MHz NMR. The GC–MS spectra were recorded using a JEOL JMS-DX 303 mass spectrometer. The UV-visible spectra were recorded on a Shimadzu UV 2200 spectrometer. Interference spectra were observed with Hitachi U-3500 UV-vis spectrometer. Gas chromatography was done on a Shimadzu GC8A with 1 m 20% SE30 and 30% Apiezon L columns. Liquid chromatography was done on a Twinkle with an Asahipak GS 310 column.

3.1. Materials

Polygermanes, $(\text{Hex}_2\text{Ge})_n$ [16], $(\text{PhMeGe})_n$ [16], and $(\text{c-HexMeGe})_n$ [30] were prepared as described.

3.2. Preparation of Poly(hexylmethylgermylene)

Poly(hexylmethylgermylene) was prepared in basically the same manner as that previously described. A sodium dispersion (3.14 g, 0.15 mol) and toluene (40 cm^3) were added to a dry 100 ml three-necked flask fitted with a condenser connected to a drying Ar inlet, pressure-equalizing dropping funnel, and a mechanical stirrer. Distilled hexylmethyldichlorogermane (12.0 g,

0.05 mol) was added via a funnel. Hexylmethyldichlorogermane was then added to the stirred dispersion over a period of 5 min. The reaction mixture turned purple immediately. After the addition of hexylmethyldichlorogermane, the reaction mixture was stirred under reflux for 2 h, and then cooled to room temperature. After treatment of the remaining with 2-propanol (30 cm^3), the reaction mixture was poured into 2-propanol (200 cm^3) with vigorous stirring, and the precipitate was gravity filtered and air-dried. The dried precipitate was dissolved in toluene (300 cm^3) at 50–60°C. After cooling, the toluene solution was washed copiously with water and was dried over sodium sulfate. The solvent was removed on a rotary evaporator and the residue dried at 80°C in a vacuum oven for 12 h to yield 0.7 g of poly(hexylmethylgermylene) of white solid. $^1\text{H-NMR}$ (δ in C_6D_6) 0.2–0.6 (m, 3H), 0.7–1.7 (m, 13H); IR (KBr, cm^{-1}) 2850–2900, 1450, 1370, 1155, 1095, 1020, 995, 935, 830, 750, 710, 650.

3.3. Study of photodecomposition of polygermane films

A thin film of polygermane was prepared by spin-coating from a 5–10% THF solution (MOC, Model/ME 300) (1000 and 2000 rpm). The film was deposited on quartz plates (10 × 30 × 1 mm) and dried under a vacuum (10^{-4} mmHg, 1 mmHg = 133.322 Pa) at room temperature. The film thickness was determined by UV-vis spectrometry (0.4–0.7 μm). The film was irradiated with a 110-W low-pressure Hg arc lamp (Sen Tokushu Kogen Co. Ltd.) at room temperature. The absorption spectrum of the film was recorded by UV and UV-vis spectrometry.

3.4. Quantum yields of polygermane films

A thin film of polygermane was irradiated with 290 nm monochromatic light. The reaction was followed by the change in the optical density at 290 nm, the reading of the meter being carried out during the course of the reaction. The quantum yield was determined by a potassium tris(oxalato)ferrate(III) actinometer. The details concerning the apparatus and operation have been published elsewhere [24].

3.5. Time-resolved optical absorption

Transient absorption spectra were measured at room temperature by using a new laser photolysis system. The system is fully integrated to a Power Macintosh 8100/100av microcomputer. Timing for laser pulsing, Xe lamp pulsing, and shutter controller are set by a Stanford Research System DG535 delay generator. The digitizing oscilloscope, monochromator, delay generator, and power supply for a photomultiplier are interfaced

to a GPIB bus. All settings on these unit are controlled directly by the computer program written by using Lab VIEW (National Instruments).

The fourth harmonic ($\lambda = 266$ nm) of a Quanta-Ray GCR-11 Nd:YAG laser with a pulse width of 5 ns was used as the exciting light source. Time profiles of the transient absorption at fixed wavelengths were recorded by a LeCroy 9362 digitizing oscilloscope connected with a photomultiplier and time-resolved spectra at several delay times were observed simultaneously by a Hamamatsu C2830 two-dimensional streak camera. Typically, 10 shots of signals were accumulated in the microcomputer. To avoid the thermal and photodegradation of the polymer matrix induced by the intense pulsed laser light, the measuring spot on the film was shifted after each excitation [31].

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References

- [1] R. West, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), *Comprehensive Organometallic Chemistry*, Vol. 2, Pergamon Press, New York, 1982, Chap. 9.4.
- [2] H. Sakurai, *Synthesis and Application of Organopolysilanes*, CMC, Tokyo, 1989.
- [3] R. West, *J. Organomet. Chem.* 300 (1986) 327 and references cited therein.
- [4] M. Ishikawa, M. Kumada, *Adv. Organomet. Chem.* 19 (1981) 51 and references cited therein.
- [5] H. Sakurai, *Yuki Gosei Kagaku Kyokaishi* 47 (1989) 1051.
- [6] R.D. Miller, J. Michl, *Chem. Rev.* 89 (1989) 1359.
- [7] M. Birot, J.-P. Pillot, J. Dunogues, *Chem. Rev.* 95 (1995) 1443.
- [8] P. Trefonas, R. West, *J. Polym. Sci.* 23 (1989) 1359.
- [9] R.D. Miller, R. Sooriyakumaran, *J. Polym. Sci. Polym. Chem. Ed.* 25 (1987) 111.
- [10] J.-C. Baumert, G.C. Bjorklund, D.H. Jundt, M.C. Jurich, H. Looser, R.D. Miller, J. Rabolt, R. Sooriyakumaran, J.D. Swalen, R.J. Twieg, *Appl. Phys. Lett.* 53 (1988) 1147.
- [11] V.M. Hallmark, C.G. Zimba, R. Sooriyakumaran, R. Müller, J.F. Rabolt, *Macromolecules* 23 (1990) 2346.
- [12] T. Hayashi, Y. Uchimaru, N.P. Reddy, M. Tanaka, *Chem. Lett.* (1992) 647.
- [13] M. Okano, K. Mochida, *Chem. Lett.* (1990) 701.
- [14] K. Mochida, H. Chiba, M. Okano, *Chem. Lett.* (1991) 109.
- [15] S. Kobayashi, S. Cao, *Chem. Lett.* (1993) 1385.
- [16] K. Mochida, H. Chiba, *J. Organomet. Chem.* 473 (1994) 45.
- [17] T. Kodaira, A. Watanabe, O. Ito, M. Matsuda, S. Tokura, M. Kira, S. Nagano, K. Mochida, *Adv. Mater.* (1995) 917.
- [18] K. Mochida, T. Ohkawa, H. Kawata, A. Watanabe, O. Ito, M. Mastuda, *Bull. Chem. Soc. Jpn.* 69 (1996) 2993.
- [19] K. Mochida, S. Nagano, S. Maeyama, T. Kodaira, A. Watanabe, O. Ito, M. Matsuda, *Bull. Chem. Soc. Jpn.* 70 (1997) 713.
- [20] K. Mochida, K. Kimijima, H. Chiba, M. Wakasa, H. Hayashi, *Organometallics* 13 (1994) 404.
- [21] T. Sanji, K. Sakamoto, H. Sakurai, *Bull. Chem. Soc. Jpn.* 68 (1995) 1052.
- [22] T. Iwatsu, Master thesis, Gakushuin University, 1996; K. Mochida, T. Iwatsu, in preparation.
- [23] S. Tolansky, *Multiple-Beam Interferometry of Surfaces and Films*, Clarendon, 1948.
- [24] S. Kato, S. Minagawa, M. Koizumi, *Bull. Chem. Soc. Jpn.* 34 (1961) 1026.
- [25] H. Ban, K. Sukegawa, *J. Appl. Polym. Sci.* 33 (1987) 2787.
- [26] N.R. Avery, in: J.T. Yates, Jr., T.E. Madey (Eds.), *Vibrational Spectroscopy of Molecular on Surfaces*, Plenum, 1987.
- [27] W.P. Neumann, *Chem. Rev.* 91 (1991) 311.
- [28] K. Mochida, I. Yoneda, M. Wakasa, *J. Organomet. Chem.* 399 (1990) 53.
- [29] P. Riviere, A. Castel, J. Satge, D. Deyot, *J. Organomet. Chem.* 264 (1984) 193.
- [30] S.S. Badesha, M. Stolka, R.J. Weagley, F.J. Roberts Jr., *Chem. Abstr.* 111 (1989) 105745k.
- [31] Y. Sakaguchi, H. Hayashi, S. Nagakura, *J. Phys. Chem.* 86 (1982) 3177.