

# Excited-State Dynamics of Conjugated Polycarbosilane Oligomers with Branched Dimethyl or Diphenyl Group

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**ABSTRACT:** Dimethyl or diphenyl branched conjugated polycarbosilane oligomers in solutions, including poly[[1,4-bis(thiophenyl)buta-1,3-diyne]-*alt*-(dimethylsilane)], poly[[1,4-bis(thiophenyl)buta-1,3-diyne]-*alt*-(diphenylsilane)], poly[[1,4-bis(phenyl)buta-1,3-diyne]-*alt*-(dimethylsilane)], and poly[[1,4-bis(phenyl)buta-1,3-diyne]-*alt*-(diphenylsilane)], were investigated by steady-state and picosecond time-resolved spectroscopies to elucidate the effect of silicon-atom introduction into the  $\pi$ -conjugated copolymer backbone and the substitution of the aromatic phenyl group on the silicon atom. The introduction of silicon atoms into  $\pi$ -conjugated copolymer backbones induces slow decay emission components with lifetimes of about 450 ps in addition to  $\pi$ - $\pi^*$  local excited-state relaxations in the time-resolved fluorescence decay profiles. The diphenyls, which are branched in the silicon atoms, bring about broad, structureless emission bands in the low-frequency region of the steady-state fluorescence spectra. However, such broad bands do not occur in the case of dimethyl branched conjugated polycarbosilane oligomers. The time-resolved and solvent-dependent studies of these bands imply that the excited-state dynamics of diphenyl branched conjugated polycarbosilane oligomers can be related to an intramolecular charge-transfer dynamics through an inductive and (*d-p*)  $\pi$ -conjugation effect between the  $\pi$ -conjugated backbone and the branched phenyl ring. © 1999 John Wiley & Sons, Inc. *J Polym Sci B: Polym Phys* 37: 2901–2908, 1999

**Keywords:** excited-state dynamics; conjugated polycarbosilane oligomers; steady-state fluorescence; fluorescence lifetime; intramolecular charge transfer

## INTRODUCTION

Conjugated organic polymers have been investigated intensively in the past few years because of their unusual electrical and optical properties. Moreover, because of their roles as model compounds for quasi-one-dimensional semiconductors, considerable interest has been directed to-

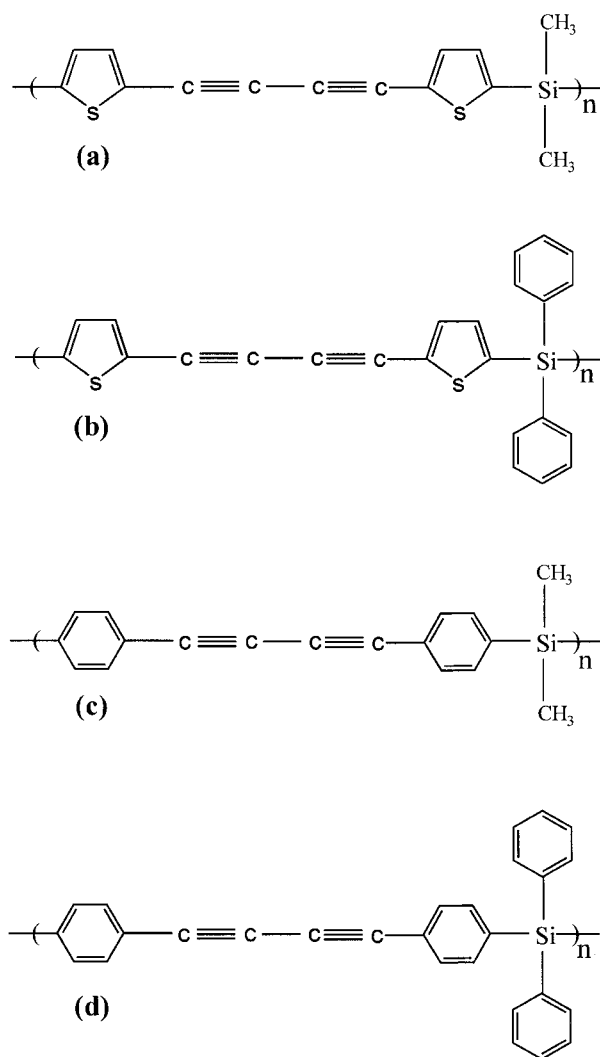
ward the studies of electrical and optical properties with long conjugated chain polymers such as polyacetylenes,<sup>1</sup> polydiacetylenes,<sup>2,3</sup> polythiophenes,<sup>4,5</sup> polyphenylenes,<sup>6</sup> and polyphenylenevinyls.<sup>7</sup> Such properties can also be tuned by the changes of the molecular compositions of the polymers. Various studies have been performed in the modifications of the chain units and the preparations of copolymers to obtain the molecular properties for the various applications and to study the rules governing energy-transport properties in these polymeric materials. Among them, the conjugated polycarbosilanes of poly(sil-

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ylenediacetylene) have shown conductivities as well as high thermal properties.<sup>8,9</sup> Also, silicon-containing poly(*p*-phenylenevinylene) copolymers have shown tunable electroluminescences for possible application to blue-light-emitting diodes.<sup>10</sup>

In this study, we were interested in the effects of silicon-atom introduction into a  $\pi$ -conjugated copolymer backbone and the effects of a  $\pi$ -conjugated functional group substitution on silicon from the viewpoint of charge-transport dynamics. Therefore, the photochemical and photophysical properties of dimethyl or diphenyl branched conjugated polycarbosilane oligomers, including poly[[1,4-bis(thiophenyl)buta-1,3-diyne]-*alt*-(dimethylsilane)] (PBTBD-DMS;  $n = 3.4$ ), poly[[1,4-bis(thiophenyl)buta-1,3-diyne]-*alt*-(diphenylsilane)] (PBTBD-DPS;  $n = 13.5$ ), poly[[1,4-bis(phenyl)buta-1,3-diyne]-*alt*-(dimethylsilane)] (PBPBD-DMS;  $n = 97.8$ ), and poly[[1,4-bis(phenyl)buta-1,3-diyne]-*alt*-(diphenylsilane)] (PBPBD-DPS;  $n = 1.3$ ), were investigated by steady-state and picosecond time-resolved fluorescence spectroscopies at room temperature. Their structures are shown in Figure 1. Because the branched dimethyl groups in Figure 1(a,c) are considered nearly not to affect the electronic states of the  $\pi$ -conjugated systems, their energy dynamics can be discussed as the introduction effect of the silicon atom into the thiophenediacetylene copolymer backbone with the comparison of the excited-state dynamics of the thiophenediacetylene copolymers, which have been studied previously by us with poly(2,5-diethynylthiophene) (PDET).<sup>11</sup> For the introduction effect of the silicon atom into the  $\pi$ -conjugated backbone, the previous report of silanylene-thiophene block copolymers indicated that the presence of one or two silicon atoms between thiophene sequences induces a strong, energetic interruption of the conjugation, but a certain through-conjugation effect apparently exists in the silanylene-interrupted polymers.<sup>12</sup> It was suggested that this was due to the participation of empty silicon *d*-orbitals in the  $\pi$ -system of the ring, and it was called (*d-p*) $\pi$ -conjugation. However, to our knowledge, a more detailed charge-transport dynamics of the silicon-containing conjugated copolymers has not been reported yet. A polar conjugation effect can be considered in their charge-transport dynamics because a silicon atom is relatively more electropositive than carbon, and inductive effects of their molecular systems should also be considered.<sup>13</sup> Therefore, in this study, we discuss the polar conjugation and the inductive effect in addition to the (*d-p*) $\pi$ -conjugation in understanding the charge-transport dynamics of the sili-



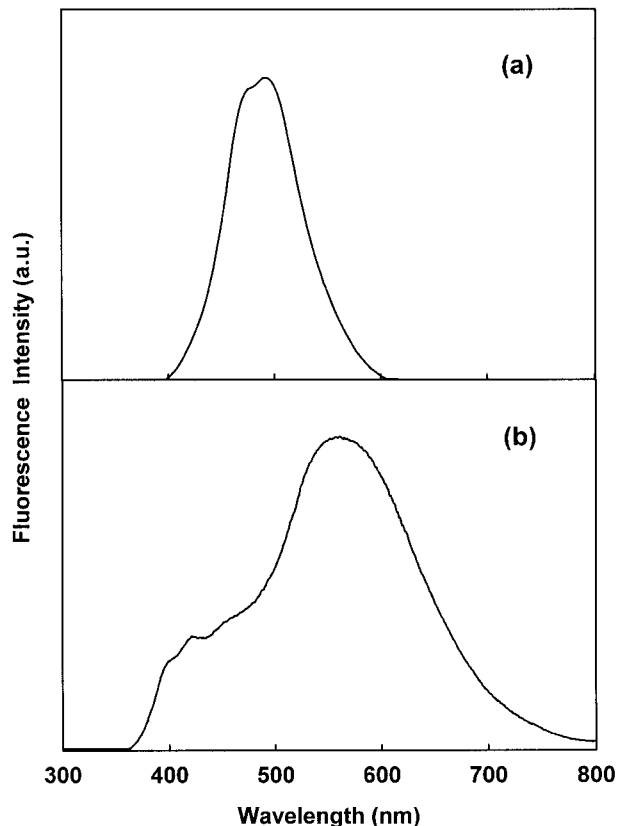
**Figure 1.** The chemical structures of conjugated polycarbosilane oligomers. (A) Poly[[1,4-bis(thiophenyl)buta-1,3-diyne]-*alt*-(dimethylsilane)] (PBTBD-DMS;  $n = 3.4$ ). (B) Poly[[1,4-bis(thiophenyl)buta-1,3-diyne]-*alt*-(diphenylsilane)] (PBTBD-DPS;  $n = 13.5$ ). (C) Poly[[1,4-bis(phenyl)buta-1,3-diyne]-*alt*-(dimethylsilane)] (PBPBD-DMS;  $n = 97.8$ ). (D) Poly[[1,4-bis(phenyl)buta-1,3-diyne]-*alt*-(diphenylsilane)] (PBPBD-DPS;  $n = 1.3$ ).

con-containing conjugated molecular systems. For the diphenyl branched conjugated polycarbosilane oligomers in Figure 1(b,d), it would be interesting also to investigate whether there are any interactions between the conjugated  $\pi$ -systems in the backbone and the  $\pi$ -orbitals in the branched diphenyl ring. We investigated it by comparing the results of their steady-state and time-resolved fluorescence measurements with those of the dimethyl branched conjugated polycarbosilane oligomers.

The results showed that the excited-state dynamics of the diphenyl branched conjugated polycarbosilane oligomers can be related to an intramolecular charge-transfer dynamics. This result can be supported by their fluorescence characteristics in polar [tetrahydrofuran (THF)] and nonpolar (*n*-hexane) solvent.

## EXPERIMENTAL

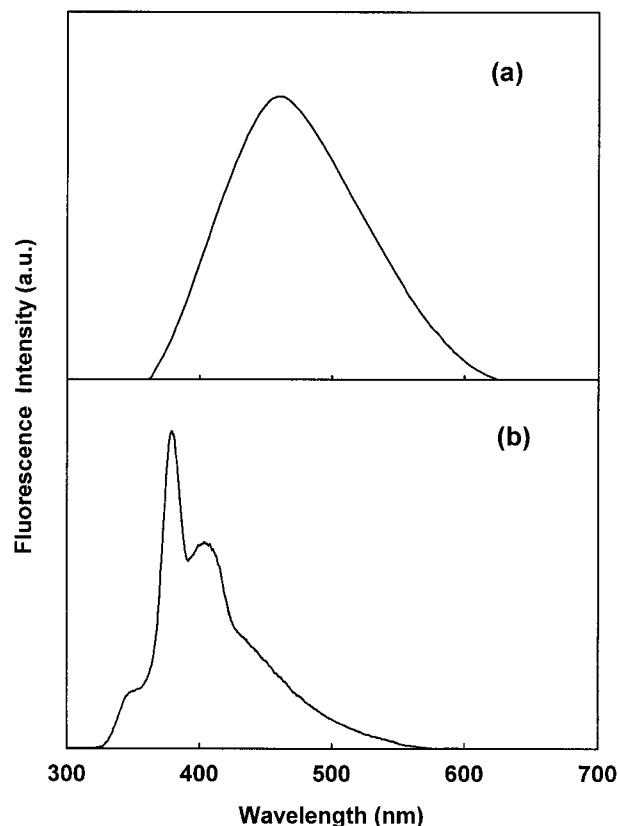
In spectroscopic studies of polymeric molecules, the main problems arise from their solubilities. Generally, polymers are likely to be nonsoluble, particularly when they consist of a large number of repeating units.<sup>14</sup> However, for this study we synthesized soluble conjugated polycarbosilane oligomers without any long alkyl chains. The synthesis and characterization of the conjugated polycarbosilane oligomers were reported previously.<sup>15</sup> The repeating unit numbers of the oligomers were determined by degree of polymerization (*n*), which was calculated by the molecular weight averaging method from the result of gel-permeable chromatography. Although the *n* values in Figure 1 were not consistent in the sample syntheses, the local effects around the silicon atoms that induce a strong energetic interruption of the conjugation were investigated in this study. The solution samples were prepared in THF (spectroscopic grade, Aldrich, Milwaukee, WI) and *n*-hexane (spectroscopic grade, Aldrich). Their concentrations were maintained at less than  $1 \times 10^{-5}$  M. The experiments were performed at room temperature. Steady-state fluorescence spectra were obtained by using a spectrofluorimeter (Hitachi F-2000, Japan). A picosecond time-correlated single-photon-counting (TCSPC) system was employed for the measurement of time-resolved fluorescence decay profiles. The TCSPC laser system utilized in this study consisted of a cavity-dumped dye laser that was synchronously pumped by a mode-locked argon-ion laser. The temporal pulse width of the excitation source was 2 to 3 ps, and the excitation wavelength was 285 nm. More detailed information on this instrument was given in a previous article.<sup>16</sup> The exponential fittings were done with iterative least-squares deconvolution fitting procedures. The fluorescence lifetimes were measured at several fixed emission wavelengths on the fluorescence spectra with the magic angle emission polarization.



**Figure 2.** Steady-state fluorescence spectra of (A) PBTBD-DMS ( $n = 3.4$ ) and (B) PBTBD-DPS ( $n = 13.5$ ).

## RESULTS AND DISCUSSION

The steady-state fluorescence spectra of PBTBD-DMS ( $n = 3.4$ ) and PBTBD-DPS ( $n = 13.5$ ) are shown in Figure 2. In Figure 2, when the spectrum of PBTBD-DMS ( $n = 3.4$ ) is compared with that of PBTBD-DPS ( $n = 13.5$ ), the following results are obtained. Although the chain length of the former is much smaller than that of the latter, bathochromic shift nearly does not occur when considering the rising point around 400 nm of both spectra. This result indicates that the effective conjugation length of PBTBD-DPS ( $n = 13.5$ ) is not much longer than that of PBTBD-DMS ( $n = 3.4$ ), although the chain length of the former is four times as long as that of the latter. However, a broad, structureless emission band, which does not appear in PBTBD-DMS, seems to occur in the low-frequency region ( $\sim 550$  nm) of PBTBD-DPS. This band is discussed in detail later with the results of the time-resolved experiments and the solvent-dependent studies. As shown in Figure 3, PBPBD-DMS ( $n = 97.8$ ) and PBPBD-DPS ( $n$

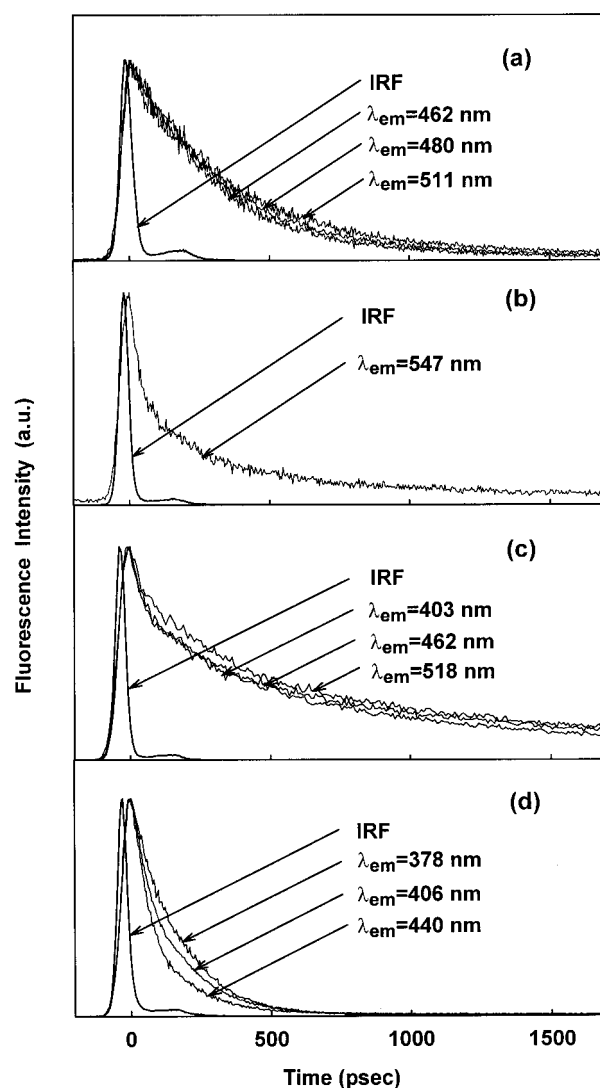


**Figure 3.** Steady-state fluorescence spectra of (A) PBPBD-DMS ( $n = 97.8$ ) and (B) PBPBD-DPS ( $n = 1.3$ ).

$n = 1.3$ ) are different in their spectral shapes. This may be due to the different conjugated chain lengths between them as well as the different substituents on the silicon atoms. Although the chain length of PBPBD-DMS is oligomeric ( $n = 97.8$ ), that of PBPBD-DPS is almost monomeric ( $n = 1.3$ ). Regarding the effects of their different chain lengths, we can consider two possible interpretations. First, because the self-trapped excitons can be generated much more in the monomer than in the oligomer,<sup>17</sup> the narrow bands in the high-frequency region of Figure 3(b) can be considered self-trapped exciton bands due to the small size of the chain length. The self-trapped exciton bands in the high-frequency region were discussed in our previous report on PDET.<sup>11</sup> Second, the emissions of PBPBD-DPS ( $n = 1.3$ ) would show molecular vibronic structures, whereas the broad emissions of PBPBD-DMS ( $n = 97.8$ ) would be characteristic of polymers with a distribution of segments and due to the denser vibronic energy states that usually come from longer molecules. Despite the band-shape

dependence on the conjugated chain lengths, the aforementioned broad, structureless band in the low-frequency region ( $\sim 450$  nm) seems to occur in PBPBD-DPS [Fig. 3(b)].

The time-resolved fluorescence decay profiles for the steady-state spectra of PBTBD oligomers are shown in Figure 4(a,b). The decays were measured at the emission wavelengths of 462, 480, and 511 nm for PBTBD-DMS and 547 nm for PBTBD-DPS. The fluorescence decay in Figure 4(b) was measured at the frequency of the broad, structureless emission band of PBTBD-DPS in Figure 2(b). The decays in Figure 4(a) reveal the



**Figure 4.** Time-resolved fluorescence decays of (A) PBTBD-DMS, (B) PBTBD-DPS, (C) PBPBD-DMS, and (D) PBPBD-DPS. IRF represents the instrument response function of the fluorescence lifetime measurement system.

**Table I.** Fluorescence Lifetimes of Conjugated Polycarbosilane Oligomers

Sample	$\lambda_{\text{em}}$ nm	Rise ( $\tau_1$ ) ps	Decay ( $\tau_2$ ) ps	Decay ( $\tau_3$ ) ps	Decay ( $\tau_4$ ) ps	$\chi^2$
PBTBD-DMS	462	<4	200 (65%)	460 (35%)		1.1
	480	<4	195 (58%)	473 (42%)		1.1
	511	<4	183 (52%)	450 (48%)		1.3
PBTBD-DPS	547	8	21 (86%)	150 (10%)	881 (4%)	1.0
PBPBD-DMS	403	<4	51 (62%)	1832 (15%)	423 (23%)	1.1
	462	<4	66 (56%)	2162 (18%)	450 (26%)	1.2
	518	<4	68 (48%)	2212 (20%)	403 (32%)	1.2
PBPBD-DPS	378	9	49 (40%)	151 (60%)		1.1
	406	9	47 (64%)	152 (36%)		1.2
	440	8	49 (85%)	155 (15%)		1.2

$I(t) = -A_1e^{t/\tau_1} + A_2e^{t/\tau_2} + A_3e^{t/\tau_3} + A_4e^{t/\tau_4}$ ;  $I(t)$ ,  $\lambda_{\text{em}}$ ,  $A$ , and  $\tau$  are the time-dependent fluorescence intensity, detection wavelength of emission, amplitude (noted as the normalized percent in the parenthesis), and lifetime, respectively. The excitation wavelength 285 nm was applied to all samples.

existence of a slow decay component in the low-frequency region; that is, the decay slows down from the high to the low frequency. However, the fluorescence decay in Figure 4(b) indicates that the broad, structureless emission band (547 nm) shown in Figure 2(b) reveals relatively very fast decay characteristics. In the experiment, the decays of PBTBD-DPS in the high-frequency region could not be obtained due to the overall weak fluorescence intensities. The decays of PBPBD-DMS in Figure 4(c) also reveal the existence of a slow decay component in the low-frequency region, which is similar to that of PBTBD-DMS. However, the decays of PBPBD-DPS in Figure 4(d) indicate the reversed result to those of the dimethyl branched conjugated polycarbosilane oligomers; that is, a fast decay component exists and increases toward the low-frequency region. The fitted parameters for the fluorescence decays are shown in Table I. In Table I, PBTBD-DMS shows a very fast rise of <4 ps and two-exponential decay characteristics of  $193 \pm 9$  and  $461 \pm 12$  ps lifetimes. Due to the resolution of the instrument, the fast rise time of <4 ps is not the absolute value; however, it can be mentioned that there exists a very fast rise component. This rise time can be considered the fluorescence build-up time of  $\pi$ - $\pi^*$  local excited-state emissions. The fast decay component of  $193 \pm 9$  ps in the high-frequency region is a value comparable with our previous report on PDET,<sup>11</sup> in which the  $\pi$ - $\pi^*$  local excited-state lifetimes of PDET show the two-exponential decay characteristics of  $139 \pm 5$  and  $205 \pm 3$  ps. However, the  $461 \pm 12$  ps decay component that dominated in the low-frequency

region is a new component that has not appeared in PDET. Therefore, this slow decay component is thought to be from the introduction of the silicon atom into the thiophene-diacetylene  $\pi$ -conjugated backbone. The introduction of the silicon atom into the  $\pi$ -conjugated backbone may induce a potentially deep-trapped state in the excited-state of this copolymer. As a comparable value of the  $461 \pm 12$  ps lifetime, the  $\pi$ - $\pi^*$  fluorescence lifetime of (4-methoxyphenyl)ethynylpentmethylidisilane at room temperature was previously reported as 600 ps by Horn et al.<sup>18</sup> This 600-ps lifetime is due to the introduction of the silicon atom into the phenylethynyl  $\pi$ -conjugated system. It was also reported that the introduction of a trimethylsilyl group into a polythiophene oligomer resulted in a slight redshift in steady-state spectra, and this is due to the participation of empty silicon  $d$ -orbitals in the  $\pi$ -system of the ring.<sup>12</sup> Therefore, it is reasonable that the deep-trapped state due to the introduction of the silicon atom into the  $\pi$ -conjugated copolymer backbone can occur by the interaction of the  $\pi$ -conjugated backbone and the empty  $d$ -orbitals of the silicon atom, a so-called ( $d$ - $p$ ) $\pi$ -conjugation. Also, when the  $461 \pm 12$  ps lifetime is considered in terms of the charge-transport dynamics, this value can be discussed as follows. In the silicon-containing conjugated polycarbosilanes, the polar conjugation and the inductive effect, in addition to the ( $d$ - $p$ ) $\pi$ -conjugation, can also be discussed. The polar conjugation between the  $\pi$ -system and the silicon atom interrupts the charge transporting in the molecular system because they are electrically connected in an alternative way. However, the ( $d$ - $p$ ) $\pi$ -conjugation

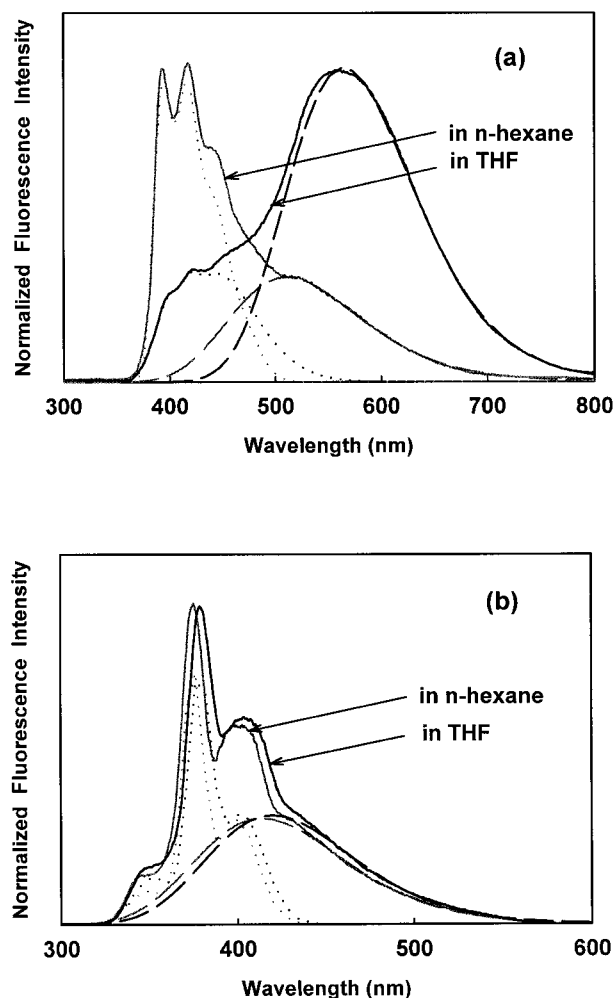
tion and the inductive effect can enhance the charge transporting because the thiophenyl group in the backbone has an electron donating ability due to its nonpaired electrons and the branched dimethyl group can also act as a weak electron donor. Thus, it is suggested that the  $461 \pm 12$  ps decay component of PBTBD-DMS is due to the overall contribution of these counteracting charge-transporting processes in the molecular system.

As shown in Table I, the fluorescence lifetimes of PBTBD-DPS, which is measured at 547 nm of the broad, structureless emission band shown in Figure 2(b), reveal a fast rise of 8 ps and three exponential decay characteristics of 21, 150, and 881 ps, whereas the  $461 \pm 12$  ps decay component that occurs in PBTBD-DMS does not appear. Because the relaxation time of 21 ps is their major amplitude, we can consider that this component comes from the energy state of the broad, structureless emission band shown in Figure 2(b) and that the 150 ps decay component comes from those of the bands in the high-frequency region. Also, the 150 ps decay component can be due to a  $\pi$ - $\pi^*$  excited-state emission of the locally  $\pi$ -conjugated backbone with the comparison of the self-trapped exciton lifetime of the  $139 \pm 5$  ps in PDET.<sup>11</sup> The 881 ps decay component is difficult to discuss accurately because it has a very small amplitude (4%). Thus, it may be due to an impurity or other minor relaxation processes. The fast 21 ps decay component corresponding to the broad, structureless emission band may be due to the diphenyl substitution on the silicon atom. This fast lifetime component implies important information on the charge-transport dynamics of this copolymer. That is, the nonexistence of the  $461 \pm 12$  ps component that appeared in PBTBD-DMS and the existence of the 21 ps component in PBTBD-DPS suggest that the electrons potentially trapped in the silicon atom of PBTBD-DPS by the polar conjugation cannot be transported into another  $\pi$ -conjugated backbone unit like the case of PBTBD-DMS but rather into the branched phenyl ring. This process can be considered an intramolecular charge-transfer process, and it would be possible when the  $\pi$ -conjugated backbone acts as an electron donor and the branched phenyl ring acts as an electron acceptor through the (*d-p*) $\pi$ -conjugation and the inductive effect in the molecular system. That is, because the branched phenyl ring is relatively more electropositive than the  $\pi$ -conjugated backbone containing the thiophene ring, the photoexcited electrons would rather transfer from the backbone

unit to the branched phenyl ring than to another backbone unit through the inductive and (*d-p*) $\pi$ -conjugation coupling effect in the molecular system.

Table I indicates that PBPBD polycarbosilane oligomers generally show similar trends to those of PBTBD. In PBPBD-DMS,  $62 \pm 9$  ps and  $2068 \pm 206$  ps lifetime emissions in the high-frequency region can be assigned as  $\pi$ - $\pi^*$  local excited-state emissions, and a  $425 \pm 24$  ps emission in the low-frequency region comes from the effect of the silicon-atom introduction into the  $\pi$ -conjugated backbone. As a comparable value of the  $2068 \pm 206$  ps lifetime in PBPBD-DMS, the fluorescence lifetime of the  $\pi$ - $\pi^*$  local excited-state emission in poly(*p*-phenyleneethynylene) has previously been reported as  $\sim 2$  ns.<sup>19</sup> In PBPBD-DPS, as mentioned in the case of PBTBD-DPS, the  $153 \pm 2$  ps lifetime in the high-frequency region occurs from  $\pi$ - $\pi^*$  local excited-state emissions of the  $\pi$ -conjugated backbone unit, and the fast rise of  $8 \pm 1$  ps and the decay component of  $48 \pm 1$  ps in the low-frequency region would also be due to an intramolecular charge-transfer emission. However, the case of PBPBD-DPS would be somewhat different from that of PBTBD-DPS. Because the phenylene unit instead of the thiophenyl unit is inserted into the  $\pi$ -conjugated backbone, the electron donation ability of the  $\pi$ -conjugated backbone would be small. Therefore, as shown in Figure 3(b), the relative intensity of the intramolecular charge-transfer emission to the  $\pi$ - $\pi^*$  local excited-state emission is smaller than that of PBPBD-DPS. This implies that the photoinduced excited-state carriers in PBPBD-DPS are more likely to be self-trapped in PBPBD backbone unit than to be transported into the branched phenyl ring.

To reconfirm the existence of the charge-transfer emission in the diphenyl branched conjugated polycarbosilane oligomers, the dependence of the charge-transfer emission on the polarity of the solvent was investigated. As shown in Figure 5(a), the intensity of the charge-transfer emission in PBTBD-DPS increases from the nonpolar solvent (*n*-hexane) to the polar solvent (THF), and the spectrum is bathochromic shifted. Also, the bathochromic shift is even larger in the charge-transfer emission than in the  $\pi$ - $\pi^*$  local excited-state emissions. These results agree well with the previous reports on other charge-transfer emissions in which the charge-transfer emissions are strengthened and stabilized in polar circumstances.<sup>20,21</sup> In the case of PBPBD-DPS, the de-



**Figure 5.** Steady-state fluorescence spectra of (A) PBTBD-DPS and (B) PBPBD-DPS in THF and *n*-hexane. The charge-transfer (---) and  $\pi$ - $\pi^*$  local excited-state (.....) emissions were separated by a band fitting process.

pendence of spectrum on the polarity of the solvent is much smaller than in PBTBD-DPS. This is due to the difference in the polarity of the  $\pi$ -conjugated backbone in PBPBD-DPS and PBTBD-DPS. Because the thiophenyl group in PBTBD-DPS is relatively more electronegative than the phenylene group in PBPBD-DPS, the charge-transfer efficiency from the  $\pi$ -conjugated backbone to the branched phenyl ring is more affected in PBTBD-DPS than in PBPBD-DPS by the polarity of the solvent.

## CONCLUSION

The steady-state and time-resolved spectroscopic studies of the dimethyl branched conjugated poly-

carbosilane oligomers such as PBTBD-DMS and PBPBD-DMS reveal slow decay components with lifetimes of about 450 ps in the low-frequency region, which did not appear in a previous study on PDET.<sup>11</sup> These components are assigned to the introduction of the silicon atom into the  $\pi$ -conjugated copolymer backbone. Namely, the introduction of the silicon atom induces a deep-trapped state in the excited state of the  $\pi$ -conjugated copolymer, and this state occurs due to the polar conjugation through the inductive and (*d-p*) $\pi$ -conjugation coupling effect in the molecular system. Different from the dimethyl branched conjugated polycarbosilane oligomers, the diphenyl branched ones in THF show broad, structureless emission bands in the low-frequency region. These bands are due to the phenyl-group substitution on the silicon atom and show the polarity dependent of the solvent and the very fast decay characteristics. As the solvent changes from the nonpolar (*n*-hexane) to the polar (THF), their intensities increase, and the positions are bathochromic shifted. In the time-resolved fluorescence measurements, they show a rise of about 10 ps and decay characteristics that are 21 ps for PBTBD-DPS and  $48 \pm 1$  ps for PBPBD-DPS. These results are consistent with the typical characteristics of intramolecular charge-transfer emissions in previous reports.<sup>20,21</sup> On the basis of these results, it is suggested that the intramolecular charge-transfer emission state exists in photoexcited PBTBD-DPS and PBPBD-DPS and this dynamics occurs because the polar conjugation of the backbone experiences the (*d-p*) $\pi$ -conjugation and the inductive effect in the molecular system. The existence of the intramolecular charge-transfer process in the diphenyl branched conjugated polycarbosilane oligomers would be meaningful in the field of conducting polymer and organometallic chemistry.

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