Bull. Chem. Soc. Jpn., ***69***, 2993—2998 (1996)

# Preparation of Branched Oligogermynes and Their Micropatterning by Ultraviolet Irradiation

**Kunio Mochida,* Tomoharu Ohkawa, Hiroki Kawata,† Akira Watanabe,†† Osamu Ito,†† and Minoru Matsuda††**

Department of Chemistry, Faculty of Science, Gakushuin University, 1-5-1 Mejiro, Toshima-ku, Tokyo 171

†Faculty of Humanities and Social Sciences, Iwate University, Ueda, Morioka 020

††Institute for Chemical Reaction Science, Tohoku University, Katahira, Aoba-ku, Sendai 980-77

(Received April 2, 1996)

Branced oligogermynes were prepared both by Wurtz coupling reactions of alkyl- and phenyl-trichlorogermanes with sodium metal and by the reaction of alkyltrichlorogermanes using of samarium(II) diiodide. Upon ultraviolet irradiation of oligo(phenylgermyne) in air, the germanium–germanium bond in an oligo(phenylgermyne) film changed into a digermoxane chain. The laser flash photolysis of the oligo(phenylgermyne) film showed the formation of a germyl radical as a reactive intermediate during photodegradation. The formation of germanium carbide (Ge–C) and germanium dioxide ($GeO_2$) was observed upon a heat treatment of unirradiated and irradiated oligo(phenylgermyne) films, respectively. A relatively high-resolution $GeC/GeO_2$ micropatterning was obtained by combining the photochemical and thermal properties of branced oligogermynes.

Recently, organometallic polymers and group-14 element (silicon, germanium, tin) backbone polymers have attracted considerable attention 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, organopolygermanes strongly absorb light in the ultraviolet (UV) and near-UV regions, owing to $\sigma$ delocalization along the linear Ge–Ge polymer backbone.[8—17] Bleaching of the absorption band is caused by a decomposition of the Ge–Ge bond under UV irradiation. These polymers are quite photosensitive, and have an attractive possibility to be used as photoresists.

In addition, Henner and co-workers have reported on the formation of ceramic residues as GeC due to crosslinking by the thermolysis of polygermanes containing a $\pi$-electron system at low temperatures.[18] However, the increase in the cross-linking degree of a polymer leads to an intractable, infusible, and insoluble net-work. It is thus necessary to synthesize a new type of polygermanes.

We herein describe the synthesis of branced oligogermynes[19—22] by the reaction of alkyl- and phenyl-trichlorogermanes with reducing agents, and the micropatterning of $GeC/GeO_2$ by photocrosslinking of the oligogermynes films under UV irradiation in the air and a following heat treatment in vacuo.

## Results and Discussion

**Synthesis of Branced Oligogermylnes.** Branced oligogermynes were prepared by Wurtz-coupling reactions of alkyl- and phenyl-trichlorogermanes with sodium metal, and by a treatment of butyltrichlorogermane using samarium(II) diiodide. A Wurtz-coupling oligomerization of alkyl- and phenyl-trichlorogermanes with sodium metal was carried out according to a method for synthesizing linear polygermanes.[16] The branced oligogermynes prepared by a Wurtz coupling had a narrow molecular-weight distribution, but were in relatively low yields.

$$\mathrm{RGeCl_3} + 3\,\mathrm{Na} \longrightarrow (\mathrm{RGe})_n + 3\,\mathrm{NaCl}$$

$$\mathrm{R} = \text{alkyl, aryl}$$

Sodium metal was employed as a dispersion, and was favored over dispersed lithium metal and sodium–potassium alloy for the molecular weight and yields of the oligogermynes. Dispersed lithium led to a low molecular weight of branced oligogermynes, and a sodium–potassium alloy clearly resulted in a degradation of the oligogermynes at elevated temperatures. A successful oligomerization of alkyl- and phenyl-trichlorogermanes was carried out at high temperature in an inert aromatic solvent, such as toluene or xylene. Oligogermynes with higher molecular weight were obtained within 2 h.

The results under optimized reaction conditions are summarized in Table 1.

The synthesis of branced oligogermynes was also examined using samarium(II) diiodide ($SmI_2$) as a one-electron reducing agent in tetrahydrofuran (THF).[23] This procedure provided a homogeneous reduction of butyltrichlorogermane under both safer and milder conditions in contrast to the sodium dispersion method. The molecular weight and yield

Table 1. Oligomerization of Alkyl- and Phenyl-trichlorogermanes and Alkali Metals and Samariumu(II) Diiodide

| Polymer | Method | $\overline{M}_w$ [a)] | $\overline{M}_n$ | $\overline{M}_w/\overline{M}_n$ | Yield/% | IP/eV [b)] |
|---|---|---|---|---|---|---|
| ($n$-BuGe)$_n$ | Na/toluene, reflux, 2 h | 3800 | 3300 | 1.2 | 39.3 | 5.18 |
|  | $SmI_2$/THF, r.t., 12 h, | 3500 | 3000 | 1.1 | 25.4 |  |
| ($t$-BuGe)$_n$ | Na/toluene, reflux, 2 h | 1300 | 1200 | 1.1 | 23.7 |  |
| ($n$-HexGe)$_n$ | Na/toluene, reflux, 2 h | 4900 | 4300 | 1.1 | 48.9 | 5.16 |
| (PhGe)$_n$ | Na/toluene, reflux, 2 h | 1700 | 1100 | 1.5 | 6.3 | 4.95 |

a) Molecular weights are relative to polystyrene standards. b) Ionization potentials were measured by using an UV photoelectron spectrometer (Riken Keiki AC-1).

of the oligogermynes obtained using of $SmI_2$ are similar to those of the Wurtz-type couplings. This result is included in Table 1.

After terminating of oligomerization, the reaction mixture was subsequently quenched by the addition of 2-propanol. The IR spectra of the oligogermynes quenched with alcohol showed a strong Ge–O–Ge band (950—1050 $cm^{-1}$)[24)] arising from the hydrolysis of unreduced germanium–chlorine (Ge–Cl) bonds. After a similar workup, the reaction mixture treated with butyllithium showed no significant digermoxane band. Generally, the NMR spectra provide the most direct information about the microstructure of branced oligogermynes. However, no satisfactory information on the microstructure of the oligomers by means of the $^1H$ and $^{13}C$ NMR spectra was obtained due to a broad resonance.

It has been reported that bromine can cleave the Ge–Cl bonds of polygermanes to give bromogermanes.[25)] Phenyltribromogermane was formed in high yields in the reaction of oligo(phenylgermyne) with bromine in 1,2-dibromoethane at 120 °C. The formation of phenyltribromogermane suggests that the isolated oligogermynes have a branced structure.

While the linear polygermanes exhibit strong $\sigma$–$\sigma^*$ transitions in the range of 300—350 nm ($\varepsilon$=2000—10000 per Ge) in the near UV,[16)] solutions of branced oligogermynes exhibit a more intense broad absorption from 200 nm ($\varepsilon$ < 10000 at 200 nm), tailing down into the visible region. The very high extinction coefficients of branced oligogermynes may be attributed to an extension of the Ge–Ge $\sigma$ conjugation effects observed in linear polygermanes into three dimension across the branced oligogermynes.

A typical elution profile of oligo(butylgermyne) from gel permeation chromatography (GPC) and its UV spectrum are shown in Figs. 1 and 2.

The branced oligogermynes are all isolated as yellow and moderately light-sensitive molecules. Most oligogermynes, except for oligo(phenylgermyne), showed poor film-forming properties.

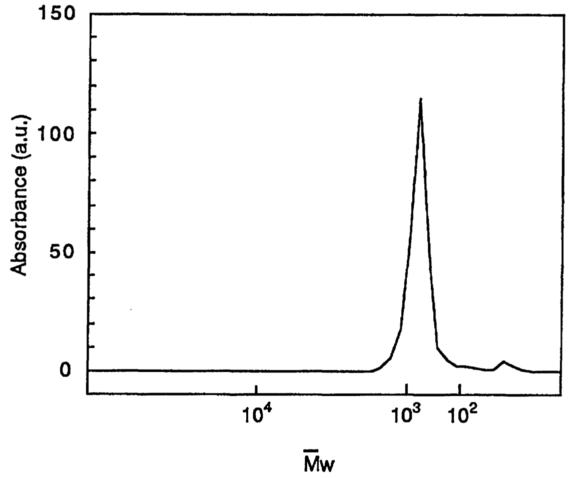

Fig. 1. Elusion profile from gel permeation chromatography of oligo(phenylgermyne). Molecular weights are relative to polystyrene standard.

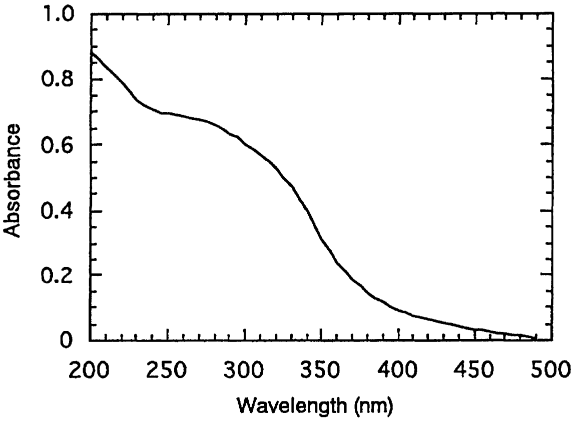

Fig. 2. UV spectrum of oligo(phenylgermyne) film.

**Photochemical Properties of Oligo(phenylgermyne).** Thin films of oligo(phenylgermyne) were prepared by spin-coating from a 5—10% THF solution. The film was deposited on quartz plates and dried under a vacuum at room temperature. The film thickness of oligo(phenylgermyne), which was determined by UV-vis spectrometry, was 0.4—0.7 μm. As expected, an oligo(phenylgermyne) film is quite light sensitive. Figure 3 shows the bleaching of a film of oligo(phenylgermyne) 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,[16)] a blue shift of their absorption maxima is caused by a Ge–Ge chain scission, which produces lower molecular-weight chain fragments.

The solid-state quantum yield for the oligo(phenylgermyne) film was measured at 290 nm by potassium tris(oxalato)ferrate(III) actinometer.[26)] In($e^{2.303\mathrm{O.D}}$-1), when plotted against $t$, must give a straight line. O.D is the

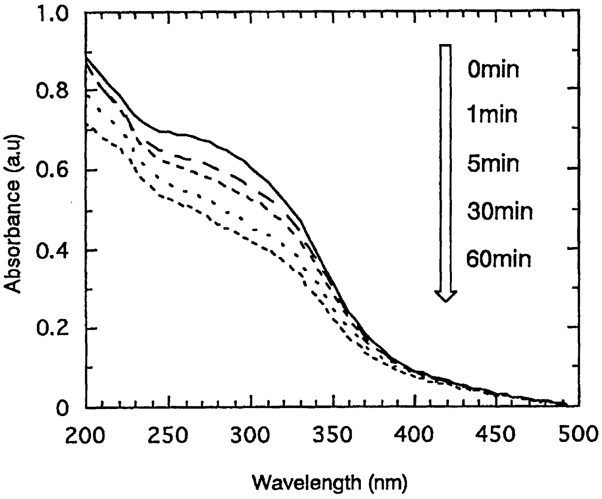

Fig. 3. UV spectra of oligo(phenylgermyne) film with successive UV irradiation.

optical density for an oligo(phenylgermyne) film. The inclination determined from the straight line corresponds to $2.302\Phi I_0\varepsilon\times10^3$. $\Phi$ is the quantum yield, $I_0$ the light intensity, and $\varepsilon$ the molar extenction coefficient of oligo(phenylgermyne). Using a chemical actinometer, the quantum yield ($\Phi$) was calculated to be $10\times\varepsilon^{-1}$. $\Phi$ for the oligo(phenylgermyne) film was determined to be $1\times10^{-3}$, assuming a value of $10^4$ at 290 nm for $\varepsilon$. The quantum yields for scission were significantly lower in the solid state. In the solid state the quantum yields were much lower (50—100 times) than the solution values for linear polysilanes[27] and branced polysilynes.[28]

In addition to UV observations, the process of photodecomposition of the oligo(phenylgermyne) film was observed by IR spectrometry. Figure 4 shows the IR spectral change of the oligo(phenylgermyne) film in the range of 500—3000 $cm^{-1}$ upon irradiation at 254 nm. Irradiation of the oligo(phenylgermyne) film in air led to the appearance of IR bands at 950—1050 $cm^{-1}$, attributed to the Ge–O–Ge bond.[24] IR bands due to the Ge–O–Ge bond increased with succesive UV irradiation.

The XPS spectra of the Ge 3d region for the oligo(phenylgermyne) film were observed both before and after UV irradiation at 254 nm, as shown in Fig. 5. The XPS spectrum before UV irradiation shows a peak at 29.8 eV and a shoulder near 32.0 eV in Fig. 5. The former is attributed to the Ge–Ge structure and the latter is the Ge–O–Ge structure. After UV irradiation in air, the peak of Ge–Ge almost disappears, and the peak of the Ge–O–Ge structure increases, as shown in Fig. 5. These results are consistent with those of the IR spectra.

To obtain information about reactive intermediates in the photooxidation of an oligo(phenylgermyne) film, the laser flash photolysis of an oligo(phenylgermyne) film was carried out in air. The laser flash photolysis ($\lambda$ =266 nm) of the oligo(phenylgermyne) film gave a transient absorption peak at ca. 350 nm, as shown in Fig. 6. The transient peak at ca. 350 nm has been assigned to that of the oligogermyl radicals by comparing its spectral characteristics with those reported for similar previously reported germyl radicals.[16] Thus, the key intermediate is oligogermyl radicals generated by a Ge–Ge bond scission in the photooxidation of the oligo(phenylgermyne) film in air.

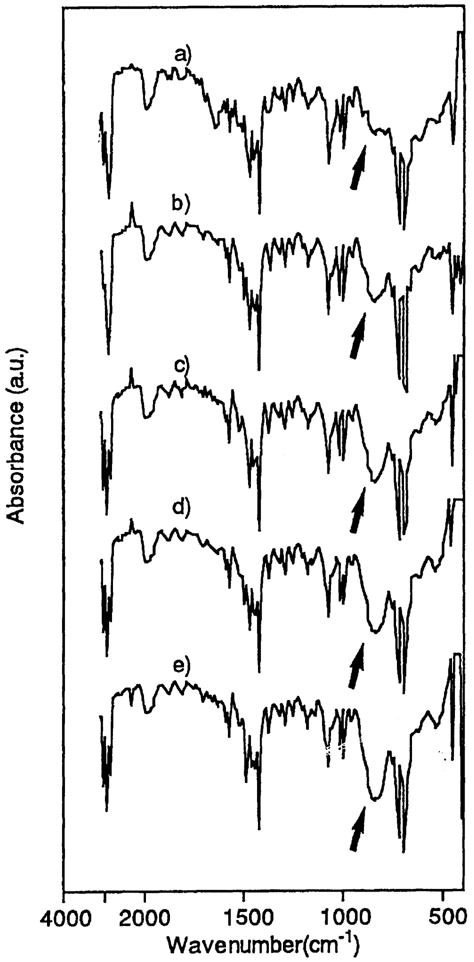

Fig. 4. IR spectra of oligo(phenylgermyne) film with successive UV irradiation.

**Thermal Properties of Oligo(phenylgermyne).** The thermal behavior of oligo(phenylgermyne) was investigated using the thermogravimetric (TG) curve and different thermal analyses (DTA) (Fig. 7). The TG curve of an oligo(phenylgermyne) film shows that two steps may be distinguished: (1) From 50 to ca. 230 °C, the weight of the polymer is constant, but begins to become less at 230 °C. (2) Above 300 °C, a fast weight loss takes place, and the oligomer loses 60% of its weight by heating under nitrogen up to 500 °C. At the same time, a large escape of benzene is detected by GC and GC-MS. Based on the volume of detected benzene it may be concluded that the degradation of oligo(phenylgermyne) involves mainly a cleavage of the germanium-phenyl bonds. Although a cleavage of the Ge–Ge bonds occurs, no low oligogermanes are detected by GC or GC-MS. The DTA of oligo(phenylgermyne) shows that the Ge-branced structure greatly changes at 340 °C. The elimination of benzene and other volatile compounds may be enhanced at 230—500 °C.

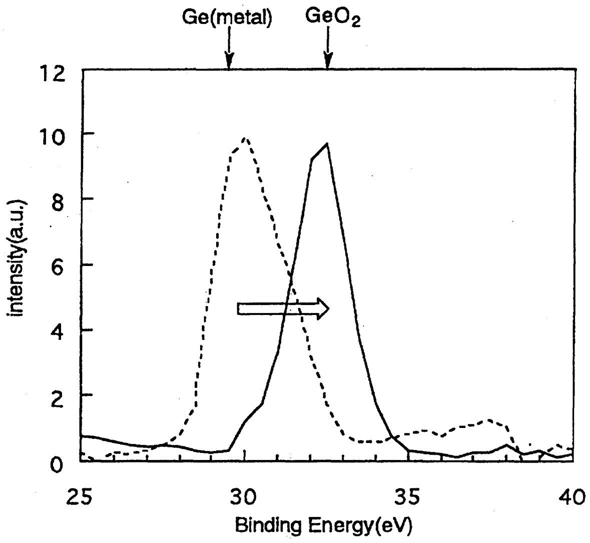

Fig. 5. XPS spectra of oligo(phenylgermyne) film before UV irradiation (····) and after UV irradiation (—) in the air.

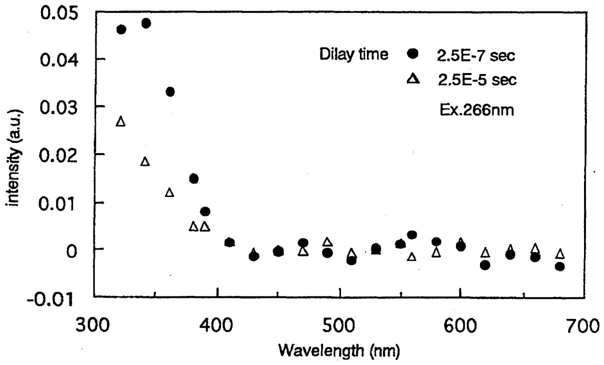

Fig. 6. Transient absorption spectra obtained by laser flash photolysis of oligo(phenylgermyne) film in the air; laser excitation at 266 nm.

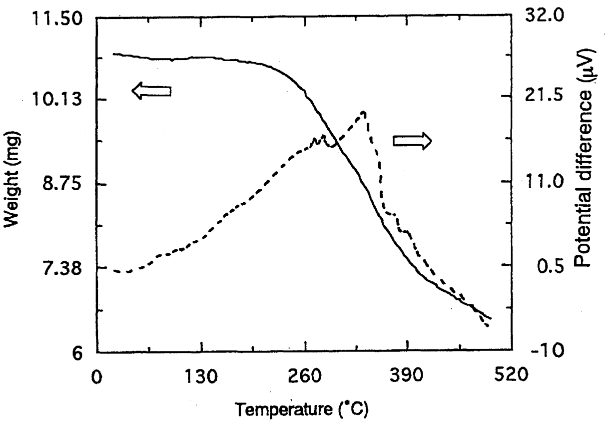

Fig. 7. Thermogravimetric (TG) curve and differential thermal analysis (DTA) for oligo(phenylgermyne) under nitrogen.

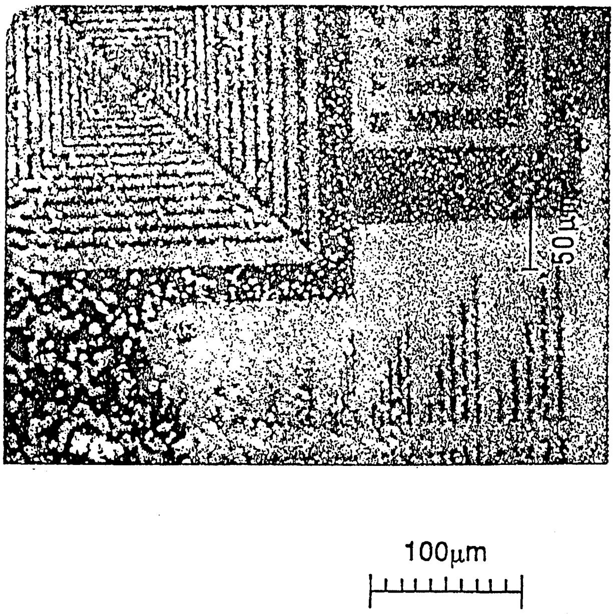

Fig. 8. Micrograph of oligo(phenylgermyne) films heat treated at 400 °C for 1 h in vacuo after UV irradiation for 10 min with photomask.

After the elimination of volatile compounds, the formation of GeC and $GeO_2$ may proceed above 500 °C. The IR spectra of residues of the oligo(phenylgermyne) by a heat treatment at 500 °C revealed the appearance of a Ge–O–Ge and GeC framework; additional NMR experiments show no proton signals. The formation mechanism of the GeC structure at high temperature is not as clear as in the poly(phenylsilyne) cases.[29)]

**GeC/GeO$_2$ Micropatterning.** As mentioned above, oligo(phenylgermyne) is UV sensitive, and is also appliciable to the precursor of GeC. These photochemical and ther-

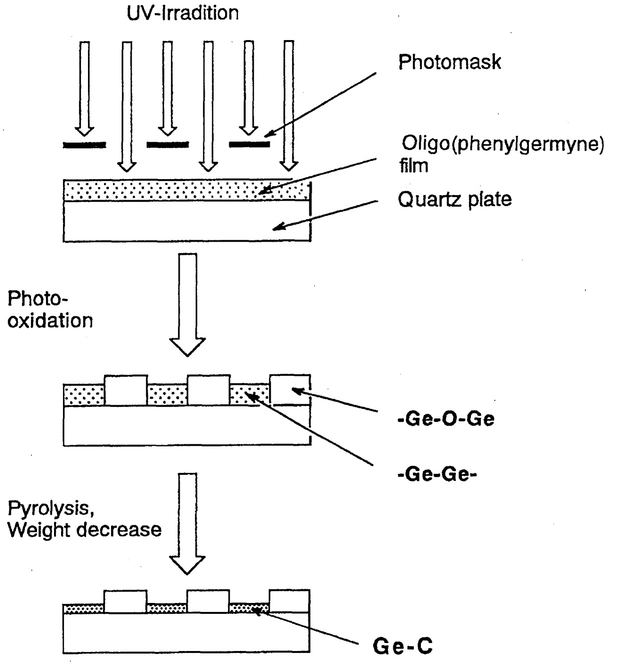

Fig. 9. Schematic diagram of the formation of GeC/GeO$_2$ micropatterning using oligo(phenylgermyne) film.

mal properties were combined to achieve micropatterning consisting of GeC and $GeO_2$ lines. Figure 8 shows a micrograph of oligo(phenylgermyne) obtained upon a heat treatment at 500 °C after UV irradiation for 10 min with a photomask. The micrograph of oligo(phenylgermyne) shows clear micropatterns where the resolution of the line and space reaches ca. 5 μm. The formation of the patterns suggests an excellent dimensional stability of oligo(phenylgermyne) due to the Ge-branced structure. No cracking or hole was observed over the entire area of GeC/$GeO_2$ patterning. A schematic representation for GeC/$GeO_2$ micropatterning using an oligo(phenylgermyne) film by UV irradiation and a heat treatment is summarized in Fig. 9. Upon a irradiation of an oligo(phenylgermyne) film, it was photo-oxidized via a germyl radical as a reactive intermediate. Oligo(phenylgermyne)/oligogermoxane micropatterns were formed upon UV irradiation with a photomask. The heat treatment in vacuo changes the oligo(phenylgermyne)/oligogermoxane micropatterns into GeC/$GeO_2$ micropatterns. GeC/$GeO_2$ micropatterning by combining the photochemical and thermal properties of branced oligogermanes is a convenient, all-dry process which has an advantage compared to a wet lithography process. Recently, SiC/$SiO_2$ and a-Si/$SiO_2$ micropatterning by a heat treatment of a poly(organosilyne) film in vacuo after a photooxidation under UV irradiation with a photomask was achieved by Watanabe and co-workers.[30—33]

## Experimental

$^1$H and $^{13}$C NMR 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 infrared spectra were recorded with a Shimadzu FT IR 4200 spectrometer. The UV and UV-vis spectra were recorded on a Shimadzu UV 2200 spectrometer. Gas chromatography was performed on a Shimadzu GC8A with 1 m 20% SE30 and 30% Apiezon L columns. Liquid chromatography was performed on a Twincle with Asahipak GS 310 column.

**Materials.** Sodium metal, potassium metal, lithium metal, magnesium metal, and a hexane solution of *n*-BuLi were commercially obtained. Ether, tetrahydrofuran, and toluene for use as a solvent were dried over a sodium wire and purified by distillation under nitrogen. *n*-$BuGeCl_3$,[34] *t*-$BuGeCl_3$,[35] *n*-$C_6H_{13}GeCl_3$,[34] and $PhGeCl_3$[34] were prepared as described.

**Preparation of Branced Oligogermanes by Wurtz Coupling.** As a representative example, the preparation of oligo(phenylgermyne) is described. Branced oligogermanes were 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 phenyltrichlorogermane (12.7 g, 0.05 mol) was added via a funnel. Phenyltrichlorogermane was then added to the stirred dispersion over a period of 5 min. The reaction mixture turned purple immediately. After the addition of phenyltrichlorogermane, the reaction mixture was stirred under reflux for 2 h, and then cooled to room temperature. First THF (50 cm$^3$), and then BuLi (0.075 mol), were added to the reaction mixture and stirred for 1 h. After the 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 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 0.8 g of oligo(phenylgermyne) of a white solid. $^1$H NMR ($\delta$ in $C_6D_6$) $\delta=7.0$ (br); $^{13}$C NMR ($\delta$ in $C_6D_6$) $\delta=128.0$; IR (neat) 2950, 1950, 1650, 1550, 1380, 1300, 1260, 1080, 1020, 1000, 730, 630 cm$^{-1}$. Anal. Found: C, 47.72; H, 3.16%. Calcd for $(C_6H_5Ge)_n$: C, 48.14; H,3.37%.

Oligo(butylgermyne): $^1$H NMR ($\delta$ in $C_6D_6$) $\delta=1.2$ (br), 3.6 (br); $^{13}$C NMR ($\delta$ in $C_6D_6$) $\delta=1.39$; IR (neat) 2950, 2930, 2850, 1630, 1460, 1080, 620 cm$^{-1}$. Anal. Found: C, 36.76; H, 6.74%. Calcd for $(n\text{-}C_4H_9Ge)_n$: C, 37.04; H, 6.99%.

Oligo(*t*-butylgermyne): $^1$H NMR ($\delta$ in $C_6D_6$) $\delta=1.2$ (br), 3.6 (br); $^{13}$C NMR ($\delta$ in $C_6D_6$) $\delta=14.4$, 23.1; IR (neat) 2950, 2930, 2350, 1950, 1610, 1490, 1460, 1360, 1270, 1080, 1050, 970, 870, 810, 780, 700 cm$^{-1}$. Anal. Found: C, 36.88; H, 6.85%. Calcd for $(t\text{-}C_4H_9Ge)_n$: C, 37.04; H, 6.99%.

Oligo(hexylgermyne): $^1$H NMR ($\delta$ in $C_6D_6$) $\delta=1.0$ (br), 1.5 (br); $^{13}$C NMR ($\delta$ in $C_6D_6$) $\delta=14.3$, 23.1, 30.1; IR (neat) 2950, 2030, 1600, 1500, 1470, 1380, 1170, 1100, 980, 940, 780, 700 cm$^{-1}$. Anal. Found: C, 45.24; H, 7.98%. Calcd for $(n\text{-}C_6H_{13}Ge)_n$: C, 45.68; H, 8.31%.

**Preparation of Oligo(butylgermyne) by Use of Samarium(II) Diiodide.** A THF solution of $SmI_2$ (3.0 mmol) was added to a dry 100 ml two-necked flask fitted with a condenser connected to a drying Ar inlet. The reaction mixture was stirred at room temperature for 12 h. BuLi (1.5 mmol) was then added to the reaction mixture. The reaction mixture was stirred for 5 min. After removing the solvent, oligo(butylgermyne) was obtained by crystallization from 2-propanol. Oligo(butylgermyne) (0.06 g) was obtained.

**Reaction of Oligo(phenylgermyne) with Bromine in 1,2-Dibromoethane.** Bromine (1.9 g, 23.7 mmol) was added to oligo(phenylgermyne) ($\overline{M}_w=1700$, 0.6 g) in 1,2-dibromoethane (20 cm$^3$) and stirred at 120 °C for 20 h. Phenyltriboromogermane (0.24 mmol) was characterized by GC and GC-MS.

**Study of Photochemical Reactions of Oligo(phenylgermyne) Film by UV.** A thin film of oligo(phenylgermyne) was prepared by spin-coating from a 5—10% THF solution. The film was deposited on quartz plates (10×30×1 mm) and dried under a vacuum (10$^{-4}$ mmHg, 1 mm Hg=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.

**A Study of Photochemical Reactions of Oligo(phenylgermyne) Film by IR.** Thin films of oligo(phenylgermyne) were prepared from a 20% toluene solution. The film was deposited onto a NaCl plate for IR use, and dried under a vacuum (10$^{-4}$ mmHg) at room temperature. This operation was repeated three times. The sample was irradiated with a 110-W low-pressure Hg arc lamp at room temperature. The change in the sample was followed by IR spectrometry.

**Quantum Yields of Oligo(phenylgermyne).** A thin film of oligo(phenylgermyne) 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.[26]

**Time-Resolved Optical Absorption.** Laser flash photolysis experiments were performed at room temperature by using the fourth harmonic ($\lambda$ =266 nm) of a Quanta-Ray (GCR-130) Nd : YAG laser as an excitatory light source. The sample was a thin film of oligo(phenylgermyne) on a quartz plate. The laser pulse was about 6 ns; details concerning the laser-photolysis apparatus and manipulation have been published elsewhere.[36)]

The authors thank Dr. Katsumi Shimoda for measuring the TG and DTA data of oligo(phenylgermyne). We also thank Dr. Kohichi Handa of Nissan Auto Co., Ltd. for measuring the XPS of oligo(phenylgermyne). This research was partially supported by a Grant-in-Aid for Scientific Research on Priority Area of Reactive Organometallics No. 05236233 for K. M. from the Ministry of Education, Science and Culture.

## References

1) R. West, "Comprehensive Organometallic Chemistry," ed by G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press, New York (1982), Vol. 2, Chap. 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), and references cited therein.

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, H. 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.*, **1992**, 647.

13) M. Okano and K. Mochida, *Chem. Lett.*, **1990**, 701.

14) K. Mochida, H. Chiba, and M. Okano, *Chem. Lett.*, **1991**, 109.

15) S. Kobayashi and S. Cao, *Chem. Lett.*, **1993**, 1385.

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.*, **1995**, 917.

18) J. F. Brefort, R. J. P. Corriu, C. Guerin, and B. J. L. Hebber, *J. Organomet. Chem.*, **464**, 133 (1994).

19) A. Watanabe, T. Komatsubara, M. Matsuda, Y. Yoshida, and S. Tagawa, *J. Photopolym. Sci. Technol.*, **5**, 545 (1992).

20) W. J. Sxymanski, G. T. Visscher, and P. A. Bianconi, *Macromolecules*, **26**, 869 (1993).

21) A. Watanabe, T. Komatsubara, M. Matsuda, Y. Yoshida, and S. Tagawa, *Macromol. Chem. Phys.*, **196**, 1229 (1995).

22) H. Kishida, H. Tachibana, M. Matsumoto, and Y. Tokura, *Appl. Phys. Lett.*, **65**, 1359 (1994).

23) Y. Yokoyama, M. Hayakawa, T. Azemi, and K. Mochida, *J. Chem. Soc., Chem. Commun.*, **1995**, 2275.

24) R. J. Cross and F. Glockling, *J. Chem. Soc. A*, **1968**, 1423.

25) M. Metlesics and H. Zeiss, *J. Am. Chem. Soc.*, **82**, 3321 (1960).

26) S. Kato, S. Minagawa, and M. Koizumi, *Bull. Chem. Soc. Jpn.*, **34**, 1026 (1961).

27) H. Ban and K. Sukegawa, *J. Appl. Polym. Sci.*, **33**, 2787 (1987).

28) A. Watanabe and M. Matsuda, *Chem. Lett.*, **1991**, 1101.

29) A. Watanabe, Y. Tsutsumi, and M. Matsuda, *Synth. Met.*, **74**, 191 (1995).

30) A. Watanabe and M. Matsuda, *Chem. Lett.*, **1991**, 1101.

31) A. Watanabe, Y. Nagai, M. Matsuda, M. Suezawa, and K. Sumino, *Chem. Phys. Lett.*, **207**, 132 (1993).

32) A. Watanabe, T. Komatsubara, O. Ito, and M. Matsuda, *J. Appl. Phys.*, **77**, 2796 (1995).

33) A. Watanabe, Y. Nagai, and M. Matsuda, *Jpn. J. Appl. Phys.*, **34**, L452 (1995).

34) "Shin Jikkenn Kagaku Kouza," Maruzen, Tokyo (1976), Vol. 12, p. 377.

35) M. Wojnowska, M. Noltemeyer, H. J. Fullgrabe, and A. Meller, *J. Organomet. Chem.*, **228**, 229 (1982).

36) A. Watanabe, T. Komatsubara, O. Ito, and M. Matsuda, *J. Appl. Phys.*, **77**, 2796 (1995).