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Influence of the π-Conjugated Carbon Moiety on the Electronic Structure of Polymeric Organosilicon Systems

Kazuyoshi Tanaka,* Keizo Nakajima, Mayumi Okada, and Tokio Yamabe

*Department of Hydrocarbon Chemistry and Division of Molecular Engineering, Faculty of Engineering,
Kyoto University, Sakyo-ku, Kyoto 606-01, Japan, and Institute for Fundamental Chemistry,
34-4 Nishihiraki-cho, Takano, Sakyo-ku, Kyoto 606, Japan*

Mitsuo Ishikawa

Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Higashi-Hiroshima 724, Japan

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The influence of a π-conjugated carbon chain embedded in the skeleton of organosilicon polymers $-[SiH_2(CH{=}CH)_x]_n-$ (x = 1-5) on the total electronic structure has been theoretically and systematically studied on the basis of the one-dimensional tight-binding self-consistent crystal orbital method. Emphasis has been put on the interchange of the σ-σ^* and the π-π^* transition energies to give the apparent band-gap value and on the degree of the σ- and π-conjugation extending along the whole polymer chain. The result indictes the following. (1) The π-π^* transition energy becomes almost the same as the σ-σ^* energy when the π-conjugated carbon chain achieves a certain length (x = 3). Such a tendency is not observed in the carbon-catenated polymers ($-[CH_2(CH{=}CH)_x]_n-$ (x = 1-5)), signifying that the σ-electrons from the silylene unit have a strong effect on the organosilicon polymer. (2) Both the σ- and the π-conjugation throughout the whole polymer chain become weaker with an increase in x. The molecular orbital levels of simplified-model molecules for the polymers dealt with here were also examined in association with (1).

Introduction

Polysilanes are currently one of the most interesting classes of polymeric materials due to their intriguing properties such as enhancement of electrical conductivity with doping, nonlinear optical properties, and so on.[1-10] Furthermore, polymeric organosilicon systems consisting of both silicon and carbon atoms have also received increasing attention, and many kinds of such polymers have been synthesized.[11-17] We have recently reported the electronic structures of simplified polymeric organosilicon systems containing both a disilanylene ($-SiH_2-SiH_2-$) unit and a π-conjugated carbon moiety such as ethenylene ($-CH{=}CH-$), ethynylene ($-C{\equiv}C-$), diethynylene ($-C{\equiv}C-C{\equiv}C-$), or phenylene and found two kinds of interesting results.[18]

First, both the highest occupied crystal orbital (HOCO) and the lowest unoccupied crystal orbital (LUCO) of these polymers are of the σ-type in spite of the presence of the π-conjugated carbon systems. The levels of the π-type CO's, the component of which mainly comes from that of the carbon moieties, are rather far from the frontier CO level. This predicts that the σ-σ^* interband transitions should be observed in the actual polymeric organosilicon systems as in the cases of polydihydrosilane and its derivatives.[19-22] Second, these organosilicon polymers tend to form pseudo π-bonding between the silicon atom and the side substituents. In the polymer skeleton, however, the pattern of the HO π-type CO shows the Si-Si antibonding pπ nature and that of the LU π-type CO the Si-Si bonding pπ nature. These results strongly suggest that the electronic properties of silicon-containing polymers are different from those of ordinary organic polymers. Therefore, it is worthwhile to examine the electronic properties of organosilicon polymers in a more detailed manner.

In this paper, we first report how the electronic structures of organosilicon polymers are affected by the π-conjugated carbon moieties, when these are incorporated into the polymer skeleton, in order to get a guiding principle toward a detailed molecular design of these polymers. Specifically, we investigate the dependence of the electronic structures of polymeric organosilicon systems on the length of π-conjugated carbon chains in their unit cells. Skeletons of the polymers examined here are expressed as $-[SiH_2(CH{=}CH)_x]_n-$ (x = 1-5; A-E). Moreover, we also checked the electronic structure of $-[CH_2(CH{=}CH)_x]_n-$ (x = 1-5; F-J). Among these 10 polymers, 4 silylene-containing polymers (x = 1-4; A-D) and 2 methylene-containing polymers (x = 1, 2; F, G) are illustrated in Figure 1.

Method of Calculation

The calculations of all the polymers were performed on the basis

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* To whom correspondence should be addressed at Kyoto University.

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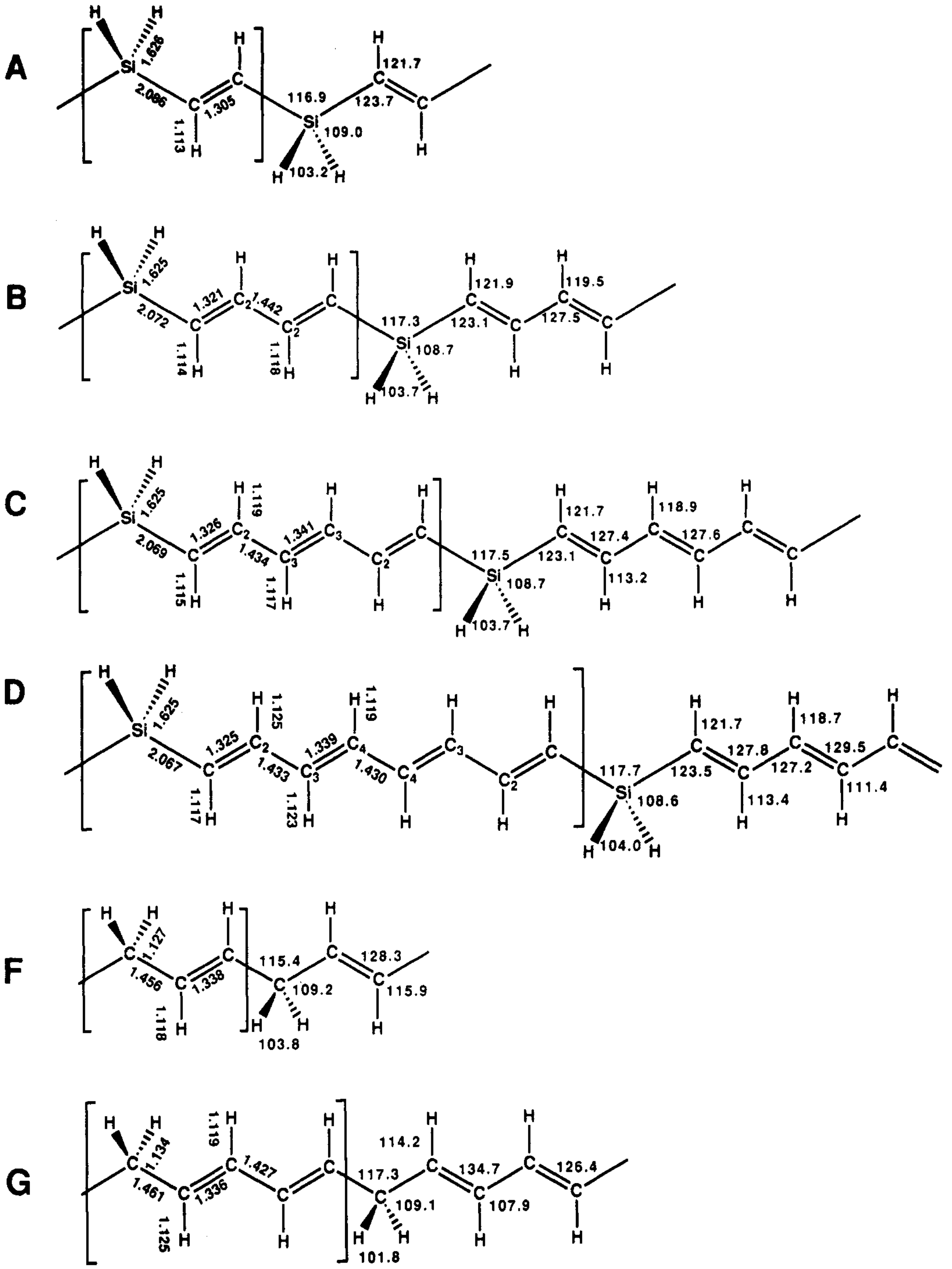

Figure 1. Skeletons of selected model polymers (see text). The bond lengths (in Å) and angles (in degrees) indicated are those obtained by the energetic optimization.

of the one-dimensional tight-binding self-consistent-field–crystal-orbital (SCF–CO) method at the level of the CNDO/2 (complete neglect of differential overlap, version 2) approximation including all the valence electrons.[23] The program employed for the present calculation is able to handle the screw axis symmetry as well as the translational symmetry.

In order to optimize the polymer skeletons of A–J, we have employed the energy gradient method.[24] The number of the representative wave vectors was chosen as 21 with regular intervals ($\pi/10a$, where a is the unit vector of the translational symmetry or the screw axis symmetry, being parallel to the polymer chain axis) in the Brillouin zone. The overlap integrals and the electron repulsion integrals were considered as far as from the third to the tenth nearest neighboring cell (ca. 36–45 Å from the central unit cell), depending on the length of the unit cell of each polymer. Polarization functions such as silicon 3d atomic orbitals (AO's) were suppressed, since it has been reported that they do not give an appreciable contribution to the electronic structures of silicon atoms in silane oligomers.[20] For the sake of reference, polydihydrosilane (PS), polyacetylene (PA), and polyethylene (PE) were also optimized on the basis of the same calculation method.

For the polymers A–C, ab initio SCF–CO calculations with the STO-3G basis set for the geometrical parameters obtained by the CNDO/2 optimization process were also carried out for the sake of comparison. The molecular orbital (MO) levels of several molecules (ethane, ethylene, and disilane) were examined by ab initio MO calculations[25] with the 3-21G* basis set by employing

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[25] The Gaussian 90 program, from the library of the Institute for Fundamental Chemistry, has been released by Carnegie Mellon University, Pittsburgh, PA.

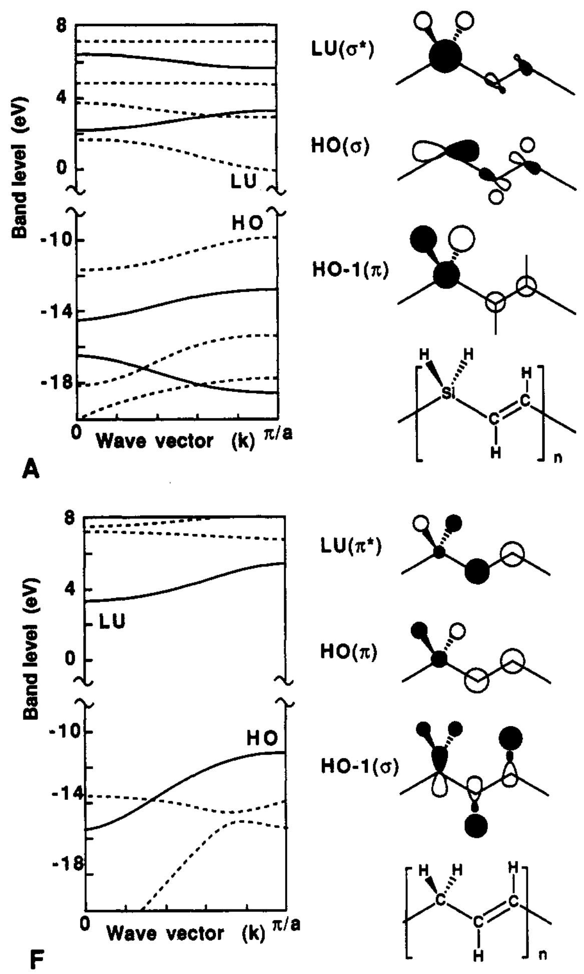

Figure 2. Band structures and the frontier CO patterns of the polymers A and F. Broken and solid lines indicate the σ and π bands, respectively.

the geometrical parameters in refs 26 and 27.

Results and Discussion

Geometries and Electronic Structures. Geometrical parameters optimized for the polymers A–D by the energy gradient method are shown in Figure 1. Optimized data for the polymers F and G are also indicated for comparison. Note that the main-chain skeletons of all the polymers possess C_s-symmetry planes within numerical error.

The Si—C and C=C bond lengths of $-[SiH_2(CH{=}CH)_x]_n-$ decrease and increase respectively, with an increase in the number of x. Thus, it is quite reasonable that the π bond order of C=C bonds, listed in Table I, decreases with an increase in x. In addition to these phenomena, the π bond order of Si–C bonds increases slightly with x. On the basis of these changes of bond lengths and π bond order, the polymers A–D are shown to be influenced by the π-conjugation effect of the $(CH{=}CH)_x$ moieties. The bond angles ∠CSiC increase slightly, depending on x. Similar changes depending on x (π bond order, bond lengths, and $\angle CC(H_2)C$ angle) are observed in the polymers F and G.

It is seen that both silicon and carbon atoms in the silylene and methylene units, respectively, tend to be positively charged. The hydrogen and carbon atoms attached to silicon atoms are negatively charged due to electron transfer from the silicon atoms.

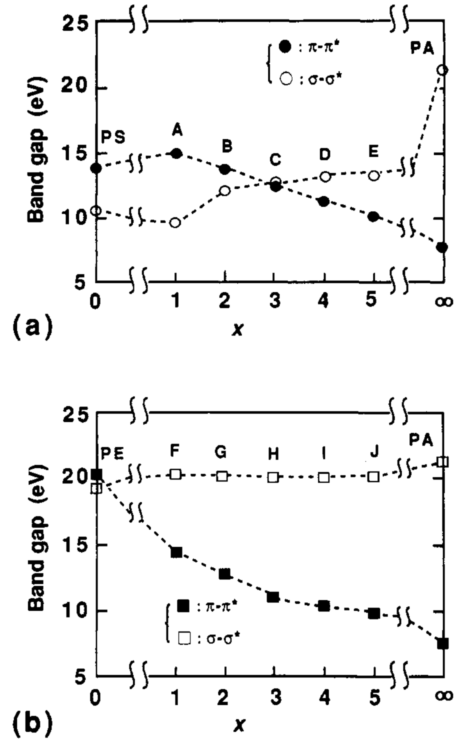

Figure 3. Changes of the σ–σ^* and the π–π^* band gaps depending on the number of x: (a) $-[SiH_2(CH{=}CH)_x]_n-$; (b) $-[CH_2(CH{=}CH)_x]_n-$.

Band Structure. The band structures and the frontier CO patterns of polymers A and F are shown in Figure 2. Since the main-chain skeletons of the present polymers are planar, the CO's can be classified into the σ and the π types. Both the HOCO and LUCO of the polymer A are of σ type, which is similar to the case for poly(disilanylene–ethenylene)[18] and PS.[19-22] From the CO patterns of A, it is noticed that its HOCO is constructed from the σ-AO's extending along the polymer chains and, moreover, that σ-AO and π-AO from the silicon atoms largely contribute to the HOCO and the (HO − 1)CO, respectively. Such σ-type HOCO and LUCO are also observed in polymer B. In polymers C–E, the π-type CO's gradually show up at the frontier level. On the other hand, the π-type HOCO and LUCO are observed in polymer F. The CO patterns of polymer F show that (1) the π-type HOCO and LUCO are mainly constructed from the π-AO of the ethylene moiety and (2) the (HO − 1)CO consists of the pσ AO's almost perpendicular to the polymer chain. The four other kinds of carbon-catenated polymers (G–J) also definitely show frontier CO's of π nature.

In total, in polymers A–E, there is a competition of σ- and π-type CO's for the frontier CO depending on x. From the present result, it seems to be justified that the π–π^* interband transition energy becomes smaller than the σ–σ^* energy for $-[SiH_2(CH{=}CH)_x]_n-$ at $x \geq 3$ as listed in Table II. The band-gap values corresponding to the σ–σ^* and the π–π^* transitions are plotted in Figure 3 for all the polymers examined here. Polymer A shows almost the same values as those for $-[SiH_2SiH_2(CH{=}CH)]_n-$ (σ–σ^*, 9.58 eV; π–π^*, 14.58 eV).[18] Note that the Hartree–Fock theory, on which the present CNDO/2 and the ab initio calculation methods are based, has a tendency toward overestimation of the band gap[28] but that there is a considerably good proportionality of the calculated and the experimental band-gap values.[29] The paths of change in

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Table I. Calculated Results of Electronic Structures[a]

	$-[SiH_2(CH{=}CH)_x]_n-$				$-[CH_2(CH{=}CH)_x]_n-$	
	A ($x = 1$)	B ($x = 2$)	C ($x = 3$)	D ($x = 4$)	F ($x = 1$)	G ($x = 2$)
π-Bond Order						
C=C	0.983	0.939	0.930 0.888	0.927 0.877	0.936	0.906
C—C		0.315	0.341	0.346 0.368		0.353
X—C[b]	0.129	0.146	0.148	0.149	0.251	0.257
X—H[c]	0.679	0.673	0.673	0.673	0.659	0.656
AO Density						
X π	0.793	0.787	0.789	0.789	0.952	0.956
σ	2.774	2.745	2.746	2.745	3.014	3.004
C π	0.994	1.015	1.018	1.019	1.016	1.000
σ	3.084	3.107	3.098	3.096	2.982	2.988
C_2 π		0.976	0.976	0.975		1.020
σ		2.979	2.984	2.984		2.978
C_3 π			0.998	1.003		
σ			2.995	2.992		
C_4 π				0.993		
σ				2.992		
Atomic Net Charge						
X	0.434	0.468	0.465	0.466	0.034	0.040
C	−0.078	−0.122	−0.116	−0.115	0.001	0.011
C_2		0.044	0.040	0.040		0.003
C_3			0.008	0.006		
C_4				0.015		
H(X)	−0.140	−0.145	−0.145	−0.146	−0.003	−0.000
H(C)	0.002	0.007	0.007	0.006	−0.015	−0.010
H(C_2)		−0.019	−0.020	−0.020		−0.024
H(C_3)			−0.006	−0.006		
H(C_4)				−0.011		

[a] The numberings of carbon atoms are designated in Figure 1. [b] X means a silicon atom in A–D and the carbon atom of CH_2 in F and G. [c] Between pπ AO and 1s AO of H.

Table II. Electronic Properties of Each Polymer[a]

	$-[SiH_2(CH{=}CH)_x]_n-$					$-[CH_2(CH{=}CH)_x]_n-$				
	A ($x = 1$)	B ($x = 2$)	C ($x = 3$)	D ($x = 4$)	E ($x = 5$)	F ($x = 1$)	G ($x = 2$)	H ($x = 3$)	I ($x = 4$)	J ($x = 5$)
σ–σ^* band gap	9.67	11.91	12.61	12.90	13.01	20.38	19.63	20.05	20.08	20.11
π–π^* band gap	15.03	13.73	12.42	11.47	10.57	14.47	12.56	11.22	10.55	9.78
HO σ bandwidth	1.90	1.13	0.81	0.44	0.19	1.14	0.20	0.17	0.05	0.03
HO π bandwidth	1.73	1.30	0.56	0.30	0.16	4.36	2.33	1.46	0.97	0.67
LU σ bandwidth	1.73	0.37	0.10	0.03	0.01	0.46	0.36	0.18	0.13	0.10
LU π bandwidth	1.03	1.21	0.78	0.45	0.26	2.04	0.93	0.44	0.26	0.15
ionization potential	9.78	11.06	11.07	10.50	9.97	11.15	10.42	9.74	9.47	9.13
electron affinity	0.11	−0.85	−1.02	−0.97	−0.60	−3.32	−2.14	−1.48	−1.08	−0.65

[a] All the values are shown in eV.

the band gaps are much different between parts a and b in Figure 3. In a series of silylene-containing polymers (Figure 3a), the π–π^* and σ–σ^* band gaps initially increase and decrease, respectively, as x is changed from 0 to 1. At greater x, their values decrease and increase, respectively. However, the σ–σ^* band-gap value changes very slowly, and the value for polymer E is actually far from that of PA. On the other hand, in Figure 3b, the π–π^* band gap decreases monotonously with an increase in x, and crossing between the π–π^* and the σ–σ^* band gaps is not seen in the range $x = 1$–5. These results signify that the influence of the σ-electrons originating from the silylene unit is rather strong and competes with that of the π-electrons provided by the carbon moiety. A similar tendency was also seen in the results of the ab initio calculations for the polymers A–C.

Other electronic properties derived from the band structures are also listed in Table II. The HO- and LU-π bandwidths as well as those of the HO- and LU-σ decrease with an increase in the number of x. Hence, the extension of the carbon-π conjugated chain moiety does not work for enhancement of the conjugation of the whole polymer. Instead, the existence of the silylene unit or the methylene unit rather helps the schnitt of both σ and π conjugations of the CO's near the frontier level, which becomes more remarkable with an increase in x. It is seen that the HO σ bandwidth of the silylene-containing polymer series for $x = 1$–5 is always larger than that of the methylene-containing polymers but that the HO π bandwidth of the former is always smaller than that of the latter.

Contributions of silylene and methylene units to the electronic densities of the HO-π and -σ CO's are illustrated in Figure 4. It is generally seen in both the $-[SiH_2(CH{=}CH)_x]_n-$ ($x = 1$–5) and the $-[CH_2(CH{=}CH)_x]_n-$ ($x = 1$–5) series that contribution from these units to the π-HOCO's becomes smaller as x increases. On the other hand, contribution of the silylene unit to the electronic densities of the σ-HOCO's is unchanged at $x \geq 3$ (ca. 25%). In the case of the methylene-containing polymer, contri-

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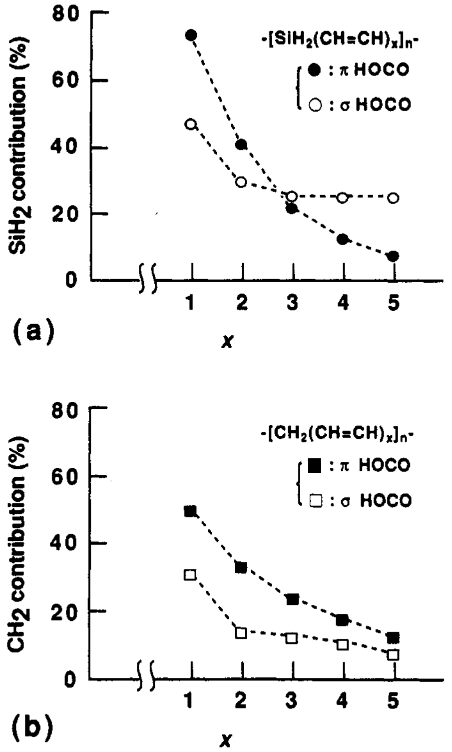

Figure 4. Change in the contributions to the electronic densities of the HO σ- and π-type CO's from silylene and methylene units of (a) $-[SiH_2(CH{=}CH)_x]_n-$ and (b) $-[CH_2(CH{=}CH)_x]_n-$.

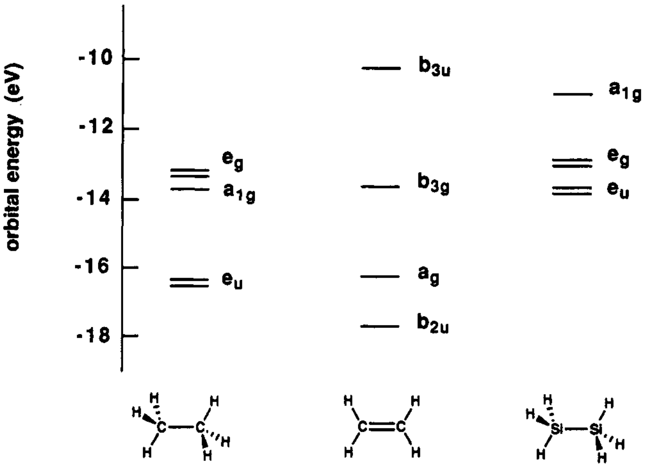

Figure 5. Occupied MO levels near the HOMO of ethane, ethylene, and disilane.

bution to σ-HOCO gradually decreases as x increases.

Comparison with Model Molecules. The dominance of either the π–π^* or σ–σ^* interband transition in the present polymeric systems could be explained by examining model molecules such as ethane, disilane, and ethylene. The energy levels of their occupied MO's are shown in Figure 5. The π-HOMO of ethylene (b_{3u}) is energetically higher than the corresponding MO of ethane (e_g). Hence, in a "synthetic" molecule from these two such as 1-butene, it is natural that its HOMO should be of π nature mainly contributed from the ethylene part. The (HO − 1)MO of such a molecule should be constructed from the e_g-type MO (another moiety of the degenerate MO) of ethane and the b_{3g} MO of ethylene, and it may well be directed perpendicular to the main chain. This orbital pattern explains well the CO patterns of the polymer F (Figure 2).

In contrast, the energy level of the HOMO of disilane (a_{1g}) is considerably higher than that of ethane. Since all the main-chain skeletons in the present polymers are coplanar, the orbital interactions near their frontier level could be understood in terms of those between b_{3u}(ethylene) and e_g(disilane) MO's or a_{1g}(disilane) and b_{3g}(ethylene) MO's. Since these completed σ- and π-type CO's exist almost at the same energy levels, it is plausible that these CO's compete for the frontier level in the polymers discussed above, which should depend on the *ratio x*.

Conclusion

We have studied the electronic structures of simplified polymeric organosilicon systems, focusing on the influence of the length of the π-conjugated carbon chain on the nature of the frontier CO's, the interband transition energy, and the conjugation extending the whole polymer chain. First, it has been clarified that, in the polymers of type $-[SiH_2(CH{=}CH)_x]_n-$ ($x = 1$–5), the σ–σ^* interband transition interchanges with π–π^* to give the band-gap value at $x = 3$. On the other hand, in the polymer series $-[CH_2(CH{=}CH)_x]_n-$, the π–π^* interband transition energy is always smaller than the σ–σ^* energy except for $x = 0$ (polyethylene). This kind of tendency can be interpreted to come from the high-lying σ-HOMO of disilane in contrast with ethane or ethylene and should be regarded to rule the electronic properties of most of the organosilicon polymers. This could justify the interpretation of the σ–σ^* interband transition frequently observed in most organosilicon polymers.

Second, both the σ- and the π-conjugation throughout the whole polymer chain become weaker with an increase in x. It has been clarified that the HO π and the HO σ bandwidths in both of these polymers become generally smaller as x increases. The present results would hopefully offer a definite guiding principle in the molecular design of organosilicon polymers.

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Registry No. $-[SiH_2(CH{=}CH)]-_n$ (SRU), 143172-38-7; $-[SiH_2(CH{=}CH)_2]-_n$ (SRU), 143172-39-8; $-[SiH_2(CH{=}CH)_3]-_n$ (SRU), 143172-40-1; $-[SiH_2(CH{=}CH)_4]-_n$ (SRU), 143172-41-2; $-(CH_2CH{=}CH_2)-_n$ (SRU), 77173-94-5; $-(CH_2CH{=}CHCH{=}CH_2)-_n$ (SRU), 40022-08-0.

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