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Synthesis, absorption characteristics and some reactions of polygermanes

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Abstract

A number of high molecular weight polygermanes were prepared by an improvement on Wurtz coupling reactions of dichlorogermanes and sodium metal, and by a method using diiodogermylene and Grignard reagents (or organolithiums). Most of the polygermanes thus prepared showed a narrow molecular distribution containing molecular weights 10^3–10^4. In solution, the polygermanes showed characteristic electronic absorption bands at 300–350 nm and were strongly thermochromic for alkyl-substituted derivatives. Photolysis of the polygermanes proceeded by both contraction of the chain with loss of diorganogermylenes and homolytic scission of the germanium–germanium σ bond.

Key words: Germanium; Polygermane; Photochemistry

1. Introduction

A relatively new class of σ-conjugated polymers, polysilanes and polygermanes, have attracted considerable interest in recent years because of their unique chemical and physical properties arising from electronic delocalization in the Group 14 element–Group 14 element σ bond [1–6]. Much attention is therefore being directed towards the development of synthetic routes, chemical and physical studies, and applications of these high molecular weight polysilanes and polygermanes. However, the study of high molecular weight polygermanes is very much limited compared with those of the polysilanes [7–11].

Previously, we have found curious spectroscopic properties of germanium–germanium σ bonds of relatively short oligogermanes [12] and the generation of germylenes and germyl radicals produced by photochemical decomposition [13]. Here, we describe an improved method of Wurtz coupling polymerization (Kipping method) and a synthetic method for polygermane using diiodogermylene, a stable inorganic germanium compound (**II**), and the electronic properties and photochemical reactions of high molecular weight polygermanes.

2. Results and discussion

2.1. *Synthesis of polygermanes*

The first substituted polygermanes were prepared by the condensation of dichlorogermanes with sodium metal as described in case of polysilanes [7].

$$R^1R^2GeCl_2 + 2Na \longrightarrow (R^1R^2Ge)_n + 2NaCl$$

Although this Wurtz-type coupling of dichlorogermanes (Kipping method) is the most practical procedure for the preparation of polygermane high polymers, there are some obvious disadvantages. It has a low tolerance for reactive functionality, stereochemical control in the polymerization is borderline, yields are usually low and depend upon the substituents on germanium, and molecular weight distributions are large [6]. To improve these problems, we carried out Wurtz-type coupling polymerization of dichlorogermanes under various experimental conditions. These results are summarized in Table 1.

First, we investigated Wurtz-type coupling of di-n-butyldichlorogermane under a variety of reaction conditions. The poly(di-n-butylgermane) produced at elevated temperatures in toluene using sodium metal in dispersion had a narrow molecular weight distribution, but was relatively low in molecular weight (entry 3). The first poly(di-n-butylgermane) prepared and isolated by Trefonas and West [7] showed a distinctly

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bimodal broad molecular distribution and molecular weights in excess of about 7.7×10^5 were obtained. The preformed sodium dispersion itself can be added to the dichlorogermane dissolved in toluene or vice versa. The inverse addition mode for the preparation of polysilanes has been reported to result in lower yields of higher molecular weight polymer, although the procedure is experimentally more difficult and hazardous than normal addition [6]. However, the inverse addition mode for the polymerization of di-n-butyldichlorogermane gave lower yields of lower molecular weight polymers under these reaction conditions (entry 4). Sodium metal was favored over lithium metal and sodium–potassium alloy for molecular weight and yields of poly(di-n-butylgermane) (entries 7 and 8). Lithium metal often results in cyclooligomerization rather than linear polymerization. Sodium–potassium alloys lead to the degradation of high molecular polygermanes.

Polygermanes were obtained in good yields by Wurtz-coupling in toluene containing a small amounts of hexamethylphosphoric triamide (HMPA) under milder conditions (entry 6). The utility of HMPA as a co-solvent appears general for the polymerization of dialkyldichlorogermanes, but the improved yields of polygermanes are accompanied by a decreasing molecular weight. Addition of relatively large amounts of 18-crown-6 resulted in poor yields and lowering of the molecular weight of polygermanes (entry 5). The results of Wurtz-type coupling of di-n-butyldichlorogermane in Table 1 may suggest that the solvent effect is more complex than simple anion activation.

In an effort to produce higher molecular weight polygermanes, dichlorodi-n-hexylgermane as a monomer was also examined under a variety of different reaction conditions (entries 10–14). In most cases, the polygermanes as isolated showed a narrow molecular distribution that contained high molecular weights ($MW > 1.0 \times 10^4$). The molecular weights are suggested to be very sensitive to the length of the substituent of dialkyldichlorogermanes [7,8]. As was shown in the polymerization of dichlorodi-n-hexylgermane, the molecular weight of the polymer became shorter at lower temperatures (entries 10, 11). Inverse addition did not improve the situation, and very little high molecular weight material was isolated as described in the case of polymerization of di-n-butyldichlorogermane (entry 12). The use of sodium–potassium alloys and the addition of 18-crown-6 in the Wurtz-coupling of dichlorodi-n-hexylgermane did not improve molecular weights and yields of the polymers (entries 13, 14). High molecular weight poly(di-n-hexylgermane) was first prepared by Miller and Sooriyakumaran in very low yield [8].

Interestingly, the molecular weights of poly(phenylmethylgermane) were found to have a marked temperature dependence (entries 15–17). Thus, the molecular weights of the polymers became longer at lower temperature. At elevated temperatures, sodium metal may lead to the degradation of the germanium–phenyl bond

TABLE 1. Polymerization of dichlorogermanes and alkali metals

Entry	Polymer	Method	λ_{max} (nm)	$\bar{M}w$ ($\times 10^3$)	$\bar{M}n$ ($\times 10^3$)	$\bar{M}w/\bar{M}n$	Yield (%)
1	$(Et_2Ge)_n$	Na/toluene, reflux, 2 h	305	3.4	2.8	1.21	11.0
2	$(Pr_2Ge)_n$	Na/toluene, reflux, 2 h	300	6.3	5.6	1.13	15.4
3	$(Bu_2Ge)_n$	Na/toluene, reflux, 2 h	325	6.8	6.4	1.06	52.5
4	$(Bu_2Ge)_n$	inverse addition reflux, 2 h	320	4.0	2.7	1.49	20.0
5	$(Bu_2Ge)_n$	Na, 18-c-6/toluene reflux, 2 h	316	3.8	1.7	2.26	8.1
6	$(Bu_2Ge)_n$	Na/toluene-HMPA 50°C, 2 h	320	3.6	2.1	1.69	40.9
7	$(Bu_2Ge)_n$	Li/toluene reflux, 2 h	320	3.6	2.5	1.47	5.0
8	$(^iBu_2Ge)_n$	Na/toluene reflux, 2 h	330	3.9	3.5	1.12	2.0
9	$(Hex_2Ge)_n$	Na/toluene reflux, 2 h	328	15.1	10.4	1.45	20.0
10	$(Hex_2Ge)_n$	Na/toluene 60°C, 2 h	325	11.4	7.8	1.46	7.8
11	$(Hex_2Ge)_n$	inverse addition reflux, 2 h	325	11.0	7.5	1.47	6.0
12	$(Hex_2Ge)_n$	Na-K/toluene reflux, 2 h	325	11.5	7.8	1.49	8.5
13	$(Hex_2Ge)_n$	Na, 18-c-6/toluene reflux, 2 h	322	7.6	4.3	1.76	5.0
14	$(PhMeGe)_n$	Na/toluene reflux, 2 h	325	2.0	0.7	2.79	20.4
15	$(PhMeGe)_n$	Na/toluene 60°C, 2 h	327	5.0	3.6	1.39	26.4
16	$(PhMeGe)_n$	Na/toluene r.t., 2 h	330	5.7	4.2	1.36	15.4
17	$(PhHexGe)_n$	Na/toluene 60°C, 2 h	355	12.5	9.1	1.37	3.3
18	$(Hex_2Ge)_n(Hex_2Si)_m$	Na/toluene, reflux 2 h	316	High			
				112.8	90.6	1.24	
				Low			7.2
				7.1	6.1	1.16	

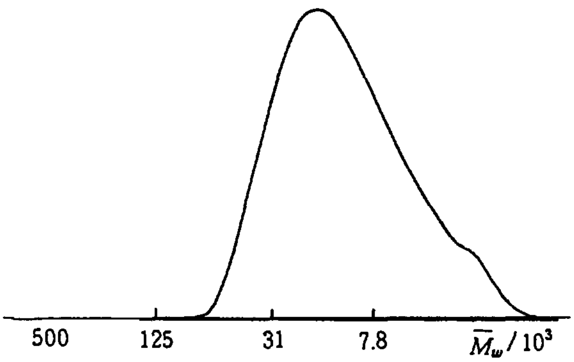


Fig. 1. Elution profile from gel permeation chromatography of $(^n\mathrm{Hex}_2\mathrm{Ge})_n$. Molecular weights are relative to polystyrene standards.

in poly(phenylmethylgermane). The first preparation of poly(phenylmethylgermane) was reported by Tanaka and *et al.* [11].

The mechanism of Wurtz-coupling polymerizations appears to be complex. The likely first step may be an electron transfer from alkali metal to form a radical anion of dichlorogermane. Condensation may take place partly on or near the alkali metal surface, and partly in solution.

Other dialkyldichlorogermanes were examined as monomers for polymerization, and the results are also summarized in Table 1. The low yields of polygermanes listed in Table 1 may be due to the formation of oligomers and low molecular weight polymers.

A typical elution profile of poly(di-n-hexylgermane) from gel permeation chromatography (GPC) is shown in Fig. 1. Unexpectedly, most of the polygermanes prepared and isolated under these experimental conditions show a monomodal molecular weight distribution in contrast with that of polysilanes.

It is well known that organogermylenes easily polymerize to give high molecular weight products [13]. Therefore, organogermylenes are very useful precursors for the preparation of polygermanes. The substituted polygermanes can also be prepared by reaction of a stable inorganic germylene, diiodogermylene, with Grignard reagents and organolithiums. The method of diiodogermylene with organometallics is experimentally easier and safer than Wurtz-type couplings. This procedure gives higher yields of relatively lower molecular weight polygermanes with narrower molecular weight distribution than the Wurtz-coupling methods. The reaction of diiodogermylene with phenyl Grignard reagents gave mainly tetraphenylgermane and hexaphenyldigermane. These results are summarized in Table 2.

$$\mathrm{GeI_2} + \text{excess } \mathrm{RMgBr(or\ RLi)} \longrightarrow (\mathrm{R_2Ge})_n$$

A typical elution profile of poly(di-n-butylgermane) from GPC is shown in Fig. 2.

Recently, Kobayashi and Cao have reported on the formation of high molecular weight polygermanes by the reaction of dichlorogermylene-1,4-dioxane complex and organolithiums [14].

2.2. Electronic properties

To investigate the delocalization of the σ electron in germanium–germanium bonds, ultraviolet and visible spectra of polygermanes were examined. The high molecular weight polygermanes showed characteristic electronic absorption bands at 300–350 nm. The values of λ_{max} are included in Tables 1 and 2.

The UV absorption bands of polygermanes depend upon the substituent group on the germanium atom as shown in Tables 1 and 2. The values of λ_{max} move to longer wavelength as the size of the alkyl group increases. This trend may be explained by the difference in the chain conformation of polygermanes with larger alkyl groups favoring a greater proportion of *trans* conformations [10]. Previously, we reported that the values of λ_{max} of permethylated oligogermanes move to longer wavelength with increasing chain length as the number of germanium atoms becomes larger [12]. Taking the UV data of permethylated oligogermanes reported previously [12] and various kinds of molecular weight polygermanes shown in Table 1, the absorption maxima of polygermanes reach a constant values (*ca.* 330 nm) as the number of germanium atoms become larger than *ca.* 20. The wavelength of absorption bands as a function of chain length for polygermanes are shown in Fig. 3.

Polygermanes with alkyl substituents in solution showed clear thermochromic behavior. For example,

TABLE 2. Reactions of $\mathrm{GeI_2}$ with Grignard reagents and organolithiums

Entry	Polymer	Method	λ_{max} (nm)	$\overline{Mw}$ ($\times10^3$)	$\overline{Mn}$ ($\times10^3$)	$\overline{Mw}/\overline{Mn}$	Yield (%)
1	$(\mathrm{Me_2Ge})_n$	MeMgBr reflux, 3 h	*ca.* 295	2.1	1.2	1.75	30
2	$(\mathrm{Me_2Ge})_n$	MeLi reflux, 3 h	*ca.* 290	2.0	1.1	1.88	19
3	$(\mathrm{Bu_2Ge})_n$	BuMgBr reflux, 3 h	*ca.* 290	2.2	1.8	1.22	55
4	$(\mathrm{Bu_2Ge})_n$	BuLi reflux, 3 h	*ca.* 290	2.2	1.7	1.28	52
5	$(\mathrm{Ph_2Ge})_n$	PhMgBr reflux, 3 h	*ca.* 300	$(\mathrm{Ph_3Ge})_2$, $\mathrm{Ph_4Ge}$			60

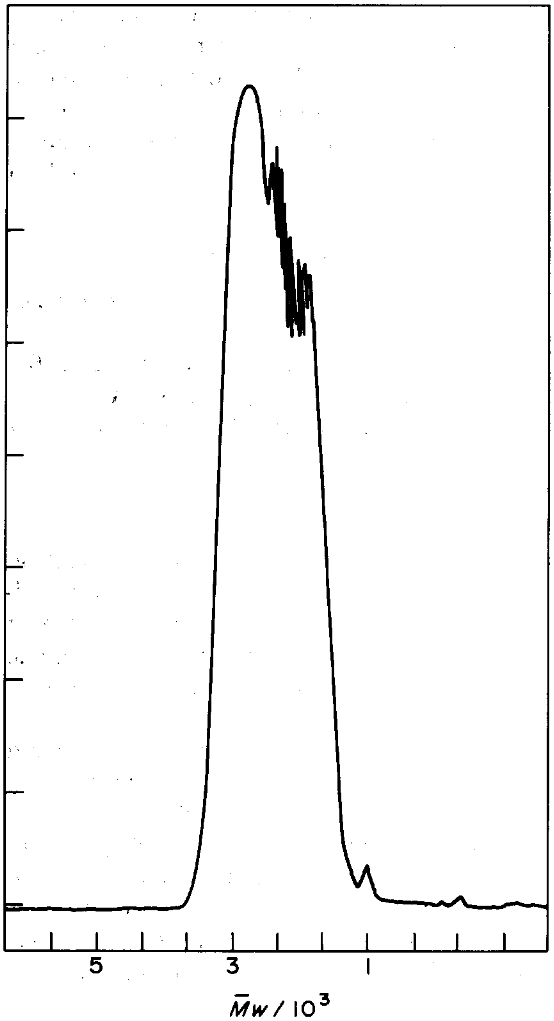


Fig. 2. Elution profile from gel permeation chromatography of $(^n\mathrm{Bu}_2\mathrm{Ge})_n$. Molecular weights are relative to polystyrene standards.

the value of λ_{max} of $(\mathrm{Hex}_2\mathrm{Ge})_n$ shifts gradually and reversibly to longer wavelength with decreasing temperature as shown in Fig. 4. Thus, one absorption band (λ_{max} 340 nm at room temperature) of $(\mathrm{Hex}_2\mathrm{Ge})_n$ disappears and a new band (λ_{max} 350 nm at −60°C) grows at longer wavelength, as the temperature decreases. The UV spectrum of $(^n\mathrm{Bu}_2\mathrm{Ge})\mathrm{n}$ also showed clear thermochromic behavior (from λ_{max} 340 nm at room temperature to 360 nm at −120°C). On the other hand, $(\mathrm{Et}_2\mathrm{Ge})_n$ and $(\mathrm{PhHexGe})_n$ did not show clear thermochromic behavior. In these polygermanes, absorption maxima steadily red shifts from the room temperature values of 300 nm for $(\mathrm{Et}_2\mathrm{Ge})_n$ (and 330 nm for $(\mathrm{PhHexGe})_n$) and approaches a limiting values of 305 nm (and 335 nm) at low temperatures. The UV spectrum of poly(phenylhexylgermane) in pentane is shown in Fig. 5.

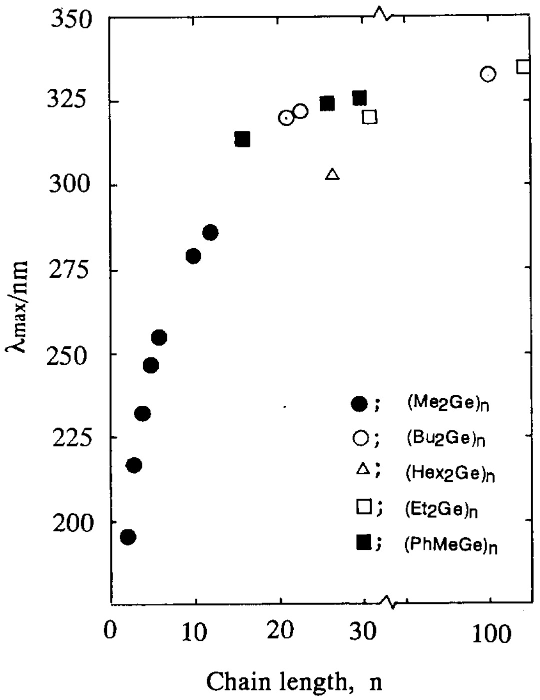
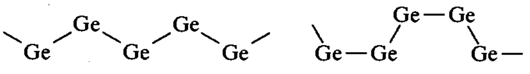


Fig. 3. Absorption wavelength maxima as a function of the oligogermane and polygermane chain length of n units.

This thermochromism reflects changes in conformation with the proportion of *trans* conformations increasing as the temperature is decreased, as shown in cases of polysilanes [6].



trans conformation *gauche* conformation

Poly(phenylmethylgermane) did not show thermochromic behavior under these experimental condi-

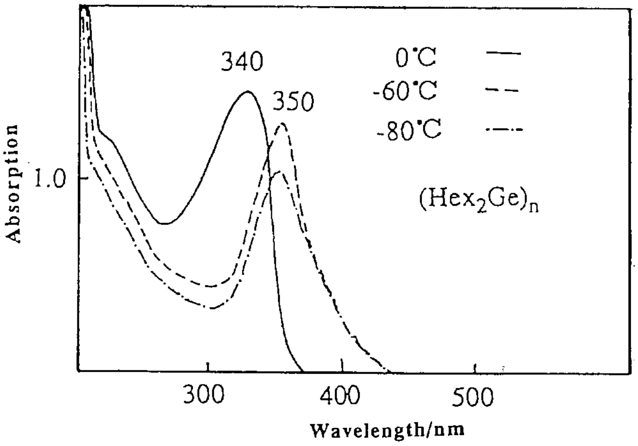


Fig. 4. UV spectra of a solution of $(^n\mathrm{Hex}_2\mathrm{Ge})_n$ in pentane.

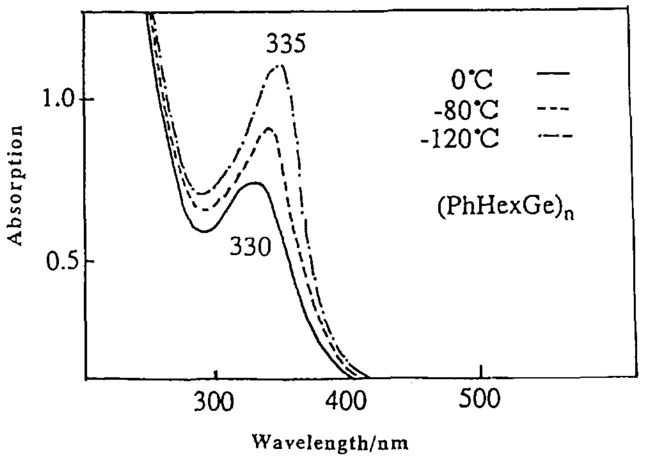


Fig. 5. UV spectra of a solution of $(PhHexGe)_n$ in pentane.

tions. It is probable that conformation of the poly(phenylmethylgermane) is fixed within the present temperature ranges.

The thermochromic behavior of films of polygermanes have also been reported [7,8,10]. Polygermanes with alkyl chains show thermochromic behavior at lower temperatures compared with polysilanes.

2.3. Photochemical reaction

As expected, the polygermanes are quite light sensitive. Upon irradiation of cyclohexane solutions of polygermanes with a 110-W low-pressure Hg arc lamp (254 nm, spiral type) at room temperature, lower molecular weight chain fragments were produced by chain scission. These phenomena were verified by GPC examination and UV spectra of the irradiated samples. As a typical example, Figure 6 shows the UV spectra of poly(di-n-hexylgermane) in cyclohexane with successive doses of broadband UV irradiation. Figure 7 also shows changes in molecular weight distribution of poly(di-n-hexylgermane) in cyclohexane upon irradiation. The photochemical degradation of polygermanes is pictured as involving homolytic scission of the germanium–germanium bond and extrusion of germylenes from the results of short-chain germanium catenates [13].

In order to obtain more information on photochemical degradation of polygermanes, reactive intermediate trapping techniques were used. A cyclohexane solution of polygermanes containing *ca.* 20 molar equivalents of 2,3-dimethylbuta-1,3-diene [15,16] was similarly irradiated. Only a trace of the expected germylene trapping compounds was detected by GC-MS. The diene sometimes is not a good trapping agent for photochemically generated germylenes [13]. However, the germylene from poly(phenylmethylgermane) reacted with the diene to give the corresponding germacyclopentene in good yield (*ca.* 40%) [17].

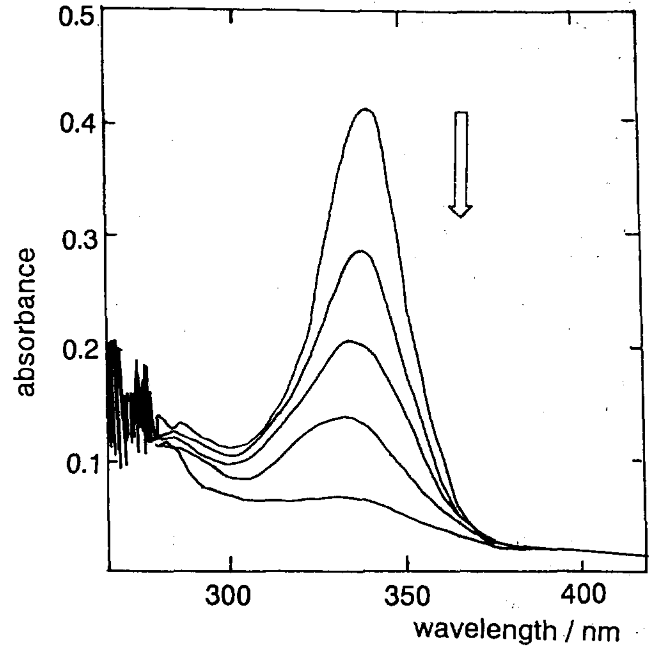


Fig. 6. UV spectra of $(^nHex_2Ge)_n$ in cyclohexane with successive doses of broadband UV irradiation.

In the presence of polyhalomethanes (carbon tetrachloride and chloroform), photolysis of a cyclohexane solution of polygermanes gave dichlorogermanes and hexachloroethane as the main products in high yields. The presence of dichlorogermanes seems to indicate the intermediacy of organogermylenes. Thus, the formation of dichlorogermanes are as a result of thermal decomposition of trichloromethylchlorogermanes, which are produced by insertion of germylene into the C–Cl bond of carbon tetrachloride [18,19] or stepwise

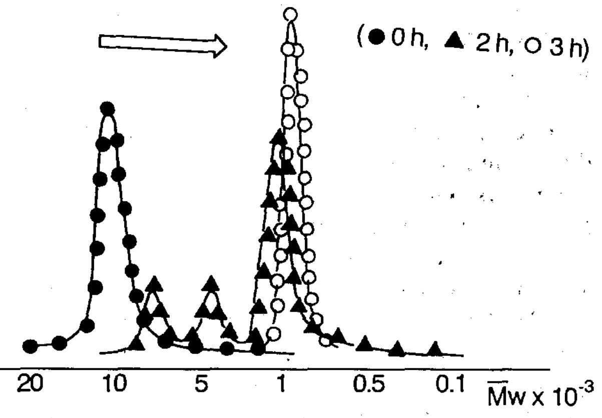


Fig. 7. Change in molecular weight distribution of $(^nHex_2Ge)_n$ ($\bar{M}w = 11.5\times10^3$, *ca.* 10 mM) in cyclohexane upon irradiation.

TABLE 3. Products and yields from photolysis of polygermanes in the presence of carbon tetrachloride in cyclohexane [a]

Polygermane	Conversion (%) [b]	Photoproducts (yields (%)) [c]	
		R_2GeCl_2	$(CCl_3)_2$
$(Et_2Ge)_n$	63.0	23.0	46.0
$(Bu_2Ge)_n$	100	80.0	46.0
$(Hex_2Ge)_n$	100	84.0	37.0
$(PhMeGe)_n$	81.0	46.0	36.0

[a] Photolysis was carried out with a 110-W low-pressure Hg arc lamp for 30–60 min at room temperature. [b] Polygermanes used in this study show a monomodal molecular weight distribution. Conversion yields were estimated by the decrease in initial GPC peak areas after irradiation. [c] Yields of photoproducts were based on the polygermanes consumed.

chlorine abstraction from carbon tetrachloride by germylene as described for silicon [20,21].

The presence of hexachloroethane is explained by the intermediacy of polygermyl radicals. Polygermyl radicals generated by homolysis of the germanium–germanium bond of the polygermanes abstract a chlorine atom from carbon tetrachloride to give polygermyl chlorides and trichloromethyl radical [22]. The trichloromethyl radical dimerizes to form hexachloroethane. High-boiling polygermyl chlorides could not be detected by means of GC and GC-MS. The photochemical results are summarized in Table 3 [23].

To obtain more information on reactive intermediates, laser flash photolysis of polygermanes was carried out. Laser flash photolysis ($\lambda = 266$ nm, pulse width 5 ns, power 10 mJ/pulse) [24] of the polygermanes (*ca.* 103 M) in cyclohexane at 293 K gave two well separated transient absorption bands at 350–370 nm and 430–460 nm, as shown in Fig. 8. The transient peak at the shorter wavelengths (350–370 nm) may be assigned to that of polygermyl radicals by comparing its spectral characteristics with those reported for similar germyl radicals [17,25,26]. The transient peaks for the polygermanes in cyclohexane decayed with second-order kinetics, suggesting the dimerization of polygermyl radicals. The assignment as a polygermyl radical was confirmed by quenching experiments using 2,3-dimethylbuta-1,3-diene and carbon tetrachloride as germyl radical quenchers. The rate constants of these transient species are summarized in Table 4. The quenching experiments for the transient absorption for the disappearance of the monogermyl radicals have been reported to be $(2.0\text{–}8.0) \times 10^8$ s^{-1} M^{-1} for carbon tetrachloride and $(1.0\text{–}1.5) \times 10^5$ s^{-1} M^{-1} for 2,3-dimethylbuta-1,3-diene [24–26]. The values of rate constants for polygermanes in Table 4 are a little larger than those reported for monogermyl radicals [24–26]. In general, the reac-

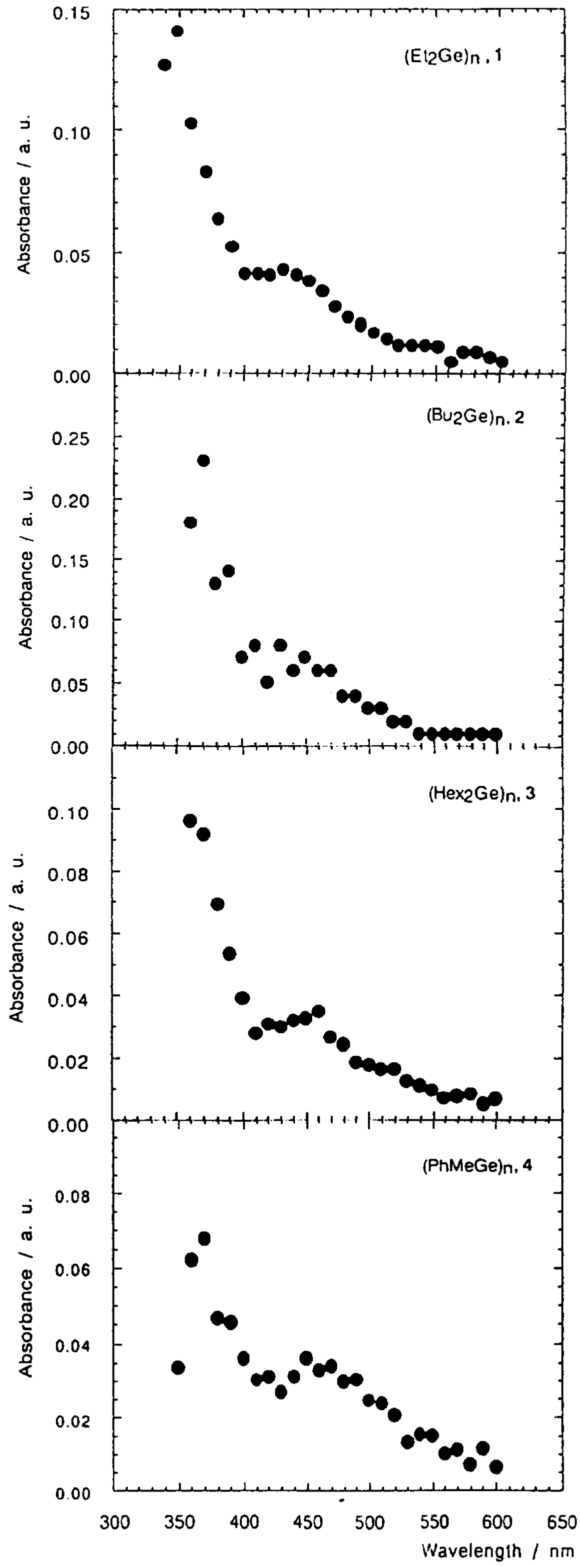


Fig. 8. Transient absorption spectra at 200 ns after photoexcitation of polygermanes (10^{-3} M) in degassed cyclohexane solution.

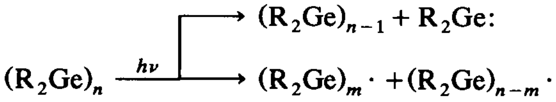
tivity of Group 14 element catenate radicals are expected to be faster that of Group 14 element centered radicals [27,28].

What is the carrier of the transients at longer wavelengths (430–460 nm)? The transient peaks from the polygermanes in cyclohexane decayed with second-order kinetics, and decayed with pseudo first-order kinetics in the presence of a large excess of carbon tetrachloride and 2,3-dimethylbuta-1,3-diene. There is a possibility of assigning the transient peak at longer wavelengths to that of a germylene by comparing its spectral positions and characteristics with those of similar germylenes previously reported [15,24–26,29–31]. However, the quenching rate constants for germylenes observed in this study are one order of magnitude faster compared with those from reported phenylated trigermanes ($k = (7.2–240) \times 10^5$ s^{-1} M^{-1} for diene and $(6.5–15) \times 10^7$ s^{-1} M^{-1} for CCl_4) [24]. The low value for the disappearance of germylenes obtained from phenylated trigermanes is probably due to the interaction of a vacant orbital of germylene with the π-system [32]. A similar phenomenon was also observed in silicon [33,34]. The experimentally determined decay constants of these transient species are also given in Table 4.

There is another possibility of assigning the transients at longer wavelengths to a polygermyl radical taking similar rate constants of the transients at shorter wavelengths. At present, the assignment of the transient at longer wavelengths is unclear.

2.4. *Mechanism of photolysis of polygermanes*

In the results obtained from the analysis of photoproducts and laser flash photolysis of high molecular weight polygermanes, both germylene extrusion and homolytic cleavage of the germanium–germanium bond are competing processes as shown in Scheme 1. A similar mechanism has been proposed for the photolysis of the silicon analogue, polysilane [6].



$$(R_2Ge)_n \xrightarrow{h\nu} \begin{cases} (R_2Ge)_{n-1} + R_2Ge: \\ (R_2Ge)_m\cdot + (R_2Ge)_{n-m}\cdot \end{cases}$$

Scheme 1.

Photolysis of polygermanes causes germanium–germanium bond cleavage to yield polygermyl radicals. In polyhalomethanes, the polygermyl radicals generated are able to abstract a chlorine atom to give the corresponding chlorides and polyhalomethyl radicals. Polyhalomethyl radicals dimerize to give the corresponding polyhaloethanes. The polygermyl radicals also add 2,3-dimethylbuta-1,3-diene to give germyl-substituted carbon radicals.

On the other hand, the photogenerated germylenes insert into the carbon–chlorine bond to afford polyhalomethylchlorogermanes. The germylene arises either from a simple extrusion process or photodecomposition of polygermyl radicals. Photochemical fragmentation of polygermyl radicals with a sequential loss of a single germylene unit may not occur [24].

3. Experimental details

^{1}H NMR spectra were recorded with a JNM-PMX 60 SI. GC-MS spectra were recorded with a Jeol JMS-DX 303 mass spectrometer. Infrared spectra were recorded with a Shimadzu FT IR 4200 spectrometer. UV and UV-vis spectra were recorded on a Shimadzu UV 2200 spectrometer. Gas chromatography was performed on a Shimadzu GC 8A with 1-m 20% SE30 and 30% Apiezon L columns. GPC was performed with JAI LC-908.

TABLE 4. Rate constants for disappearance of the transients in the photolysis of polygermanes in cyclohexane at 293 K

Polygermane	λ_{max} (nm)	k/ϵ (cm s^{-1}) [a]	Rate constant (s^{-1} M^{-1})	
			CCl_4	Diene
$(Et_2Ge)_n$	430	1.1×10^6 (at 460 nm)	1.0×10^9	8.4×10^7
	350	1.8×10^5 (at 370 nm)	7.7×10^8	8.3×10^7
$(Bu_2Ge)_n$	450	2.4×10^5 (at 450 nm)	9.2×10^8	3.1×10^7
	370	5.1×10^5 (at 370 nm)	1.1×10^9	2.5×10^7
$(Hex_2Ge)_n$	460	1.5×10^5 (at 450 nm)	1.3×10^9	4.0×10^7
	360	2.3×10^4 (at 360 nm)	9.5×10^8	3.7×10^7
$(PhMeGe)_n$	440	4.1×10^5 (at 450 nm)	1.6×10^8	2.2×10^8
	360	3.1×10^5 (at 370 nm)	4.0×10^8	3.4×10^8

[a] k is the rate constant of second-order decay and ϵ is the molar extinction coefficient.

3.1. Materials

Sodium metal, potassium metal and lithium metal were commercially obtained. Toluene, cyclohexane, HMPA, 2,3-dimethylbutadiene, CCl_4, iso-PrOH, and 18-crown-6 were purified prior to use. Et_2GeCl_2l [35], $^{n}Pr_2GeCl_2$ [36], $^{n}Bu_2GeCl_2$ [37], $^{i}Bu_2GeCl_2$ [38], $^{n}Hex_2GeCl_2$ [8], $PhMeGeCl_2$ [39], Hex_2SiCl_2 [40] and GeI_2 [41] were prepared as described in the cited references.

3.2. Preparation of phenylhexyldichlorogermane

Phenylhexyldichlorogermane was obtained by chlorodephenylation of hexyltriphenylgermane (40.0 g, 0.10 mol) with dry hydrogen chloride in the presence of a catalytic amount of aluminum chloride in chloroform (200 ml). The degree of chlorodephenylation was examined by GC. The solvent was removed and fractional distillation gave 21.3 g (0.07 mol, 70.0% yield) of phenylhexyldichlorogermane, b.p. 105°C/3 mmHg. ^{1}H NMR ($CDCl_3$): δ 0.6–1.9 (m, 13H); 7.0–7.9 (m, 5H). n_D 1.5271. IR (neat): 3050, 2900, 2830,1420,1080, 980, 720 cm^{-1}; M$^+$ 306. Anal. Found: C, 47.44; H, 6.12. $C_{12}H_{18}GeC_{12}$ calcd.: C, 47.14; H, 5.93%.

3.3. Preparation of poly(diorganogermanes) from dichlorogermanes and sodium

As a representative example, the preparation of poly(di-n-hexylgermane) is described. Poly(diorganogermanes) were prepared basically in the manner described by Miller and Sooriyakumaran [8]. The sodium dispersion (2.46 g, 0.107 g atom) and toluene (20 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 mechanical stirrer. Distilled dichlorodi-n-hexylgermane (16.4 g, 0.052 mol) was added *via* the funnel. The dichlorogermane was then added to the stirred dispersion over 5 min. The reaction mixture turned purple immediately. After the addition of dichlorogermane, the reaction was stirred under reflux for 2 h. The mixture was cooled to room temperature. After hydrolysis of isopropyl alcohol (20 cm^3), the reaction mixture was poured into isopropyl alcohol (400 cm^3) with strong stirring, and the precipitate was gravity filtered and air dried. The dried precipitate was dissolved in toluene (500 cm^3) at 50–60°C. After removing the solvent, 4.2 g of poly(di-n-hexylgermane) was obtained. ^{1}H NMR ($CDCl_3$): δ 0.90 (t); 1.33 (br m). IR (neat): 2900, 2850, 1460, 1370, 1155, 1095, 1020, 995, 935, 830, 750, 710, 650 cm^{-1}. Poly(diethylgermane): ^{1}H NMR ($CDCl_3$): δ 1.17 (br m). IR (neat): 2900, 2850, 1450, 1420, 1370, 1220, 1200, 1010, 940, 790, 670 cm^{-1}. Poly(di-n-propylgermane): ^{1}H NMR ($CDCl_3$): δ 0.97 (t); 1.47 (br m). IR (neat): 2850–2945, 1450, 1400, 1370, 1330, 1200, 1060, 1000, 850, 780, 730, 680 cm^{-1}. Poly(di-n-butylgermane): ^{1}H NMR ($CDCl_3$): δ 0.90 (t); 1.30 (br m). IR (neat): 2900, 2830, 1450, 1370, 1270, 1160, 1070, 990, 950, 840, 650 cm^{-1}. Poly(di-isobutylgermane): ^{1}H NMR ($CDCl_3$): δ 0.97 (m); 1.07 (m); 1.27 (s). IR (neat): 2850–2950, 1450, 1395, 1370, 1350, 1300, 1200, 1150, 1070, 1020, 810, 740, 680 cm^{-1}. Poly(phenylmethylgermane): ^{1}H NMR ($CDCl_3$): δ 0.3 (br m); 7.0 (br m). IR (neat): 2850–3050, 1570, 1480, 1420, 1290, 1250, 1220, 1075, 1050, 1020, 990, 840, 750, 720, 680 cm^{-1}. Poly(di-n-hexylsilyl)(di-n-hexylgermane): ^{1}H NMR ($CDCl_3$): δ 0.87 (br t); 1.27 (br m). IR (neat): 2820–2900, 1450, 1360, 1320, 1230, 1150, 1090, 1030, 980, 930, 880, 820, 750, 710, 650 cm^{-1}. Poly(phenylhexylgermane): ^{1}H NMR ($CDCl_3$): δ 0.77 (br m); 7.00 (br m). IR (neat): 3020, 2900, 2830, 1570, 1470, 1450, 1420, 1370, 1295, 1250, 1150, 1090, 1070, 1020, 990, 950, 830, 720, 680 cm^{-1}.

3.4. Preparation of poly(di-n-hexylgermane) from dichlorodi-n-hexylgermane and sodium–potassium alloy

Sodium (1.4 g, 0.06 g atom)–potassium (0.02 g) alloy and toluene (20 cm^3) were added to a dry 100-ml three-necked flask fitted with a condenser connected to a drying inlet, dropping funnel, and mechanical stirrer. Distilled dichlorodi-n-hexylgermane (10 g, 0.03 mol) was added to *via* the funnel. The subsequent procedure was the same as described above for the preparation of poly(di-n-hexylgermane) from dichlorodi-n-hexylgermane and sodium dispersion.

3.5. Preparation of poly(di-n-hexylgermane) from dichlorodi-n-hexylgermane and sodium metal in the presence of 18-crown-6

Poly(di-n-hexylgermane) was prepared from dichlorodi-n-hexylgermane (10 g, 0.03 mol), sodium metal (1.4 g, 0.06 g atom) and 18-crown-6 (8 g, 0.03 mol).

3.6. Preparation of poly(di-n-butylgermane) from di-n-butyldichlorogermane and sodium metal in toluene/HMPA

Poly(di-n-butylgermane) was prepared from di-n-butyldichlorogermane (22.0 g, 0.07 mol), sodium dispersion (4.1 g, 0.18 g atom), toluene (20 cm^3) and HMPA (5 cm^3).

3.7. Reactions of diiodogermylene with Grignard reagent and organolithium

As a representative example, the preparation of poly(di-n-butylgermane) is described. Diiodogermylene (1.0 g, 3 mmol) and dry ether (2 cm^3) were added to a dry 30-ml two-necked flask equipped with a condenser and addition funnel. Butylmagnesium bromide prepared from butyl bromide (2.8 g, 20 mmol) and magnesium metal (0.5 g, 20 mmol) was added to this solution under nitrogen. The reaction mixture was refluxed for 3 h. After hydrolysis with water, the reaction mixture was extracted with ether. The organic layer was dried over magnesium sulfate. The products were analyzed by NMR, IR and GPC. Poly(dimethylgermane): ^{1}H NMR ($CDCl_3$): δ 0.20 (s); 0.30 (s); 0.37 (s). IR (neat): 2900, 2870, 1400, 1220, 820, 745 cm^{-1}.

3.8. *Photochemical reactions of a cyclohexane solution of polygermanes in the presence of carbon tetrachloride*

The polygermanes (*ca.* 2–3 mg, *ca.* $(1.2–3.8) \times 10^{-4}$ M) was dissolved in dry cyclohexane (2 cm^3) containing carbon tetrachloride (100 mg) in a quartz tube. The tube was degassed in a vacuum and replaced with argon. The sample was irradiated with a 110-W low-pressure Hg arc lamp (Sen Tokushu Kogen Co. Ltd.) at room temperature for 30 min. After irradiation, the photo-products were identified by comparing the retention times on GLC and GC-MS with those of authentic samples. Dichlorogermanes and hexachloroethane were mainly formed.

3.9. *Time-resolved optical absorption*

The sample was placed in a quartz cell with an optical length of 5 mm and was degassed by four freeze-pump-thaw cycles. The concentrations of the polygermanes were *ca.* 10^{-3} M. Laser flash-photolysis experiments were performed at room temperature by using the fourth harmonic (266 nm) of a Quanta-Ray DCR-1 Nd:YAG laser as an excitatory light source. The laser pulse was about 5 ns, and the details of the laser photolysis apparatus have been published elsewhere [19]. The signals were monitored by a Tektronix 485 oscilloscope (350 MHz) and recorded by an Iwatsu DM-901 digital memory (10 ns/point, 8 bit) controlled by a NEC PC 8801 microcomputer.

3.10. *Absorption spectra of polygermanes*

Polygermane (*ca.* 10 mg) was dissolved in pentane (*ca.* 10 cm^3) in a quartz cell connected to a Pyrex tube as the upper part. The cell was degassed in a vacuum and replaced with argon. The cell was introduced into an Oxford cryostat. The UV spectra were recorded on a Shimadzu UV 2200 spectrometer.

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