A Two-Species Model of Polymer Morphology: Implications for Electroluminescent Polymer Design and Processing

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The luminescent efficiency of conjugated polymer films has been shown to depend heavily on processing conditions [1], making it clear that packing of the polymer chains in the solid state is an important factor in their excited state behavior. We have done systematic studies of how the photophysics of model phenylene vinylene polymers varies as the morphology is varied in solution by deliberate introduction of a poor solvent that induces aggregation [2]. The resulting changes in spectroscopy and luminescence quantum yield provide us with insight into what are desirable and undesirable chain configurations and how to adjust processing conditions to obtain them in films. Moreover, an understanding of the spectroscopy gives us an excellent diagnostic for the quality of a film without complex measurements of solid state quantum yields.

Figure 1 illustrates the effect of mixing a poor solvent with a good one in solutions of MEH-PPV that have been adjusted to have the same absorbance at the excitation wavelength (400 nm). The poor solvent causes chain aggregation that results in a red shift and threefold reduction in fluorescence quantum yield. This is typical of films of MEH-PPV relative to solutions in good solvents. Based on analogous results with trimers of MEH-PPV that are too short to fold, we believe the red shift and quantum yield decreases are both due to multiple chain aggregation rather than conformational changes in single chains. What is surprising is that the spectrum in mixed solvents can be perfectly decomposed into linear combinations of the emission spectrum in the good solvent and that in the poor solvent. This is also true of the absorption spectra [4].

Our explanation of these phenomena is as follows. The red shift is a result of increased conjugation length caused by packing-induced steric hindrance of the phenyl ring torsional motion that otherwise limits the π orbital delocalization. The reduction in quantum yield has to do with the formation of interchain species in high quantum yield that relax nonradiatively when the chains are aggregated [5].

Evidence that the sample can be viewed as merely two independently addressable conformations of polymer rather than a broad inhomogeneous distribution is provided by Figures 2 and 3. In figure 2, we show that the bluest part of the luminescence in a mixed solvent sample (540 nm) can only be excited by a spectrum considerably bluer than the absorption. Excitation spectra monitored at various places in the red are identical since these correspond primarily to emission from aggregated regions. Neither excitation spectrum matches the absorption which is composed of both species. A more dramatic confirmation of the two species concept is provided by Figure 3 where the luminescence stimulated by a 550 nm "dump" beam in a mixed solvent sample does not resemble the sample's emission spectrum but rather that of a polymer in a good solvent. Only the species that can emit at 550 nm are affected and these are the fraction that are not aggregated, their spectrum being like those in a good solvent. Further studies of excited state decay dynamics and single chain spectroscopy [6] confirm our basic picture. We will discuss how this information can be used as a film diagnostic and as a basis for emissive polymer design.

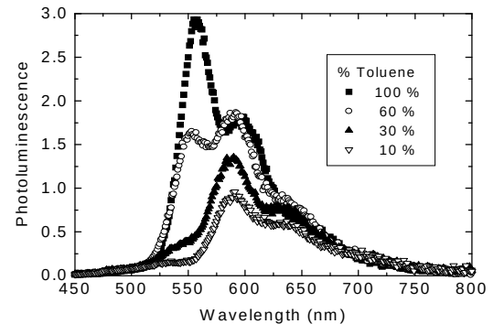

Figure 1. Photoluminescence spectra of MEH-PPV in mixed solvents of toluene and hexane. The concentrations of polymer are adjusted so that absorbances are equal at 400 nm, the excitation wavelength.

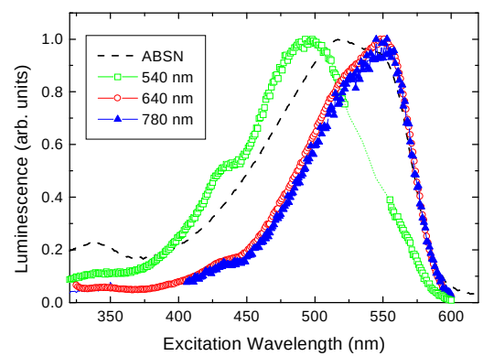

Figure 2. Photoluminescence excitation and absorption spectra of MEH-PPV in 60 % toluene/40 % hexane.

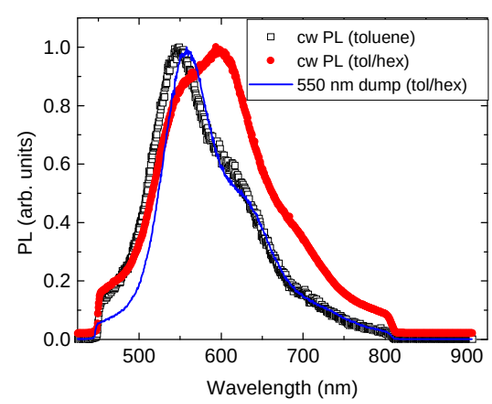

Figure 3. Steady state emission spectra of MEH-PPV in toluene and 60 % toluene/40 % hexane solvents compared with the stimulated emission depleted photoluminescence spectrum of the mixed solvent sample. Stimulated emission dump pulse is 100 fs duration with wavelength of 550 nm and 5 ps after 100 fs, 400 nm excitation.

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