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Nonlinear Optical Susceptibility of Oligo- and Polygermanes

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Third-order nonlinear susceptibilities ($\chi^{(3)}$) for thin films of oligo- and polygermanes were measured in the range of 0.6—86×10^{-12} esu. A measured $\chi^{(3)}$ of 86×10^{-12} esu for a polygermane–polysilane random copolymer, coploy(methylphenylsilylene/methylphenylgermylene), was the largest ever reported for transparent polymers in the visible spectral region.

Recently, organometallic polymers and group-14 element backbone polymers have attracted considerable attention as new materials for nonlinear optics. Promising candidates for nonlinear optics must have large nonlinear optical susceptibilities (χ) and must be readily processable.[1—4] σ-Conjugated polymers such as polysilanes and polygermanes have nonlinear optics as well as unique physical, chemical, and optical properties arising from σ-electron delocalization through the silicon–silicon and germanium–germanium bonds.[5—13]

The polysilanes and polygermanes are transparent in the visible range and have strong absorption bands in the near ultraviolet region markedly different from carbon based π-conjugated polymers. While the nonlinear optical properties of polysilanes have been extensively investigated, there have been few reports on those of polygermanes.[14—18] We herein describe results of third harmonic generation (THG) measurements on thin films of oligo- and polygermanes, and related compounds.

Results and Discussion

Synthesis of oligo- and polygermanes for THG measurments was done by a method for synthesizing linear polygermanes.[10—12] Thus, polygermane homopolymers, poly(methylphenylgermylene), $(PhMeGe)_n$, (**1**) and poly(dihexylgermylene), $(n\text{-}Hex_2Ge)_n$, (**2**), and a copolymer with polysilane, copoly(methylphenylsilylene/methylphenylgermylene), $(PhMeSi)_n$–$(PhMeGe)_m$, (**3**) were prepared by condensation of the corresponding dichlorogermanes and dichlorosilanes with sodium metal in toluene. The polymer **3** prepared is a random copolymer. Branched oligogermyne, oligo(phenylgermyne), $(PhGe)_n$, (**4**) was also prepared by coupling reactions of trichlorophenylgermane with sodium metal as described previously.[19] Oligo(digermylene–π-electron system)s, oligo(digermylene–1,3-phenylene), $(1,3\text{-}(C_6H_4)(GeMe_2)_2)_n$, (**5**) and oligo(digermylene–1,2-phenylene), $(1,2\text{-}(C_6H_4)(GeMe_2)_2)_n$, (**6**) were prepared by treatment of di-Grignard reagents with 1,2-dichlorotetramethyldigermane. The oligo- and polygermanes were fractionated by precipitation from toluene with 2-propanol. The molecular weights of the polymers were measured by gel permeation chromatography using polystyrene samples for calibration. The polymers prepared by methods of Wurtz coupling and Grignard reagents had a narrow molecular weight distribution, but were in relatively low yields. Figure 1 shows absorption spectra of films of the polymers **1**—**6**. The polygermane homopolymer **1**, **2**, and copolymer with polysilane **3** have characteristic electronic absorption bands at 280—339 nm. The poly(dihexylgermylene) **2** shows two absorption peaks at 325 and 345 nm as shown in Fig. 1. Branched oligogermanes **4** and oligo(digermylene–π-electron system)s **5**, **6** have a more intense broad absorption from 200 nm ($\varepsilon < 10000$ at 200 nm), tailing down into the visible region. The molecular weight ($\overline{M}_w$) and absorption maxima (λ_{max}) of the polymers are summarized in Table 1.

Thin films of the samples were prepared by spin-coating from toluene solution. The films were deposited on quartz plates (10×30×1 mm) and dried under vacuum (10^{-4} mmHg, 1 mmHg = 133.322 Pa) at room temperature. The samples were homogeneous and transparent in the visible range. The film thickness of the samples is given by Eq. 1, where l is the film thickness of the sample, N is the number of interference peaks, n is the refractive index of the sample ($n = 1.6$ for the polygermane homopolymer and copolymer with polysilane), θ is the angle of incidence ($\theta = 5°$, $\sin^2\theta = 0.008$ or 0), and λ_1 and λ_2 are the first and the last peaks in the interference spectrum observed by UV-vis spectrometry, respectively.[20]

$$l = (N-1) \times \left(2\sqrt{n^2 - \sin^2\theta}\right)^{-1} \times \left(\frac{1}{\lambda_1} - \frac{1}{\lambda_2}\right)^{-1} \times 10^{-3}. \quad (1)$$

The film thickness of the samples measured on quartz plates was included in Table 1.

THG measurements were done at room temperature using

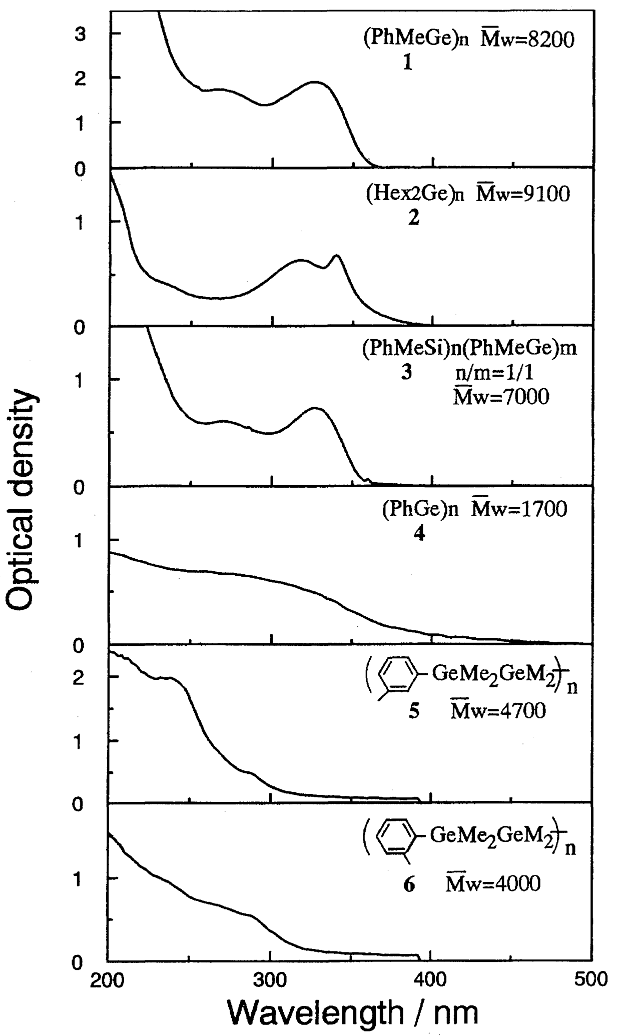


Fig. 1. Absorption spectra of thin films of polygermane homopolymers **1**, **2**, copolymer with polysilane **3**, oligogermyne **4**, and oligo(digermylenephenylene)s **5**, **6**.

the Maker fringe technique at 1064 nm. The sample consisted of an oligo- or polygermane thin film on a quartz plate and was rotated along an axis parallel to the fundamental beam polarization direction. The third-harmonic signal was recorded as a function of the angle of incidence. The fundamental 1064 nm radiation was provided by a Q-switched Nd : YAG laser operated at a repetition rate of 10 Hz and a pulse duration of 5 ns.

Figure 2 shows third-harmonic Maker fringe data for various molecular weight polygermane homopolymers **1**, **2**, a polygermane copolymer with polysilane **3**, a branched oligogermyne **4**, and oligo(digermylene–π-electron system)s **5**, **6**, and that of the silica substrate (SiO_2). The third-order nonlinear optical susceptibility $\chi^{(3)}$ for thin films of **1**—**6** is given by Eq. 2, where $\chi_s^{(3)}$ is the susceptibility of the silica substrate ($\chi_s^{(3)}=3.1\times10^{-14}$ esu at 1064 nm), $I_{3\omega}$ and $I_{3\omega,s}$ are the third harmonic intensities at the angle of incidence ($\theta=0°$) (Maker fringe data) for the reference (silica) and sample, respectively, l is the thickness of the polymer film, and $l_{c,s}$ is the coherence length[21] ($l \ll l_{c,s}$).

$$\chi^{(3)} = \frac{2}{\pi}\chi_s^{(3)} \times \left(\sqrt{I_{3\omega}/l}\right) \times \left(\sqrt{I_{3\omega,s}/l_{c,s}}\right)^{-1}. \qquad (2)$$

The measured third-order nonlinear optical susceptibilities $\chi^{(3)}$ of the polymers **1**—**6** at 1064 nm are summarized in Table 1. Experimental error is about 5—10%. The observed $\chi^{(3)}$ values of the polymers in this study may be increased by resonance because the values of λ_{max} for the polymers **1**—**6** are not very far from 355 nm (third-harmonic of Nd : YAG laser). The values of $\chi^{(3)}$ in the vicinity of the three-photon resonance can be approximated using Eq. 3, where E_{ng} is the energy at the value of λ_{max} and Γ is the n-state width for the oligo- and polygermanes.[13]

$$\chi^{(3)}(-3\omega;\ \omega,\omega,\omega)$$
$$\propto \left((E_{ng}-3\omega-i\Gamma)\times(E_{ng}-\omega)\times(E_{mg}-2\omega)\right)^{-1}. \qquad (3)$$

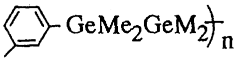
For example, polygermanes **1** and **2** have a value of λ_{max} at 325 nm so that $\chi^{(3)}$ $(-3\omega;\ \omega,\omega,\omega)$ is approximately estimated to be 1.5×10^{-12} esu. This calculated value, however, may be too large. In fact, Baumert and co-workers have studied the effects of resonant increases and nonresonant $\chi^{(3)}$ for poly(dihexylsilylene) at 1064 and 1907 nm, respectively, and found only a small contribution of resonant to $\chi^{(3)}$.[14] Therefore, resonance may be neglected.

The nonlinear optical measurement on group-14 element backbone polymers was first reported by Kajzar and coworkers.[13] They reported that the value of $\chi^{(3)}$ for poly(methylphenylsilylene) was 1.5×10^{-12} esu at 1064 nm measured by the Maker fringe technique. Somewhat larger $\chi^{(3)}$ values for poly(methylphenylsilylene) and poly(dihexylsilylene) at 1064 nm in the region of $(4.6—11)\times10^{-12}$ esu at 1064 nm have been reported by Baumert and coworkers.[14] They found that these values of $\chi^{(3)}$ depended on the film thickness and decreased as the thickness of the polymers increased. The $\chi^{(3)}$ value of $(3.3—6.5)\times10^{-12}$ esu for poly(dihexylgermylene) at 1064 nm was also studied by the same authors.[14] Recently, we have reported the $\chi^{(3)}$ for polygermane homopolymers ($(Bu_2Ge)_n$ ($\overline{M}_w=6.8\times10^3$, $\overline{M}_w/\overline{M}_n=1.1$), $(Hex_2Ge)_n$ ($\overline{M}_w=11.5\times10^3$, $\overline{M}_w/\overline{M}_n=1.5$), and $(PhMeGe)_n$ ($\overline{M}_w=9.0\times10^3$, $\overline{M}_w/\overline{M}_n=1.3$) and a copolymer with polysilane $(Hex_2Si)_n$–$(Hex_2Ge)_m$ ($\overline{M}_w=112.8\times10^3$, $\overline{M}_w/\overline{M}_n=1.2$) measured by the Maker fringe technique in the region of $(1.6—5.2)\times10^{-12}$ esu at 1064 nm.[18]

As shown in Table 1, the values of $\chi^{(3)}$ for polygermane homopolymers **1** and **2** were $(25—31)\times10^{-12}$ esu and $(5—63)\times10^{-12}$ esu, respectively. They are roughly dependent on $\overline{M}_w$ of the polymers and are largest recorded for a group-14 element backbone homopolymers in the visible spectral region. This value of $\chi^{(3)}$ for **1** is 20-fold larger than that (1.6×10^{-12} esu) for **1** previously reported. This may be due to the change in the polygermane backbone conformation and anisotropy of polygermane thin film dependent on the solvent used for spin-coating.

The characterisitic features observed in the absorption spectra of thin films of **1** and **2** prepared by spin-coating in toluene, in comparison with those in isooctane,[18] may be summarized as follows: (a) original absorption bands of **1**

Table 1. Third-Order Nonlinear Optical Susceptibilities $\chi^{(3)}$ at 1064 nm for Oligo- and Polygermanes **1**—**6** at Room Temperature

Polymer	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$	λ_{max}	Film thickness	$\chi^{(3)}$ a)
	$\times 10^3$		nm	µm	$\times 10^{-12}$ esu
$(PhMeGe)_n$	2.0	2.7	324	0.6	25
1	5.0	1.4	324	0.6	28
	8.2	1.6	325	0.6	31
$(Hex_2Ge)_n$	6.2	1.5	310, 340	0.3	5
2	9.1	1.7	325, 345	0.4	63
	15.9	1.2	325, 345	0.4	31
$(PhMeGe)_n(PhMeSi)_m$					
3 n/m=3/1	6.8	1.6	327	0.3	57
=1/1	7.0	1.8	327	0.4	46
=3/1	21.2	6.4	333	0.3	86
$(PhGe)_n$	1.7	1.5	-b)	0.5	1.1
4	1.7	1.5	-b)	0.1	3.9
					
5	4.7	1.6	286	0.4	1.0
					
6	4.0	1.3	-b)	0.2	2.7

a) Corrected $\chi^{(3)}$ are about 10% lower. b) No λ_{max}.

and **2** shift slightly to longer wavelengths and clearly increase in intensity and (b) the ratio of second bands to original bands of **2** increase. From the study of thermochromic behavior of polysilanes[5,22] and polygermanes,[10,11] it is clearly that original and second absorption bands reflect helical-*gauche* and all-*trans* states, respectively. In transition of helical-*gauche* to all-*trans* states, the intensity of original bands increases and then decreases along with appearance of a new band at longer wavelengths. Taking these results into consideration, the conformation of polygermane films prepared in toluene is consist of helical-*gauche* and all-*trans* states. Therefore, it would be considered that the large values of $\chi^{(3)}$ of **1** and **2** in this study are attributed to all-*trans* conformation of the germanium backbone.

Similar large values of $\chi^{(3)}$ were measured for a polygermane copolymer with polysilane **3** in the region of $(46—86)\times 10^{-12}$ esu. On the other hand, the measured values of $\chi^{(3)}$ for a branched oligogermyne **4** and oligo(digermylene–π-system)s **5**, **6** are in the same range of $(0.6—2.7)\times 10^{-12}$ esu; such values indicate less σ electron delocalization along the germanium–germanium bonds for **4**, and along the π systems for **5**, **6**.

Oligo- and polygermanes absorb the light strongly in the near UV region with transparency throughout the visible; they are sensitive to UV lamps. Their molecular polarizability is strongly anisotropic and conformationally dependent, and electronic effects of the substituent on germanium atoms are transmitted over large distances along germanium chromophore. Oligo- and polygermanes also show relatively thermal stability and fairly resistant of oxidation.[19] In addition, they represent large third-order nonlinear optical susceptibilities in this study.

Experimental

^{1}H 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-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 Twincle with an Asahipak GS 310 column.

Materials. Polygermane homopolymers, ($(PhMeGe)_n$ and $(Hex_2Ge)_n$),[12] and branched oligophenylgermyne ($(PhGe)_n$),[19] were prepared as described.

Preparation of Copoly(methylphenylgermylene/methylphenylsilylene) by Wurtz Coupling. Copoly(methylphenylgermylene/methylphenylsilylene) was prepared in basically the same manner as that previously described.[12] A sodium dispersion (4.4 g, 0.19 mol) and in toluene (30 cm^3) was added to a dry 100 ml three-necked flask fitted with a condenser connected to a dry Ar inlet, pressure-equalizing dropping funnel, and a mechanical stirrer. Distilled (dichloro)methylphenylsilane (7.6 g, 0.04 mol) and (dichloro)methylphenylgermane (10 g, 0.04 mol) were then added to a stirred dispersion over a period of 5 min. The reaction mixture turned purple immediately. The reaction mixture was stirred under reflux for 2 h, and then hydrolyzed with 2-propanol (200 cm^3). The precipitate was gravity-filtered and again dissolved in toluene at 80 °C. After cooling, the toluene solution was washed copiously with water and dried over anhydrous sodium sulfate. The solvent was removed on a rotary evaporator and the residue was dried at 80 °C in a vacuum oven for 5 h to yield 0.1 g of copoly(methylphenylgermylene/methylphenylsilylene). ^{1}H NMR ($CDCl_3$) δ=0.5—0.7 (3H), 6.1—7.8 (5H); IR (KBr) 3070—2851, 1483, 1427, 1260, 1246, 1098, 1082, 1026, 999, 783, 761, 729, 696, 669 cm^{-1}.

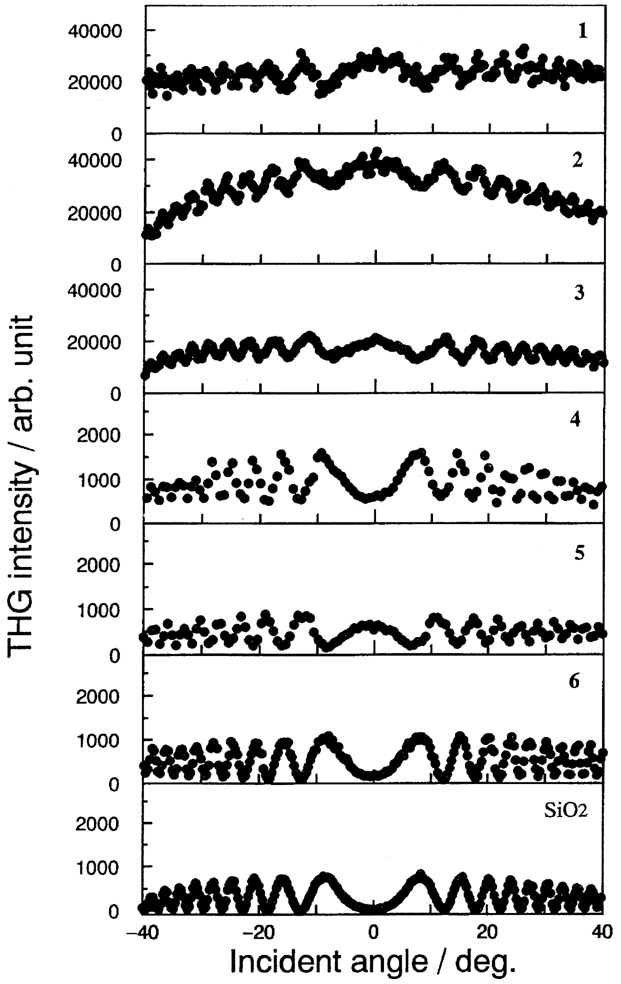


Fig. 2. Third-harmonic Maker fringe data for **1**—**6** and for SiO$_2$.

Preparation of Oligo(digermylene-1,3-phenylene) and Oligo-(digermylene-1,2-phenylene). As a representive example, the preparation of oligo(digermylene-1,3-phenylene) is described. Magnesium (0.97 g, 40 mmol) and *m*-dibromobenzene (4.72 g, 20 mmol) in THF (5 cm^3) were added to a dry 100-ml three-necked flask fitted with a condenser connected to a dry Ar inlet, pressure-equalizing dropping funnel, and a mechanical stirrer. Distilled 1,2-dichlorotetramethyldigermane was added via a funnel to a di-Grignard reagent. The reaction mixture was stirred with refluxing for 20 h. After hydrolysis with water, the organic layer was extracted with toluene. The organic layer was washed copiously with water and dried over anhydrous sodium sulfate. The solvent was removed on a rotary evaporator and the residue was recrystallized with ethanol. The solid was dried at 80 °C in a vacuum oven for 5 h. ^{1}H NMR (CDCl$_3$) δ=0.63 (s, 3H), 7.46 (m, 5H); IR (KBr), 2970, 827, 787, 780, 596 cm^{-1}.

Third-Harmonic Generation Measurements of Oligo- and Polygermanes. Thin films of oligo- and polygermanes prepared by spin-coating from 10% toluene solution were deposited on quartz plates by using a spinner (MOC, Model/ME 300) (1000 and 2000 rpm) and dried under a vacuum. THG measurement was done using the Maker fringe technique at 1064 nm. The film of sample was rotated along an axis parallel to the fundamental beam polarization direction. The fundamental radiation was provided by a Q-switched Nd : YAG laser (Spectron SL412-10, repetition rate of 10 Hz, a pulse duration of 5 ns). The third signal was recorded as a function of the angle of incidence.

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