

Electronic Structure of Polycarbosilane Studied by UV Photoelectron Spectroscopy

Yoko Sakurai,^{*,†} Daisuke Yoshimura,[†] Hisao Ishii,[†] Yukio Ouchi,[†] Hiroaki Isaka,^{‡,§} Hiroyuki Teramae,^{‡,¶} Nobuo Matsumoto,^{‡,○} Shinji Hasegawa,[§] Nobuo Ueno,^{||} and Kazuhiko Seki[⊥]

Department of Chemistry, Graduate School of Science, Nagoya University, Furocho, Chikusa-ku, Nagoya 464-8602, Japan, NTT Basic Research Laboratories, Morinosato-Wakamiya, Atsugi, Kanagawa 243-0198, Japan, Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan, Department of Materials Technology, Faculty of Engineering, Chiba University, Chiba 263-8522, Japan, and Research Center for Materials Science, Nagoya University, Furocho, Chikusa-ku, Nagoya 464-8602, Japan

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An ultraviolet photoelectron spectroscopic study was performed to examine the electronic structure of poly-(1,1,2,2-tetramethyldisilylenemethylene), $[(\text{SiMe}_2)_2\text{CH}_2]_n$, which consists of repeating Si–Si–C units. We compared the observed spectra to reported gas-phase spectra of Si_2Me_6 and $\text{Si}_4\text{Me}_{10}$ and theoretical molecular orbital calculations. Theoretical calculations by the *ab initio* and PM3 methods agree well with the observed spectra, which enabled assignment of the observed spectral features. The broad peak derived from Si–Si bond orbitals in polycarbosilane suggests that Si–Si units, which are separated by carbon atoms, still interact with each other, to form σ -conjugation through the backbone. The observed ionization threshold energy of the polycarbosilane $[(\text{SiMe}_2)_2\text{CH}_2]_n$ is 6.4 eV. The dispersion of the highest valence band of polycarbosilane is less than that of polysilane, indicating that the degree of σ -conjugation of polycarbosilane is smaller than that of polysilane.

I. Introduction

Silicon-backboned polymers have unique electronic structures in which σ -electrons are delocalized along the polymer chain,¹ with energy and electronic properties comparable to those of π -electrons in π -conjugated carbon-based polymers. Based on this analogy, this delocalization is called σ -conjugation, and these polymers have attracted attention as a new class of electronically functional materials, with potential applications as photoresists, conducting polymers, and initiators of polymerization.² However, control of their electronic structure is important for such applications. Various attempts have been made to control the degree of σ -conjugation in polysilanes, e.g., by modifying the conformation and by introducing functional substituents.^{3–5}

Another way to change the degree of σ -conjugation is to replace the Si atoms by foreign atoms. Such studies initially involved homopolymers formed by heavier analogues of Si, i.e., Ge and Sn.^{6–9} However, the electronic structures of polysilane and polygermane are similar, due to the small difference in the

energy of the atomic orbitals (AOs) between Si and Ge atoms.^{6,7} Similar results were obtained for Sn, with only a small difference in the lowest excitation energies (0.2–0.5 eV) compared to those of the corresponding polysilanes.^{8,9} The electronic structures of copolymers of Si and Ge are also similar to those of polysilane or polygermane homopolymers.⁶

On the other hand, the electronic structure of polycarbosilane with a backbone formed by Si and C atoms is expected to be significantly different from those of homopolymers, due to the large AO energy difference between Si and C atoms. This trend can be seen by comparing the Pauling electronegativities of C(2.55), Si(1.90), Ge(2.01), and Sn(1.96).¹⁰ Isaka et al. showed that the electronic structure of polycarbosilane formed by repeating Si–Si–C units, poly(1,1,2,2-tetramethyldisilylenemethylene) $[(\text{SiMe}_2)_2\text{CH}_2]_n$, is actually different from those of polysilane and polyethylene based on electronic absorption spectra and theoretical calculations.¹¹

To obtain further insight into the copolymers, in this work we investigated the electronic structure of this polycarbosilane studied by Isaka et al. using UV photoelectron spectroscopy (UPS). By comparing the obtained UPS spectra with those of related compounds and theoretical calculations, we could assign the observed spectral features. We also compared the electronic structure of this polycarbosilane with those of polysilane $(\text{SiH}_2)_n$, polyethylene $(\text{CH}_2)_n$, and polysiloxane. In the last case, σ -conjugation is broken because of the large difference in atomic orbital energy between Si and O.

II. Experimental Section

$[(\text{SiMe}_2)_2\text{CH}_2]_n$ was synthesized by Wurtz coupling with crown ether.¹¹ The molecular weight obtained by GPC measurement based on a polystyrene standard was $M_n = 1.3 \times 10^5$ ($M_w/M_n = 4.6$). The samples used in the UPS measurements were

* Author to whom correspondence should be addressed at Department of Chemistry, Graduate School of Science, Nagoya University, Furocho, Chikusa-ku, Nagoya 464-8602, Japan. Fax: +81-52-789-2944. E-mail: sakurai@mat.chem.nagoya-u.ac.jp.

† Department of Chemistry, Graduate School of Science, Nagoya University.

‡ NTT Basic Research Laboratories, Morinosato-Wakamiya.

§ Institute for Molecular Science.

|| Chiba University.

⊥ Research Center for Materials Science, Nagoya University.

¶ NTT Communications Corporation, 3-20-2, Nishi-Shinjuku, Shinjuku Tokyo 163-1422, Japan.

○ ATR Adaptive Communications Laboratories, 2-2 Hikaridai, Seika-cho Soraku-gun, Kyoto 619-0288, Japan.

○ Shonan Institute of Technology, 1-1-25, Nishikaigan, Tsujidou, Fujisawa, Kanagawa 251-8511, Japan.

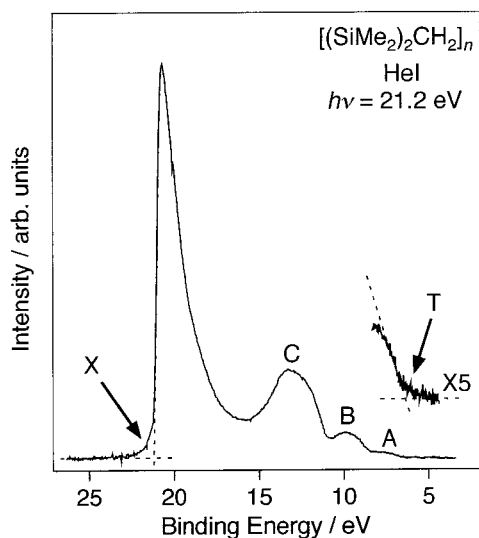


Figure 1. UPS spectrum of $[(\text{SiMe}_2)_2\text{CH}_2]_n$ at $h\nu = 21.22$ eV. The abscissa is the binding energy relative to the vacuum level.

prepared on a copper disk by spin-coating a drop of 0.2 wt % toluene solution. UPS spectra were measured using two apparatuses. One consists of a rare-gas resonance lamp capable of producing a HeI (21.22 eV) line and a retarding-field type electron analyzer. The base pressure of the chamber was in the 10^{-8} Torr range. The photoelectron spectra were obtained using the ac modulation technique,^{12,13} with a peak-to-peak modulation of 0.2 V. An advantage of the retarding-field type analyzer is that we can accurately determine the ionization threshold energy due to the high accuracy of the binding energy relative to the vacuum level, which is based on the simple geometry of the energy analyzer. The other UPS apparatus is an angle-resolved UPS system at BL8B2 of the UVSOR synchrotron radiation facility at the Institute for Molecular Science. Synchrotron radiation monochromatized with a plane grating monochromator¹⁴ impinged on the sample, and the energy of photoelectrons was analyzed with a hemispherical electrostatic analyzer. The base pressure of the measurement chamber was in the range of 10^{-10} Torr. An advantage of this system is that we can probe most of the valence band using high-energy photons. The energy resolution of both apparatuses was about 0.2 eV, as determined by the Fermi edge of gold. No detectable damage of the sample by photon irradiation was observed.

III. Calculations

The molecular orbital calculations were performed with the ab initio crystal orbital method^{15,16} and semiempirical PM3 method.¹⁷ The ab initio crystal orbital method was applied to infinite polymer chains using the 3-21G basis set. The geometry was optimized by the energy gradient method for the all-trans conformer which was revealed by X-ray diffraction for the $[(\text{SiMe}_2)_2\text{CH}_2]_n$ crystal.¹⁸ Density of states (DOS) was determined by Brust's histogram method.¹⁹ PM3 calculation was performed with the MOPAC package on an oligomer with five monomer units. DOS was derived by convolution of delta functions at each orbital energy by a Gaussian function with a full width at half-maximum (fwhm) of 0.8 eV.

IV. Results and Discussion

The UPS spectrum of polycarbosilane using HeI (21.22 eV) is shown in Figure 1, where the abscissa is the binding energy

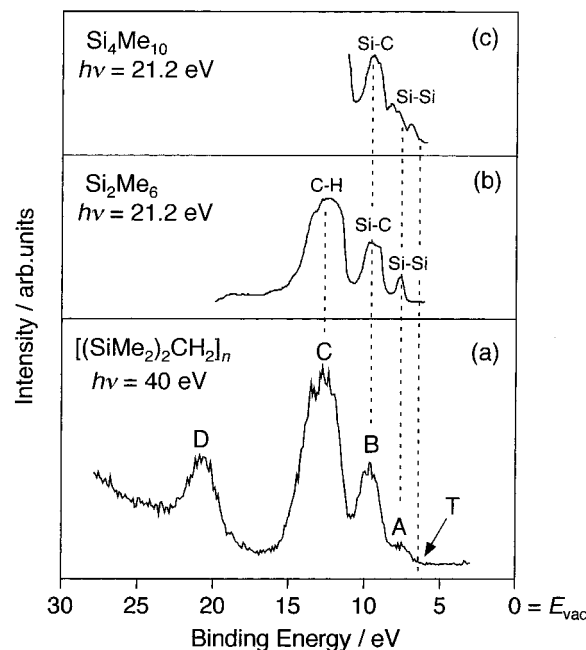


Figure 2. (a) UPS spectrum of $[(\text{SiMe}_2)_2\text{CH}_2]_n$ at $h\nu = 40$ eV, (b) and (c) gas-phase UPS spectra of Si_2Me_6 and $\text{Si}_4\text{Me}_{10}$, respectively, at $h\nu = 21.2$ eV.

TABLE 1: Binding Energies of UPS Spectral Features of $[(\text{SiMe}_2)_2\text{CH}_2]_n$

feature	E_B/eV	assignment
T	6.4	Ionization threshold
A	7.5	Si-Si and Si-C bonds
B	9.6	Si-C bonds
C	12.8	C-H bonds
D	20.7	C2s

E_B relative to the vacuum level:

$$E_B = h\nu - E_k$$

where $h\nu$ is photon energy and E_k is the kinetic energy of a photoelectron measured from the left-hand cutoff X, which corresponds to $E_k = 0$. The right-hand cutoff T corresponds to the maximum E_k . The energies of these cutoffs were determined by linear extrapolation of the spectrum, as shown in Figure 1. The value of E_B at T gives an ionization threshold energy of 6.4 eV for this polycarbosilane.

The UPS spectrum of polycarbosilane $[(\text{SiMe}_2)_2\text{CH}_2]_n$ at a higher photon energy $h\nu = 40$ eV is shown in Figure 2a, where again the abscissa is E_B relative to the vacuum level. In the spectra in both Figures 1 and 2a, we see three features labeled A, B, and C. Their energies agree well between the two figures. In the spectrum in Figure 2a, we see an additional peak D at a higher binding energy. The values for these features are listed in Table 1 with their assignments given below.

For assignment of the observed spectral features, we first compared the spectrum in Figure 2a with the reported gas-phase UPS spectra of $\text{Si}_2(\text{CH}_3)_6$ and $\text{Si}_4(\text{CH}_3)_{10}$,²⁰ which are shown in Figure 2b,c. In this figure, the assignments of the peaks are shown by the types of bonds from which the levels forming the peaks are derived.²⁰ The energies of the gas-phase spectra are shifted by 1.1 eV to align the Si-C peak with the 9.5 eV peak in the spectrum of polycarbosilane. Comparison of these spectra, shown by the broken lines in the figure, suggests that peaks A, B, and C can be assigned to the levels derived from the Si-Si, Si-C, and C-H bond orbitals, respectively. Peak

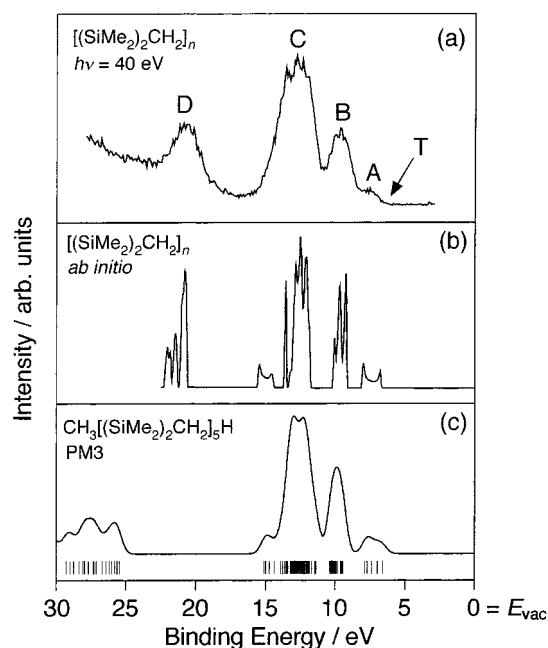


Figure 3. (a) UPS spectrum of $[(\text{SiMe}_2)_2\text{CH}_2]_n$ at $h\nu = 40$ eV, (b) the calculated DOS by 3-21G ab initio calculation for $[(\text{SiMe}_2)_2\text{CH}_2]_n$, and (c) the calculated DOS by PM3 calculation for $\text{CH}_3[(\text{SiMe}_2)_2\text{CH}_2]_5\text{H}$ pentamer.

A in the spectrum of polycarbosilane is broader than the Si–Si peak in the spectrum of $\text{Si}_2(\text{CH}_3)_6$. While this is partly due to the peak-broadening observed for the solid state,^{21,22} there is also a contribution from the splitting of levels by σ -conjugation, which we will discuss later. This suggests that Si–Si bonds still interact with each other through the inserted carbon atoms, to form σ -conjugation over the backbone.

Next, in Figure 3 we compare the UPS spectrum at $h\nu = 40$ eV with the DOS derived from ab initio and PM3 calculations for the polymer chain and the pentamer, respectively. For the PM3 results, the energies of the occupied orbitals are also shown with vertical bars on the energy axis. The energy scale of the DOS derived from ab initio calculation is reduced to 83% for a better fit with the observed spectrum. The calculated results agree well with the UPS spectrum, except for the high binding energy part in the PM3 calculation at 25–30 eV. On the basis of this correspondence, we can assign feature A of the observed spectrum to the levels formed by the combined contributions from the Si–Si and Si–C bonds in the backbone, feature B, to the levels from Si–C bonds in both the backbone and the side chain, feature C, to the levels from C–H bonds, and feature D, to the levels from C2s atomic orbitals. These results agree well with the assignments based on the above-mentioned comparison with the spectra of permethylated silanes (Figure 2b,c),²⁰ except that the theoretical calculation indicates a contribution from the Si–C bonds in the backbone in feature A, in addition to that from Si–Si bonds.

The energy-band structure of the parent polycarbosilane $[(\text{SiH}_2)_2\text{CH}_2]_n$ obtained from ab initio calculations is shown in Figure 4c. For comparison, the band structures of the parent polysilane $(\text{SiH}_2)_n$ and polyethylene $(\text{CH}_2)_n$ are also shown in Figure 4a,b, respectively.^{16,23} In these band structures, the highest valence band has significant dispersion to wave vector k . This band is mainly formed from the p orbitals with their axes along the main chain. In polyethylene, the width of these bands is large, indicating effective interaction among the C2p orbitals. In polysilane, the width is slightly smaller than this. The dispersion in polycarbosilane is even smaller than that in

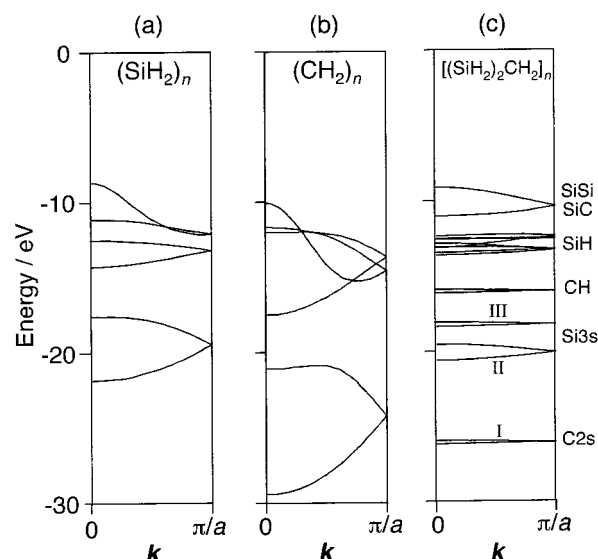


Figure 4. Electronic band structures of (a) polysilane, (b) polyethylene, and (c) polycarbosilane by ab initio calculations.

TABLE 2: Ionization Threshold Energies of Polymers (in eV)

polymer	$(\text{CH}_2)_n$	$[(\text{SiMe}_2)_2\text{CH}_2]_n$	$(\text{SiMe}_2)_n$	$(\text{SiMe}_2\text{O})_n$
I_{th}	8.5	6.4	5.9	8.3
ref	28	present work	26	27

polysilane. These results suggest that polycarbosilane exhibits σ -conjugation along the backbone, but the degree of conjugation is smaller than those in polyethylene and polysilane.

There are many bands at the higher binding energy region in Figure 4c. According to previous reports,^{21,24–30} the pair of bands centered at –20 eV in $(\text{SiH}_2)_n$ (Figure 4a) and the pair centered at –25 eV in $(\text{CH}_2)_n$ (Figure 4b) are derived from the Si3s and C2s AOs, respectively. In $[(\text{SiH}_2)_2\text{CH}_2]_n$ the pair of bands at –26 eV (I in Figure 4c) and the four bands at around –18 to –20.5 eV (II and III) can be assigned as the C2s- and Si3s-derived bands, respectively. Bands II and III should be due to the bonding and antibonding contributions of the two Si3s orbitals in a Si–Si unit. The C2s-derived band is very flat with a very small bandwidth, indicating that the interaction among the C2s orbitals through two Si atoms is weak. On the other hand, the interaction among the Si3s-derived Si–Si bond orbitals through a C atom seems to be stronger, as seen in the greater width of bands II compared to bands I. The total width of the Si3s-derived bands II and III is comparable to that of polysilane, confirming the reasonably effective conjugation through C atoms. The bands in the region between –16 eV and –13 eV should mainly come from the bond orbitals in the Si–H and C–H bonds.

We compared the ionization threshold energies (I_{th}) of polycarbosilane $[(\text{SiMe}_2)_2\text{CH}_2]_n$, polydimethylsilane $(\text{SiMe}_2)_n$, polyethylene $(\text{CH}_2)_n$, and poly(dimethylsiloxane) $(\text{SiMe}_2\text{O})_n$. The values of I_{th} for these polymers are deduced from UPS experiments,^{24,31,32} and are listed in Table 2. The value of $I_{\text{th}} = 6.4$ eV for this polycarbosilane is slightly larger than that for polydimethylsilane (5.9 eV), and still smaller than that for polyethylene (8.5 eV). On the other hand, in poly(dimethylsiloxane), the σ -conjugation of the backbone is broken by oxygen atoms with large electronegativity inserted between the Si–Si pairs, as indicated by the much smaller value of the reported bandwidth.³³ This weak σ -conjugation and the inductive effect of the electron-withdrawing oxygen atoms lead to the large value of $I_{\text{th}} = 8.3$ eV.³¹

These results clearly demonstrate that the electronic structure and degree of σ -conjugation can be significantly modified by inserting or substituting heteroatoms into the polysilane backbone, and also show the possibility of controlling and optimizing the electronic structure and electronic properties.

V. Conclusion

The electronic structure of Si₂C-type polycarbosilane was studied by UV photoelectron spectroscopy. The features in the UPS spectra were assigned based on comparison with the data of related compounds and with the density of states derived from molecular orbital calculations. The obtained electronic structure was compared to those of related polymers. The HOMO of polycarbosilane is formed by Si–Si and Si–C bond orbitals in the backbone, retaining some degree of σ -conjugation of the backbone. The degree of σ -delocalization was found to be intermediate between those of polysilane and polysiloxane, as verified by examination of the energy band structure obtained from ab initio calculations and also by the values of I_{th} . These results indicate the possibility of controlling and optimizing the electronic structure of these polymers by proper insertion or substitution by atoms of other elements.

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