

Correlation between Energy Transfer and Phase Separation in Emissive Polymer Blends

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Poly(phenylene vinylene) (PPV) is the first conjugated polymer used in the light-emitting devices.¹⁻⁶ However, the polymer is insoluble, intractable, infusible, and thus cannot be easily processed by the conventional spin-coating. One of the most studied PPV derivatives which are soluble in organic solvents is poly[2-methoxy-5-(2'-ethyl)hexoxy-1,4-phenylenevinylene] (MEH-PPV).^{7,8}

Significant enhancement in the efficiency of light emission can be achieved by blending two emissive polymers.⁹⁻¹¹ In particular, the quantum efficiency of MEH-PPV was highly improved by blending with the blue-emissive poly[1,3-propanedioxy-1,4-phenylene-1,2-ethylene-(2,5-bis(trimethylsilyl)-1,4-phenylene)-1,2-ethylene-1,4-phenylene] (DSiPV).¹²⁻¹⁴ The blend systems showed light emission from MEH-PPV with enhanced efficiency without any emission from DSiPV. The relative quantum efficiencies increased, reaching the maximum for the weight ratio of MEH-PPV:DSiPV = 1:15, of which the electroluminescence was almost 500 times larger than that of the sole MEH-PPV, even though the threshold voltages in the blend systems became larger as the composition ratio of DSiPV was increased. The picosecond time-resolved fluorescent decay profiles of the blend polymers showed that the decay lifetime of MEH-PPV was increased with the weight fraction of DSiPV.¹⁵ These indicate that the energy transfer between the two polymers is enhanced and the intermolecular quenching is reduced with increasing the weight ratio of DSiPV, thus the emission intensity from MEH-PPV is increased.

In order to fully understand the blending in the light emission of the polymers, more systematic approach is required. Poly[1,8-octanedioxy-1,4-phenylenevinylene-2-methoxy-5-(2'-ethyl)hexoxy-1,4-phenylenevinylene] (MEH-DPV), which is analogous to the blue-emissive polymer previously reported by Zyung *et al.*,¹⁶ was synthesized in our laboratory (Figure 1). The only difference between the two polymers is the length of the non-conjugated segment: the non-conjugated hydrocarbon of MEH-DPV consists of eight methylene groups while that of the reported analog consists of three methylene groups. The increased hydrocarbon chain length of the non-conjugated segment improves solubility of the polymer but lowers the glass transition temperature. The blend films composed of MEH-PPV and MEH-DPV showed photoluminescence (PL) originated from either MEH-PPV or both of the polymers, depending on the relative ratio of the two components. This observation could be explained in

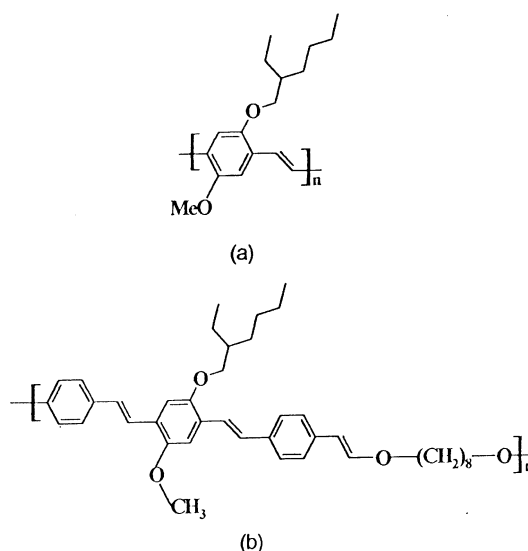


Figure 1. Chemical structures of (a) MEH-PPV and (b) MEH-DPV.

terms of the phase separation or miscibility of the two polymers in the blend surface, which is dependent on the ratio of the two components.

Experimental Section

Measurements. The chemical structures of the synthesized compounds were verified by using the JASCO FT-infrared spectrophotometer and the JEOL-JMN EX-400 (400MHz) NMR spectrometer. Thermal transition and degradation of the polymers were measured by employing a differential scanning calorimeter (DuPont TA2100). The absorption spectra of the samples were obtained with an UV-visible spectrophotometer (Hewlett and Packard 8452A diode array). The PL spectra of polymer films were obtained with the JOBIN-YVON double monochromator (He-Cd, 325 nm, 30 mW). Surface phases of the polymer blends were studied by lateral force microscopy (LFM, PSI auto-probe LS).

Synthesis. 2,5-Bis(chloromethyl)-1,4-[methoxy-(2'-ethyl)hexoxy]benzene was prepared and polymerized in the presence of potassium *t*-butoxide in tetrahydrofuran (THF) to obtain the MEH-PPV as a red solid.¹⁷ MEH-DPV was also synthesized by employing the procedure reported previ-

ously¹⁶, and obtained as a yellow solid by precipitating the reaction mixture from methanol. The number- and weight-average molecular weight of the MEH-DPV were determined with gel permeation chromatography (calibrated with polystyrene in THF) to be 7,000 and 13,000, respectively.

Preparation of polymer films for measurements. Polymer blend solutions were prepared by dissolving two different polymers in various weight ratios in chloroform. For absorption spectra, the polymer solutions (0.1 wt%) were cast on an UV quartz cell and dried in air. For PL spectra, the polymer solutions (0.5 wt%) were cast on glass plates, dried in air, and further dried in a vacuum oven at 40 °C for 7 h. For the LFM experiment, the blended polymer solutions (0.1 wt%) were cast on indium-tin-oxide coated glass at 2000 rpm for 30 s, dried in air, and further dried in a vacuum oven at 40 °C for 7 h.

Results and Discussion

The FT-IR spectrum of the MEH-DPV showed that the characteristic absorption peaks at 1700 and 2730 cm^{-1} for the aldehyde groups in 1,8-bis(4-formylphenoxy)octane almost disappeared, whereas a new peak at 959 cm^{-1} appeared (data not shown). This indicates that the polymerization reaction was nearly completed and the conformations of MEH-DPV are mainly *trans*-vinylene. Differential scanning calorimetry (DSC) revealed that the MEH-DPV undergoes the glass and the melting transitions at 40 °C and 112 °C, respectively. Thermal gravitational analysis showed no significant weight loss up to 400 °C, indicating that the polymer is thermally quite stable.

The energy transfer in the blends usually occurs from the material with larger $\pi \rightarrow \pi^*$ gap (acting as a donor) to the material with smaller $\pi \rightarrow \pi^*$ gap (acting as an acceptor). The energy transfer rate is also of crucial importance in determining its efficiency. The rate constant of the energy transfer can be expressed by the following equation which is based on the Forster theory,^{18,19}

$$k = (1/\tau)(R_0/R)^6,$$

where R is the distance between the two chromophores, and τ is the fluorescence lifetime of the donor in the presence of the acceptor. The R_0 is the characteristic transfer distance, which is related to the spatial overlaps between donor emission and acceptor absorption. Thus, in general, the energy transfer between donor and acceptor chromophores in the polymer blends depends on both the intermolecular distance between the donor and acceptor molecules and the spectral overlap between the donor emission and acceptor absorption.

The optical absorption and PL spectra of the MEH-DPV films are shown in Figure 2(a). The MEH-DPV film shows the $\pi \rightarrow \pi^*$ transition peak at 410 nm with the edge at 450 nm, and the emission peak at 498 nm, which is almost the same as the reported analog.¹⁶ The spectral overlap of the MEH-DPV emission with the MEH-PPV absorption is clearly shown in Figure 2(b). One can see a considerable

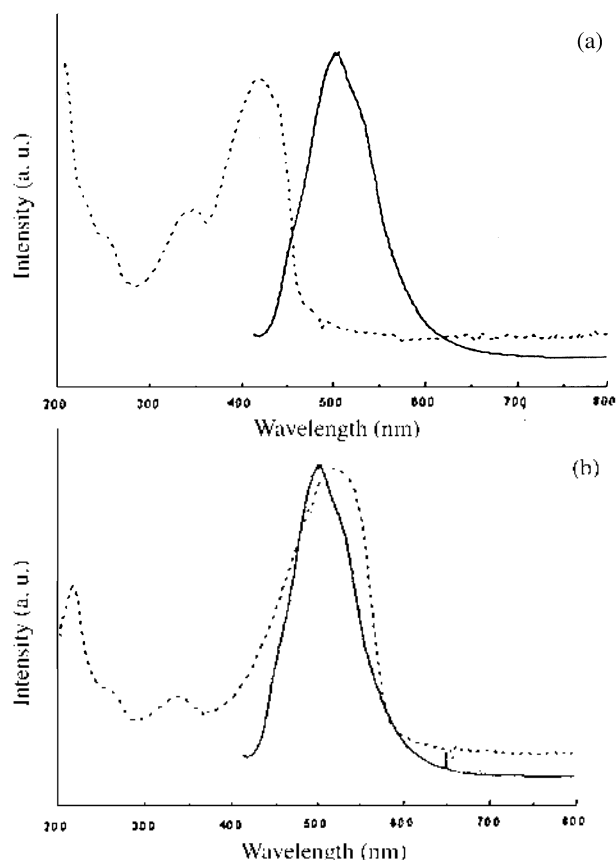


Figure 2. (a) The optical absorption (···) and PL (—) spectra of MEH-DPV. (b) the MEH-PPV absorption (···) with MEH-DPV emission (—)

overlap between the MEH-DPV emission and the MEH-PPV absorption. This suggests that the energy transfer may occur from the excited MEH-DPV (donor) to MEH-PPV (acceptor) in the ground state as long as the distance between the two chromophores is short enough in the blend films.

Figure 3 shows the PL spectra of the blended polymer films composed of MEH-PPV and MEH-DPV in different ratios. The blend film of the two polymers in equal amounts shows a PL maximum at 590 nm corresponding to the emission of MEH-PPV, indicating that the energy transfer occurs from the photo-excited MEH-DPV to MEH-PPV. However, when the ratio of the two components is 1 : 2 or greater, the blended polymer films show two emission maxima at about 500 and 620 nm corresponding to the emissions originated from MEH-PPV and MEH-DPV, respectively. This result indicates that the energy transfer between the two polymers is prohibited in the blend films containing such high fractions of MEH-DPV. The absence of the energy transfer between the two different polymers may be due to the possible micro-phase separation in the blends such that the spatial overlaps are minimized.

As mentioned above, the spectral overlap between the MEH-DPV emission and the MEH-PPV absorption seems to be large enough for the energy transfer to occur. However, in the blends of MEH-DPV and MEH-PPV, the energy

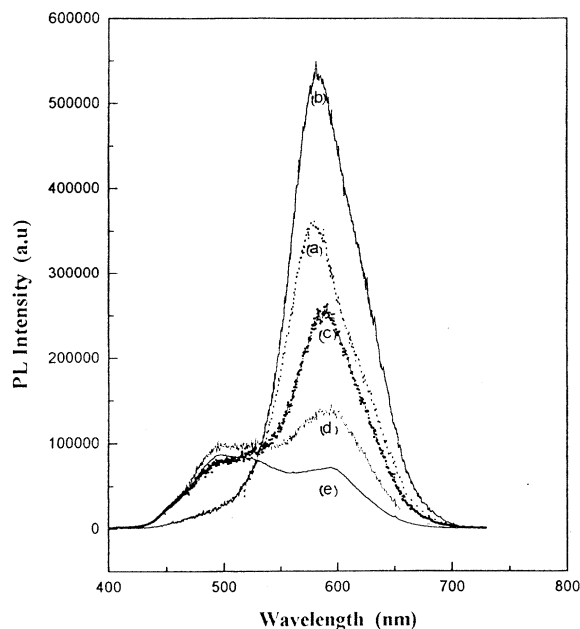


Figure 3. PL spectra of the blended polymer films composed of MEH-PPV/MEH-DPV in different ratios: (a) 1/0, (b) 1/1, (c) 1/2, (d) 1/9, and (e) 1/15.

transfer occurred only when MEH-DPV : MEH-PPV is 1 : 1 among the blending ratios employed. This suggests that the spatial overlaps also play a crucial role in the energy transfer. One may speculate that MEH-DPV and MEH-PPV are not homogeneously mixed and phase-separated in the blends except when the two polymers are blended in equal amounts.

In order to confirm the correlation between the spectral overlaps and spatial overlaps, *i.e.*, the phase separation in the blend systems, LFM was employed. The LFM image in Figure 4(a) shows that the surface of the blend film appears to be relatively homogeneous when MEH-PPV and MEH-DPV are blended in equal weight ratio. However, one can clearly see that the film surfaces are not homogeneous when the weight ratio is 1 : 2 or greater. This trend is exactly correlated to the PL spectra in different weight ratios of the two polymer blends. Thus the PL enhancement by the energy transfer can be observed when the spectral overlaps between donor emission and acceptor absorption take place, and simultaneously the blending materials are reasonably well-mixed at least at the film surface such that the rate constant, k , can be maximized by the spatial overlaps.

The LFM images, however, represent the only surface morphology of the films, and may not be sufficient for evaluation of the miscibility of the bulk materials. Thus, DSC experiment was carried out to see how the melting transition of MEH-DPV is affected by MEH-PPV in the blend since the endothermic transition peak is clearly seen in the thermograms (data not shown). The appearance of the transition peak as well as the transition temperature range of MEH-DPV was not much altered by incorporation of MEH-PPV even though the transition peak size decreased progressively as the proportion of MEH-DPV in the blends decreased.

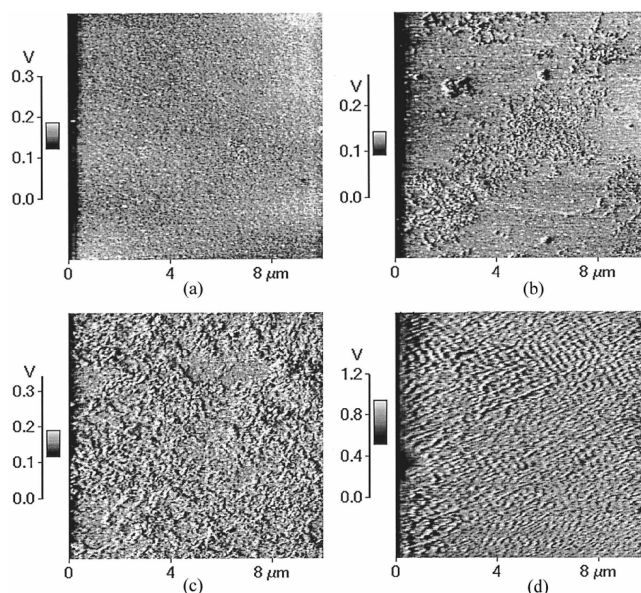


Figure 4. LFM images of blended films composed of MEH-PPV/MEH-DPV in different ratios: (a) 1/1, (b) 1/2, (c) 1/5, and (d) 1/9

This result suggests that the two polymers in the bulk are not mixed and phase-separated.

However, as the proportion of MEH-DPV in the blends was decreased, the transition enthalpy of MEH-DPV component was also decreased significantly. If there is no interaction between the two polymers, the transition enthalpy of MEH-DPV should be unchanged. This means that the two polymers in the bulk interact each other somehow such that the melting transition of MEH-DPV is prohibited and the degree of prohibition is dependent on the proportion of MEH-PPV. When the two polymers are present in equal amounts, the interaction between the two polymers may be so much that they may be relatively well-mixed enough for the energy transfer to occur at the film surface, because the PL occurs nearly at the surface of the film. Furthermore, the miscibility at the film surface could be different from that in the bulk due to the tendency of the surface to possess a minimized surface free energy.

In conclusion, we prepared a new blue-emissive polymer, MEH-DPV, in order to see the PL enhancement of the MEH-PPV in the blends of the two polymers. However, the PL of the MEH-PPV was enhanced only when the two polymers were blended in equal amounts, and the blend polymer films containing higher ratios of the MEH-DPV showed two PL maxima corresponding to each component. The LFM revealed that the surface of the polymer films is relatively homogeneous when the two polymers were mixed in equal amounts while the film surfaces appeared to be phase-separated when MEH-DPV is present in larger amounts than MEH-PPV, even though the two polymers in the bulk are phase-separated in all the composition ratios employed. Thus we clearly demonstrated that the correlation between the surface phase miscibility and the spectral overlap between donor emission and acceptor absorption plays a crucial factor to enhance the PL efficiency in polymer

blends.

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