Mechanism of Electron and Hole Localization in Poly(dimethylsilane) Radical Ions

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The mechanism of excess electron and hole localizations in radical ions of poly(dimethylsilane) (PDMS) has been investigated by means of molecular dynamics (MD) and extended Hückel methods. Oligo(dimethylsilane) composed of 100 monomer units of dimethylsilane, $CH_3(Si(CH_3)_2)_nCH_3$ (n = 100), were used as a model of PDMS. Both wings of the oligomer were capped by a methyl group. First, the geometry of PDMS with a regular all-trans form was fully optimized by $MM2^+$ energy gradient method. Next, the MD calculation was carried out for PDMS at 300 K. The structure of PDMS was gradually deformed as a function of simulation time, especially the dihedral angle of Si−Si−Si−Si backbone that was randomized. At time zero when the structure has the regular all-trans form, both the excess electron and hole were completely delocalized on the Si backbone of PDMS. After thermal activation, the localization of the electron and hole was found. The mechanism of the localization was discussed on the basis of theoretical results.

1. Introduction

Polysilanes have been extensively investigated because of their potential utility as hole and electron transport materials in organic multilayer light emitting diodes, one-dimensional semiconductors, photoresist materials, and high-density optical data storage materials.[1−5] It has been believed that the σ-electron of polysilane is strongly delocalized along the polymer chain. However, recent experiments for radical ions of polysilanes have revealed that both conduction electron and hole are localized in a few silicon atoms.[6−9] Kumagai et al. measured electron spin resonance (ESR) and absorption spectra of radical ions of poly(cyclohexamethysilane). Their experiments indicate that the excess electron and hole are localized on a few silicon atoms (about 6 monomer units). Irie et al. measured the absorption spectra of radical ions of poly(methyl-*n*-propylsilane)s with a low molecular weight and suggested that both excess electron and hole are localized on 16 silicon atoms of the polymer.[6]

In previous papers,[10−13] we investigated the electronic states and structures of oligo[dimethylsilane] radical ions using density functional theory. The oligomer composed of 32 monomer units was examined as the oligomer chain. It was found that the excess electron and hole are fully delocalized along the Si−Si main chain if the oligomer has a regular all-trans form. This result is inconsistent with the experiments. Thus, the reason why the excess electron is localized in the polymer chain is still unclear.

To elucidate the electron localization in polysilanes, we investigated preliminarily the electronic states of middle-sized oligosilanes using molecular dynamics (MD) and extended Hückel methods.[14] Oligo[hydrogenated silanes], $H(SiH_2)_nH$ (n = 32 and 64), were examined as a model polymer. As a preliminary result, it was found that deformation of main chain causes both excess electron and hole localization.

In the present study, the similar technique is extended to the more relevant polysilane system. Radical ions of poly(dimethylsilane), $CH_3(Si(CH_3)_2)_nCH_3$ (PDMS, n = 100) are examined in the calculations. This polymer is one of the typical polysilanes used as one-dimensional semiconductors, photoresist, and high-density optical data storage materials. Therefore, elucidation of the localization mechanism in PDMS is important to develop the high-performance polysilane materials.

The electronic states of neutral oligosilanes have been investigated by ab initio calculations.[15−16] Michl and co-workers investigated conformers of n-$Si_6(CH_3)_{14}$ using ab initio, molecular mechanics (MM), and additive increment method.[15] It was found that the all-transoid is the most stable conformer. Recently, conformational dependence of $Si_4(CH_3)_{10}$ on UV absorption has been investigated using singly excited configuration interaction calculation.[16] The all-transoid form is the most stable as well as n = 6. The excitation energies of ($\sigma\sigma^*$ and $\sigma\pi^*$) are not dependent on conformational change, but oscillator strengths are strongly affected. More recently, they have investigated three conformers of n-$Si_4(CH_3)_{10}$ using CASSCF method, and have shown that the excitation energies and ionization potentials are slightly affected by the conformational change. Also, the effects of conformations in neutral state are clearly elucidated by their calculations. Thus, information on the electronic structures of neutral oligosilanes has been accumulated from theoretical points of view. On the other hand, a few theoretical works have been carried out for radical ions of oligosilanes despite its importance.[17,18] In particular, the localization mechanism of hole and electron in polysilane is still unclear.

2. Method of Calculations

An oligosilene composed of 100 monomer units of dimethylsilane capped by methyl groups in chain end, $CH_3(Si(CH_3)_2)_n$-CH_3 (n = 100) denoted by PDMS was used as a model of poly(dimethylsilane). The structure of PDMS with all-trans form was fully optimized using $MM2^+$ method. From the optimized structure, MD calculations were carried out to obtain the structures affected by thermal activation. We used 300 K for the simulation temperature, and time step was fixed to 0.5 fs. The temperature of the system is defined by

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$$T = \frac{1}{3Nk}\langle\sum_{i=1}^{M} m_i v_i^2\rangle \quad (1)$$

where M is the number of atoms of the system, v_i and m_i are the velocity and mass of the *i-th* atom, respectively, and k is Boltzmann's constant. After the MD calculations, the geometrical conformations were selected, and then spin densities were calculated using the extended Hückel molecular orbital (EHMO) method. The electronic states of the polymers were calculated using *Gaussian 03* program package.[19] More details of the method for the dynamics calculation are described elsewhere.[20-24]

3. Results

A. Structure of PDMS at 300 K. The structure of PDMS is fully optimized by means of the $MM2^+$ method. To elucidate thermal effect on the structure of PDMS, the $MM2^+$-MD simulation is carried out for PDMS at 300 K. The snapshots of PDMS at 300 K are given in Figure 1. At time zero, the structure of PDMS is assumed to be a regular all-trans form, which is the most stable form of PDMS. After thermal activation, the Si backbone and side chains are gradually deformed. The rotation of the methyl group and deformation of the dihedral angle are found at 0.50 ps. At time = 2.0 ps, the structure of PDMS is randomly deformed as shown in this figure. The dihedral angles of the polymer chain are plotted in Figure 2 as a function of time. Two dihedral angles for Si−Si−Si−Si backbone, D(48−49−50−51) and D(52−53−54−55), are selected as sample angles where numbers in parentheses mean the position of the Si atom along the chain. The dihedral angles are distributed in the range 143−180° at 300 K. The bond lengths are also fluctuated by thermal activation. The variation of the vibration is 2.3−2.6 Å at the steady state (1.0−3.0 ps). The change of geometrical parameters indicates that the structure of PDMS is largely fluctuated by thermal activation at 300 K, especially the dihedral angle is strongly fluctuated due to the single bond.

B. Electron Localization of Radical Anion of PDMS. The spin densities of excess electron on radical anion of PDMS are calculated by means of the EHMO method. The structures of PDMS at time = 0.0, 0.05, 0.1, 0.5, and 1.0 ps are selected as sampling points, and then the spin densities are calculated by EHMO. The dihedral angles at the sampling points are illustrated in Figure 3. The angle is 180.0° at time zero, meaning that the Si backbone takes a regular all-trans form. After thermal activation, the dihedral angles are gradually randomized. The amplitudes of the dihedral angles at 0.05 and 0.10 ps are 5° (175−180°) and 16° (164−180°), respectively. At 1.0 ps, the angles are fully randomized (amplitude is 47°).

The spin densities plotted as a function of the position of the Si atom (m) are given in Figure 4. The spin density at time zero is fully delocalized along the polymer chain ($m = 1-100$). The structure of PDMS is the regular all-trans form at time zero. By the thermal activation, the distribution of spin density is drastically changed as a function of time. The excess electron is suddenly localized in the site $m = 19-24$ at 0.05 ps. At 1.0 ps, the excess electron is also localized in the site $m = 64-77$. By comparing the distributions of spin densities and dihedral angles, it is suggested that the excess electron is localized in continuous disorder site where dihedral angles are randomly distributed along the chain.

C. Hole Localization in the Radical Cation of PDMS. The spin densities in the radical cation of PDMS are given in Figure 4 (lower panel). The hole (spin density) is completely delocalized along the polymer chain at time zero. By thermal activation, the hole is rapidly localized on the Si atoms with $m = 80-100$ at time = 0.05 ps, indicating that the hole is localized in the polymer chain as well as the excess electron. However, the localization site is much different from the electron. Also, it should be emphasized that localization width of hole ($\Delta m = 20$) is significantly wider than that of the excess electron. For example, the localization width for excess electron is $\Delta m = 6$ at 0.05 ps.

D. Short-Time Propagation. To elucidate the mechanism of electron and hole localization in more detail, variation of spin densities is monitored in shorter time scale (0.0−30 fs). The distributions of dihedral angles at time = 0, 10, 20, and 30 fs are plotted in Figure 5. At 10 fs, the dihedral angles are distributed with narrow amplitude (176−180°). The amplitude increases gradually with increasing time. The angles are distributed in the range 172−180° at 30 fs.

The spin densities of excess electron and hole are plotted in Figure 6. As clearly shown in this figure, the excess electron is already localized at 10 fs, indicating that the excess electron can localize at very short time propagation. On the other hand, the spin density for the hole is widely distributed in the range $m = 18-80$ at 10 fs. These results indicate that a slight disorder of dihedral angle causes electron localization in polysilanes, whereas the localization of hole needs large magnitude of disorder.

E. Effects of Artificial Defect on the Localization. In the previous section, the disorder sites in the polymer chain were generated by thermal activation. Hence, the disorder sites are widely distributed over the chain. In this section, the electron and hole localizations in a model polymer are investigated. First, the model polymer with $n = 100$ is divided to two parts (A and B). In part A, the geometry of 40 monomer units ($m = 1-40$) is fixed to the optimized geometry with regular all-trans form during the MD calculation. On the other hand, all geometrical parameters in part B ($m = 41-100$) are full-dimensionally treated in the MD calculation. An expanded view of the structure of the model polymer obtained by the MD calculation at 300 K is illustrated in Figure 7 (upper figure). The dihedral angle and spin densities of excess electron and hole are plotted in Figure 7 (middle and lower panels, respectively). The dihedral angles in the left half of the model polymer ($m = 1-40$) are fixed to 180°, while those in right half ($m = 41-100$) are randomly distributed in the range 150−180° at 300 K. The spin densities in the model polymer show that the excess electron (anion) is distributed in the part of the regular all-trans form, whereas the spin density (hole) of the cation is distributed in the part of the random region. This result indicates that the localization sites for excess electron and hole are different each other in polysilanes.

4. Discussion

A. Summary of the Present Study. In the present study, the mechanism of the electron and hole localizations in charged polysilanes was investigated by means of both MD and EHMO methods. The results obtained can be summarized as follows.

(1) The excess electron and hole are localized by continuous disorder along the polymer chain. The random distribution of dihedral angles for Si main chain causes mainly the localization in polymer.

(2) Localization lengths for the excess electron on the Si main chain are significantly shorter than that of hole.

(3) The localization positions for electron and hole are different from each other. The electron is not always located in the same place as hole.

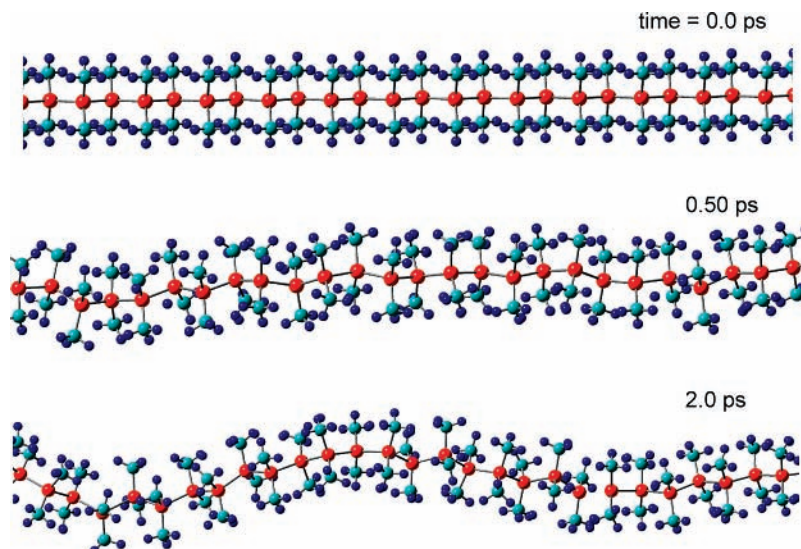

Figure 1. Snapshots of poly(dimethylsilane) calculated by means of $MM2^+$-MD method at 300 K. 25−30 monomer units around the central position of $CH_3(Si(CH_3)_2)_nCH_3$ ($n = 100$) are only illustrated. Regular all-trans form is assumed for the initial structure at time zero.

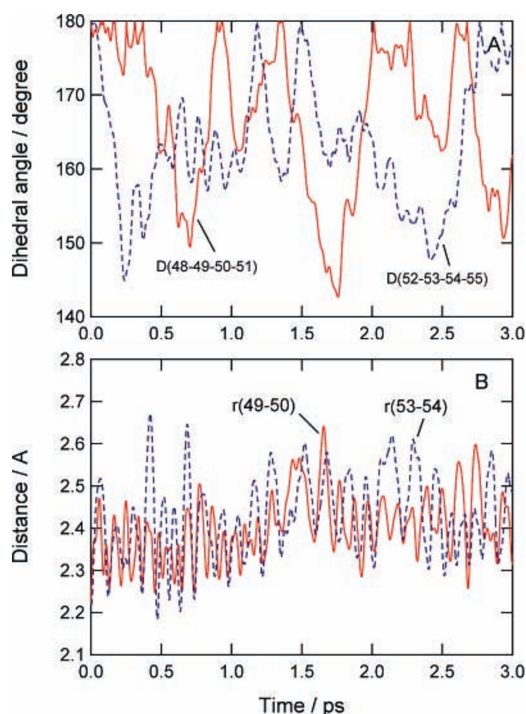

Figure 2. Results of $MM2^+$-MD calculation at 300 K. Two dihedral angles (A) and two bond distances (B) are only plotted as sample results.

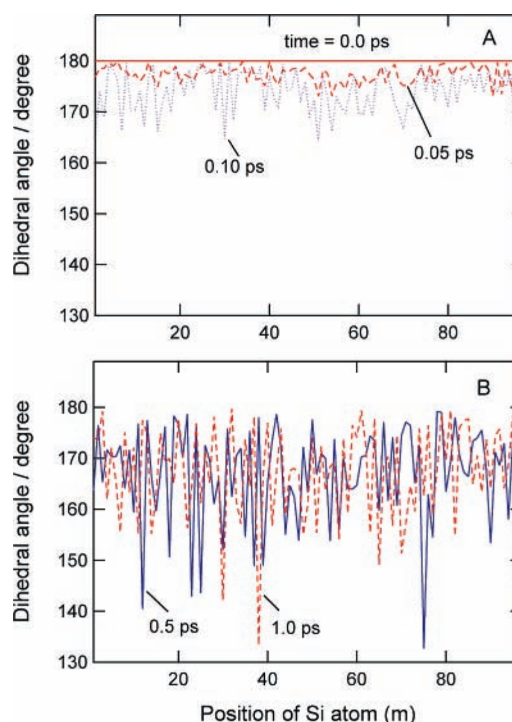

Figure 3. Distributions of dihedral angles plotted as a function of position of Si atoms obtained by the $MM2^+$-MD calculation at 300 K. Sampling times are (A) 0.0, 0.05, and 0.10 ps and (B) 0.5 and 1.0 ps.

These results strongly suggest that the delocalization of excess electron and hole is possible in the case of polysilanes without random distribution of dihedral angle. Introduction of steric side chain to polysilane would be effective to develop the ideal one-dimensional polysilane.

B. Mechanism of the Localization. On the basis of the present calculations, a model for the excess electron and hole localization in PDMS is proposed in this section. Figure 8 shows schematic illustrations for the model of the localization. If the polysilane has a regular all-trans form in all regions, both excess electron and hole are fully delocalized along the polymer chain. However, in the actual system the continuous disorder of the dihedral angle is caused by thermal activation. Therefore, the electron and hole are localized in the specific sites of the polymer chain.

C. Comparison with Previous Studies. *Mechanism of the Localization.* Mechanisms of the electron and hole localization have been investigated mainly for polyacetylene, which is a one-dimensional polymer and analogous to polysilane. Tanaka et al. calculated the electronic states of polyacetylene by means of a simple Huckel method.[25] The polymer composed of 300 units of monomer was chosen as a model of the polyacetylene. The values of Coulomb (α) and resonance (β) integrals were randomly generated to represent a random system. It was suggested that the random arrangement of α and β values causes the electron localization in polyacetylene. In addition, they pointed out that Anderson localization mechanism[26] is important in the electron localization in polyacetylene. Recently, Johansson and Larsson have investigated the electronic structure of

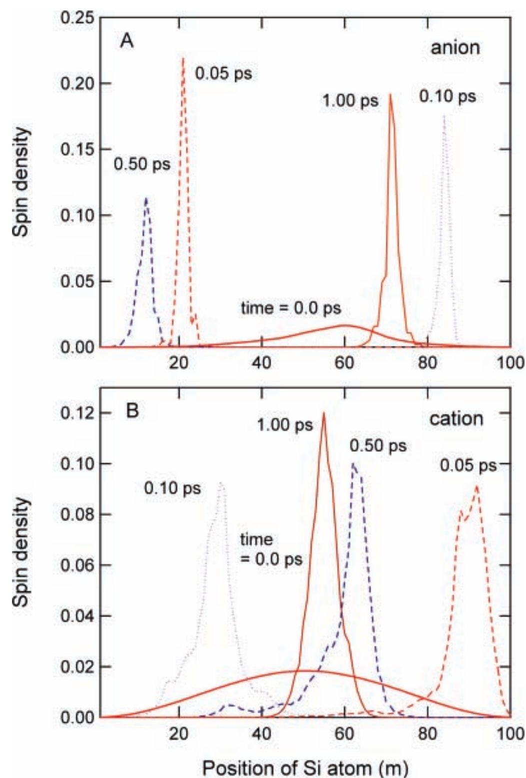

Figure 4. Spin densities for the excess electron in anion radical (A) and hole in cation radical (B) of $CH_3(Si(CH_3)_2)_nCH_3$ ($n = 100$) at the sampling time.

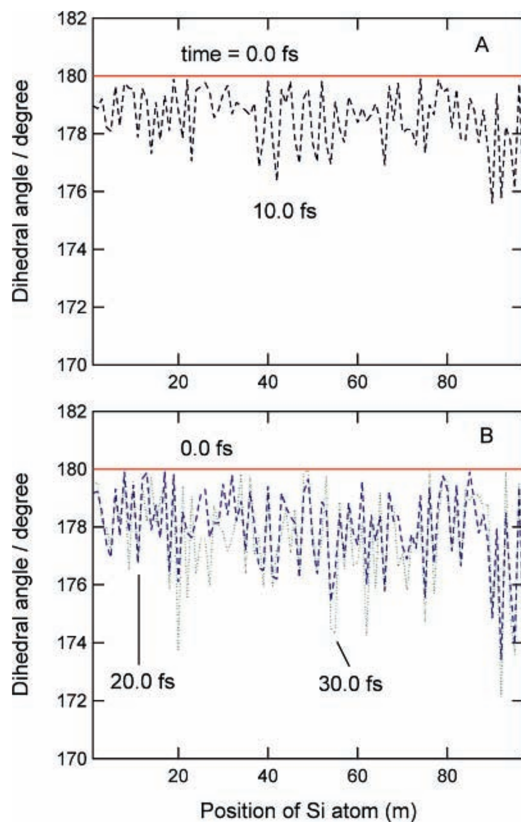

Figure 5. Distributions of dihedral angles in the short time propagation plotted as a function of position of Si atoms obtained by the MM2$^+$-MD calculation at 300 K. Sampling times are (A) 0.0 and 10 ps, and (B) 20 and 30 fs.

polythiophene (PTP) and oligothiophenes using localized electron models combined with the Su−Schrieffer−Heeger (SSH)

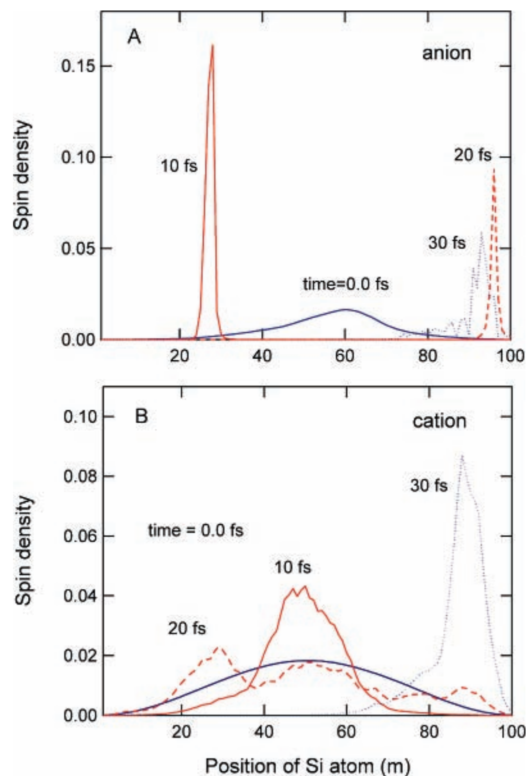

Figure 6. Spin densities for the excess electron in anion radical (A) and hole in cation radical (B) in short-time propagation.

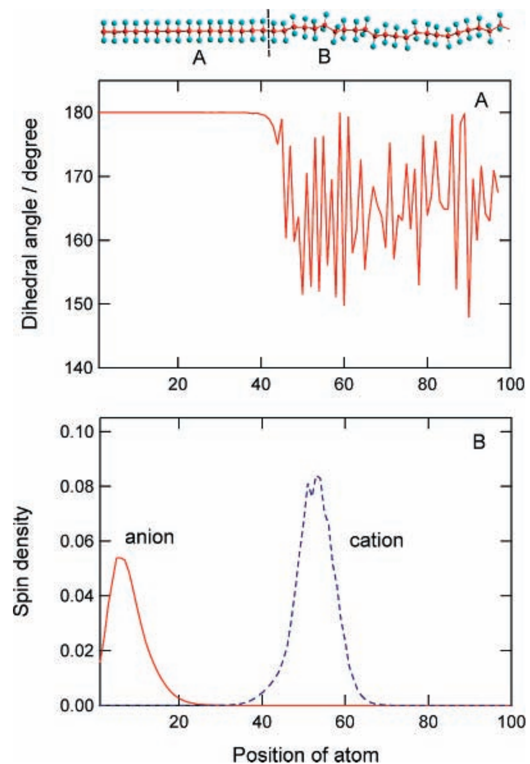

Figure 7. Distributions of dihedral angles of model polymer having an artificial defect obtained at 300 K (A) and spin densities for anion and cation (B). A snapshot of the model polymer at 300 K is illustrated in upper figure.

model. In PTP, an electron hole was found to localize over about five thiophene units.[27]

For polysilanes, the studies for electron localization is quite limited. Tilgner et al. investigated the electronic states of poly(di-*n*-hexylsilane) in solid solution from both experimental and

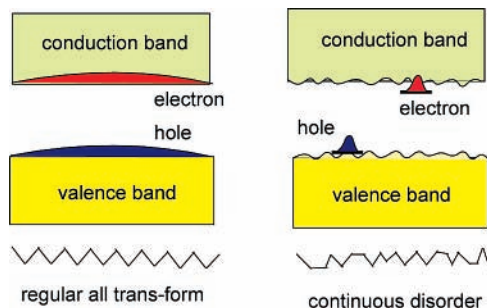

Figure 8. Schematic illustration of the model for electron and hole localization in polysilanes.

theoretical points of view.[28,29] They pointed out that the excitation is localized by a continuous disorder of main chain. Their model is very similar to the Anderson localization model. The similar conclusion was obtained by Ichikawa et al. using ESR spectra of ion radicals of oligo- and polysilanes.[30] The experiments are consistent with our model.

Localization Lengths. The localization lengths (Δm) of excess electron, hole, and electronic excitation have been reported by several authors. From the ESR measurement for ion radicals of polysilanes, Kumagai et al. suggested that the excess electron and hole are localized in a part of the polymer chain composed of a few silicon atoms ($\Delta m = 6$).[9] Irie et al. measured electron absorption spectra of radical ions of oligo- and poly(methyl-*n*-propylsilane)s in rigid matrices at 77 K.[6] They found that the spectra is saturated at $n = 16$ (where n means the number of monomer units). The present calculations showed that the electron and hole are localized in a few silicon atoms ($\Delta m = 6-20$). This result agrees well with their experiments. Frey et al.[31] suggested that holes in the valence band of polysilanes show hole-hopping type conduction, but excess electrons injected to a conduction band do not contribute to electric conduction. More recently, Saxena et al. measured UV spectra of rodlike polysilanes and suggested that exiton in the polysilane without defect is widely extent in the polymer chain.[32] This result is consistent with the present result that localization of holes is longer than that of excess electron.

In previous work,[14] we investigated preliminarily the electron localization in the medium-sized oligosilanes ($n = 32$ and 64) using MM2-MD and EHMO. Hydrogenated polysilane, $H(SiH_2)_nH$ ($n = 32$ and 64), was used for a model polymer. The localization was found along the polymer chain. However, the localization lengths ($\Delta m = 20$) are longer than the present value ($\Delta m = 6-20$) in dimethylsilane $CH_3(Si(CH_3)_2)_nCH_3$ ($n = 100$). This difference is caused by the effect of methyl substitution in the polysilanes and a different number of monomer units.

D. Final Remarks. In the present study, several approximations were introduced to calculate the structures and electronic states of charged polysilanes. We used the extended Huckel molecular orbital (EHMO) method to obtain the spin densities of excess electron and hole because the system is significantly large. This method is effective to obtain a qualitative property of the electronic state. However, the EHMO method overestimates slightly the localization length of hole and electron in the ion radicals of polysilane, as shown in Supporting Information. Therefore, the qualitative feature for the spin density obtained in the present calculation may be effective. Next, we assumed that the structures for ionic states are the same as that of the neutral one. However, this effect is negligibly small as shown in our previous papers.[11-12] Despite several approximations that are introduced here, the results enable us to obtain valuable information on the mechanism of excess electron and hole localization in actual polysilanes.

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Supporting Information Available: Figures of spin density distributions calculated by means of EHMO, ROHF, MP2, B3LYP, and PW91PW91 methods are given as Figures S1 and S2. These materials are available free of charge via the Internet at http://pubs.acs.org.

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