Electronic Structures of Organosilicon Polymers Containing Thienylene Units

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The electronic structures of simplified poly(disilanylene(thienylene)$_n$) ($n = 1-5$) have been studied in detail on the basis of the one-dimensional tight-binding self-consistent field–crystal orbital method. The result suggests that the sp^3-hybridized orbital of silicon atoms almost cuts off the π-conjugation occurring from the thienylene units. The $\pi-\pi^*$ interband transition energy becomes smaller with an increase of n (number of thiophene rings), while the $\sigma-\sigma^*$ one shows almost no change. Electronic structures of poly(ethylene(thienylene)$_n$) ($n = 1-3$), poly(silylene(thienylene)$_n$) ($n = 1$), and polythiophene have also been examined for comparison.

Introduction

In recent years polysilane (PS) and its derivatives have been studied from both theoretical and experimental points of view.[1] It is understood that there is a strong σ-conjugation throughout the main chain of PS.[2,3] This is quite different from the ordinary organic electrically conducting polymers with developed π-conjugation[4] and has stimulated a variety of studies with respect to PS including semiconducting behavior,[5,6] enhancement of electrical conduction with doping,[7] photoconduction,[8–10] nonlinear optical properties,[11] and thermochromism.[12]

However, there is not much possibility of effectively controlling the electronic properties of PS except by the modification of a substituent group attached to the silicon atoms. In this respect, organosilicon polymers containing both silicon and carbon atoms in the main chain have received increasing attention, since these systems have the potential to be chemically modified in a more flexible manner than PS. Along this line, several numbers of organosilicon polymers, which consist of the combination of regular alternation of a disilanylene ($-SiR_2-SiR_2-$) unit and a carbon π-conjugated moiety such as ethenylene ($-CH{=}CH-$), ethynylene ($-C{\equiv}C-$), diethynylene ($-C{\equiv}C-C{\equiv}C-$), butenyne ($-C{=}C-C{\equiv}C-$), or phenylene in the main chain have been synthesized.[13–18] These polymers show electrically conducting properties ($\sigma = 10^{-2}-10^{-4}$ S/cm in vacuo) at room temperature upon doping with SbF_5.[13–18] The electronic structures of these polymers have also been studied to clarify the fundamental difference between the π-bonding behavior of such silicon-containing polymers and the ordinary organic π-conjugated polymers.[19,20]

In the last several years, a similar class of polymers containing the combination of thienylene and silylene units in the main chain have been prepared.[21–24] More recently, a series of poly(disilanylene(thienylene)$_n$) (PDST-n; $n = 1-5$) have been synthesized and their various optical properties have been examined.[25,26] This is of particular interest since polythienylene (PT) is one of the most stable conductive polymers in air and is

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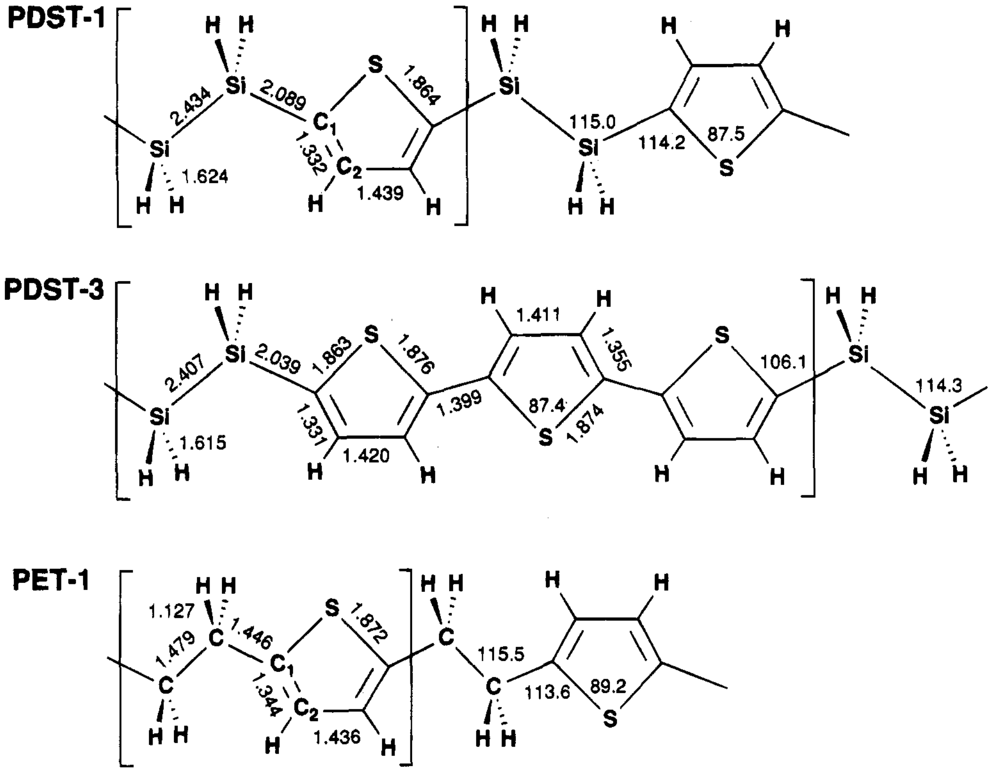

Figure 1. Skeletons of PDST-1, PDST-3, and PET-1 (see text). The bond lengths (Å) and angles (deg) indicated are those obtained by the energetical optimization.

applicable to various electronic devices such as a field-effect transistor[27] and electrochromic element.[28] In this paper we report the electronic structures of PDST-*n*, some of the representative structures of which are illustrated in Figure 1. For comparison, those of poly(ethylene(thienylene)$_n$) (PET-*n*; $n = 1-3$), poly(silylene(thienylene)$_n$) (PST-*n*; $n = 1$), and PT have also been examined. Although the actual PDST-*n* series have been synthesized with different substituents such as methyl, ethyl, butyl, or phenyl groups in the disilanylene unit, here we employ hydrogen atoms for these side substituents for simplicity.

Method of Calculation

All of the calculations were performed on the basis 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.[29] The program employed for the present calculation is able to handle the screw axis symmetry as well as the translational symmetry. The energy gradient method[30] was employed in order to optimize the polymer skeleton of PDST-*n* and PET-*n* ($n = 1-3$). For PDST-4 and PDST-5, the polymer structures were constructed from the optimized one of PDST-3.

The number of 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 the fourth nearest neighboring cell at a maximum (ca. 20–30 Å from the central cell on average). Polarization functions such as silicon 3d atomic orbitals (AOs) were suppressed, since it has been pointed out that these do not give an appreciable contribution to the electronic structure of silicon atoms in silane oligomers.[31] In fact, the calculation for PDST-1 including the silicon 3d AOs has resulted in a small drawback of positive charge on Si atoms (from 0.343 without 3d to 0.238 with 3d) and in a slight change in the $\sigma-\sigma^*$ type band gap (from 10.66 to 9.31 eV). Although a remarkable change was only seen in the AO component in the lowest unoccupied crystal orbital (LUCO) upon the introduction of 3d AOs, this feature almost does not matter in the present work.

For some selected polymers (PDST-2, PET-2, and PST-1), 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. No serious change was seen in the results of the semiempirical and the ab initio calculations. For instance, the π-bonding natures in PDST-2, PET-2, and PST-1 are listed in Table 1, where both of these calculation results clearly indicate the cutoff of the π-conjugation of thienylene moiety by sp^3-bonding at silylene and/or methylene moieties, as will be later discussed.

Results and Discussion

Optimized Geometries. The planarity of the polymer skeleton of PDST-1 was first checked prior to the

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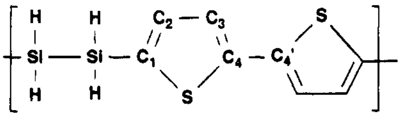
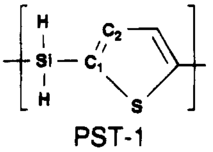
Table 1. Comparison of the π-Bonding Nature on the Semiempirical (S) and the ab Initio (A) Results

	PDST-2[a]		PET-2[b]		PST-1[a]	
	S[c]	A[d]	S[c]	A[d]	S[c]	A[d]
S—C_1	0.258	0.026	0.260	0.025	0.253	0.024
S—C_4	0.245	0.022	0.241	0.022		
C_1=C_2	0.892	0.170	0.863	0.167	0.907	0.175
C_2—C_3	0.392	0.049	0.412	0.053	0.360	0.044
C_3=C_4	0.844	0.160	0.832	0.157		
C_4—C_4'	0.370	0.034	0.383	0.039		
C_1—Si (C_1—C for PET-2)	0.147	0.005	0.255	0.007	0.143	0.004
Si—Si (C—C for PET-2)	0.140	0.002	0.197	0.0001		

[a] For the atomic numberings, see the figures below. [b] For the atomic numberings, see those of PDST-2 below. [c] π-Bond order. [d] π-Atomic orbital bond population; this value is smaller than the π-bond order due to the multiplication by the overlap integral.



PDST-2



PST-1

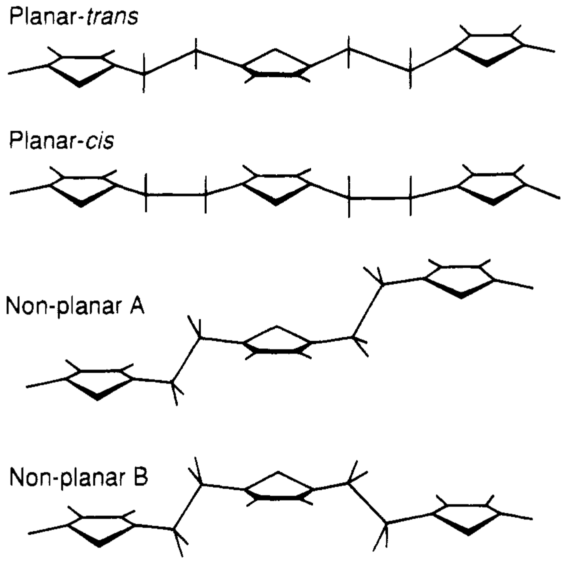


Figure 2. Four kinds of schematic conformations of PDST-1 examined, in which the unit cell contains a disilanylene and a thienylene units. Atomic notations are abbreviated.

optimization process of all the polymers treated in the present work. Four kinds of the conformations of PDST-1, illustrated in Figure 2, were energetically optimized to reveal that the planar-*trans* form is energetically most stable (see Table 2). Hence all the other polymers were submitted to the energetical optimization by starting from the planar-*trans* conformations.

Optimized geometrical parameters of planar-*trans* PDST-1 and PDST-3, for instance, along with PET-1 are also shown in Figure 1. In these planar structures two Si or C atoms lie on almost the same plane within ±0.1 Å as that of the thienylene unit. The Si—C and the Si—Si bond lengths of PDST-*n* decrease with an increase in *n*. On the other hand, the geometry of the thiophene rings does not show a remarkable difference with a change in *n*.

Electronic Structures. The band structures of PDST-1, PDST-3, and PET-1 are shown in Figure 3.

Table 2. Relative Energies of Four Types of Conformations of PDST-1

conformations[a]	relative total energy[b] (eV)
planar-*trans*	0
planar-*cis*	1.55
non-planar A	0.06
non-planar B	0.10

[a] See Figure 2. [b] Positive values indicate instability of the total energy per unit cell compared with zero.

Since all of the present polymers possess the approximate C_s symmetry, the energy bands can be classified into σ- and π-types. It is seen that the nature of both the highest occupied (HO) and the lowest unoccupied (LU) bands changes from σ-type to π-type with an increase in *n* in PDST-*n*, due to the development of the π-conjugation within the thiophene rings. The energy levels of the σ-type bands do not change much from PDST-1 to PDST-3, while π-type bands move considerably. The π-type bands of PET-1 are at the same level as those of PDST-1, and the σ-type bands lie at the lower level. The energy difference of the levels of the HO π-type and the next HO π-type bands varies according to the polymer types. In PDST-1, for instance, these two bands are almost degenerate due to the characteristics of the accompanied COs.

The electronic properties derived from the band structure are listed in Table 3. Since the Hartree–Fock theory, on which the present SCF–CO method is based, has a tendency toward overestimation of the band gap,[33] the π–π* and σ–σ* gap energies have been proportionally scaled so as to reproduce the experimental values of PT and PS.

It is seen that the value of the π–π* gap of PDST-*n* decreases as the number of thiophene rings increases, whereas that of the σ–σ* gap does not change too much. The π–π* gap values of PET-*n* change in a manner similar to those of PDST, while the σ–σ* gap values remain larger than the π–π* gap ones. Note that the calculated band gap (σ–σ*) of PS previously reported[19] is on the same level with that of PDST-1. Moreover, the HO bandwidths of PT (π) and PS (σ) are much wider than those of PDST-*n* and PET-*n*.

It is noteworthy that the π–π* gap values of $(-SiH_2-(CH{=}CH)_2-)_n$[20] and PST-1 are similar to that of PDST-1. This signifies that the π–π* gap of a polymeric organosilicon-containing π-conjugated moiety in the polymer main chain is rather independent of the number of silicon atoms in the silylene unit, in agreement with our previous work.[19] It is seen from the occupied bandwidth that PDST has more complete σ-conjugation and less complete π-conjugation than PET. This suggests that the π-conjugation of the thienylene moiety is cut off by sp^3-bonding at silylene and/or methylene moieties but with a little bit different manner. A similar tendency was also seen in the results of the ab initio calculations for PDST-2, PET-2, and PST-1, as described above.

Orbital Patterns. In Figure 4 the oribital patterns examined for the both the σ- and π-type COs are shown. In PDST-1, the σ-type HOCO and σ-type LUCO become the actual HOCO and LUCO respectively. It is noted that the σ-type HOCO is mainly constructed from the combination of the pσ-orbitals extending along the

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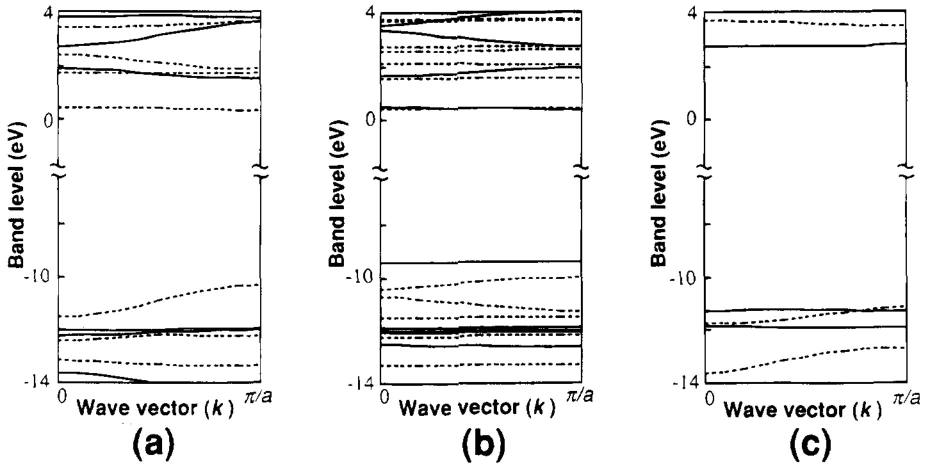

Figure 3. Band structures of (a) PDST-1, (b) PDST-3, and (c) PET-1. Solid and dashed lines indicate π- and σ-bands, respectively.

Table 3. Electronic Properties of Each Polymer[a]

	PDST-1	PDST-2	PDST-3	PDST-4	PDST-5	PET-1	PET-2	PET-3	PST-1	PT
					HO Bandwidth[b]					
π-type	0.01	0.01	≈0*	≈0*	≈0*	0.03	0.01*	0.06*	0.06	4.19
σ-type	1.20*	0.97*	0.41	0.13	0.06	0.61*	0.36	0.26	1.57*	0.74
					LU Bandwidth[b]					
π-type	0.39	0.29	0.07*	0.04*	0.02*	0.04*	0.08*	0.07*	0.94	6.72
σ-type	0.11*	0.02*	0.01	≈0	≈0	0.21	0.03	0.03	0.10*	0.52
					Band Gap					
π−π* type[c]	13.49 (4.79)	11.59 (4.11)	9.80 (3.48)	9.36 (3.32)	8.72 (3.09)	13.97 (4.96)	11.18 (3.97)	9.65 (3.42)	13.73 (4.87)	7.27 (2.58)
σ−σ* type[d]	10.66 (4.12)	10.20 (3.94)	10.42 (4.03)	10.55 (4.08)	10.66 (4.10)	14.59 (5.64)	13.32 (5.15)	13.02 (5.03)	10.63 (4.11)	13.02 (5.03)
experimental[e]	4.60	3.62	3.19	2.99	2.90					2.58
ionization pot.	10.34	9.84	9.43	9.17	8.84	11.15	9.93	9.25	9.98	8.15
electron affinity	−0.31	−0.36	−0.36	−0.19	0.12	−2.70	−1.26	0.41	−0.65	0.88

[a] All the values are shown in electronvolts. [b] The asterisk indicates the value with respect to the actual HO or LU band. [c] The values in parentheses are reestimated by a proportional scaling to the value obtained for PT.[32] [d] The values in parentheses are reestimated by a proportional scaling to the value obtained for PS.[1,19] [e] Based on the measurements of λ_{max}.[25]

polymer main chain, being similar to that in PS. Note that this pσ-orbital interaction passes through the C—S—C single-bond route in the thienylene moiety not through the C=C double bonds. On the other hand, the σ-type LUCO localizes mainly on the 3s AO of Si atoms and 1s AO of H atoms with an antibonding property, giving no intercell interactions.

The coefficients of the π-type HOCO are large on C atoms and small on Si with antibonding characteristics at the Si—Si and C—Si bonds and pseudo π-bonding at the Si—H bond. On the contrary, the π-type LUCO pattern is mainly located on Si atoms, Si—Si and Si—H being bonding and antibonding natures, respectively. The π-type HOCO pattern at $k = 0$ of PDST-1 is rather concentrated on the S atom in the thiophene ring, which resembles the pattern of the HO molecular orbital (HOMO) of a thiophene molecule.[34] This strongly suggests that the disilanylene unit in PDST-1 works as a connector which hardly allows π-conjugation between separated thiophene moieties.

The CO patterns of PDST-3 basically resemble those of PDST-1 but show more characteristic aspects. Both the π-type HOCO and LUCO, being the actual HOCO and LUCO of PDST-3, respectively, are concentrated on the thienylene unit but scarcely on the Si atoms. Thus the delocalization of π-electrons between thiophene-ring moieties is suppressed even if each moiety becomes larger. These phenomena explain the smaller width of the HO π-band compared with that of PDST-1. The σ-type HOCO is less satisfactorily conjugated at the inter-thiophene ring part, yielding a HO σ-bandwidth smaller that that for PDST-1, as seen in Table 3. The σ-type LUCO is constructed from only the antibonding combination of 3s and 1s AOs of Si and the H atom at the disilanylene moiety. Such a feature of the σ*-band has been observed in the previously reported organosilicon polymers containing ethenylene or phenylene instead of thienylene.[19]

The patterns of the π-type HOCO and the π-type LUCO of PET-1 are essentially the same as those of PDST-1. Generally, it is seen that σ-conjugation is more developed in the PDST-*n* series than in PET-*n*. The σ-type HOCO of PET-1 has a remarkably large CO coefficient on the S atom, which makes the HO σ-bandwidth considerably narrow, being about half that of PDST-1 (see Table 3). The σ-type LUCO is completely different from that of PDST-1, since the former is almost concentrated on the S atom and is slightly on C atoms in the thiophene ring.

Distribution of Electrons. The π-bond orders, AO densities, and atomic net charges of PDST-1, PET-1, and PST-1 are listed in Table 4. The π-conjugation in PET-1 prevails over those in PDST-1 and PST-1. There is not much difference in the π-conjugation between PDST-1 and PST-1. With respect to PDST-3, the π-conjugation within a thienylene moiety becomes stronger than in PDST-1.

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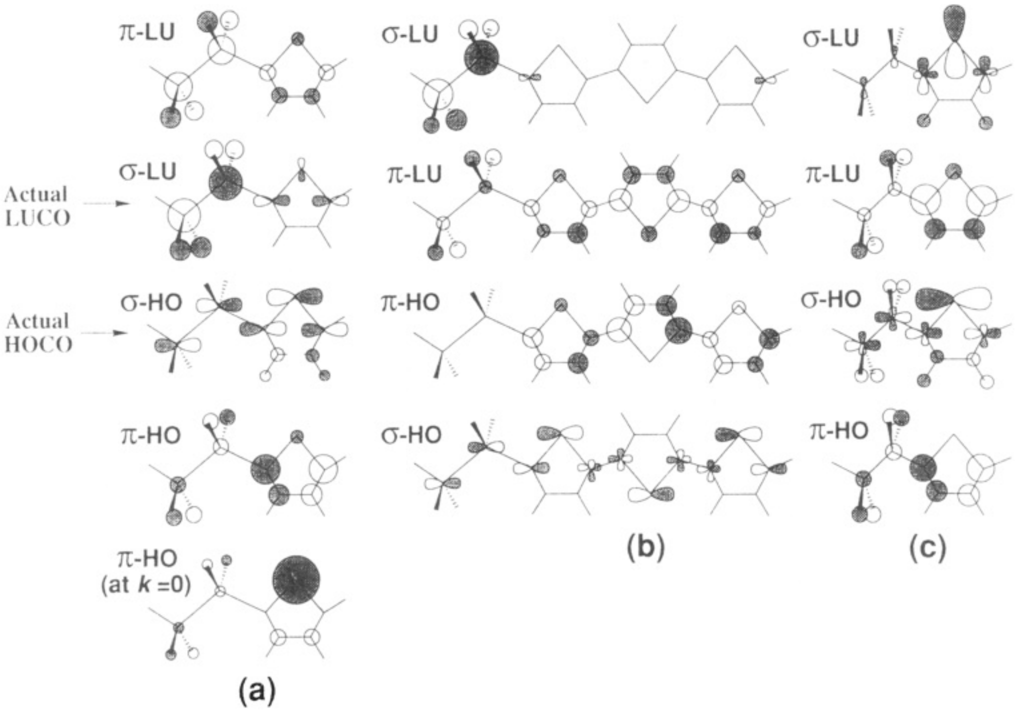

Figure 4. Patterns of the π-type and the σ-type HOCO and LUCO of (a) PDST-1, (b) PDST-3, and (c) PET-1. Note that there is the Fermi level between the second and third rows. The polymer skeletons are the same as those shown in Figure 1.

Table 4. Calculated Results of Electronic Structures of Selected Polymers[a]

		PDST-1	PET-1	PST-1
π-bond order	Si—Si (C—C for PET-1)	0.137	0.189	
	Si—C (C—C for PET-1)[b]	0.143	0.259	0.143
	thiophene ring			
	S—C	0.247	0.258	0.253
	C=C	0.907	0.872	0.907
	C—C	0.359	0.391	0.360
AO density	Si(C)[c] π	0.821	0.966	0.802
	σ	2.836	3.005	2.673
	S π	1.899	1.893	1.894
	σ	4.199	4.273	4.224
	C1 π	1.025	1.023	1.030
	σ	3.036	2.918	3.052
	C2 π	1.017	1.052	1.016
	σ	2.969	2.961	2.963
atomic net charge	Si(C)[c]	0.343	0.029	0.525
	S	−0.098	−0.166	−0.188
	C_1	−0.061	0.059	−0.082
	C_2	0.014	−0.013	0.021
	H[d]	−0.118	0.003	−0.137
	H[e]	−0.010	0.001	−0.008

[a] The numbering of carbon atoms is designated in Figure 1 and the footnotes of Table 1. [b] Between Si (or C) and the thiophene ring. [c] Carbon atoms in parentheses signify those in the ethylene unit of PET-1. [d] Attached to the disilanylene or ethylene unit. [e] Attached to the thiophene ring.

From the atomic net charge it is seen that Si atoms are positively charged (+0.343) in PDST-1, as usual, and the C atoms corresponding to the Si atom are almost neutral (+0.029) in PET-1. In PDST-1 Si atoms donate electron to H atoms bonding to Si and to the adjacent thiophene moiety. In PST-1 the Si atom is more positive (+0.525), due to the loss of σ-electrons. From the balance of the atomic charge of H bonding to Si, the σ electron of the Si atom is mainly transferred to the adjacent thiophene moieties.

Assignment of UV Spectra. Strong UV absorption spectra have been observed in tetraethyl-substituted PDST-*n* ($n = 1-5$) on the disilanylene unit, as shown in Figure 5. It is clearly seen that the position of $\lambda_{\max}$ is red-shifted with an increase in n. This result is in good agreement with the calculated $\pi-\pi^*$ interband transition, as shown in Figure 6. Incidentally, this assignment can be confirmed in Br-terminated thiophene oligomers[35] as well as the ordinary thiophene oligomers,[36] both of which show strong absorptions with wavelengths similar to that of PDST-*n*. Furthermore, no large shift of this absorption wavelength will be expected upon the change into the phenyl-substituent group attached to Si atoms of PDST-*n* in contrast with phenyl-substituted polysilane.[37] This prediction is based on the expectation of a small orbital interaction between

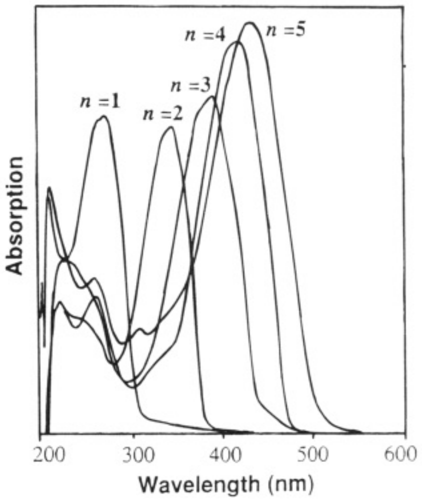

Figure 5. UV spectra of tetraethyl-substituted PDST-*n* (adapted from ref 25).

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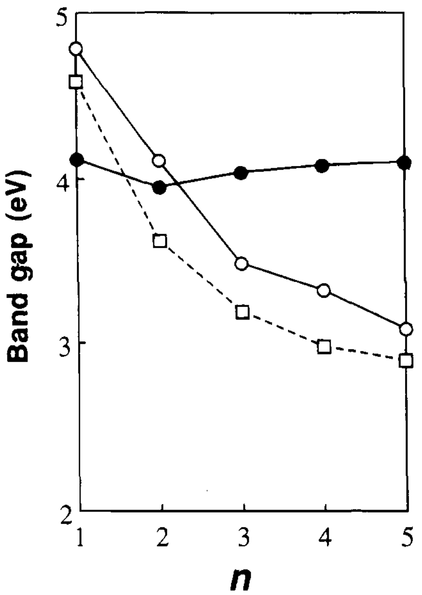

Figure 6. Changes of the $\sigma-\sigma^*$ (black circles) and the $\pi-\pi^*$ (white circles) band gaps (scaled values; see Table 3) of PDST-n. The squares indicate the experimental values of λ_{max} in Figure 5. The lines are guides for the eye.

a thiophene ring and a phenyl-substituent group, as illustrated in Figure 7. As a matter of fact, there has been observed only a 10-nm shift of λ_{max} upon the introduction of two phenyl-substituent groups into PDST-1.

Conclusion

We have studied the electronic structures of simplified poly(disilanylene(thienylene)$_n$) (PDST-n; n = 1−5) and the related polymers such as poly(ethylene(thienylene)$_n$) (PET-n; n = 1−3) and so on. There are four major findings in the present work: (1) In both the PDST-n and PET-n series, the $\pi-\pi^*$ band gap energies decrease upon the increase in n. On the other hand, the $\sigma-\sigma^*$ ones remain almost constant.

(2) The PDST-n series have more complete σ-conjugation and less complete π-conjugation throughout the whole polymer chain compared with the PET-n series.

(3) The actual HOCO and LUCO interchange from the σ-type to the π-type upon the increase in n. This obviously signifies that π-conjugation in PDST-n becomes strengthened at the thienylene unit.

(4) The experimentally observed λ_{max} of PDST-n is interpreted as the $\pi-\pi^*$ band gap.

Further research on the electronic structures of PDST-n in, for instance, the p-doped state would be of interst. These will be reported in the near future.

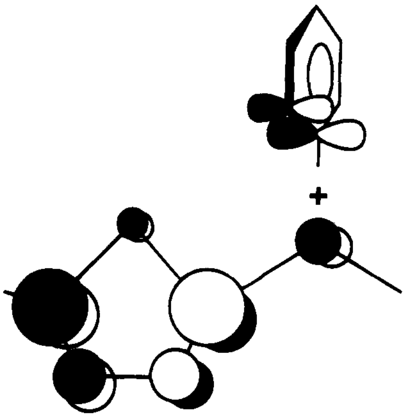

Figure 7. Orbital interaction between a phenyl substituent and a Si atom in PDST-1.

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