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Electronic Properties of p-Type Doped Copolymers Consisting of Oligothienylene and Disilanylene Units

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In association with the previous theoretical prediction on the ferromagnetic spin correlation in p-type doped poly[disilanylene(thienylene)$_n$] (PDST-*n*, $n = 1-5$), we have actually prepared these samples and examined their electronic properties by the combination of cyclic voltammetry (CV), ultraviolet−visible−near-infrared (UV−vis−NIR), electron spin resonance (ESR), and infrared (IR) spectroscopic measurements. It has been confirmed that electrons are removed mainly from oligothienylene units. A spin generated by the doping was found to be localized at 3p$_\pi$-atomic orbitals (AOs) of sulfur atom at $n = 1$. For $n = 2-5$ a spin was the polaronic π-spin delocalized within an oligothienylene unit. These natures of radical spins are in accordance with the previous theoretical study. However, the spin concentration of p-type doped polymers was considerably small (1 spin/ca. 400 oligothienylene units), possibly due to the aggregation of the oligothienylene units around the dopant and to the degradation of disilanylene units. No signs of ferromagnetic interaction has been observed yet due to such small spin concentrations.

1. Introduction

In recent years, organic ferromagnets are one of the subjects of increasing interest.[1] The organic ferromagnets so far succeeded in preparation are organic crystals consisting of the built-in radicals such as nitroxide radical molecules[2−4] and the charge-transfer complex such as, e.g., tetrakis(dimethylamino)ethylene−C_{60}.[5,6] On one hand, realization of ferromagnetic state in a polymer is of strong interest, since a polymer has several advantages such as the ease of fabrication not requiring care for subtle crystal structure and the possibility of preparing the material with large area. The main strategy to endow organic polymers with ferromagnetic spin correlation is based on the idea of topological correlation of the localized spins via the through bond interaction,[7,8] like *m*-phenylcarbene oligomers ($S = 4$).[9] On the other hand, polaronic ferromagnet polymer involving delocalized polaronic spins generated by chemical doping has been proposed.[10] In this type of polymer spins generated in the spin supplier unit (e.g., polyene) interact ferromagnetically through the coupling unit (e.g., *m*-phenylene). In fact, certain polymers with ferromagnetic spin alignment ($S = {}^5/_2$ at maximum) have been synthesized along this strategy.[11]

Recently we have proposed, by extending this polaronic ferromagnet model, copolymers consisting of π-conjugated unit as the spin supplier and of non-π-conjugated unit with several sp^3-hybridized atoms as the spacer toward a new candidate for a polymeric organic ferromagnet.[12] The interaction between polaronic spins generated in spin supplier units by p-type doping is tunable by changing the length and atomic species of the spacer unit. On the basis of this prospect, polymeric organosilicon systems consisting of regularly aligned disilanylene and π-conjugated units (Figure 1) have been examined,[12] since it has been made clear that the electronic structures of these neutral polymers are rather well localized with a large bandgap and small

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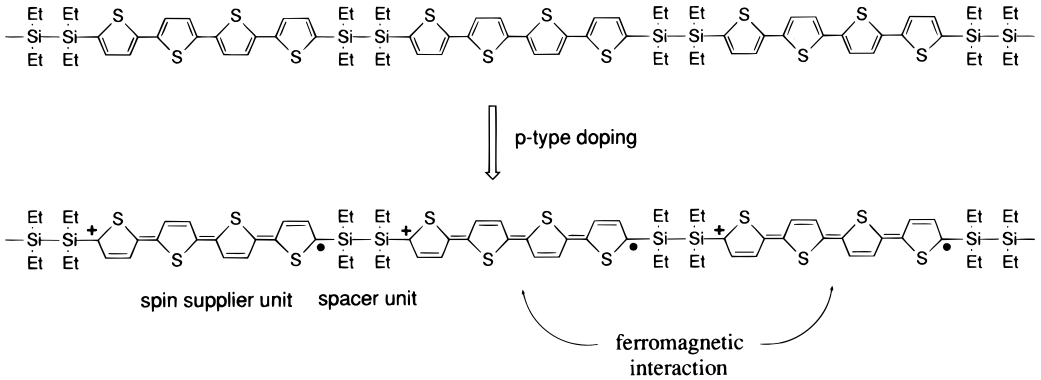

Figure 1. Illustrative description of the polaronic ferromagnet. In this model, the polaronic spins are generated in each oligothienylene unit (spin supplier unit) by chemical doping and these spins interact ferromagnetically through a disilanylene unit (spacer unit).

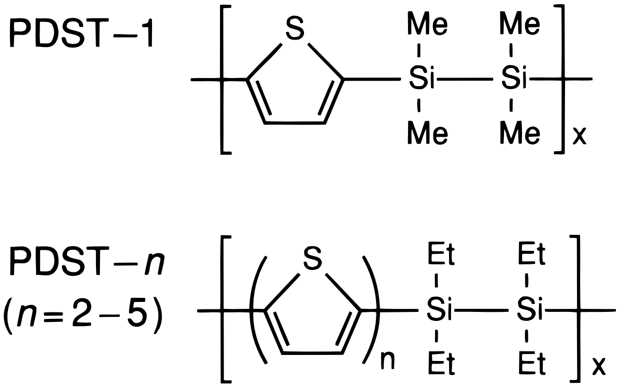

Figure 2. Chemical structures of poly[disilanylene(thienylene)$_n$] (PDST-*n*).

bandwidths indicative of weak interaction between the σ- and the π-units.[13] In fact, the electrical conductivity of the SbF_5-doped poly[disilanylene(thienylene)][14,15] and poly[disilanylene(phenylene)][16] is not remarkably high (10^{-3}−10^{-5} S/cm) comparing with those of the doped polythiophene (PT)[17] and poly(*p*-phenylene) (PPP, 10^0−10^2 S/cm).[18] Furthermore, pseudo-π-conjugation in disilanylene unit is smaller than in ethylene one.[13] One-dimensional unrestricted Hartree−Fock crystal orbital calculations have shown two types of spins in the cationic states of poly[disilanylene(thienylene)$_n$] (PDST-*n*, $n = 1-3$).[12] One is the spin localized on a sulfur atom in PDST-1 and another delocalized over the carbon skeletons in an oligothienylene unit in PDST-*n* for $n \geq 2$. The overall calculation in ref 12 has suggested the cationic PDST-3 is the most promising candidate with ferromagnetically correlated polarons.

In the present article we report actual preparation of cationic PDST-*n* ($n = 1-5$). To elucidate the nature of spins generated and the nature of interaction working among the spins, we have performed an experimental investigation on the cationic PDST-*n* ($n = 1-5$; see Figure 2) doped by electron-accepting nitrosyl tetrafluoroborate ($NOBF_4$) so as to analyze their electronic properties. Their electrochemical behavior of PDST-*n* with respect to the length of oligothienylene unit *n* is examined with the use of cyclic voltammetry (CV) and their electronic structures are characterized based on the ultraviolet−visible−near-infrared (UV−vis−NIR) and the electron spin resonance (ESR) spectroscopic measurements. Finally, we mention the degradation of the disilanylene unit upon the doping confirmed by the infrared (IR) absorption spectra.

2. Experimental Section

PDST-1 was synthesized by the condensation reaction of 2,5-bis(chlorodiethylsilyl)thiophene with sodium. PDST-2 and PDST-4 were prepared by the reaction of 1,2-bis[2-(5-bromothienyl)]tetraethyldisilane (**1**) and 1,2-bis[5-(5′-bromo-2,2′-bithienyl)]tetraethyldisilane (**2**) with 1 equiv of magnesium in THF, followed by treatment of the resulting solutions with a $NiCl_2$(dppe) catalyst in a sealed degassed tube. PDST-3 and PDST-5 were synthesized by cross coupling of the corresponding di-Grignard reagents obtained from **1** and **2** with 2,5-dibromothiophene in the presence of the nickel catalyst. The detailed conditions are reported in the literature.[19−22]

For the CV measurements a conventional combination of a potentiogalvanostat (Nikko NPGS-301) and a function generator (Nikko NFG-3) was employed, and dry benzonitrile solution containing 1 M of oligothienylene unit and 0.1 M of *n*-tetrabutylammonium tetrafluoroborate (n-Bu_4NBF_4) as the electrolyte was examined with a potential scan rate of 50 mV/s. The saturated caromel electrode (SCE) was used as a reference electrode and Pt wires were used as a counter and a working electrodes.

UV−vis−NIR spectrum was recorded on a Shimadzu UV365 spectrophotometer. The spectroscopic grade of dichloromethane (CH_2Cl_2) solution was used as the solvent without further purification. Polymer was dissolved in CH_2Cl_2 with the concentration of 4×10^{-5} M of the oligothienylene unit. Such dilute concentration was adopted so that interchain interaction may be neglected. The chemical doping was performed by injecting CH_2Cl_2 solution of $NOBF_4$ (3×10^{-2} M) with a microsyringe into the polymer solution. Three levels of the dopant concentration based on the prepared molar ratio of the dopant to the oligothienylene unit, that is, lightly ($NOBF_4$/oligothienylene unit = 1−20), intermediately (20−40), and heavily (40−100) doped states are considered in the present study.

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(22) The molecular weights based on the polystyrene standards are PDST-1: $M_w = 20\,000$ ($M_w/M_n = 3.8$),[20] PDST-2: 53 000 (4.0),[21] PDST-3: 47 000 (3.4),[21] PDST-4: 29 500 (3.8),[21] PDST-5: 17 000 (2.1).[21]

Table 1. CV Data (in V vs SCE)

PDST-*n*	E^{ox}_1	E^{ox}_2	E^{red}_1	E^{red}_2
$n = 1$				
$n = 2$	1.32	1.54[a]		
$n = 3$	1.12	1.34		
$n = 4$	1.03	1.25		
$n = 5$	1.02	1.22	0.97	1.21

[a] Very weak.

ESR spectrum was mainly recorded on a JEOL RE-2X spectrometer at the X band (9.1 GHz) in the temperature range 123−293 K. The sample was doped by CH_2Cl_2 solution of $NOBF_4$ in an ESR quartz tube followed by the removal of the solvent under vacuum, and then sealed under vacuum. The doping degree is classified into three levels as described above. The $CuSO_4{\cdot}5H_2O$ crystal was used as the reference for the calculation of spin concentration and the Mn^{2+}−MgO solid solution was used for the determination of the peak-to-peak line width (ΔH_{pp}) and the g value. For several samples, the ESR spectra were measured down to 4.5 K by using a Varian E-112 with an Oxford cryogenic system.

The Fourier transform (FT) IR spectra were measured on a BIO-RAD FTS-30 FT-IR spectrometer. The $NOBF_4$-doped samples were prepared in the CH_2Cl_2 solution. After evaporation and drying under vacuum, the sample was mixed with KBr to make a pellet, which was subjected to the IR measurement. The KBr used had been pretreated at 300 °C in vacuo to eliminate the moisture included.

3. Results and Discussion

3.1. CV Measurements. The results of CV measurements for each polymer in 0.1 M *n*-Bu_4NBF_4/benzonitrile solution with the scan rate of 50 mV/s are listed in Table 1. Selected CV curves are shown in Figure 3. PDST-1 did not show any redox waves within the present scan range appropriate to the solvent and PDST-2, -3, and -4 showed relatively small and broad oxidizing waves without the reducing wave. In PDST-5 two clear oxidizing waves along with two reduction peaks were seen. Values of the first oxidation potential (E^{ox}_1) of PDST-2−5 are quite similar to those of the corresponding α,α′-bis(trimethylsilyl)-substituted bithiophene (1.46 V vs SCE), terthiophene (1.21 V), quaterthiophene (1.04 V), and quinquethiophene (0.98 V).[23] Note these values of PDST-*n* decrease as the number of the thiophene ring increases. It is thus understood that in PDST-*n* electrons are electrochemically removed mainly from oligothienylene units and not from disilanylene units, which signifies the π-conjugation along the whole polymer chain is weak. Note that the easiness of oxidation in the oligothienylene unit compared with the disilanylene unit is consistent with our previous calculation results.[12] The difficulty of extracting an electron from PDST-1 is closely related to the large ionization potential of a thiophene molecule. The fact that oxidation currents of the PDST-*n* are relatively lower than those of the corresponding genuine oligothiophene solutions with the same concentration[24] suggests conglomerates of oligothienylene units even in the dilute solution due to macromolecular structure of PDST-*n*. The conglomerates possibly impede the oxidation of each thienylene unit in a chain. Moreover, solubility of the polymers could also cause difficulty in obtaining clear peaks.

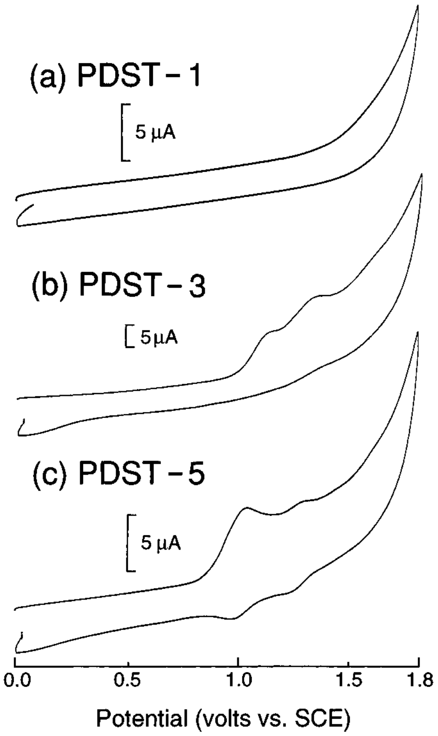

Figure 3. Selected CV diagrams of (a) PDST-1, (b) PDST-3, and (c) PDST-5 in 0.1 M *n*-Bu_4NBF_4/CH_2Cl_2 solution. Scanning rate was 50 mV/s.

Absence of reducing waves corresponding to the oxidizing ones in PDST-2, -3, and -4 would be explained in terms of the degradation of the Si−Si bond, since insoluble dark brown powder was observed after the cycle. This dark brown powder cannot be analyzed due to its small amount. Degradation of Si chain caused by the CV has been observed in several organosilicon polymers.[25] Polymerization reaction eventually forming PT is also possible as it has been reported that PT film can be electrochemically synthesized from dimethylbis(2-thienyl)silane[26] or 2,5-bis(trimethylsilyl)thiophene.[27] In any case, as the polymers convert to insoluble components by such reactions, the apparent reducing wave should become weak. Two reducing waves of PDST-5, however, suggest that the doped quinquethienylene unit can be more stable than the shorter oligothienylene units of PDST-2, -3, and -4.

3.2. Optical Absorption Measurements. The electronic structures of p-type doped PDST-*n* have been examined in detail by the UV−vis−NIR spectrum. The optical absorption peak positions of the heavily doped polymers are listed in Table 2 with those of the corresponding oligothiophenes for comparison. The λ_{max} values of the π−π* transition peak in the neutral PDST-*n* are found to be red-shifted compared with the corresponding neutral oligothiophenes probably due to extension of the π-conjugation through the hyperconjugation in disilanylene unit as mentioned before and also due to the electron-donating nature of silicon atom.[13]

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Table 2. Peak Positions of Pristine and Heavily Doped PDST-*n* and the Corresponding Oligothiophene (in nm)

PDST-*n*	pristine[a]	heavily doped[b]			oligothiophenes	pristine	lightly doped[c]		heavily doped[c]	
n = 1	273 (transparent)	(transparent)			thiophene	215[e]				
n = 2	343 (transparent)	442[d] (pale yellow)			bithiophene	302[f]	400[h]			
n = 3	389 (pale yellow)	441 (dark orange)	617		terthiophene	350[g]	579[h]	886[h]		
n = 4	412 (yellow)	441 (dark brown)	664	1137	quaterthiophene	388[g]	670[h]	1117[h]	667[h]	725[h]
n = 5	427 (yellow)	478 (green-blue)	780	1406	quinquethiophene	403[g]	747[h]	1347[h]	795[h]	873[h]

[a] In parentheses are shown color of the solution of pristine PDST-*n*. [b] In parentheses are shown the color of the heavily doped PDST-*n* solution. [c] Definition of the doping degree does not necessarily agree with that for PDST-*n*. [d] Very weak. [e] Taken from ref 28. [f] Taken from ref 29. [g] Taken from ref 30. [h] Taken from ref 31.

In general, by oxidization, color of the oligothiophene solutions changed from yellow (or orange) to dark green (or dark blue)[32] being similar to PT solution. For instance, poly(3-heptoxy-4-methylthiophene) solution shows a color change from orange-yellow to blue-green.[33] The changes in the electronic spectra of oligothiophenes caused by the p-type doping have been understood in a qualitative manner by change in the energy levels of the frontier molecular orbitals (MOs).[23,30,31,34,35] For example, α,α′-dimethyl quinquethiophene (5T) shows two peaks at 747 and 1347 nm in its cationic state (polaronic state, $5T^{\bullet +}$) and one at 873 nm in its dicationic state (bipolaronic state, $5T^{2+}$) by continuous doping as shown in Table 2.[31]

The change in peak position upon the doping degree for PDST-3, -4, and -5 are shown in Figure 4. The color change of PDST-*n* upon the doping is also listed in Table 2. The main $\pi-\pi^*$ transition splits upon the doping. Although the original transition peak causes the blue-shift and decrease in intensity by the doping, a newly appearing peak at about 440 nm grows and is red-shifted by a little in PDST-5 as seen in Figure 4 and Table 2. The former can be interpreted by the stabilization of the highest occupied (HO) π-type crystal orbital (CO) consisting mainly of oligothienylene units caused by the extraction of electron upon the doping. The latter peak could be associated with the $\pi-\pi^*$ transition of the oligothienylene unit with quinoid structure because it is known that the chemical doping induces a structural change in PT from aromatic to less stable quinoid structure, giving smaller excitation energy. This peak is also observed in the doped oligothiophene solution, even though its intensity is much weaker than that of PDST-*n*.[31] The new peak at 617 nm of heavily doped PDST-3 can be considered as the polaronic state of terthienylene unit, although another weak absorption around 886 nm[31] is absent. New peaks of heavily doped PDST-4 observed at 664 and 1137 nm can be also attributed to the polaronic state of quaterthienylene unit,[31] since these peaks increase simultaneously with doping proceeds. In PDST-5, the heavily doped state can be ascribed to the mixed version of the polaronic and the bipolaronic states of quinquethienylene units because a peak at 1406 nm was reduced by the heavy doping.

Comparison of the optical spectra with those of the corresponding oligothiophenes leads to three apparent differences: (i) in the pristine polymers there occurs red-shift of the main $\pi-\pi^*$ transition by about 20−60 nm compared with the oligothiophene, (ii) a larger amount of the dopant than that in the oligothiophene is required to yield the new absorption peak at the low-energy region corresponding to the cationic (polaronic) or the dicationic (bipolaronic) states of oligothienylene units, and (iii) even after addition of the dopant to such larger

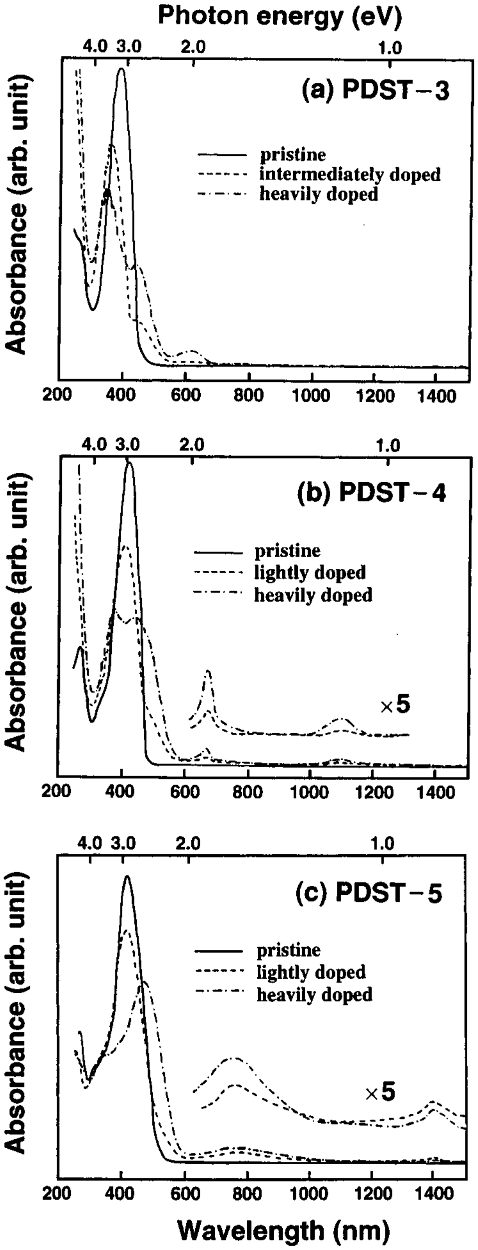

Figure 4. UV−vis−NIR spectra of the pristine and the $NOBF_4$-doped (a) PDST-3, (b) PDST-4, and (c) PDST-5. Note there are three levels of the doping degrees (see Experimental Section).

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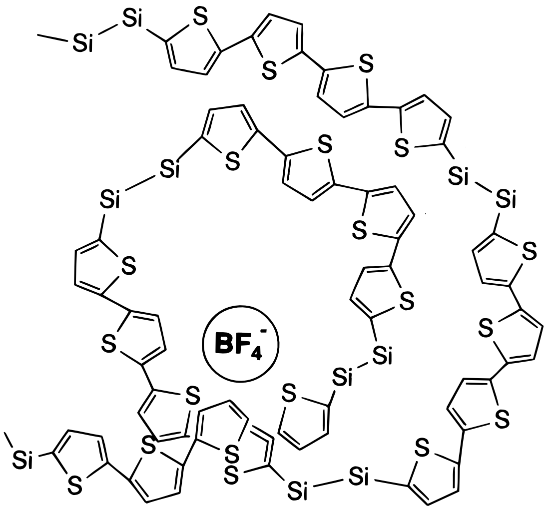

Figure 5. Schematic illustration of conformation of the doped PDST-4 in the solution. Oligothienylene units in a chain are considered to surround the dopant (BF$_4^-$ ion) and to aggregate. This conformation may give partially charged states in oligothienylene units.

amount, the new absorption peaks are much weaker and relatively broader than those of the oligothiophene.

From the CV results, it is hard to remove electrons from each oligothienylene unit of PDST-*n*. We conjecture this is owing to the macromolecular structure of PDST-*n* shown, for instance, in Figure 5. In the polymer solution, even though the solution is dilute, some oligothienylene units of one chain could surround the BF$_4^-$ ion or, in other words, the oligothienylene units aggregate around the dopant. On the other hand, in a dilute solution of oligothiophene such aggregation would not occur due to the absence of closely located oligomers. Small charge transfer (CT) between a BF$_4^-$ ion and each oligothienylene unit results in several numbers of the partially charged units. However, in the heavily doped state, it can be expected the portion of the aggregation becomes small since dicationic (bipolaronic) state was observed in heavily doped PDST-5. In addition, oxidation of disilanylene units occurs in the heavily doped state, resulting in the scission at disilanylene, as discussed in section 3.4. Therefore, several reasons accounting for the above differences between PDST-*n* and oligothiophenes can be considered. In the case of neutral PT solution, the chain has been pointed out not to be exactly linear but to be coiled and tangled from a thermochromic effect,[36] but the aggregation around a dopant (Figure 5) has not been reported in the doped solution.

3.3. ESR Measurements. The nature of spins generated in doped PDST-*n* (powder sample) with NOBF$_4$ was examined by ESR measurements. Note that there were detected no appreciable spin concentrations of each pristine PDST-*n*. It is clear that the peak-to-peak line width (ΔH_{pp}) decreases with increase in *n* for both the lightly and the heavily doped samples from the data in Table 3. It should be noted that all the measured samples were free from metallic impurities since no broad signal (>1000 G[37]) was observed. The following relationship (Ohnishi's formula[38]) between ΔH_{pp} and the length of oligothienylene units *n* was satisfied in the lightly doped PDST-*n*:

$$\Delta H_{pp} \propto n^{-1/2} \tag{1}$$

This *n* dependence of the line width strongly suggests that the spins generated are mostly confined in an oligothienylene unit but not in a disilanylene unit. Relationship 1 excludes the formation of PT. Moreover, there should be no silyl radicals, since they are so unstable that oxidation of disilanylene unit easily leads to the degradation,[39] if any, as is discussed later. Larger ΔH_{pp} values of the heavily doped sample than those of the lightly doped one can be explained in terms of the spin–orbit interaction in the former, since the probability of location of the spin on the BF$_4^-$ ion becomes larger as the doping proceeds. A slight discrepancy from relationship 1 found in the heavily doped samples could be attributed to the stronger spin–orbit interaction.

The *g* values of doped PDST-1 and heavily doped PDST-2 were relatively large (~2.003) and that of the heavily doped one was slightly larger than that of the lightly doped one for all the samples. The large *g* value of doped PDST-1 is in agreement with the theoretical prediction in which the spin strongly localizes on a sulfur atom.[12] Thus it can be concluded that a considerably large spin–orbit coupling constant of sulfur atom (ζ_S = 382 cm^{-1})[40,41] eventually gives the large *g* value of the doped PDST-1. The calculations have also clarified that the spins of PDST-2 and PDST-3 have polaronic nature delocalizing over the carbon atoms in an oligothienylene unit.[12] Being consistent with this, *g* values of doped PDST-*n* approaches that of a free electron with acquiring mobility as *n* increases. Difference of *g* values between the lightly and the heavily doped samples can also be explained by the spin–orbit coupling through, mainly, fluorine atoms (ζ_F = 270 cm^{-1})[40,41] in BF$_4^-$ ion.

The spin concentrations (*N*s) were found to be considerably small, coinciding with the CV and UV–vis–NIR data, and there was only 1 spin/2000 thiophene rings in maximum (1 spin/400–500 oligothienylene units), while the doped PT has been reported to have 1 spin/670 rings.[42] Furthermore, the N_s value of doped PDST-*n* is lower than that of the doped oligothiophene by about 1 order of magnitude.[32] The partially charged oligothienylene unit model shown in Figure 5, therefore, may account for these small N_s values. The contribution of oligothienylene units with bipolaronic state, which can also explain the small N_s value, is supposed to be very small from the very weak bipolaronic band (see

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Table 3. ESR Data at Room Temperature of Doped PDST-*n* with NOBF$_4$ (Values in Parentheses Are Those Measured at 123 K)

PDST-*n*	doping degree	ΔH_{pp} (G)	*g*-value	N_s (spins/g-polymer)	N_s (spins/oligthienylene unit)[a]
$n = 1$	lightly	8.58 (9.77)	2.0031 (2.0027)	9.8×10^{16} (2.4×10^{17})	3.0×10^{-5}
	heavily	8.72 (10.08)	2.0032 (2.0031)	1.0×10^{16} (5.3×10^{16})	3.0×10^{-6}
$n = 2$	lightly	5.30 (6.27)	2.0022 (2.0022)	1.1×10^{18} (2.2×10^{18})	6.0×10^{-4}
	heavily	6.31 (5.25)	2.0029 (2.0030)	7.7×10^{16} (1.8×10^{17})	4.0×10^{-5}
$n = 3$	lightly	3.97 (4.65)	2.0021 (2.0022)	1.4×10^{18} (3.0×10^{18})	1.0×10^{-3}
	heavily	5.66 (6.00)	2.0024 (2.0024)	2.8×10^{18} (6.3×10^{18})	2.0×10^{-3}
$n = 4$	lightly	2.63 (3.12)	2.0022 (2.0022)	2.2×10^{18} (4.4×10^{18})	1.8×10^{-3}
	heavily	3.66 (4.39)	2.0026 (2.0028)	9.5×10^{17} (2.1×10^{18})	8.0×10^{-4}
$n = 5$	lightly	2.03 (2.67)	2.0018 (2.0019)	2.0×10^{18} (4.9×10^{18})	1.9×10^{-3}
	heavily	2.59 (3.12)	2.0025 (2.0027)	2.6×10^{18} (5.9×10^{18})	2.5×10^{-3}

[a] Ratio of the number of spins to oligothienylene units at room temperature.

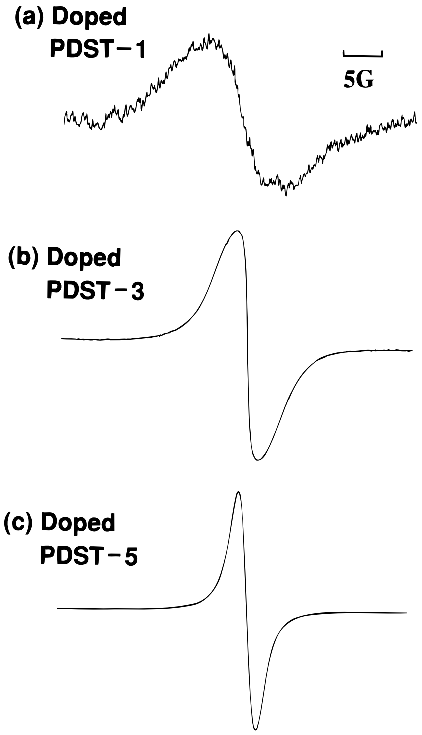

Figure 6. ESR spectra of lightly NOBF$_4$-doped (a) PDST-1, (b) PDST-3, and (c) PDST-5 powders measured at room temperature.

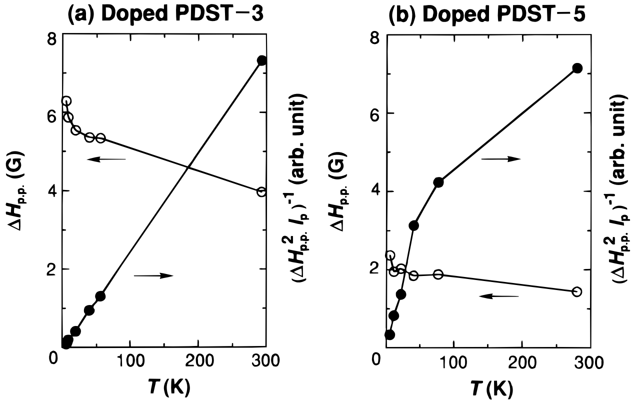

Figure 7. Temperature dependence of the peak-to-peak line width (ΔH_{pp}) and the reciprocal of the peak intensity derived from $(I_p\Delta H_{pp}{}^2)^{-1}$ of lightly doped (a) PDST-3 and (b) PDST-5. The lines are the guide for eyes.

Figure 4) compared with that of the genuine oligothiophene.[29–31]

The line width of the doped PDST-*n* slightly increased under 60 K as seen in Figure 7, where the results of lightly doped PDST-3 and -5 are representatively shown. On the other hand, the *g* value was rather independent of temperature for almost all the doped samples (see Table 3). The broadening at lower temperature can be explained in terms of the suppression of the motional narrowing. Reciprocal ESR intensity, $(I_p\Delta H_{pp}{}^2)^{-1}$, where I_p is the full height of the ESR differential curves, were found to increase approximately linearly with increasing temperature for lightly doped PDST-2, -3, and -4 (see Figure 7a for PDST-3). This is in good agreement with the Curie law and indicative of no magnetic correlation. Lightly doped PDST-5 showed two types of Curie spins in the higher and the lower temperature regions as seen in Figure 7b, which again suggests no magnetic correlation. In addition, there was not seen any signal corresponding to $\Delta m_s = \pm 2$ at about 1500 G characteristic of the triplet state even at 4.5 K. These facts suggest that there are no ferromagnetic interactions among the polaronic spins. This absence of ferromagnetism probably comes from the quite low spin concentration (1 spin/400 oligothienylene units in maximum) generated in doped PDST-*n*.

3.4. IR Measurements. Although formation of PT has been denied based on the ESR spectral measurement, there still remains possibility of degradation of the polymer due to cleavage of a Si−Si bond by the doping. For instance, it has been reported that a UV irradiation causes scission of the Si−Si bond in PDST-1 and poly(disilanylene(phenylenes)) to make silole (−Si−OH) and siloxane (−Si−O−Si−) fragments.[21] Note that the heavy doping brings about the scission of the Si−Si bond cleavage, by removing electrons from σ-type HOCO with the bonding nature between the 3p$_\sigma$ orbitals of each silicon atom as well as the removal from π-type HOCO, whereas UV irradiation excites electrons in the σ-type HOCO to the σ-type LUCO with the antibonding nature between 3s orbitals of silicon atoms, resulting in the degradation of the Si−Si chain.[12,13,21] The IR spectra of both the pristine and NOBF$_4$-doped PDST-5 are shown in Figure 8. The pristine sample gave peaks at 704 and 794 cm^{-1} and at 3062 cm^{-1} attributed to the out-of-plane vibration and the stretching, respectively, of C−H at the β-positions of 2,5-disubstituted thiophene. The bands appearing at 2871−2951 and 1410−1500 cm^{-1} are assigned to the C−H stretching of ethyl group and the β-(C−H) in-plane vibration of thiophene rings, respectively. In the doped sample, strong CT bands were newly observed at 1000−1400 cm^{-1}, being characteristic of the doped PT[43,44] as well as the doped 5T[30,45] irrespective of the dopant species. Moreover, the peak

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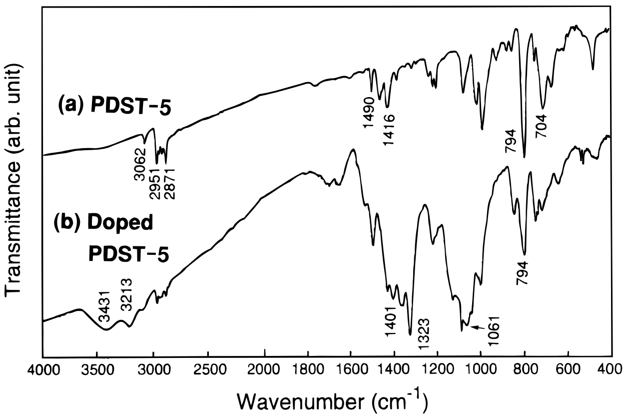

Figure 8. IR spectra of (a) pristine and (b) NOBF$_4$-doped PDST-5 samples.

at 1061 cm^{-1} and a broad band at 3210−3430 cm^{-1} seems to indicate the presence the Si−O−Si and Si−OH bonds, respectively,[46] arising from the degradation mentioned above. Since the cross-linking as well as the aggregation is supposed to occur, one cannot treat PDST-*n* simply as an α,α′-bis(siloxy)oligothiophene.

4. Concluding Remarks

The electronic properties of p-type doped poly[disilanylene(thienylene)$_n$] (n = 1−5) have been studied based on the CV, UV−vis−NIR, ESR, and IR measurements. The oxidation is concluded to occur mainly at oligothienylene units, generating π-type spins as has been predicted by the previous theoretical study. The spin generation, however, has been found to be rather difficult since oligothienylene units in a chain could aggregate and surround the dopant ion, resulting in a partially charged state as suggested by the UV−vis−NIR spectra. Oxidation of disilanylene units could also occur followed by a Si−Si bond cleavage based on the IR spectral measurement. Being consistent with our previous theoretical prediction, polaronic spins delocalizing over the carbon skeleton of an oligothienylene unit have been observed for n = 2−5 and the spin localized on a sulfur atom observed for n = 1. Delocalization of the spin in an oligothienylene unit has also been confirmed from the n dependence of the ESR line width. The larger g value and line width observed in the heavily doped sample compared with those of the lightly doped one suggest the spin−orbit interaction due to increasing possibility of the spins locating on the dopant ion. Since the spin concentrations are considerably small, ferromagnetic interaction among the polaronic spins has not yet been observed.

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