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The inhomogeneity in conjugated polymer blend films

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Abstract

Conjugated polymer blend films are studied by time-resolved fluorescence and near-field scanning optical microscopy. Phase separations were directly observed by NSOM. The domains are found to be composed of different fractions of the two constituent polymers. The composition of the domains and the domain structure alter as a function of blend ratio. Surface roughness and optical contrast exhibit similar trend at the change of blend ratio. At 4 : 1 ratio, both have higher contrasts. For low PdOPV ratio, the two polymers are mixed homogeneously. As the concentration of PdOPV increases, condensed phase of PdOPV is formed. © 1998 Elsevier Science B.V. All rights reserved.

The potential applications of conjugated polymers light-emitting diodes (LEDs) have attracted much attention recently [1]. The basic structure of these LEDs consists of polymers of thickness around 100 nm sandwiched between positive and negative electrodes. When the LED is turned on, large electric field (10^5 – 10^6 V/cm) is applied on the active layer of the polymer film [2]. Thus, roughness of the layer affects the local electric field distribution. Moreover large electric fields tend to break the thinner parts of the layer, consequently, short circuiting the LED [2,3]. The flatness of polymer layer is crucial for the reliability of organic LED. Hence, it is important to investigate the variations in thickness of the polymer film at a nanometer length scale. Near-field scanning optical micro-

scopy with the capability of simultaneous imaging of topographic and optical variation offers a useful tool for investigating the morphology of these organic films.

Various applications of LEDs require broad emission spectrum which can be obtained by blending the polymers with different energy gap [4,5]. If phase separation occurs in the blend film, the color emitting by the polymer LED can be partly controlled by the applied voltage. On the other hand, if the polymer blend is relatively homogeneous, efficient energy transfer will reduce emission from the high-gap polymer and enhance emission from the low band gap polymer. The polymer blend device can also be used as photoreceiver [6,7]. The charged donor–accepter pairs are generated by incident light, which subsequently separate and are transported to the electrodes. The surface flatness as well as the mixing uniformity are important parameters for the performance of these devices.

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In this paper, we present a study of conjugated polymer thin films by time-resolved fluorescence spectroscopy (PL) and near-field scanning optical microscopy (NSOM). The surface flatness and local structural of the blend films comprising of PPV copolymer and PdOPV in various weight ratios (PPV copolymer vs. PdOPV) were examined. Time-resolved PL was used to probe the energy transfer in the polymer blends, while NSOM was used to measure the surface flatness and phase separations.

Poly(dioctyloxy phenylene vinylene) (PdOPV) was prepared by the method similar to Holmes [8] and Wudl [9]. PPV copolymer contains repeating units of finite conjugated chain and non-conjugated chain segments, which emit blue light. The synthesis of PPV copolymer was carried out in accordance with the method given by Karasz [10]. PPV copolymer and PdOPV were dissolved in chloroform and then mixed at various ratios. To prepare thin films, the solutions were spin cast on a cover glass. The polymer film has a thickness about 100 nm. The absorption and fluorescence spectra of both pure PPV copolymer and PdOPV films are shown in Fig. 1. There is a substantial overlap between the emission of PPV copolymer and the absorption of PdOPV. This overlap ensures Förster-type energy transfer from PPV copolymer to PdOPV, if the mixture is homogeneous.

We used NSOM operated at 514.5 nm to study the morphology of the samples. The details of our NSOM setup have been published elsewhere [11]. Fig. 2 shows the absorption and topographic images of two samples with different blend ratios. The data indicates that the films form domains with different ratios of the constituents. Since the PPV copolymer does not absorb at 514.5 nm, the bright area corresponds to mostly the PPV copolymer while the dark area corresponds to that of PdOPV. The comparison of Fig. 2a and Fig. 2b further suggests that the domain structures vary slightly as the mixing ratio is changed. It should be noted here that films comprising of only one type of polymer were also studied for comparison, which showed no structures in the NSOM image. The domain size is about several-hundred nanometers. In addition, the 1:1 ratio film exhibits a higher transmission contrast between different domains. It is important

Fig. 1. The absorption and fluorescence spectra of pure (a) PPV copolymer and (b) PdOPV films.

to note that the NSOM images do not exhibit one to one correspondence between the topographic images. The lack of correlation between the NSOM images and topography can be explained if the films are not composed of single-domain layers along their thickness. However, the film thickness (100 nm) is less than the domain size (400 nm). Thus, we ruled out the probability of the existence of more than one layer in the film thickness. Further studies using time-resolved PL should provide more insight on the near-field results.

Time-resolved fluorescence measurements were carried out using time-correlated single-photon counting. The time resolution of the instrument was 100 ps. The samples were excited by 395 nm radiation, which is near the absorption peak of PPV copolymer. Experiments were first performed on the samples containing only one type of polymer. These results provided a basis for understanding the more complicated behaviors of blend films. In addition, the intra vs. inter-chain effects were studied by polymers in solution and in thin-film phases. Both PPV copolymer and PdOPV behave very differently in the condensed phase and in dilute solution phase. While PPV copolymer in dilute solution shows the fluorescence lifetime of 1.1 ns. The thin-films exhibit wavelength dependent fluorescence dynamics. The decay of thin films at 480 nm can be fitted by two exponential with lifetimes of 0.3 and 0.9 ns, respectively. For PdOPV, the fluorescence lifetime is about

Fig. 2. Transmission NSOM and topographic images of the blend films. The blend ratios of PPV copolymer to PdOPV are (a) 1 : 1 and (b) 14 : 1, respectively. The dimension of the scan area is $2\ \mu\text{m} \times 2\ \mu\text{m}$.

0.5 ns in dilute solution. The decay dynamics in the thin-film phase can be fitted by two exponential functions with lifetime of 0.2 and 0.6 ns, respectively. These results indicate that in the condensed phase, additional non-radiative channels due to inter-chain interactions decrease the fluorescence lifetime.

Fig. 3 shows the fluorescence decay dynamics of samples with different blend ratios monitored at (a) 480 nm, near the fluorescence peak of PPV copolymer, and (b) 580 nm, the fluorescence peak of

PdOPV. The fluorescence dynamics represent the relaxation of excited states in PPV copolymer (480 nm) and PdOPV (580 nm), respectively. Note that the fluorescence dynamics in pure PPV copolymer films (solid line) exhibits a fast initial relaxation time of 0.3 ns, and a slow relaxation time of 0.9 ns. With a small concentration of PdOPV in the blend film (14 : 1 ratio), the relaxation in PPV copolymer exhibits a single exponential behavior with lifetime of 0.5 ns. This is different from the complicated behaviors in PPV copolymer films. In

Fig. 3. The fluorescence decay of blend films measured at the emission peak of (a) PPV copolymer (480 nm) and (b) PdOPV (580 nm). Note that in (b) the vertical scale is the absolute intensity of fluorescence. The three curves correspond to different blend ratios of PPV copolymer and PdOPV as – 1 : 1 (dash line), 14 : 1 (dot square), and pure PPV copolymer (solid line), respectively.

particular, the relaxation is slower than the initial decay in PPV copolymer films. This result implies that the presence of a small amount of PdOPV prohibits the condensation of PPV copolymer. Compared to the pure copolymer film, the fluorescence intensity of 14 : 1 blend film at 580 nm appears to be increased. The PL decay at this wavelength is a single exponential relaxation with lifetime of about 0.5 ns.

With further increase in the concentration of PdOPV, the relaxation in PPV copolymer became faster. Shown in Fig. 3, the decay dynamics of 1 : 1 films can be fitted by two decay lifetimes of 0.2 and 0.6 ns. Note that the initial fast relaxation, that is similar to that in the pure PdOPV films, are observed in 4 : 1, and higher PdOPV ratio films. In

addition, the fluorescence at 580 nm exhibits the initial fast relaxation similar to that in pure PdOPV films. These results imply that (1) the energy transfer from PPV copolymer to PdOPV dominates the initial relaxation in PPV copolymer, and (2) there exists a phase with structure similar to that of pure PdOPV film in this film. In addition, at $t = 0$ ns, the fluorescence intensity of PdOPV in the 1 : 1 ratio film is only 3.5 times as large as that of 14 : 1 film. This result suggests more efficient energy transfer in the dilute blend films (14 : 1). It should be noted that the fluorescence dynamics of acceptor is not affected by energy transfer. The decay dynamics in PdOPV influences merely by the local structure of PdOPV. Hence, time-resolved fluorescence is a sensitive tool to investigate the local structure of PdOPV. On the other hand, the decay dynamics in PPV copolymer is influenced by the local structure of PPV copolymer, and the energy transfer to PdOPV. It is not easy to probe the local structure of PPV copolymer by time-resolved PL in this study.

A comparison of the NSOM images with the time-resolved fluorescence provides us some insight on the nanometer scale structures of the blend films. In the films with 14 : 1 ratio, the domains appear to have formed with different constitutions. However, neither PPV copolymer nor PdOPV are in condense phase. This suggests that the domains are constituted of different fractions of the two polymers. In the film with higher PdOPV ratio, PdOPV forms the condense phase.

Recently, atomic force microscopy was used to probe the phase separation of non-conjugated polymer blend films [12]. Since AFM really measures the surface roughness, it is interesting to investigate the correlation between the surface roughness and optical signal variation. Fig. 4 shows the surface roughness and optical signal contrast of various blend films measured by the NSOM. Both contrasts were calculated from the root mean square of the whole scan area. The data shows that the trends of the changes are the same for both contrasts. The 4 : 1 film exhibits higher contrast than the other blend films. Since concentration variation as well as surface-roughness contributes to the optical signal, the optical contrast represent the combined effects of constituent and

Fig. 4. The surface roughness and optical signal contrast as a function of blend ratio. The contrasts were calculated from the root mean square of the whole areas.

surface-roughness variations. However, the surface roughness and optical images are not one-to-one correspondence (see Fig. 2). The fact that optical and surface contrasts vary the same way indicates that in average, the constituent and the surface-variations change the same way.

In conclusion, phase separations in conjugated polymer blend films were observed. The domains are composed of different fractions of the two constituent polymers. The composition as well as structure of the domains, vary with the blend ratio.

In the film of 4 : 1 ratio, surface roughness and optical contrast are higher than the other blend films. In addition, in the film with low PdOPV concentration (14 : 1), two polymers are mixed homogeneously. As the concentration of PdOPV increases, condensed phase of PdOPV is formed.

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