Time-Resolved Emission Anisotropic Studies of Silylene-Diphenylene Copolymers: Energy Migration along the σ - π Conjugated Chain

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The excited-state dynamics of silylene-diphenylene copolymers, $-[(SiMe_2)_m-(C_6H_4)_2]_n-$, m = 1, 2, 3, 4, and 6, was studied by picosecond time-resolved emission anisotropy. The emission depolarization within 100 ps suggested the effective energy migration along the σ - π conjugated silylene-diphenylene chain.

The electron delocalization between Si-Si σ band and π system is called σ - π conjugation, and the system has been extended to the σ - π conjugated polymers.[1-3] The visible emission of conjugated polymers has been investigated for the purpose of the application to luminescent devices. The dynamics of excited energy of the conjugated polymers is characterized by the energy migration along the polymer chain.[4] The effective energy migration to an emission site enhances the emission intensity. The evidence for the existence of the energy migration has been reported for π -conjugated polymers and σ -conjugated polysilanes.[5,6] However, there are few studies on the excited-state dynamics of the σ - π conjugated polymers. In this paper we report the picosecond time-resolved anisotropic studies of silylene-diphenylene alternating copolymers $-[(SiMe_2)_m-(C_6H_4)_2]_n-$ with the dimethylsilylene chain length m = 1, 2, 3, 4, and 6 which are denoted by PSi1, PSi2, PSi3, PSi4, and PSi6, respectively. The effect of the silylene chain length on the energy migration was investigated.

The silylene-diphenylene copolymers were obtained by the reaction of 1,6-dilithiodiphenyl with α, ω -dichloropermethylated oligosilanes, $Cl-(SiMe_2)_m-Cl$ (m = 1, 2, 3, 4, and 6). The details of the experimental procedures are described elsewhere.[7,8]

The time-resolved emission spectra were measured using an argon ion laser pumped Ti: sapphire laser (1.6 ps fwhm, Spectra-Physics, Tsunami 3950-L2S) with a pulse selector (Spectra-Physics, Model 3980), a harmonic generator, and a streak scope (HAMAMATSU, C4334-01). The system enables photon counting measurements at simultaneous multiple wavelengths. Typical instrument response function for this apparatus is 20 ps and the time resolution of the detection within 5 ps can be obtained by using the deconvolution technique.

In a previous study, we reported the absorption spectra and the thermochromism of silylene-diphenylene copolymers.[7] The absorption maxima of the silylene-diphenylene copolymers showed red shift with increasing the silylene chain length. The absorption maxima of PSi1, PSi2, PSi3, PSi4, and PSi6 are 269, 281, 283, 285, and 287 nm, respectively. Emission spectra of silylene-diphenylene copolymers exhibit similar red shift as shown in Figure 1. The emission maxima are 320, 380, 385, 391, and 409 nm for PSi1, PSi2, PSi3, PSi4, and PSi6, respectively. There is a discontinuous change of the emission spectral shape between PSi1 and PSi2. The former shows a rather sharp emission spectrum with vibrational structures, while the latter shows a broad and structureless one similar to PSi3, PSi4, and PSi6. Such a broad emission spectrum for aromatic organosilicon compounds has been attributed to an intramolecular CT excited state resulting from the charge transfer between the Si-Si σ -unit and the aromatic unit.[9-13] The emission spectrum of PSi1 is analogous to that of diphenyl, which suggests the π - π * characteristics of the excited state. The broadness of the emission spectra is caused by the intramolecular CT excited state of the σ - π conjugated silylene-diphenylene copolymers with m larger than 2.

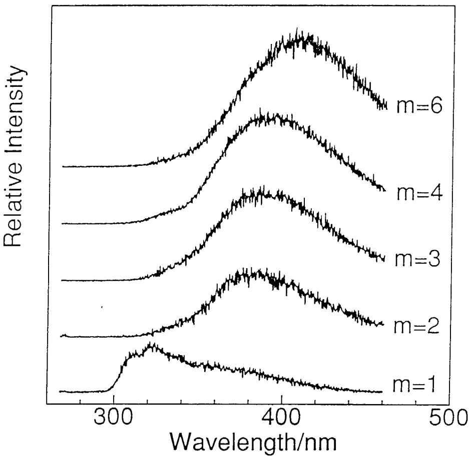

Figure 1. Time-resolved emission spectra for silylene-diphenylene copolymers in the time-domain of 0.00-0.20 ns upon excitation at 255 nm at 295 K in THF solution.

The emission decay curves of the silylene-diphenylene copolymers are non-exponential as shown in Figure 2. Similar non-exponential decays have been reported for π -conjugated poly(phenylacetylene) and σ -conjugated polysilyne.[4-6] The distribution of electronic levels in the excited state and the energy transfer or migration from the higher to lower energy level within the same chain cause the non-exponential decay.[4,5] In Figure 1, PSi1 and the others exhibit different excited-state dynamics. The emission decay curves can be fitted by assuming the sum of two exponential decays with lifetimes τ_1 and τ_2: PSi1 (72.3 ps, 1.40 ns), PSi2 (40.3 ps, 0.52 ns), PSi3 (68.0 ps, 0.53 ns), PSi4 (74.7 ps, 0.62 ns), and PSi6 (117.1 ps, 0.69 ns) at 361 nm. PSi1 shows a clear τ_1 risetime of 72.3 ps and the rather longer lifetime τ_2 than the other copolymers (m $\geqq$ 2). The τ_1 and τ_2 increase in order of the dimethylsilylene chain length m except PSi1. The discontinuous change of the emission decay between PSi1 and the other copolymers can be explained by considering the intramolecular CT excited state when the dimethylsilylene chain length m is longer than 2. The time-resolved emission spectra of silylene-diphenylene copolymers (m $\geqq$ 2) showed the CT emission just after the laser excitation.

The excited energy may be trapped at the CT site following

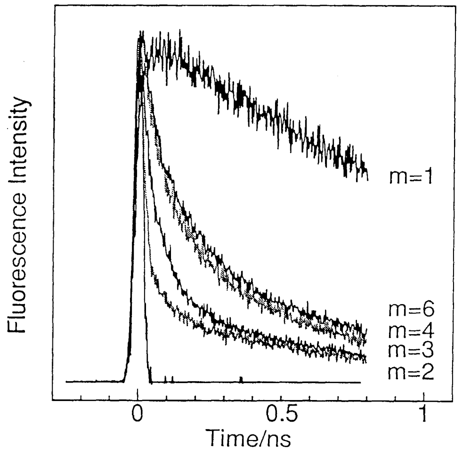

Figure 2. Emission decay profile monitored at 361 nm for silylene-diphenylene copolymers by the excitation at 255 nm at 295 K in THF solution.

the energy migration along the σ - π conjugated chain. The molecular orbital (MO) calculations (ZINDO method) on the ground and first excited states of a model compound (Me_7Si_3-$(C_6H_4)_2$-Si_3Me_7) suggest that the MO with delocalized electrons over the Si-Si bonds and the diphenyl ring in the ground state changes into the MO with the localized electrons near the diphenyl-Si bond in the excited state. As a conformation of the CT excited state, an in-plane conformation where the σ (Si-Si) bond is coplanar with the aromatic ring has been proposed.[10,11,13] The deviation from the in-plane conformation causes the difference of the emission lifetime.[11] In the case of silylene-diphenylene copolymers, there is a distribution of the conformation in the CT excited state along the polymer chain, which causes the non-exponential emission decay. The excited energy is trapped at a pre-formed CT site following the energy migration along the σ - π conjugated chain. The CT site acts as a deep trapping site for the excited state. The difference of the lifetime among the silylene-diphenylene copolymers (m = 2, 3, 4, and 6) may be due to the density of the CT trapping site, where PSi2 has the highest electron density of diphenyl-Si bond and shows the shortest lifetime. The emission decay of PSi1 at 361 nm is complicated, where there is a risetime of 72.3 ps. Such rising of the emission was not observed at the shorter wavelength near 310 nm. The risetime may be related with the energy migration from the shorter conjugated sequences to the longer conjugated sequences which act as a shallow trapping site.

The energy migration processes are evidenced by time-resolved emission anisotropic studies. Time-dependent emission anisotropy, r(t), is obtained from the standard equation $r(t) = (I_{\parallel} - G I_{\perp}) / (I_{\parallel} + 2 G I_{\perp})$, where $I_{\parallel}$ and $I_{\perp}$ are the emission decays polarized parallel and perpendicular to the polarization vector of the exciting light, respectively, G is an experimentally determined correction factor for the instrumental anisotropy.[4,5] In rigid glass (2-methyltetrahydrofuran at 77 K) where the depolarization by the molecular motion is removed, the depolarization is caused only by the energy migration along the polymer chain. Figure 3 shows the time-resolved fluorescence anisotropy of silylene-diphenylene copolymers. The anisotropy decays exhibit the depolarization within 100 ps by the energy migration. The remaining polarization anisotropy after 200 ps decreases with increasing the silylene chain length m. This result suggests the enhancement of the σ - π conjugation and the energy migration with increasing the silylene chain length.

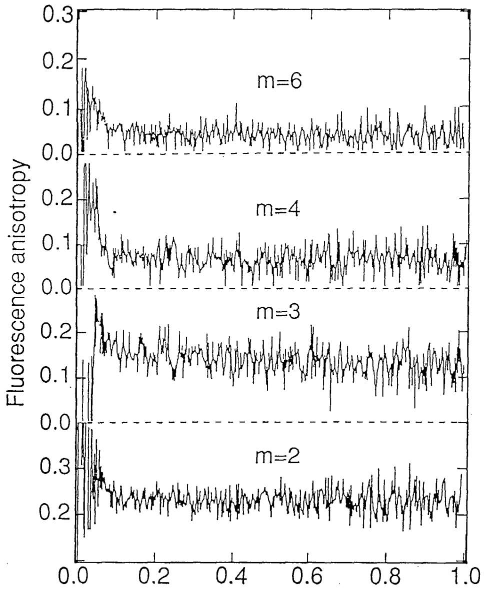

Figure 3. Time-resolved emission polarization anisotropy decays for silylene-diphenylene copolymers at monitoring wavelength of 400 nm by the excitation at 255 nm at 77 K in 2-methyltetrahydrofuran.

References and Notes

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