APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 11, 949–955 (1997)

Micropattern of GeO_2/GeC Lines Prepared by UV Irradiation and Heat Treatment of Polygermane Copolymers of Methylphenylgermylene/Phenylgermyne Units

Kunio Mochida,* Shuh-saku Nagano,[1] Hiroki Kawata,[2] Masanobu Wakasa[3] and Hisaharu Hayashi[3]

[1] Department of Chemistry, Faculty of Science, Gakushuin University, 1-5-1 Mejiro, Toshima-ku, Tokyo 171, Japan
[2] Faculty of Humanities and Social Sciences, Iwate University, Ueda, Morioka 020, Japan
[3] The Institute of Physical and Chemical Research (Riken), Wako, Saitama 351-01, Japan

Upon ultraviolet irradiation of polygermane copolymers of methylphenylgermylene/phenylgermyne units $(PhMeGe)_n(PhGe)_m$ in air, the germanium–germanium bond in the copolymer film changed into a digermoxane chain. Laser flash photolysis of the copolymer film showed the intermediacy of polygermyl radicals generated by Ge–Ge bond homolysis. The XPS showed the formation of germanium carbide (GeC) and germanium dioxide (GeO_2) upon heating the unirradiated and irradiated copolymer $(PhMeGe)_n(PhGe)_m$ films, respectively. A relatively high-resolution micropattern of GeC/GeO_2 was obtained by combining the photochemical and thermal properties of the copolymers of methylphenylgermylene/phenylgermyne units. © 1997 John Wiley & Sons, Ltd.

Appl. Organometal. Chem. **11**, 949–955 (1997)
No. of Figures: 7 No. of Tables: 1 No. of Refs: 25

Keywords: polygermane copolymers; micropatterning; photo-oxidation; heat treatment

Received 19 March 1997; accepted 15 May 1997

INTRODUCTION

Recently, Group 14 element (silicon, germanium)–Group 14 element bond backbone polymers have been a subject of considerable interest as a new class of soluble, film-forming polymers due to both their rather remarkable chemical, physical and optical properties and their potential technological utility.[1–7] Among them, the Ge–Ge backbone in polygermanes acts as an intense ultraviolent (UV) chromophore, and the position of the absorption maximum (λ_{max}) is dependent on the chain length of the polymer. The λ_{max} value of the polygermanes moves to longer wavelength and finally reaches a constant value at 320–330 nm with increasing chain length. Therefore, the polygermanes are quite photosensitive under UV irradiation with photoscission processes.[8–17] There are attractive possibilities for the use of these polygermanes as mid- and deep-UV photoresists, as sensitive photoinitiators for olefin polymerizations and for other applications.

In addition, the formation of ceramic residues as GeC due to crosslinking by thermolysis of polygermanes containing π-electron systems has been reported by Henner and co-workers.[18] Previously, we have reported on the formation of micropatterns of GeC/GeO_2 by photocrosslinking branched oligo(phenylgermyne) film under UV irradiation and subsequent heat treatment *in vacuo*.[19] On the other hand, micrography of poly(methylphenylgermylene) was unclear because its molecular weight decreased to 50% and a ceramic film could not be obtained after UV irradiation and heat treatment.

In this paper, we describe micrography of GeC/GeO_2 using polygermane copolymer, $(PhMeGe)_n(PhGe)_m$. Polygermane copolymers of methylphenylgermylene/phenylgermyne units, $(PhMeGe)_n$ $(PhGe)_m$, are thermostable due to the

---

* Correspondence author: Kunio Mochida.

Contract grant sponsor: Ministry of Education, Science and Culture; Contract grant number: 08554024.

Ge-network structure, and a ceramic film can be obtained by heat treatment *in vacuo* without thermal oxidation or photocrosslinking. The polygermane copolymers $(PhMeGe)_n(PhGe)_m$ with a Ge-network structure are very photoactive under UV irradiation.

RESULTS AND DISCUSSION

Synthesis of polygermane homopolymers and copolymers

Polygermane homopolymers, poly(methylphenylgermylene) $(PhMeGe)_n$ (**1**) and poly(phenylgermyne) $(PhGe)_n$ (**5**) and polygermane copolymers of methylphenylgermylene/phenylgermyne units $(PhMeGe)_n(PhGe)_m$ (**2, 3** and **4** for $n/m = 4{:}1$, 3:2 and 2:3, respectively) were synthesized by Wurtz coupling reactions of phenyl-substituted dichlorogermanes and trichlorogermanes with sodium metal in toluene.[16] The polygermane homopolyers **1** and **5** and copolymers **2–4** were fractionated by precipitation from toluene with 2-propanol. Molecular weights and distributions of the polygermanes **1–5** were determined by gel-permeation chromatography (GPC) analysis using polystyrene samples for calibration. The polygermanes **1–5** prepared by Wurtz coupling reactions had a narrow molecular weight distribution and were in 7–64% yields. Figure 1 shows absorption spectra of films of polygermane homopolyers **1** and **5** and copolymers **2–4**. The linear polygermane film of **1** had a characteristic electronic absorption band at 325 nm, exhibiting a strong σ(Ge–Ge)–σ^* transition. The branched polygermyne film of **5** exhibited a broad absorption from 200 nm, tailing down into the visible region. For polygermane copolymers **2–4**, the absorbance of the absorption band at 325 nm decreased and broad absorption with tailing into 400–500 nm increased with an increasing proportion of $(PhGe)_m$ in the polymers, as shown in Fig. 1. The molecular weight (M_w), yields and absorption maxima (λ_{max}) of the polygermanes **1–5** are summarized in Table 1.

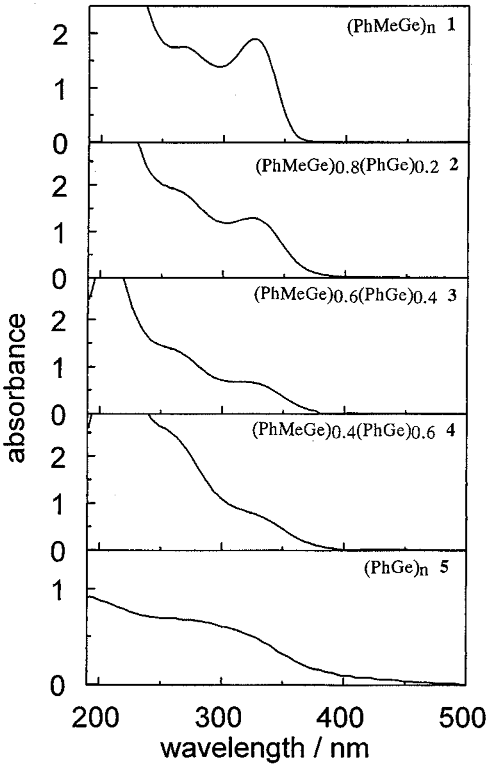

Figure 1 Absorption spectra of films of polygermanes **1–5**.

The phenyl-substituted polygermane homopolymers and copolymers prepared in this study were very photoactive and soluble in common

Table 1. Properties of polygermanes **1–5**

Polymer	$\bar{M}_w$[a]	$\bar{M}_w/\bar{M}_n$	λ_{max} (nm)[b]	Yield (%)
1 $(PhMeGe)_n$	5400	1.4	325	15
3 $(PhMeGe)_{0.8}(PhGe)_{0.2}$	3600	1.7	322	31
3 $(PhMeGe)_{0.6}(PhGe)_{0.4}$	2700	1.5	320 (s)[c]	56
4 $(PhMeGe)_{0.4}(PhGe)_{0.6}$	2000	1.5	—[d]	64
5 $(PhGe)_n$	1700	1.5	—[d]	7

[a] Molecular weights are relative to polystyrene standards.
[b] In films.
[c] Shoulder.
[d] No λ_{max}.

organic solvents, and showed film-forming properties.

Photochemical properties of polygermane copolymers

The thin films of polygermanes prepared by spin-coating from tetrahydrofuran (THF) solution were homogeneous and transparent in the visible range. The film thickness determined by UV–Vis spectrometry, was 0.4–0.7 μm.[20]

As expected, films of polygermane homopolymers and copolymers **1–5** are quite sensitive to UV light. As a typical example, Fig. 2 shows the bleaching of film of $(PhMeGe)_{0.6}(PhGe)_{0.4}$, **3**, by irradiation with a 110-W low-pressure mercury-arc lamp ($\lambda = 254$ nm) at room temperature in air. The absorption edge extending to 400 nm shifted to a shorter wavelength with decreasing absorbance. The bleaching of the polygermane films is caused by the photodecomposition of the Ge–Ge chain. The change of absorbance at λ_{max} with UV irradiation time is shown for $(PhMeGe)_n(PhGe)_m$ films **1–4** in Fig. 3: the intensity of absorbance of films of $(PhMeGe)_n(PhGe)_m$ decreased with increasing proportion of $(PhGe)_m$. After UV irradiation for 1 min, the polymer films were dissolved in THF. GPC showed that the molecular weights of copolymers **3** and **4** were almost constant, but that of **1** decreased to $M_w = 2000$ (*ca* 50%).

The solid-state quantum yield for films of polygermane copolymers **2–4** in comparison with that of homopolymers **1** and **5** was measured at 290 nm.[21] A plot of ln (exp 2.303O.D.-1) against *t* must give a straight line where O.D. is the optical density for a polygermane film. The inclination determined from the straight line corresponds to $2.303\phi I_0\varepsilon\times 10^3$, where ϕ is the quantum yield, I_0 the light intensity and ε the molar extension coefficient of the polygermane film. Using a chemical actinometer, the quantum yield (ϕ) for the copolymer **3** was calculated to be $15.9\times\varepsilon^{-1}$. The value of ϕ for the copolymer **3** film was determined to be 0.069, assuming an ε value of *ca.* 2300 at 290 nm. Similarly, the values of ϕ for the homopolymers and copolymers **1–5** were determined to be 0.007, 0.0022, 0.0069, 0.0289 and 0.001, respectively. The quantum efficiencies for photodegradation in $(PheMeGe)_n(PhGe)_m$ films were relatively low, between 0.002 and 0.03, depending on the ratio of $(PhMeGe)_n$ to $(PhGe)_m$. Interestingly, the quantum yields of the copolymers **2–4** films are higher than those of the homopolymers **1** and **5** films in this study.

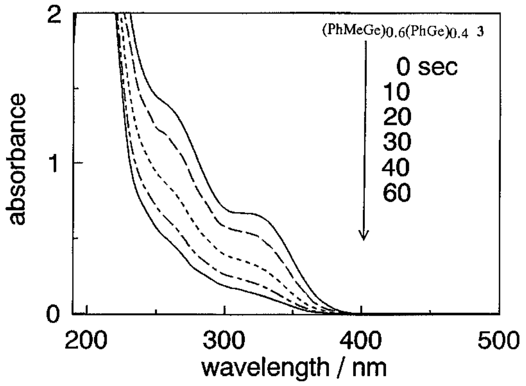

Figure 2 UV spectra of films of the copolymer **3** with successive UV irradiation.

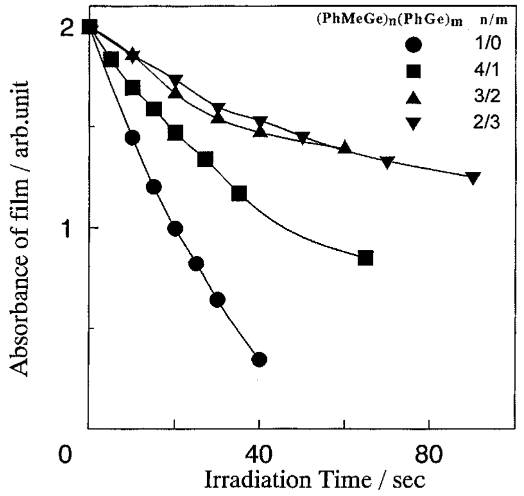

Figure 3 Change of absorbance at λ_{max} vs irradiation time for the films of **1–4**.

In addition to UV observations, the process of photodegradation of the polygermane films was observed by X-ray photoelectron spectroscopy (XPS) spectra.[22] Figure 4 shows XPS spectra of the Ge 3d region for the film of **3** observed before and after UV irradiation at 254 nm. The XPS spectra show a peak at 29.8 eV and at 32.0 eV before and after UV irradiation, respectively, as shown in Fig. 4. The peak at 29.8 eV is attributed to the Ge–Ge structure of **3** and that at 32.0 eV is the Ge–O–Ge structure. After UV irradiation of **3** film for 10 min in air, the Ge–Ge peak almost disappeared, and the Ge–O–Ge peak increased, as shown in Fig. 4. The XPS spectra showed that the Ge–Ge bonds of polygermane copolymer films easily changed into Ge–O–Ge

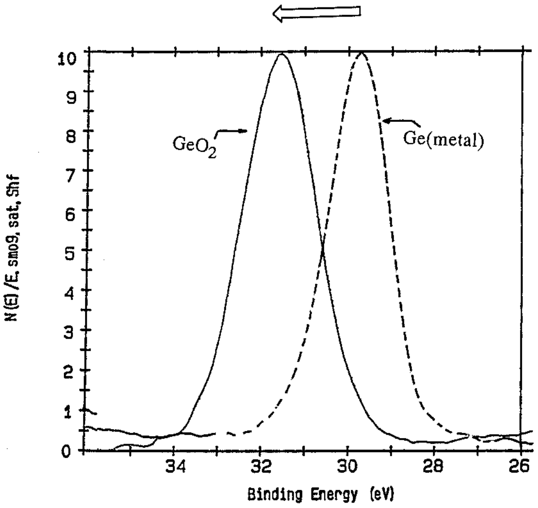

Figure 4 XPS spectra of the copolymer **3** film before UV irradiation (...) and after UV irradiation (——) in the air.

chains.

The transient absorption spectra were measured by laser flash pohtolysis ($\lambda = 266$ nm, pulse width 5 ns, power 10 mJ/pulse) of the polygermane copolymer films in air to obtain information on reactive intermediates in the photodegradation. The laser flash photolysis of **3** film, as a typical example, at 293 K gave a broad transient absorption band at *ca* 340 nm after excitation at 200 ns and 22 μs, as shown in Fig. 5. The signals at *ca* 340 nm showed a rapid rise and subsequent decay. The transient peaks at *ca* 340 nm may be assigned to the polygermyl radicals from comparison of their spectral characteristics with those of similar ones previously reported.[16,23] Thus, the key intermediate comprises polygermyl radicals generated by a Ge–Ge bond scission in the photodegradation of the polygermane films in air. Therefore, the Ge–O–Ge backbone polymers must be produced by photo-oxidation via the reaction of polygermyl radicals with oxygen.

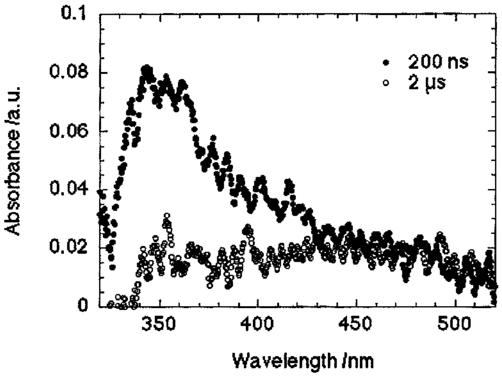

Figure 5 Transient absorption spectra obtained by laser flash photolysis of the copolymer **3** film in air after excitation at 200 nm and 22 μs.

Thermal properties of polygermane copolymer

The thermal properties of polygermanes **2–4** were investigated by the thermogravimetric (TG) curve and different thermal analysis (DTA). As a typical example of the copolymers, TG and DTA spectra of **4** are shown in Fig. 6. Two steps might be distinguished: (1) from 50 to 230 °C, the weight of **4** was almost constant, but started to decrease at 230 °C; (2) at above 250 °C, a relatively fast weight loss took place, and the copolymer **4** lost 50% of its weight by heating under nitrogen to 520 °C. At the same time, the generation of benzene was detected by GC and GC–MS. The DTA of the copolymer **4** showed that the Ge–Ge structure changed around 360 °C. Other films of polymers **1–3** and **5** showed similar thermal behaviour: their weight loss began at 285, 275, 250 and 230 °C, respectively, and their residue volumes decreased around 50% up to *ca.* 500 °C.

After the elimination of volatile compounds such as benzene at 500 °C, a GeC and GeO_2 framework may form. In fact, IR and NMR spectra of residues of the copolymers **2–4** by a heat treatment at 500 °C revealed the appearance of a Ge–O–Ge and GeC framework. The formation mechanism of the GeC structure at high temperature is not clear as in the case of polysilanes.[24]

GeC/GeO$_2$ micropatterning of copolymers

As mentioned above, the germanium–germanium bond in the copolymer of methylphenylgermylene/phenylgermyne units **2–4** films changed into a digermoxane chain (Ge–O–Ge) by UV irradiation of the copolymer thin films in air. The formation of germanium carbide (Ge–C) and germanium dioxide (GeO_2) upon heating the unirradiated and irradiated copolymer films was observed. These photochemical and thermal properties of the copolymers **2–4** were combined to achieve micropatterning consisting of GeC and GeO_2

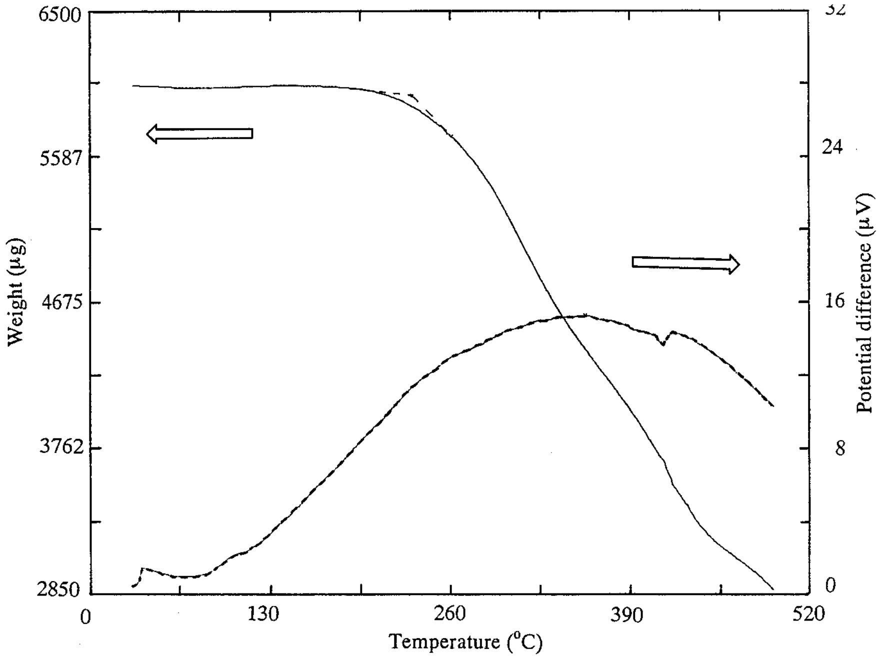

Figure 6 Thermogravimetric (TG) curve and differential thermal analysis (DTA) for the copolymer **4** film under nitrogen.

lines.

Figure 7 shows the micrograph of $(PhMeGe)_n$ (**1**) and $(PhMeGe)_{0.6}(PhGe)_{0.4}$ (**4**) obtained upon a heat treatment at 500 °C after UV irradiation for 10 min with a photomask according to the previously reported procedure.[19] The micrograph of the copolymer **4** showed clear micropatterns where the line and space resolution reached *ca* 5 μm. On the other hand, the micrograph of **1** was unclear. The heat treatment of $(PhMeGe)_n$ was carried out with the temperature changing between 300 and 500 °C, but only unclear patterns were obtained. The formation of the patterns suggests an excellent dimensional stability of the copolymer **4** due to the Ge network. No cracking or hole formation was observed over

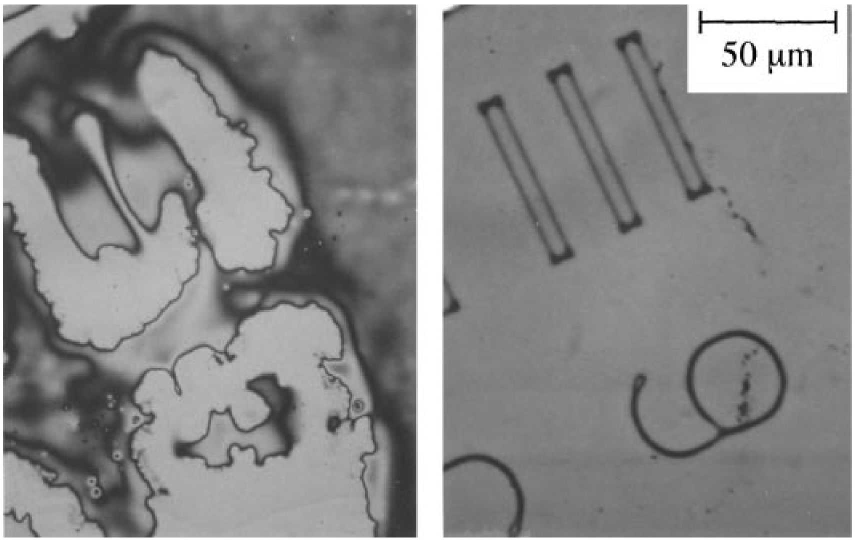

Figure 7 Micrograph of polymers **1** (left) and **4** (right) films heat-treated at 500 °C for 1 h *in vacuo* after UV irradiation for 10 min with a photomask.

the entire area of GeC/GeO_2 patterning.

In conclusion, the micrograph of $(PhMeGe)_n$ alone was unclear owing to absence of formation of ceramic films, but that of copolymers $(PhMeGe)_n(PhGe)_m$, in which more than 30% phenylgermyne $(PhGe)_m$ was involved, showed clear patterns with resolution of *ca*. 5 μm. This GeC/GeO_2 micropatterning using copolymers of methylphenylgermylene/phenylgermyne units is a convenient, totally dry process which has an advantage in comparison with a wet lithography process.

EXPERIMENTAL

Instrumentation

^{1}H NMR spectra were recorded with a Varian Unity–Inova 400 MHz NMR spectrometer. 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 a Hitachi U-3500 UV–visible spectrometer. Gas chromatography was performed on a Shimadzu GC8A with 1 m 20% SE30 and 30% Apiezon L columns. Liquid chromatogrpahy was performed on a Twincle with an Asahipak GS 310 column.

Materials

Polygermanes, $(PhMeGe)_n$[16] and $(PhGe)_m$[19] were prepared as described in the literature.

Preparation of poly(methylphenylgermylene)–poly(phenylgermyne)

Polygermane copolymers, $(PhMeGe)_n(PhGe)_m$ ($n/m = 4{:}1$, 3:2, 2:3) were prepared in basically the same manner as that previously described.[16] A sodium dispersion (3.14 g, 0.15 mol) and toluene (40 cm^3) were added to a dry 100-cm^3 three-necked flask fitted with a condenser connected to a drying argon inlet, a pressure-equilizing dropping funnel and a mechanical stirrer. Distilled methylphenyldichlorogermane (7.0 g, 0.03 mol) and phenyltrichlorogermane (5.1 g, 0.02 mol) were added to the stirred dispersion over a period of 5 min. The reaction mixture turned purple immediately. After the addition of chlorogermanes, the reaction mixture was stirred under reflux for 2 h, and then cooled to room temperature. After hydrolysis of 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 with water and 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 $(PhMeGe)_{0.6}(PhGe)_{0.4}$ as a white solid. ^{1}H NMR (δ) in C_6D_6 ppm): 0.8–1.2 (m, 9H), 5.8–7.9 (m, 22H); IR (KBr, cm^{-1}): 2903, 1579, 1482, 1429, 783, 729, 696, 577, 455.

Methods

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 mm × 30 mm × 1 mm) and dried under 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 mercury-arc lamp (Sen Tokushu Kogen Co. Ltd) at room temperature. The absorption spectra of the film were recorded by UV and UV–vis spectrometry.

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 with a potassium tris)oxalato)ferrate(III) actinometer. The details concerning the apparatus and operation have been published elsewhere.[21]

Time-resolved optical absorption

Transient absorption spectra were measured at room temperature with a laser photolysis system. The system was fully integrated to a Power Macintosh 8100/100av microcomputer. Timings for laser pulsing, xenon lamp pulsing and shutter control were set by a Stanford Research System DG535 delay generator. The digitizing oscilloscope, monochrometer, delay generator and power supply for a photomultiplier were interfaced to a GPIB bus. All settings on these units were controlled directly by the computer program written 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 means of a Hamamatsu C2830 two-dimensional streak camera. Typically, ten shots of signals were accumulated in the microcomputer. To avoid the thermal and photo-degradation of the polymer matrix induced by the intense pulsed laser light, the measuring spot on the film was shifted after each excitation.[25]

Acknowledgements The authors thank Mr Katsumi Ogi (Mitsubishi Material Co. Ltd) for measuring the XPS of polygermane films. We also thank Dr Masakatsu Shimoda (Ricoh Co. Ltd) for measuring the TG and DTA data of polygermane films. This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture (No. 08554024). We thank Mitsubishi Material Co. Ltd for providing us with germanium tetrachloride.

REFERENCES

1. R. West, *Comprehensive Organometallic Chemistry,* Wilkinson, G., Stone, F. G. A. and Abel, E. W. (eds) Pergamon, New York, 1982, Vol. 2, Chapter 9.4.
2. H. Sakurai, *Synthesis and Application of Organopolysilanes,* CMC, Tokyo, 1989.
3. R. West, *J. Organomet. Chem.* **300**, 327 (1986) and references cited therein.
4. M. Ishikawa and M. Kumada, *Adv. Organomet. Chem.* **19** 51 (1981) and references cited therein.
5. H. Sakurai, *Yuki Gosei Kagaku Kyokaishi,* **47**, 1051 (1989).
6. R. D. Miller and J. Michl, *Chem. Rev.* **89**, 1359 (1989).
7. M. Birot, J.-P. Pillot and J. Dunogues, *Chem. Rev.* **95**, 1443 (1995).
8. P. Trefonas and R. West, *J. Polym. Sci.* **23**, 1359 (1989).
9. R. D. Miller and R. Sooriyakumaran, *J. Polym. Sci., Polym. Chem. Ed.,* **25**, 111 (1987).
10. J.-C. Baumert, G. C. Bjorklund, D. H. Jundt, M. C. Jurich, L. Looser, R. D. Miller, J. Rabolt, R. Sooriyakumaran, J. D. Swalen and R. J. Twieg, *Appl. Phys. Lett.* **53**, 1147 (1988).
11. V. M. Hallmark, C. G. Zimba, R. Sooriyakumaran, R. Miller and J. F. Rabolt, *Macromolecules* **23**, 2346 (1990).
12. T. Hayashi, Y. Uchimaru, N. P. Reddy and M. Tanaka, *Chem. Lett.* 647 (1992).
13. M. Okano and K. Mochida, *Chem. Lett.* 701 (1990).
14. K. Mochida, H. Chiba and M. Okano, *Chem. Lett.* 109 (1991).
15. S. Kobayashi and S. Cao, *Chem. Lett.* 1385 (1993).
16. K. Mochida and H. Chiba, *J. Organomet. Chem.* **473**, 45 (1994).
17. T. Kodaira, A. Watanabe, O. Ito, M. Matsuda, S. Tokura, M. Kira, S. Nagano and K. Mochida, *Adv. Mater.* 917 (1995).
18. J. L. Brefort, R. J. P. Corriu, C. Guerin and B. J. L. Henner, *J. Organomet. Chem.* **464**, 133 (1994).
19. K. Mochida, T. Ohkawa, H. Kawata, A. Watanabe, O. Ito and M. Mastuda, *Bull. Chem. Soc. Jpn.* **69**, 2993 (1996).
20. Jikken Kagaku Kouza, Vol. 13, Japan Chemical Society, Maruzen, Tokyo, 1990, p. 74.
21. S. Kato, S. Minagawa and M. Koizumi, *Bull. Chem. Soc. Jpn.* **34**, 1026 (1961).
22. Jikken Kagaku Kouza, Vol. 13, Japan Chemical Society, Maruzen, Tokyo, 1990, p. 411.
23. K. Mochida, K. Kimijima, H. Chiba, M. Wasaka and H. Hayashi, *Organometallics* **13**, 404 (1994).
24. A. Watanabe, Y. Tsutsumi and M. Matsuda, *Synth. Methods.* **74**, 191 (1995).
25. Y. Sakaguchi, H. Hayashi and S. Nagakura, *J. Phys. Chem.* **86**, 3177 (1982).