Conjugated Polymers

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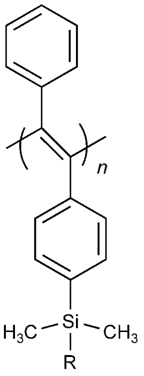
Correlation of Intramolecular Excimer Emission with Lamellar Layer Distance in Liquid-Crystalline Polymers: Verification by the Film-Swelling Method**

*Wang-Eun Lee, Jin-Woo Kim, Chang-Jin Oh, Toshikazu Sakaguchi, Michiya Fujiki, and Giseop Kwak**

π-Conjugated polymers composed of coplanar aromatic rings in the main chain, such as polythiophene, polyfluorene, polyphenylene, polyphenylenevinylene, and polyphenylene-ethynylene, are generally stiff, rigid rodlike chain molecules with planar geometries and strong intermolecular interactions, which lead to a highly cofacial chain packing in the solid state.[1] Although such a stacked chain structure is essential for effective intermolecular charge-carrier transport in an active layer within thin-film organic devices such as photovoltaic cells[2] and field-effect transistors (FETs),[3] this cofacial packing structure is not preferable for high quantum efficiency in the solid state because it results in self-quenching as the intermolecular excimers have an extremely low transition energy in a nonradiative process.[4] Thus, the design highly emissive conjugated polymers has been intensively studied to date.[5]

Unsubstituted polyacetylene is not emissive and mono-substituted polyacetylenes are almost non-emissive without the aid of side-chain fluorophores. Unusually, however, disubstituted acetylene polymers exhibit intense fluorescence (FL) in a wide visible range from blue to green-yellow.[6] This unusual FL emission has been assumed to be based on the effective exciton confinement within the main chain because of the steric hindrance and/or intramolecular electron interactions of bulky aromatic substituents such as phenyl rings.[7] Very recently, Tang and co-workers clarified the idea that the FL emission of disubstituted acetylene polymer derivatives originates from intramolecular excimers because of the face-to-face stacking of the phenyl rings.[8] Thus, in order to further precisely design the optimized molecular structure for highly emissive, substituted acetylene polymers in the solid state, it is crucial to know what influences the intramolecular excimer emission in films, as well as to further understand how the intramolecular excimer forms in films. XRD and dynamic fluorescence spectroscopy studies accompanied with film-swelling experiments revealed that the intramolecular excimer emission of diphenylacetylene polymer derivatives in films is significantly influenced by the lamella layer distance. The origin of this effect will be also described in detail.

Diphenylacetylene polymer derivatives (polymers **1**–**3**) show lyotropic liquid crystallinity. In films, these polymers have lamellar layer structures with long distance spacing of about 22.0, 14.9, and 13.0 Å, respectively.[9] These interlayer distances are much greater than the interplanar distances (3.0–4.0 Å) needed for an effective intermolecular π–π interaction.[10] Also, these polymer chains are highly twisted because of the steric repulsion between the two bulky phenyl groups and its backbone is essentially non-coplanar with the phenyl ring.[7g] Theoretically, the fully extended polymer chains are approximately greater than 1 μm in length.[11] Thus, the polymers should be wormlike chain molecules with a relatively weak intermolecular interaction and a relatively nonplanar geometry, which lead to an unstacked chain conformation in the solid state.



1: R = octadecyl
2: R = octyl
3: R = methyl

Herein, we discuss the correlation between the lamellar layer distance (LLD) and FL properties of such unusual, unstacked, π-conjugated polymers. Figure 1 shows the FL

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[*] W.-E. Lee, J.-W. Kim, C.-J. Oh, Prof. G. Kwak
Department of Polymer Science, Kyungpook National University
1370 Sankyuk-dong, Buk-ku, Daegu 702-701 (Korea)
Fax: (+82) 53-950-6623
E-mail: gkwak@knu.ac.kr
Prof. T. Sakaguchi
Department of Materials Science and Engineering
University of Fukui, Bunkyo, Fukui 910-8507 (Japan)
Prof. M. Fujiki
Nara Institute of Science and Technology
8916-5 Takayama, Ikoma, Nara 630-0101 (Japan)

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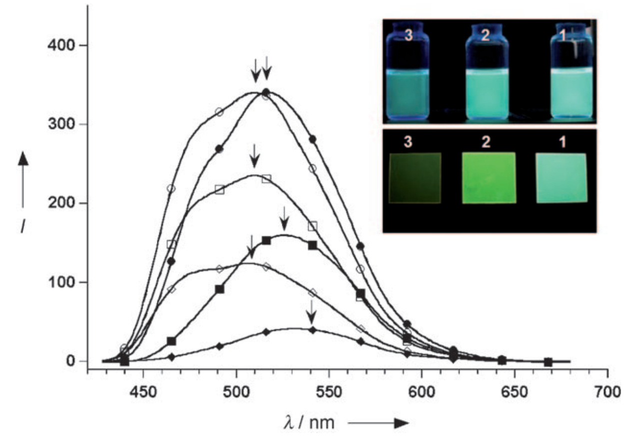

Figure 1. Fluorescence emission spectra (excited at 420 nm) and emission colors (excited at >450 nm) of **1**–**3** in solution (concentration 1.0×10^{-6} M in toluene, ○ **1**; □ **2**; ◇ **3**) and film (thickness 100 nm, ● **1**; ■ **2**; ◆ **3**). The arrows indicate $\lambda_{max,em}$.

emission spectra and emission color photographs of the polymers in films and solution. The difference in FL maximum wavelength ($\lambda_{max,em}$) of **1**, which has the longer LLD, is not so large between films and solution (505 nm in solution; 510 nm in film). In addition, the FL emission of **1** is quite intense in film as well as in an ideal solution (quantum emission yield $\Phi_{em}=20.3\,\%$ in film; 53 % in dilute cyclohexane solution).[9b] The intense emission of **1** in film can be observed by the naked eye. On the other hand, both **2** and **3**, which have shorter LLDs, show quite different FL properties between films and solution. For example, the FL emission of **3** in solution is quite intense in the sky blue region ($\lambda_{max,em}=505$ nm; $\Phi_{em}=27\,\%$ in cyclohexane solution),[9b] while in film the FL emission is much weaker and shifts from sky blue to green-yellow ($\lambda_{max,em}=540$ nm; $\Phi_{em}=1.2\,\%$ in film). The $\lambda_{max,em}$ values of **2** in solution and film are significantly different (505 and 525 nm, respectively; $\Phi_{em}=38\,\%$ in cyclohexane solution; 16.4 % in film).[9b]

It should be noted that the $\lambda_{max,em}$ values of these all the polymers in solution are almost the same at about 505 nm and the emission colors are all close to blue, but the emission bands in films shift to shorter wavelengths as the LLD increases (**1** > **2** > **3**) and their emission colors are completely different from each other (**1**: sky blue; **2**: blue-green; **3**: green-yellow). It is very unusual that the slight change in alkyl chain length within the side chain significantly influences the emission wavelength and intensity of the polymer derivatives in films. Although in our previous study[11] this effect was thought to be due to the chain entanglement that occurs exclusively in **3**, the behavior of the polymers was not still clarified and it may be reasonable to think that the FL emission property of such diphenylacetylene polymer derivatives is closely correlated to their LLDs.

We wished to investigate why **3** shows significantly different FL properties in solution and films, unlike **1**. As mentioned above, this effect should not be due to intermolecular π–π stacking interactions because the polymer chains should not be stacked in films. To rationalize the behavior of **3** and to understand the alkyl side-chain length effect on the emission properties of the polymers, we focused our interest on the FL origin of the substituted diphenylacetylene polymers. As already reported by Tang and co-workers, diphenylacetylene polymer derivatives exhibit an excimer emission that arises from the intramolecular phenyl–phenyl stack in the side chains.[8] Such an intramolecular excimer emission should be concentration-independent. In fact, when the concentration of the present polymers **1**–**3** was varied from 10^{-6} to 10^{-3} M, their spectral profile remained unchanged, with neither blue- nor red-shift in the peak maximum. Unusually, the full width at half-maximum (FWHM) of the emission spectra decreased as the concentration was increased (Figures S1–S3 in the Supporting Information). In theoretical calculations, the energy-minimized 10-mer model of **3** certainly showed the phenyl–phenyl stack structure in the side chains although the stack structure, which involves two or three phenyl rings, was discontinuously connected (Figure S4 in the Supporting Information). These results indicate that the polymer emission comes mainly from the intramolecular excimer, and also agree with those of Tang and co-workers on other diphenylacetylene polymer derivatives.[8]

The electron density and electronic structure of such an intramolecular excimer may be influenced by the changes in intermolecular distance and molecular conformation.[12] In fact, when π-conjugated fluorophore molecules and polymers adopt a highly twisted structure at an isolated state and also have a bulky substituent, the resulting aggregated nanoparticles display a remarkably enhanced emission relative to the isolated molecules in an ideal solution. This emission enhancement is now thought to arise from the following factors: 1) the intramolecular rotation restriction (molecular perturbation inhibition) and conformational planarization occur together with a decrease in the intermolecular distance in the course of aggregation or crystallization.[12c–e] 2) Both the twisted structure and the bulky substituent prevents intermolecular π–π stacking interaction to restrain the self-quenching. These phenomena are referred to as aggregation-induced emission enhancement (AIEE) and crystallization-induced emission enhancement (CIEE), respectively. Similarly, the present polymers also have a highly twisted main-chain structure and two bulky phenyl rings. These facts suggest that the intramolecular rotation barrier energy and the stack degree of the phenyl rings in the polymers may vary along with changes in the LLD, and may influence the intramolecular excimer emission.

To confirm this hypothesis, we carried out film-swelling experiments of **3**, which has a shorter LLD, together with an XRD study. Polymer **3** has an extremely large fractional free volume (FFV) of about 0.26 in films. The large FFV helps various chemicals to easily diffuse into its films because of the high porosity at the molecular level. We used paraffin oil as a poor solvent for swelling. For example, Figure 2 shows the XRD patterns of **3** in film before and after swelling with paraffin oil. A sharp signal is clearly seen at 6.9° before swelling, with a corresponding distance of approximately 13 Å, while the diffraction peak shifts to a lower angle by 2.9° after swelling and the signal is seen at 4.0° with a corresponding distance of approximately 22 Å. This value indicates that

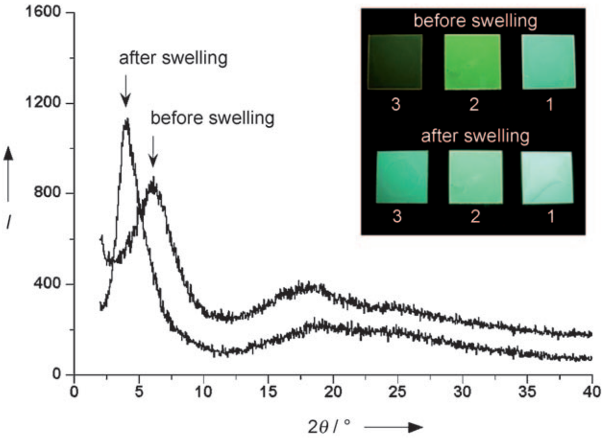

Figure 2. Wide-angle X-ray diffraction (WAXD) patterns of **3** in cast film (thickness 1.0 μm) before and after swelling in paraffin oil. Inset: Changes in emission color of **1**–**3** in the cast film after swelling in paraffin oil (film thickness 100 nm, excited at > 450 nm).

the LLD in **3** is increased by swelling. Simultaneously, the FL intensity significantly increased with swelling (before swelling: $\Phi_{em} = 1.2\,\%$; after fully swelling: $\Phi_{em} = 11.1\,\%$) and the FL emission band shifted to blue by 30 nm and the emission color changed from green-yellow to sky blue. It should be noted that the X-ray diffraction peak of **3** that appears in the swollen film corresponds to that (4°, 22 Å) of **1** in an unswollen film and that the FL intensity and the emission color ($\lambda_{em,max}$) of **3** in the swollen film are almost same as those of **1** in an unswollen film. In addition, the polymer **2** showed similar results when the film was swollen by paraffin oil. This result strongly supports the idea that the increase in the FL intensity and the change in emission wavelength along with swelling are ascribed to the increase in the length of LLD. Therefore, the oscillator strength and the radiative electronic energy transition of the intramolecular excimer in the poly(diphenylacetylene) derivatives can be modulated by the change in LLD length.

To gain further insight into the change in fluorescence properties along with the change in the LLD in the swelling process of **3**, we performed dynamic fluorescence spectroscopy to accompany the swelling experiments using the polymer films of **3**. Table 1 summarizes the fluorescence lifetimes of **3** before and after swelling in decane and paraffin oil. The photoemission decay of **3** before swelling obeyed a triexponential decay, while a biexponential was required to adequately fit the observed decay dynamics of the swollen film. The emission of **3** before swelling is characterized by a shorter fluorescence lifetime (τ_1) as well as longer ones (τ_2, τ_3) whereas the emission after swelling comes exclusively from the longer-lived excited species (τ_2, τ_3). This result means that the shorter-lived emission excited species of **3** in the unswelled film was formed because of a rapid energy migration into the energy trapping sites, while the polymer film swelling restrained generation of the shorter-lived excited species. Presumably, the degeneration of the shorter-lived excited species is due to the fact that the cross-sectional phenyl–phenyl stack area decreases with an increase in LLD along with the degree of swelling in order to restrain the formation of excimers of energy trapping sites (Figure 3).

Table 1: Fluorescence lifetimes of **3** in cast films before and after swelling.[a]

Polymer film	$\tau_1(f_1)$ [ns]	$\tau_2(f_2)$ [ns]	$\tau_3(f_3)$ [ns]	χ^2
unswollen	0.120(0.39)	0.411(0.46)	1.302(0.15)	1.873
swollen in decane		0.611(0.71)	1.524(0.29)	1.656
swollen in paraffin oil		0.901(0.50)	1.866(0.50)	1.750

[a] Film thickness = 1.0 μm. Wavelength monitored = 550 nm, τ_1, τ_2, and τ_3 are lifetimes (ns), f_1, f_2, and f_3 are fractional intensities, and χ^2 is the reduced chi-square value.

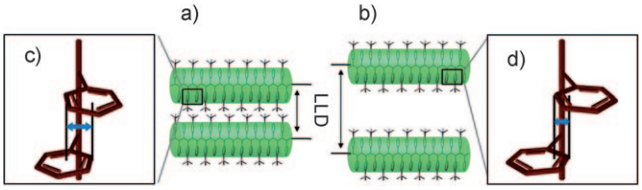

Figure 3. Representation of changes in lamella layer structure before swelling (a), after swelling (b), and cross-sectional phenyl–phenyl stack area before swelling (c) and after swelling (d). In (c) and (d), the blue arrow indicates the stack area of the phenyl rings.

According to our previous results, the emission of **1** with the larger LLD in an unswollen film was mainly due to an extremely longer-lived excited species (lifetime: 1.43 nm; fractional intensity: > 0.99).[9b] In fact, the dynamic fluorescence property of **3** in the swollen film is very similar to that of **1** in the unswollen film. In their previous study on aggregation of poly(diphenylacetylene) (PDPA) derivatives, Tang and co-workers reported that the shrinkages in the molecular volumes along with aggregation of PDPA physically forces the phenyl rings to come closer to each other, thus leading to an increase in molecular electron density because of their π-electron communications and hence results in a red shift in FL emission spectra.[8b] Although the aggregation is the opposite phenomenon to swelling, the result of Tang and co-workers implied that steric crowding in the PDPA chains plays a key role in FL emission properties.

It should be also noted that the fluorescence lifetime of **3** is longer in the film swollen by paraffin oil rather than in the film swollen by decane. Actually, the I/I_0 ratio, where I_0 and I are intensities at $\lambda_{em,max}$ before and after swelling in paraffin oil, respectively, was estimated to be 7.8 and greater than that of decane (I/I_0 ratio = 6.1). This result can be explained as follows: Paraffin oil is composed of longer, bulkier, and branched hydrocarbon alkane chains with approximate carbon numbers higher than C_{16}. The molecular size and viscosity of paraffin oil are much greater than those of the C_{10} chain of decane. Thus, the degree of swelling of **3** in paraffin oil may be greater than that in decane and thus the increase of LLD is also greater. The intramolecular rotation freedom of the phenyl–phenyl structure of **3** may be further restricted in the more viscous paraffin oil compared to decane and thus FL quenching that arises from the molecular perturbation of the phenyl rings is lower in paraffin oil than in decane. This hypothesis supports the above-mentioned idea that the intramolecular excimer emission is significantly dependent on the length of the LLD. The results also suggest the possibility of potential applications using **3** as a fluorescent viscosity sensor material with a molecular size recognition function.

In conclusion, we have shown that the intramolecular excimer emission of lyotropic liquid crystalline poly(diphenylacetylene) derivatives in films is intrinsically correlated with lamella layer distance and can be modulated by the film-swelling method. This result is expected to be very helpful in the molecular designs for chemical-stimuli sensor materials with high responsivity to various organic solvents as well as for light-emitting materials with high emission quantum efficiency. Above all, polymer **3** is expected to be very useful as a sensor material to distinguish the differences in molecular size and viscosity. The study on viscosity sensor applications of **3** is currently underway.

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