

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231398024>

# Electronic Structure of Oligosilane and Polysilane Radical Anions As Studied by Electron Spin Resonance and Electronic Absorption Spectroscopy

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY · DECEMBER 1994

Impact Factor: 2.78 · DOI: 10.1021/j100101a005

---

CITATIONS

17

---

READS

7

4 AUTHORS, INCLUDING:



[Hitoshi Koizumi](#)

Hokkaido University

69 PUBLICATIONS 597 CITATIONS

SEE PROFILE

# Electronic Structure of Oligosilane and Polysilane Radical Anions As Studied by Electron Spin Resonance and Electronic Absorption Spectroscopy

Jun Kumagai, Hiroshi Yoshida, Hitoshi Koizumi, and Tsuneki Ichikawa\*

Faculty of Engineering, Hokkaido University, Sapporo 060, Japan

Received: March 24, 1994; In Final Form: September 29, 1994<sup>®</sup>

The electron spin resonance (ESR) and the electronic absorption spectra of poly(cyclohexylmethylsilane) and poly(methylphenylsilane) radical anions in a cryogenic 2-methyltetrahydrofuran solid have been compared with those of permethyloligosilanes  $[\text{Si}_n(\text{CH}_3)_{2n+2}]$ ,  $n = 4-6$  for elucidating the electronic structure of polysilane radical anions. The spectra of the polysilane radical anions are very similar to each other and also to those of the oligosilane radical anions in which an unpaired electron occupies not an antibonding  $\sigma^*(\text{sp})$  orbital but a pseudo- $\pi(\text{p})$  orbital composed of antibonding Si–Si and antibonding Si–C orbitals. The polysilane radical anions show axially symmetric ESR spectra with  $g_{\perp} = 2.0023$  and  $g_{\parallel} = 2.0064$  and the electronic absorption spectra composed of UV and near-IR bands. Analysis of the ESR and the absorption spectra shows that the unpaired electron of the polysilane radical anions is not delocalized all over the polymer chain but is confined in only a part of the polymer chain, probably around the elongated Si–Si bond of a branched polymer chain.

## Introduction

Polysilanes are  $\sigma$ -conjugated polymers composed of Si–Si skeletons and organic side chains. Recently they have attracted much attention because of their potential utility as one-dimensional conductors, photoresists and radiation resists, nonlinear optical materials, and high-density optical data storage materials (for recent review, see refs 1 and 2). The expectation of polysilane as an electron conductor by doping an electron donor or acceptor is based on the tacit assumption that an excess electron or hole is delocalized over the polymer chain or a polymer segment through the  $\sigma$ -conjugation. The polymer does not show a high electroconductivity if the electron or hole is localized on a small part of the polymer chain. To elucidate the electronic structure of the radical anion and cation of polysilane is therefore important for realizing the one-dimensional conductor.

The electronic structures of radical anion and cation have been studied by measuring their electronic absorption spectra. Since the radical ions in liquid solution are not stable enough to measure the steady-state spectra,<sup>3</sup> they are generally generated by  $\gamma$ -irradiation of the solid solution of polysilanes at cryogenic temperature or by pulse radiolysis of the liquid solution. In these solutions the radical anion is generated by attachment of an electron which is ejected from the solvent molecule by ionizing radiation. The radical cation is also obtained in a similar way by electron transfer from the polymer to the solvent radical cation.

Ban et al. measured the transient absorption spectra of polysilanes in organic solutions after electron beam irradiation and found that the radical cation and anion of polysilanes show strong UV absorption bands.<sup>4,5</sup> They attributed the bands to the electronic transition of the delocalized unpaired electron on the Si skeleton. Irie et al. measured the transient and the steady-state absorption spectra of polysilane radical ions with alkyl and aryl side groups.<sup>6,7</sup> In addition to the UV bands, they found a near-IR band for the radical cation of polysilane with aryl side groups. They attributed the near-IR band to charge resonance between two aryl groups. They also measured the absorption spectra of radical anion and cation of cyclic oligo-

meric dimethylsilanes and found that both the ions show the absorption bands in UV and near-IR regions.<sup>8</sup> They failed, however, to detect IR bands for the radical cation and anion of polyalkylsilanes and the radical anion of polyarylsilanes. Very recently, Ushida et al. reported that the sharp near-IR band is observed not only for the radical cation of polyarylsilanes but also generally for all the polysilane radical cations and anions so far examined.<sup>9</sup> They attributed the sharp band as a charge resonance arising from charge resonance interaction between adjacent  $\sigma$ -conjugated polymer segments, just like the charge resonance band for diphenylmethyl radical ions.<sup>10</sup>

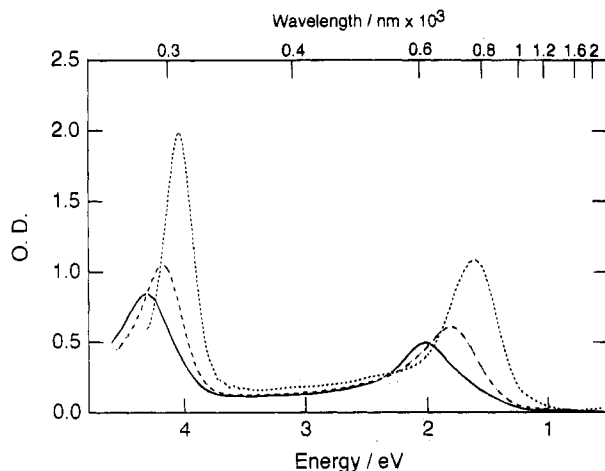
Discussion on the electronic structure so far mentioned is based on the assumption that the unpaired electron of the radical ions is significantly delocalized over the polymer skeleton. The validity of this basic assumption is, however, not examined yet. The absorption spectra include information on both the ground and the excited states so that it is difficult to extract the information only on the electronic structure of the ground state radical ions. The ground-state electronic structure is possible to be obtained by analyzing their ESR spectra. In the present paper the ESR and electronic absorption spectra of the radical anions of poly(cyclohexylmethylsilane) and poly(methylphenylsilane) and of oligomeric dimethylsilanes are analyzed for elucidating the electronic structure of the radical anions.

## Experimental Section

Permethyloligosilanes,  $\text{Si}_n(\text{CH}_3)_{2n+2}$  where  $n$  ranges from 4 to 6, were synthesized from the coupling of  $\text{Si}(\text{CH}_3)_3\text{Cl}$  and  $\text{Si}_m(\text{CH}_3)_{2m}\text{Cl}_2$  by Wurtz-type reaction and purified by fractional distillation.<sup>11</sup> Poly(cyclohexylmethylsilane) was synthesized from dichlorohexylmethylsilane by Wurtz-type reaction in mixed solvent (toluene:*n*-heptane = 0.85:0.15) with Na alloy and 15-crown-5-ether under the reflux condition.<sup>12</sup> The crude polymer was purified by repeated precipitations from chloroform solution into methanol. Poly(methylphenylsilane) was kindly supplied from Dr. N. Kushibiki. The average number of Si atoms composing the polymer main chains is approximately 80 for both polymers.

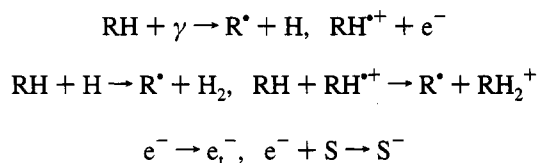
Fractionally distilled 2-methyltetrahydrofuran (MTHF) was vacuum-distilled with Na–K alloy as a drying agent and then deaerated by freezing–pumping–thawing cycles. The dried and

<sup>®</sup> Abstract published in *Advance ACS Abstracts*, November 1, 1994.

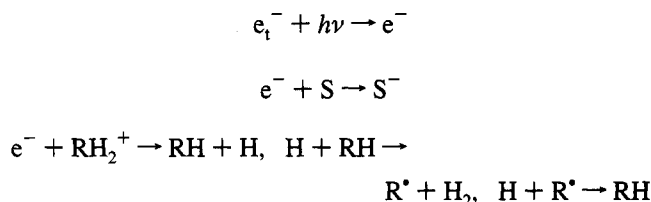


**Figure 1.** Electronic absorption spectra at 77 K for  $\gamma$ -irradiated 2-methyltetrahydrofuran matrix containing  $5 \times 10^{-2}$  mol/dm<sup>3</sup> of (—) Si<sub>4</sub>(CH<sub>3</sub>)<sub>10</sub>, (---) Si<sub>5</sub>(CH<sub>3</sub>)<sub>12</sub>, and (···) Si<sub>6</sub>(CH<sub>3</sub>)<sub>14</sub> observed after photobleaching the trapped electron.

deaerated MTHF solution of oligosilane or polysilane in a sealed high-purity Suprasil quartz cell was irradiated in the dark at 77 or 4.2 K with a <sup>60</sup>Co  $\gamma$ -ray source. Trapped electrons in the irradiated samples were eliminated by photoillumination of the samples with near-IR light of the wavelength longer than 700 nm. The radiation—chemical process induced by  $\gamma$ -irradiation of the sample is



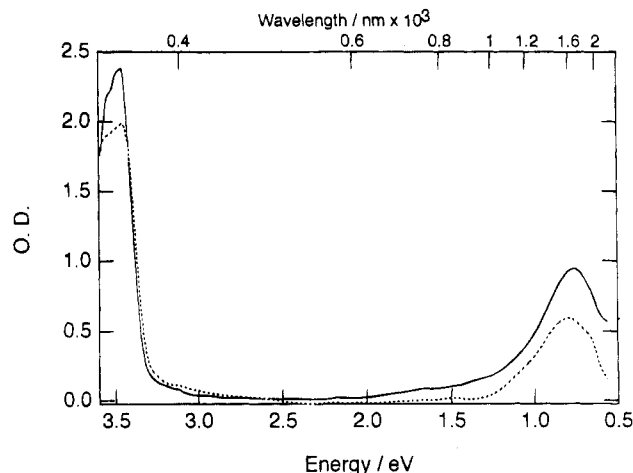
Photoillumination of the sample with  $\lambda > 700$  nm causes



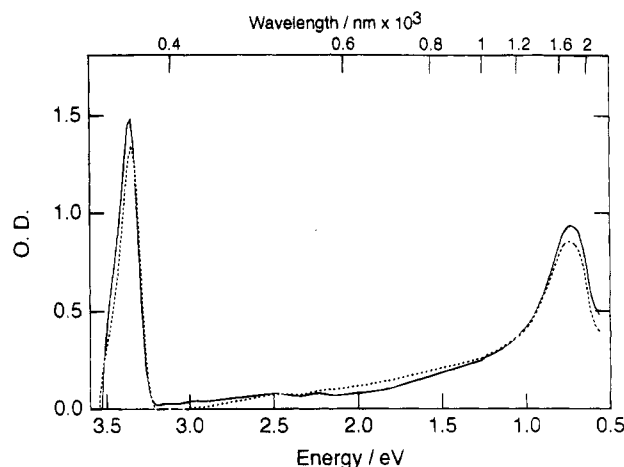
where RH, S, and  $e_t^{-}$  denote solvent (MTHF) molecules, solute (oligosilane or polysilane) molecules, and a trapped electron, respectively. The electronic absorption spectra were measured at 77 or 4.2 K with a Shimadzu MPS 3000 spectrophotometer.<sup>13</sup> The ESR spectra were measured at 77 K with a Varian ESR spectrometer. For eliminating coexisting solvent radicals in polysilane samples, the samples were exposed to the atmosphere for a short period and then plunged into liquid nitrogen.

## Results

**Electronic Absorption Spectra.** Figure 1 shows the absorption spectra of the oligosilane sample  $\gamma$ -irradiated at 77 K. The coexisting trapped electron was eliminated by illuminating the samples with near-IR light with the wavelength longer than 700 nm. The spectra are composed of two bands: visible or near-IR and UV ones. Similar spectra have been observed for the radical anions of cyclic methylsilane (Me<sub>2</sub>Si)<sub>n</sub>, where  $n$  ranges from 5 to 7.<sup>7,14</sup> Increase of the spectral intensity with the molecular weight is due to increase of the electron scavenging efficiency of the oligosilanes, since the increase accompanied the concomitant decrease of the trapped electron with the



**Figure 2.** Electronic absorption spectra for 4.2 K  $\gamma$ -irradiated 2-methyltetrahydrofuran matrix containing  $5 \times 10^{-2}$  mol/dm<sup>3</sup> of poly(cyclohexylmethylsilane) observed at 4.2 K (—) and 77 K (---) after photobleaching the trapped electron.

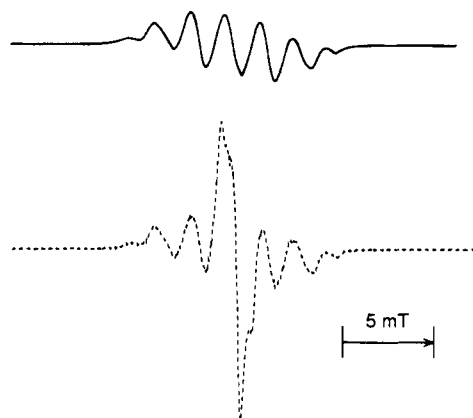


**Figure 3.** Electronic absorption spectra for 4.2 K  $\gamma$ -irradiated 2-methyltetrahydrofuran matrix containing  $5 \times 10^{-3}$  mol/dm<sup>3</sup> of poly(methylphenylsilane) observed at 4.2 K (—) and 77 K (---) after photobleaching the trapped electron.

absorption maximum at 1200 nm. The electron affinity of the oligosilanes probably increases with the length of the Si—Si chain. Red shift of both the UV and the near-IR bands with increasing chain length is due to increase of the  $\sigma$ -conjugation. Illumination of the samples with visible light ( $360 \text{ nm} < \lambda$ ) caused the disappearance of the radical anions due to photoelectron detachment from the radical anions.

Figures 2 and 3 show the absorption spectra of poly(cyclohexylmethylsilane) and poly(methylphenylsilane) samples  $\gamma$ -irradiated at 4.2 K. The coexisting trapped electron was eliminated by illuminating the samples with visible light. The spectra are composed of near-IR and UV bands. Increase of polymer concentration caused enhancement of the two bands accompanying the concomitant decrease of the trapped electron. The observed spectra are therefore attributable to the polysilane radical anions generated by electron capture of the polymers. Photobleaching of the polymer radical anions with visible light was much slower than that of the oligosilane radical anions, which suggests that the electron affinity of the polysilanes (ionization potential of the polysilane radical anions) is much larger than that of the oligosilanes.

Similarity of the spectral shape for poly(cyclohexylmethylsilane) and poly(methylphenylsilane) radical anions indicates that the orbitals relating to the electronic transitions are not on the side chains but on the Si—Si skeletons. The shape and



**Figure 4.** ESR spectra at 77 K for  $\gamma$ -irradiated (—) neat 2-methyltetrahydrofuran and (---) the 2-methyltetrahydrofuran solution of  $1 \times 10^{-1}$  mol/dm<sup>3</sup>  $\text{Si}_4(\text{CH}_3)_{10}$  after photobleaching the trapped electron.

location of the UV bands are close to those of the parent neutral polymers, which suggests that the bands correspond to the transition of an electron in the HOMO orbitals. The red shift of the bands from the neutral polymers indicates the increase of the HOMO energy due to electronic repulsion by the additional excess electron.

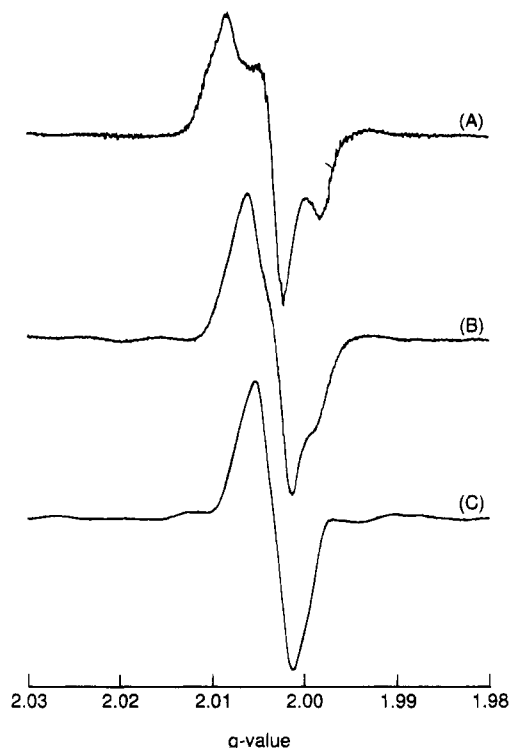
The structural relaxation of ionic species generated at 4.2 K in a rigid matrix is generally prohibited due to high rigidity of matrix,<sup>15</sup> so that warming of a sample from 4.2 to 77 K generally causes an irreversible blue shift of the absorption spectrum of the ionic species due to decrease of the ground-state electronic energy by the structural relaxation. However, as shown by broken spectra in Figures 2 and 3, warming of the samples to 77 K causes no change of the absorption spectra. These results suggest that the radical anions take the stable structure already at 4.2 K. The radical anions completely disappeared by charge recombination when the samples were warmed in the atmosphere a few minutes.

The similarity of the absorption spectra between the oligosilane and the polysilane radical anions strongly suggests that the near-IR band of the polysilanes, which has been assigned as an intersegment charge resonance band,<sup>9</sup> is attributable to the same type of transition as that of the oligosilanes.

**ESR Spectra.** Shown in Figure 4 are the ESR spectra for neat MTHF and for the  $\text{Si}_4(\text{CH}_3)_{10}$  sample  $\gamma$ -irradiated and measured at 77 K. The trapped electron was completely eliminated by illuminating the sample with near-IR light. The ESR spectrum of neat MTHF is composed of septet lines due to MTHF radical. The ESR spectrum for the oligosilane sample is composed of sharp central one attributable to the radical anion of  $\text{Si}_4(\text{CH}_3)_{10}$ , in addition to the septet lines due to the coexisting MTHF radical. The central spectrum disappeared when the sample was illuminated with visible light.

Figure 5 shows the ESR spectra of oligosilane radical anions obtained by subtracting the septet lines from the observed ESR spectra for the oligosilane samples  $\gamma$ -irradiated and measured at 77 K. The  $g$  anisotropy of radical anions decreases with increasing chain length. The average  $g$  factor,  $\bar{g}$ , of the radical anions ranges between 2.003 and 2.004, which accords well with the  $g$  factor of the chemically prepared decamethylcyclopentasilane radical anion ( $g = 2.0032$ ) in a liquid solution.<sup>14,16</sup>

The LUMO of oligosilanes and polysilanes is an  $\sigma^*(\text{sp})$  orbital, which is composed of  $\text{sp}^3$  hybrid atomic orbitals generated from two antibonding  $\text{sp}^3$  Si—Si orbitals on the same Si atom.<sup>17,18</sup> Since the Fermi contact term of the  $^{29}\text{Si}$  atom (natural abundance = 4.7%) is 121.8 mT, the oligosilane radical anions  $[\text{Si}_n(\text{CH}_3)_{2n+2}]^-$  must show satellite lines with the



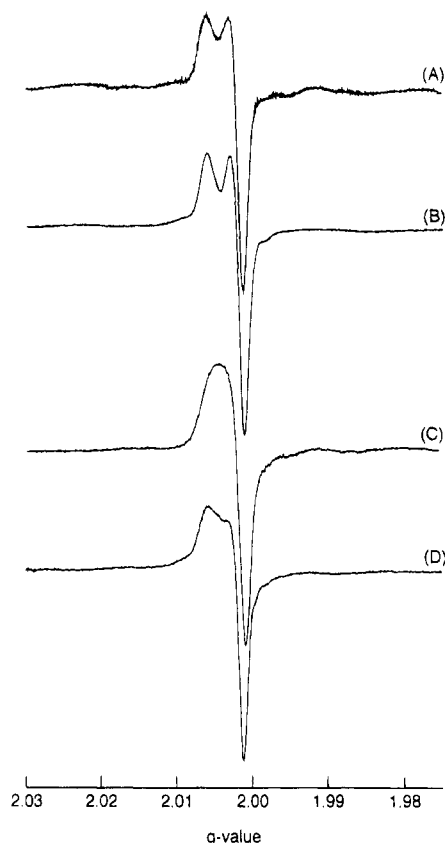
**Figure 5.** ESR spectra of (A)  $\text{Si}_4(\text{CH}_3)_{10}$ , (B)  $\text{Si}_5(\text{CH}_3)_{12}$ , and (C)  $\text{Si}_6(\text{CH}_3)_{14}$  radical anions obtained by subtracting the spectrum of solvent radical from the observed spectra.

hyperfine splitting constant of approximately  $121.8/(2n)$  mT, if the SOMO of the oligosilane radical anions is the same as the LUMO of the neutral oligosilanes. However, no satellite line was observed for all the oligosilane radical anions examined. The appearance of no satellite line clearly indicates that the SOMO of the radical anions is not the LUMO of the neutral molecules but a  $\pi$ -type orbital containing no 3s atomic orbital of the Si atoms. The SOMO orbital of the decamethylcyclopentasilane radical anion has been suggested to be a  $\pi$ -type orbital composed of 3p and 3d atomic orbitals of the Si atoms.<sup>14</sup>

Figure 6 shows the ESR spectra of the poly(cyclohexylmethylsilane) and the poly(methylphenylsilane) samples obtained by subtracting the spectrum of the MTHF radical from the observed spectra. Also shown in Figure 6 are the neat spectra of the polysilane radical anions obtained at 77 K after 15 s exposure of the irradiated sample to the atmosphere. The spectral shapes are the same as those obtained by subtracting the contribution of the MTHF radical. Exposure of more than 15 s caused significant decrease of the radical anion, though the spectral shapes were unchanged. These results support that the central spectra remaining after the thermal annealing are due to the polysilane radical anions. The excess negative charge on the polymer is probably surrounded by polymer chains which prevents the approach of the counteraction  $\text{RH}_2^+$  and slows the charge recombination reaction. The ESR spectra of the radical anions are axially symmetric with  $g_{\parallel} = 2.0064$  and  $g_{\perp} = 2.0023$ . The spectral shapes of the poly(cyclohexylmethylsilane) and the poly(methylphenylsilane) radical anions are very similar to each other, which also suggests that the excess electron is mainly on the Si—Si chain.

## Discussion

Table 1 summarizes the spectroscopic data of the oligosilane and the polysilane radical anions. The electronic structure of the radical anions can be determined by analyzing these data in the following way: Both the present solid-state and the



**Figure 6.** ESR spectra at 77 K of poly(cyclohexylmethylsilane) radical anion obtained (A) by subtracting the spectrum of solvent radical from the observed spectrum and (B) by thermal annealing of the sample for 15 s in the atmosphere, and of poly(methylphenylsilane) radical anion obtained (C) by subtracting the spectrum of solvent radical from the observed spectrum and (D) by thermal annealing of the sample for 15 s in the atmosphere.

**TABLE 1: Optical and ESR Parameters for Oligosilane and Polysilane Radical Anions**

compound	UV band/eV	near-IR band/eV	g tensor <sup>b</sup>
Si <sub>4</sub> (CH <sub>3</sub> ) <sub>10</sub>	4.31 (5.28) <sup>a</sup>	2.02	$g_{xx} = 1.9979$ $g_{yy} = 2.0037$ $g_{zz} = 2.0082$
Si <sub>5</sub> (CH <sub>3</sub> ) <sub>12</sub>	4.18 (4.96)	1.81	$g_{xx} = 1.9992$ $g_{yy} = 2.0032$ $g_{zz} = 2.0061$
Si <sub>6</sub> (CH <sub>3</sub> ) <sub>14</sub>	4.04 (4.77)	1.62	$g_{xx} \approx g_{yy} \approx g_{zz}$ $\bar{g} = 2.0032$
[−SiCH <sub>3</sub> C <sub>6</sub> H <sub>11</sub> −] <sub>n</sub>	3.50 (3.80)	0.79	$g_{xx} = g_{yy} = g_{\perp} = 2.0023$ $g_{zz} = g_{\parallel} = 2.0064$
[−SiCH <sub>3</sub> C <sub>6</sub> H <sub>5</sub> −] <sub>n</sub>	3.35 (3.65)	0.72	$g_{xx} = g_{yy} = g_{\perp} = 2.0023$ $g_{zz} = g_{\parallel} = 2.0064$

<sup>a</sup> Values in parentheses are the energy of UV bands for neutral compounds. <sup>b</sup> The *x*–*y* plane for the tensor is the molecular plane of the Si–Si chain.

previous liquid-state ESR studies on the oligosilane radical anions indicate that an unpaired electron does not occupy the LUMO orbital of the parent oligomer molecule but a  $\pi$ -type orbitals composed of 3p orbitals of the Si atoms. Although Carberry et al. suggested the contribution of the 3d orbitals to the SOMO orbitals,<sup>14</sup> the contribution may not be important since the radical anions show very small *g* anisotropy.

Figure 7 shows the electronic structure of the linear oligosilane or polysilane obtained by a simple LCBO (linear combination of bonding orbitals)<sup>17</sup> method in which the occupied and the vacant orbitals of the linear silanes are composed of bonding and antibonding Si–Si  $\sigma$  orbitals, respectively. A more complex

calculation does not change the orbital feature.<sup>1,17,18</sup> The HOMO and LUMO orbitals are composed of bonding  $\sigma_{\text{Si-Si}}(\text{p}_x)$  orbitals and antibonding  $\sigma^*_{\text{Si-Si}}(\text{sp}_y)$  orbitals, respectively. The SOMO orbital of the radical anion is not the same as the LUMO orbital of the neutral silane. Since the SOMO orbital of the radical anion contains no 3s orbital, it is necessary to eliminate the s orbitals from the LUMO orbital by adding the other orbitals which are orthogonal to the occupied orbitals. A SOMO orbital without a 3s orbital is constructed by adding two antibonding Si–C orbitals to the LUMO orbitals, as

$$\begin{aligned} \frac{1}{\sqrt{3}}\sigma^*_{\text{Si-Si}}(\text{sp}_y) + \frac{1}{\sqrt{3}}\{\sigma^*_{\text{Si-C}_1}(\text{sp}^3) + \sigma^*_{\text{Si-C}_2}(\text{sp}^3)\} = \\ \frac{1}{\sqrt{3}}\left\{-\frac{1}{\sqrt{2}}s + \frac{1}{\sqrt{2}}p_y\right\} + \frac{1}{\sqrt{3}}\left[\frac{1}{\sqrt{2}}\left\{\frac{1}{2}s + \frac{1}{2}p_y + \frac{1}{\sqrt{2}}p_z\right\} + \right. \\ \left. \frac{1}{\sqrt{2}}\left\{-\frac{1}{2}s_{C_1} + \frac{1}{2}p_{y,C_1} + \frac{1}{\sqrt{2}}p_{z,C_1}\right\}\right] + \frac{1}{\sqrt{3}}\left[\frac{1}{\sqrt{2}}\left\{\frac{1}{2}s + \frac{1}{2}p_y - \right. \right. \\ \left. \frac{1}{\sqrt{2}}p_z\right\} + \frac{1}{\sqrt{2}}\left\{-\frac{1}{2}s_{C_2} + \frac{1}{2}p_{y,C_2} - \frac{1}{\sqrt{2}}p_{z,C_2}\right\}\right] = \sqrt{\frac{2}{3}}p_y - \\ \frac{1}{\sqrt{24}}(s_{C_1} + s_{C_2}) + \frac{1}{\sqrt{24}}(p_{y,C_1} + p_{y,C_2}) + \frac{1}{\sqrt{12}}(p_{z,C_1} - p_{z,C_2}) \end{aligned} \quad (1)$$

The above atomic orbitals compose an antibonding pseudo- $\pi$  orbital,  $\pi'_{\text{Si-Si}}(\text{p}_y)$  on the Si skeleton. The spin density of the unpaired electron in the 2s orbital of a carbon atom is derived from eq 1 to be  $1/(24n)$ , where *n* is the number of Si atoms in the oligosilane. The radical anion is therefore expected to give a <sup>13</sup>C isotropic hyperfine splitting of  $119/(24n)$  mT.

Although the hyperfine splitting of the oligosilane radical anions was impossible to be measured due to broad line shape of the ESR spectra, the hyperfine splitting for decamethylcyclopentasilane radical anion in liquid has been reported. The SOMO pseudo- $\pi$  orbital of the cyclosilane radical anion must be different from that of the linear oligosilane radical anions. The stability of the  $\pi'_{\text{Si-Si}}(\text{p}_y)$  orbital decreases with increasing number of cis conformation in the main chain, since the cis conformation generates the nodal point of the pseudo- $\pi$  orbital. Cyclosilanes are composed of all cis conformation, so that the SOMO orbital of the radical anion is not the  $\pi'_{\text{Si-Si}}(\text{p}_y)$  orbital but a  $\pi'_{\text{Si-C}}(\text{p}_z)$  orbital which is composed of antibonding  $\sigma^*_{\text{Si-C}_1}$  and  $\sigma^*_{\text{Si-C}_2}$  orbitals, as

$$\begin{aligned} \pi'_{\text{Si-C}}(\text{p}_z) = \sqrt{\frac{1}{2}}\{\sigma^*_{\text{Si-C}_1}(\text{sp}^3) - \sigma^*_{\text{Si-C}_2}(\text{sp}^3)\} \\ = \sqrt{\frac{1}{2}}p_y + \frac{1}{4}\{-s_{C_1} + s_{C_2} + p_{x,C_1} - p_{x,C_2} + \sqrt{2}p_{y,C_1} + \\ \sqrt{2}p_{y,C_2}\} \end{aligned} \quad (2)$$

The cyclosilane radical anion composed of *n* Si atoms is expected to give a <sup>13</sup>C hyperfine splitting of  $119/(16n)$ . The observed hyperfine splitting of the decamethylcyclopentasilane radical anion is 1.6 mT,<sup>14,16</sup> which compares well with the calculated value of 1.5 mT.

Stabilization of the pseudo- $\pi$  orbital arises from the expansion of the atomic orbitals on the Si atoms by the excess electron. Because of repulsive interaction by an excess negative charge, the atomic orbitals of the radical anion are more diffusive and  $\pi$ -type interactions between the atomic orbitals are stronger than those of neutral molecule. The SOMO orbital therefore changes from  $\sigma^*_{\text{Si-Si}}(\text{sp}_y)$  to  $\pi'_{\text{Si-Si}}(\text{p}_y)$ , which is otherwise unstable because of the mixing of high-energy antibonding Si–C orbitals.

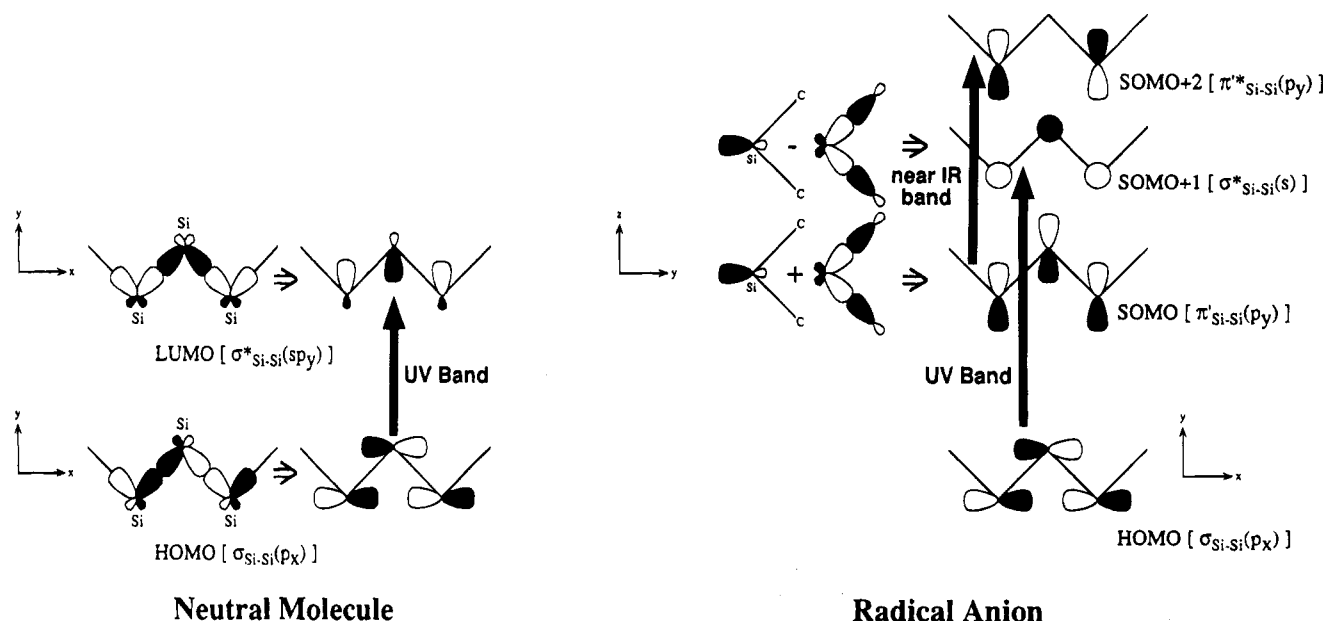


Figure 7. A schematic deviation of the molecular orbitals of oligosilane and polysilane and their radical anions.

Mixing of the LUMO and the antibonding Si–C orbitals of the neutral linear silanes generates another orbital, antibonding  $\sigma^*_{\text{Si-Si}}(s)$  orbital, as

$$\frac{1}{\sqrt{3}}\sigma^*_{\text{Si-Si}}(sp_y) - \frac{1}{\sqrt{3}}\{\sigma^*_{\text{Si-C}_1}(sp^3) + \sigma^*_{\text{Si-C}_2}(sp^3)\} = -\sqrt{\frac{2}{3}}s + \frac{1}{\sqrt{24}}(s_{C_1} + s_{C_2}) - \frac{1}{\sqrt{24}}(p_{y,C_1} + p_{y,C_2}) - \frac{1}{\sqrt{12}}(p_{z,C_1} - p_{z,C_2}) \quad (3)$$

which may compose a SOMO+1 orbital. As seen from Figure 7, the optical transition between HOMO and SOMO is symmetrically forbidden whereas the transition between HOMO and SOMO+1 is optically allowed. The UV bands of the radical anions therefore correspond to HOMO to SOMO+1 transition.

The near-IR bands can be assigned to be pseudo- $\pi \rightarrow$  pseudo- $\pi^*$  transition by analyzing the  $\mathbf{g}$  tensor of radical anions. The principal values of the  $\mathbf{g}$  tensors of the radical anions are derived from the ground-state and the excited-state molecular orbitals of the unpaired electron,  $\psi_0$  and  $\psi_k$ , respectively, by calculating the spin-orbit interaction between the unpaired electron and the Si atoms as<sup>19</sup>

$$\Delta g_{uu} = g_{uu} - 2.0023 = 2.0023\zeta \sum_{k \neq 0} [\langle \psi_0 | \sum_{i=1}^n \tilde{l}_{u,i} | \psi_k \rangle \langle \psi_k | \sum_{i=1}^n \tilde{l}_{u,i} | \psi_0 \rangle (E_0 - E_k)] \approx -2.0023\zeta \sum_{k \neq 0} \left( \frac{[\sum_{i=1}^n \langle C_{0,i} \chi_{0,i} | \tilde{l}_{u,i} | C_{k,i} \chi_{k,i} \rangle]^2}{E_0 - E_k} \right) \quad (4)$$

where

$$\psi_0 = \sum_{i=1}^n C_{0,i} \chi_{0,i}, \quad \psi_k = \sum_{i=1}^n C_{k,i} \chi_{k,i}$$

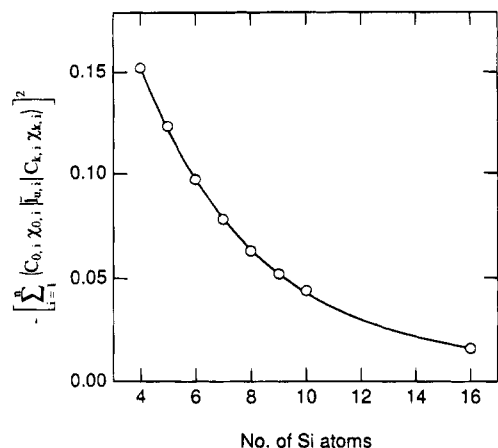
$u$  denotes  $x$ ,  $y$ , or  $z$ ,  $\zeta = 149 \text{ cm}^{-1}$  is the spin-orbit coupling constant of the Si atoms,  $E_0$  and  $E_k$  are the orbital energies of the unpaired electron for the ground state and the  $k$ th excited

state, respectively, and  $\chi_{k,i}$  is the atomic orbital of the  $i$ th Si atom. Equation 4 indicates that only  $\Delta g_{zz}$  has the value different from zero when the atomic orbitals on the Si atoms do not contain  $p_z$  orbitals. Moreover, since the value of  $\langle C_{0,i} \chi_{0,i} | \tilde{l}_{u,i} | C_{k,i} \chi_{k,i} \rangle$  is always imaginary, contribution of the  $k$ th excited state to  $\Delta g_{uu}$  is negative if the orbital energy of the unpaired electron in the  $k$ th excited state is higher than that in the ground state.

As shown in Table 1, the polysilane radical anions do not show negative  $\Delta g_{uu}$  values, which indicates that the value of  $\langle C_{0,i} \chi_{0,i} | \tilde{l}_{u,i} | C_{k,i} \chi_{k,i} \rangle$  is negligibly small when  $E_k$  is larger than  $E_0$ . The SOMO+ $n$  orbitals are therefore composed of  $3s$  and/or  $3p_y$  atomic orbitals of the Si atoms, and the near-IR band corresponds to the pseudo- $\pi$  to a pseudo- $\pi^*$  transition. Excited-state orbitals of the unpaired electron contributing to the spin-orbit coupling is the occupied orbitals of the ground-state radical anion. The occupied orbitals are composed of  $3s$ ,  $3p_x$ , and  $3p_y$  orbitals of the Si atoms, so that the angular momentum operator  $\tilde{l}_{u,i}$  giving the value  $\langle C_{0,i} \chi_{0,i} | \tilde{l}_{u,i} | C_{k,i} \chi_{k,i} \rangle \neq 0$  is only  $\tilde{l}_{z,i}$ . The  $g_{\parallel}$  and the  $g_{\perp}$  components for the radical anions are therefore assigned to  $g_{zz}$  and  $g_{xx} = g_{yy}$  components, respectively.

The oligosilane radical anions show axially symmetric ESR spectra with one negative  $\Delta g_{uu}$ . This is because the  $\pi'$  orbitals of the radical anions contain significant amount of  $3p_z$  orbitals. The operator effective for the spin-orbit coupling with the  $3p_z$  and  $3p_y$  orbitals is  $\tilde{l}_{x,i}$ . The negative  $\Delta g_{uu}$  for the radical anion therefore corresponds to  $\Delta g_{xx}$ . Increase of the  $|\Delta g_{xx}|$  value with decreasing molecular size of the oligosilane is caused by the increase of the contribution of  $3p_z$  atomic orbitals in the  $\pi'$  orbitals. Contribution of the repulsive interaction between electrons to the total electron energy is larger for smaller oligosilanes. The repulsive interaction may be decreased by adding  $3p_z$  orbitals to the atomic orbitals of the unpaired electron, which is originally composed of  $3p_y$  orbitals. The contribution of  $3p_z$  orbitals in the  $\pi'$  orbitals therefore increases with decreasing molecular size.

The sharp near-IR bands and the axially symmetric ESR spectra of the polysilane radical anions indicate that the unpaired electron is not delocalized all over the Si–Si chain but is localized on a part of the chain. As mentioned in the previous section, the near-IR band of the radical anions corresponds to the transition of the unpaired electron from the pseudo- $\pi$  to pseudo- $\pi^*$  orbitals. Since both the orbitals are composed of



**Figure 8.** Degree of spin-orbit interaction as a function of the number of Si atoms in linear oligosilanes.

the same antibonding  $\sigma^*$  orbitals, like  $\pi-\pi^*$  transitions for polyene molecules, the transition energy rapidly decreases with increasing chain length and is almost zero for the radical anions composed of about 80 Si atoms. The near-IR band of the polysilane radical anions is therefore assigned to the pseudo- $\pi \rightarrow$  pseudo- $\pi^*$  transition of the unpaired electron which is localized to some extent on the polymer chain.

The  $g$  anisotropy of the polysilane radical anions also support the localization of the unpaired electron. The degree of spin-orbit coupling is roughly estimated by calculating the value of  $-\sum_k [\sum_{i=1}^n \langle C_{0,i} \chi_{0,i} | \tilde{I}_{u,i} | C_{k,i} \chi_{k,i} \rangle]^2$  in eq 4. As shown in Figure 8, the value of this term rapidly decreases with the number of Si atoms in the polymer. Observed decrease of  $g$  anisotropy for the oligosilane radical anion with increasing chain length supports this conclusion. The anisotropic ESR spectra of the polysilane radical anions therefore indicates that the unpaired electron is localized on a part of the polymer chain.

Another evidence supporting the localization of the unpaired electron is that only holes are mobile in charge transporting and photoconducting experiments.<sup>20,21</sup> Electrons injected or excited into the conduction band are trapped so quickly that no current corresponding to negative charge carrier is detected in time-of-flight measurements.

The most probable candidate for the trapping centers is a branched polymer chain. Excited polysilanes are known to show sharp and broad emissions.<sup>22-26</sup> The sharp emission is generally agreed to be due to the lowest  $\sigma^*_{\text{Si-Si}}(\text{sp}_y)-\sigma_{\text{Si-Si}}(\text{p}_x)$  transition. The origin of the broad emission has not been clarified yet. However, recent NMR and IR studies on the structural defects in polysilanes strongly suggest that the emission is due to the transition of the excited electron which is localized around a lengthened Si-Si bond at a branched polymer chain.<sup>27</sup> It is therefore very probable that the unpaired electron of the polysilane radical anions is also localized around the elongated Si-Si bond. T-shaped pseudo- $\pi$  orbitals with essentially the same orbital nature as those for the linear silanes are possible to be generated around the branch with the molecular plane perpendicular to that of the main chain.

Another candidate for the trapping centers is polymer segments composed of several Si atoms. However, the sharp

near IR bands and anisotropic ESR spectra may not be expected from such a trap center. Although a short segment is desirable for explaining the observed spectra, it is not suitable for trapping the excess electron. The electron affinity of the oligosilane and therefore the polymer segments increases with the number of Si atoms composing the chain or segment, respectively, so that the unpaired electron is stably localized in the longest segment composed of more than 20 atoms.<sup>28</sup> The unpaired electron in such a long segment is expected to give a very low optical transition energy and an isotropic ESR spectrum, which contradict with the experimental observation.

**Acknowledgment.** The authors thank Dr. Hiroto Tachikawa for stimulating discussions on the electronic structure of polysilane. This work was supported by Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan.

## References and Notes

- (1) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359 and references therein.
- (2) Michl, J. *Synth. Met.* **1992**, *49-50*, 367 and references therein.
- (3) Carberry, E.; West, R.; Glass, G. *J. Amer. Chem. Soc.* **1969**, *91*, 5440.
- (4) Ban, H.; Sukegawa, K.; Tagawa, S. *Macromolecules* **1987**, *20*, 1775; **1988**, *21*, 45.
- (5) Ban, H.; Tanaka, A.; Hayashi, N.; Tagawa, S.; Tabata, Y. *Radiat. Phys. Chem.* **1989**, *34*, 587.
- (6) Irie, S.; Oka, K.; Irie, M. *Macromolecules* **1988**, *21*, 110.
- (7) Irie, S.; Irie, M. *Macromolecules* **1992**, *25*, 1766.
- (8) Irie, S.; Oka, K.; Nakao, R.; Irie, M. *J. Organomet. Chem.* **1990**, *388*, 253.
- (9) Ushida, K.; Kira, A.; Tagawa, S.; Yoshida, Y.; Shibata, H. *Proc. Am. Chem. Soc. Div. Polym. Mater.* **1992**, *66*, 299.
- (10) Shida, T. *Electronic Absorption Spectra of Radical Ions*; Physical Science Data 34; Elsevier: Amsterdam, 1988.
- (11) Kumada, M.; Ishikawa, M. *J. Organomet. Chem.* **1963**, *1*, 153.
- (12) Miller, R. D.; Thompson, D.; Sooriyakumaran, R.; Fickes, G. N. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 813.
- (13) Ogasawara, M. In *Handbook of Radiation Physics and Chemistry*; Tabata, Y., Ed.; CRC Press: Boca Raton, FL, 1991; Chapter III.B.8.
- (14) Carberry, E.; West, R.; Glass, G. *J. Am. Chem. Soc.* **1969**, *91*, 5446.
- (15) Yoshizaki, M.; Ogasawara, M.; Yoshida, H. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3143.
- (16) Kirste, B.; West, R.; Kurreck, H. *J. Am. Chem. Soc.* **1985**, *107*, 3013.
- (17) Bock, H.; Ensslin, W. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 404.
- (18) Takeda, K.; Shiraishi, K. *Phys. Rev. B* **1989**, *39*, 11028.
- (19) Stone, A. J. *Proc. R. Soc. London* **1963**, *A271*, 424.
- (20) See refs 236-241 in ref 1.
- (21) Frey, F.; Möller, M.; de Haas, M. P.; Zenden, N. J. P.; Schouten, P. G.; van der Laan, G. P.; Warman, J. M. *Macromolecules* **1993**, *26*, 89.
- (22) Kagawa, T.; Fujio, M.; Takeda, K.; Matsumoto, N. *Solid State Commun.* **1986**, *57*, 635.
- (23) Harrah, L. A.; Zeigler, M. J. *J. Polym. Sci., Polym. Lett.* **1987**, *25*, 205; *Macromolecules* **1987**, *20*, 601.
- (24) Michl, J.; Downing, J. W.; Kararsu, T.; McKinley, A. J.; Poggi, G.; Wallraff, G. M.; Sooriyakumaran, R.; Miller, R. D. *Pure Appl. Chem.* **1988**, *60*, 959.
- (25) Ito, O.; Terazima, M.; Azumi, T.; Matsumoto, N.; Takeda, N.; Fujino, M. *Macromolecules* **1989**, *22*, 1718.
- (26) Ito, O.; Terazima, M.; Azumi, T. *J. Am. Chem. Soc.* **1990**, *112*, 444.
- (27) Fujiki, M. *Chem. Phys. Lett.* **1992**, *198*, 177.
- (28) Morton, J. R. *Chem. Rev.* **1964**, *64*, 453.
- (29) Kim, Y. R.; Lee, M.; Thorne, J. R. G.; Hochstrasser, R. M.; Zeigler, J. M. *Chem. Phys. Lett.* **1988**, *145*, 75.