Radical Anions of Oligogermanes, $Me(Me_2Ge)_nMe$ (n=2,3,5, and 10) Generated by Pulse Radiolysis

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Radical anions of permethylated oligogermanes, $Me(Me_2Ge)_n$-Me (n=2, 3, 5, and 10), by pulse radiolysis technique showed two transient absorption bands in the UV-Vis and NIR regions. Their absorption maxima shifted to longer wavelengths with increasing the Ge-Ge chain in the permethylated oligogermanes.

A new class of soluble and film-forming group 14 element (silicon and germanium) backbone polymers has been the subject of considerable interest in recent years due to both their unique physical, chemical, and optical properties and their potential technological utility.[1-14] These remarkable properties originate from the characteristic electronic structure. The electronic spectra of group 14 element polymers have strong absorption bands in the near ultraviolet (UV) region due to the delocalization of σ electrons into group 14 element-group 14 element bonds.[4,11] Their ionization potentials (IP's) have 5-8 eV and approximately 5 eV lower than those of the corresponding alkanes. Because of these electron delocalization characteristics, group 14 element backbone polymers are expected to undergo readily one-electron oxidation and reduction to form radical cations and radicals anions, respectively. The radical ions of group 14 element compounds play an increasingly important role in the chemistry of group 14 elements. However, the study of radical ions of oligo- and polygermanes is very much limited compared with those of the corresponding silicon compounds.[16,17] In this paper, we first report the generation of radical anions of permethylated oligogermanes, $Me(Me_2Ge)_nMe$ (n=2, 3, 5, and 10), by pulse radiolysis technique, and discuss the σ electron delocalization of the Ge-Ge bonds in the radical anions.

Linear permethylated oligogermanes, $Me(Me_2Ge)_nMe$ (n=2, 3, 5,and 10) used for the pulse radiolysis study were synthesized by Wurz coupling reactions of trimethylchlorogermane (Me_3GeCl) and dimethyldichlorogermane (Me_2GeCl_2) with lithium metal in THF and were purified by preparative GPC (>99.5%).[18] Radical anions of $Me(Me_2Ge)_nMe$ were generated by using the linear accelator system (LINAC) (28 MeV single pulse electron beam, 2 ns pulse width).

The transient absorption spectra of $Me(Me_2Ge)_nMe$ (n=2, 3, 5, and 10) (0.1 M) in THF at 293 K immediately and at 80 ns after an electron pulse are shown in Figure 1. These differences in spectra before and after pulse irradiation, therefore, represent the newly produced germanium radical anion species.

Radical anions of permethylated oligogermanes are produced by the reaction with the solvated electron generated by electron pulse radiation.[19] Pulse radiolysis of the THF solution of $Me_3GeGeMe_3$ gave a sharp transient peak at 267 nm with a subband at 305 nm and an additional broad peak around 1200 nm, as shown in Figure 1. By the addition of an electron scavenger, CCl_4, the transient peaks at 267 and ca. 305 nm disappeared. This result confirms that both bands are due to the radical anion of $Me_3GeGeMe_3$. On the other hand, the broad

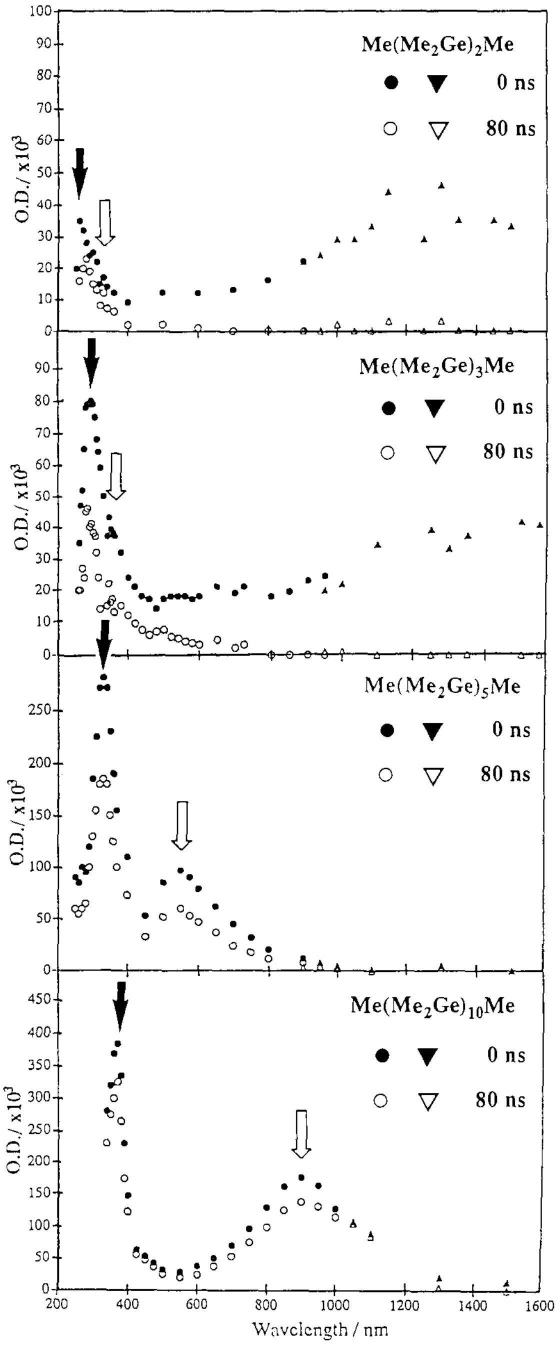

Fig. 1. Transient absorption spectra of radical anions of $Me(Me_2Ge)_nMe$ (n=2, 3, 5, and 10) immediately and at 80 ns after pulse.

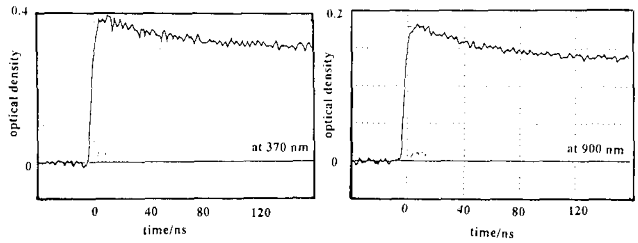

Fig. 2. The absorption profile recorded at (a) 370 and (b) 900 nm representing the decay of the transients for $Me(Me_2Ge)_{10}Me$ in THF

Table 1. The value of λ_{max} for radical anions of $Me(Me_2Ge)_nMe$ (n=2, 3, 5, and 10)

$Me(Me_2Ge)_nMe$	λ_{max}/nm		IP/eV^b
	neutral molecule^a	radical anion	
n=2	197	267, ca. 305	8.58
=3	217	291, ca. 345	8.15
=5	246	330, 545	7.67
=10	286	400, 900	5.55^c

^{a}In cyclohexane. ^{b}HeI UPS. ^{c}AC-1.

peak around 1200 nm with half-life of ca.4 ns is ascribed to that of the solvated electron from its spectral characteristics.[19] For the radical anion of $Me(Me_2Ge)_3Me$, sharp transient peaks at 291 nm with a subband at ca. 345 nm assigned to its radical anion and an additional broad peak around 1200 nm assigned to the solvated electron were observed. Radical anions of $Me(Me_2Ge)_nMe$ (n=5 and 10) showed two well-resolved transient peaks at 330 and 545 nm, and at 400 and 900 nm, respectively. The broad peak around 1200 nm observed for $Me(Me_2Ge)_nMe$ (n=2 and 3) disappeared for $Me(Me_2Ge)_nMe$ (n=5 and 10) owing to the high intensity of absorbance of their radical anions. As a typical example, the time dependence of the transient peaks for $Me(Me_2Ge)_{10}Me$ is shown in Figure 2.

As the chain length of permethylated oligogermanes increased from $Me(Me_2Ge)_2Me$ to $Me(Me_2Ge)_{10}Me$, these two absorption peaks shifted to longer wavelength. Thus, the transient peaks at shorter wavelengths gradually shifted from 267 nm to 370 nm. On the other hand, the shift of the transient peaks at longer wavelengths accelerated from 305 nm to 900 nm with a broader spectral shape. The absorbance of transient peaks also increased with increasing the chain length. The values of absorption maxima (λ_{max}) for the radical anions of permethylated oligogermanes are summarized in Table 1, together with those of neutral molecule and their IP's. As the chain length increased, the value of half-life of $Me(Me_2Ge)_nMe$ gradually increased.

The formation of the radical anion by pulse radiolysis induces the SOMO (singly occupied molecular orbital) between HOMO and LUMO. The radical anion shows a HOMO → SOMO transition at higher energy region and a SOMO → LUMO transition at the lower energy region. Both absorption bands ascribed to the radical anions of $Me(Me_2Ge)_nMe$ exhibit a bathochromic shift as the chain length increases, as shown in Table 1. The delocalized Ge-Ge chain of the extra charge probably causes this bathochromic shift. Saturation of the bathochromic shift for the radical anion of the polygermanes seems to require ca. 20-30 Ge-Ge bonds, compared with the absorption bands of higher molecular weight polygermane radical anions.[20] The intensity of absorbance of the transient peaks between $Me(Me_2Ge)_2Me$ and $Me(Me_2Ge)_{10}Me$ suggests that the extra charge of the oligogermane radical anions can be delocalized on the relatively long germanium chain.[4] Ban, Tagawa, and co-workers have reported on the pulse radiolysis of THF solutions of permethylated oligosilanes, $Me(Me_2Si)_nMe$ (n=4-6), in UV regions. However, anion radicals of $Me(Me_2Si)_nMe$ (n=2 and 3) could not be observed.[21]

So far as we are aware, this work represents the first observation of radical anions of permethylated oligogermanes, $Me(Me_2Ge)_nMe$ (n=2, 3, 5, and 10) in the wavelength regions between 300 and 1600 nm. The present finding should reveal the excited and charged states of the group 14 element oligomers.

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