

Solid-state-concentration effects on the optical absorption and emission of poly(*p*-phenylene vinylene)-related materials

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We present measurements of the optical absorption and emission properties of poly(*p*-phenylene vinylene) (PPV)-related materials focusing on the differences between molecules isolated by dispersion in an inert host and concentrated molecular films. Optical absorption spectra, photoluminescence (PL) spectra, PL efficiency, and time-resolved PL spectra of dilute blends of PPV oligomers with 2–5 phenylene-phenyl rings are compared with those of dense oligomer and polymer films. In dilute oligomer-poly(methyl methacrylate) (PMMA) blends with high PL efficiency, the PL decay is exponential, independent of both temperature and oligomer length. This implies that the fundamental radiative lifetime of PPV oligomers is essentially independent of oligomer length. Concentrated spin-cast oligomer films and polymers have a faster and strongly temperature-dependent PL decay that approaches that of the dilute oligomer results at low temperature. The differences in PL decay correspond to changes in PL efficiency. The efficiency of the oligomer-PMMA blend is high and only weakly temperature dependent, whereas that of concentrated films is lower and strongly temperature dependent, decreasing by more than a factor of 3 from 10 to 350 K. The quenching of the PL efficiency in concentrated films is due to migration to extrinsic, impurity related centers as opposed to an intrinsic intermolecular recombination process. The PL spectrum of a dilute oligomer blend redshifts substantially, both as the excitation energy is decreased and as the emission time increases. This spectral redshift is due to disorder-induced site-to-site variation and not to diffusion to lower-energy sites. In contrast, no spectral shift with excitation energy or emission time was observed for dense oligomer films. [S0163-1829(96)03132-3]

I. INTRODUCTION

Since the invention of efficient, low-molecular-weight, organic light-emitting diodes (LED's) by Tang and Van Slyke¹ there has been considerable progress toward using organic materials for display applications.² Polymer-based organic LED's were discovered by Burroughes *et al.* some years later and have stimulated a new wave of interest in this field.³ Polymer devices have now been demonstrated with internal quantum efficiencies of up to 4%,⁴ operating voltages below 5 V, emission wavelengths throughout the visible spectrum,^{3–7} and operating lifetimes beyond 1200 h.⁸ The simplest organic LED's consist of a thin, light-emitting organic film sandwiched between two metal electrodes. Even in these structures there is a need for a better understanding of the mechanisms of operation and methods to control the electrical and optical properties of the organic film to optimize charge injection, charge transport, charge recombination, and light-emission processes.

In this work we focus on the optical absorption and emis-

sion properties of dilute blends and concentrated, spin-cast films of a series of poly(*p*-phenylene vinylene) (PPV) oligomers and compare these results with those of pure polymer films. By studying dilute blends of oligomers we distinguish the intrinsic properties of isolated molecules from those effects involving intermolecular interactions. Since conjugated polymers generally contain conformational defects that effectively segment the polymer into a set of smaller conjugated units, investigating the properties of the oligomers as a function of their length and concentration provides a basis to understand the properties of related polymer materials.

In dilute oligomer-poly(methyl methacrylate) (PMMA) blends with high photoluminescence (PL) efficiency, the PL decay is exponential, independent of both temperature and oligomer length. Thus the fundamental radiative lifetime of PPV oligomers is essentially independent of oligomer length. By contrast there is a substantial redshift of the absorption and emission energies as a function of oligomer length. Concentrated spin-cast oligomer films and polymers have a faster and strongly temperature-dependent PL decay that ap-

proaches that of the dilute oligomer results at low temperature. The differences in PL decay correlates with changes in PL efficiency. The efficiency of the oligomer-PMMA blend is high and only weakly temperature dependent, whereas that of concentrated films is lower and strongly temperature dependent, decreasing by more than a factor of 3 from 10 to 350 K. The quenching of the PL efficiency in concentrated films is due to migration to extrinsic, impurity related centers. The PL spectrum of a dilute oligomer blend redshifts substantially, both as the excitation energy is decreased and as the emission time increases. This spectral redshift is due to disorder-induced site-to-site variation and is not due to diffusion to lower-energy sites. No spectral shift with excitation energy or emission time was observed for dense oligomer films.

Poly(1,4-phenylene vinylene) (PPV) and poly[2-methoxy, 5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) polymers have properties characteristics of both oligomer blends and concentrated oligomer films. The PL lifetime and efficiency of PPV is similar to that of the concentrated oligomer films, while MEH-PPV is analogous to the isolated oligomers in PMMA blends. MEH-PPV, with its bulky side groups that serve to isolate the polymer chains, behaves more like the oligomer blend samples than PPV for which no side groups are present.

The paper is organized as follows. Section II describes the materials studied, their chemical synthesis, the film forming procedures, and the apparatus used in obtaining the absorption and emission spectra. Section III reviews the basic properties of the investigated materials and presents the absorption, PL spectrum, PL transient decay, and integrated PL intensity of dilute blends and concentrated films. Section IV discusses these results in the context of disorder and the degree of interaction among the molecular sites. Section V summarizes the paper.

II. EXPERIMENTAL APPROACH

We investigated the properties of *trans*-stilbene, PPV oligomers containing between three and five phenylene-phenyl rings and with tertiary butyl substituents at the 3 and 5 positions of the terminal phenyl rings (OPV), MEH-PPV, and PPV. The chemical structure of the oligomers is shown in the inset of Fig. 1. PMMA was used as the host material for the oligomer blends.

The shortest oligomer, *trans*-stilbene, was purchased from Aldrich. The synthesis of the *t*-butyl substituted oligo(phenylene vinylene) with between three and five phenylene-phenyl rings is described elsewhere.⁹ The MEH-PPV was synthesized by treating 1-methoxy, 4-(2-ethylhexyloxy), 2,5-bis-(chloromethyl) benzene in the presence of 10 mol % anthracene with a threefold excess of potassium-tert butoxide in anhydrous tetrahydrofuran at 0 °C for 18 h followed by precipitation into methanol. Poly(*p*-phenylene vinylene) was prepared via the standard tetrahydrothiophenium leaving-group precursor polymer.¹⁰

Films of oligomer-PMMA blends, 0.5–1.5 μm thick, were spin cast from tetrahydrofuran (THF) solutions [0.1 wt % *trans*-stilbene or 1 wt % oligomer ($n=3-5$), 10 wt % (PMMA)] onto sapphire substrates. Only homogeneous

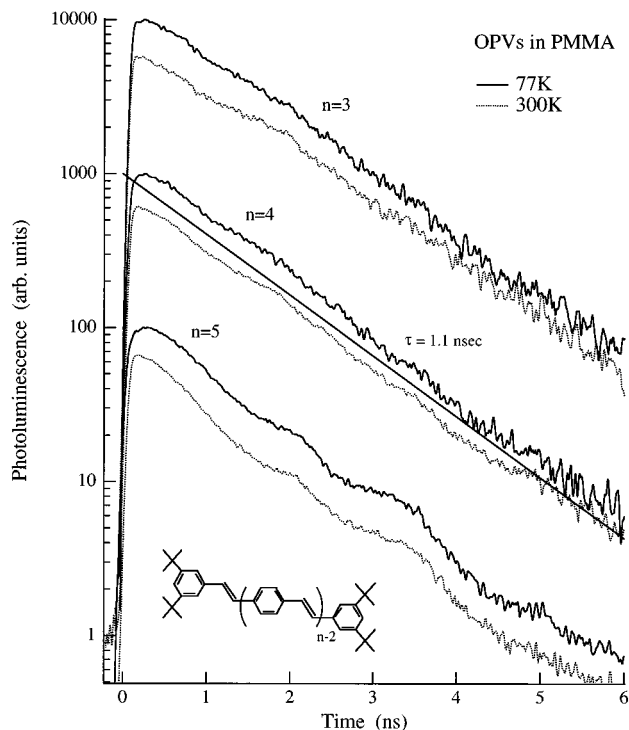


FIG. 1. Transient photoluminescence decay at 77 and 300 K of films of OPV- (with $n=3-5$) PMMA blends. The curves are displaced for clarity. The chemical structure of the oligomers is shown in the inset.

blends were investigated. Due to their low solubility homogeneous blends could not be produced from oligomers with six or more phenylene-phenyl rings. Pure oligomer films, 30–70 nm thick, were spin cast from THF solutions (1–5 wt % oligomer). Thin films of MEH-PPV, 100 nm thick, were spin cast onto sapphire or infrasil substrates from *p*-xylene solutions (1–2 wt % polymer). PPV films were prepared by thermal conversion of films of precursor polymers spin-cast from methanol solutions. The conversion to PPV was performed under dynamic vacuum at 250 °C for 12 h. Pure films of PPV oligomers and PPV are polycrystalline with crystal sizes of the order of 10 nm for PPV.¹¹ The oligomer blends and MEH-PPV were amorphous.¹² All samples were fabricated in an argon glove box and measured in vacuum cryostats preventing exposure to ambient oxygen and water.

Transient photoluminescence measurements were performed using the second harmonic of a model-locked Ti:sapphire laser producing 100-fs pulses at 100 MHz and a micro-channel plate mounted on a 0.75-m monochromator. The system response was roughly exponential with a decay time of 70 ps. The same setup was used with either phase-sensitive detection or photon-counting techniques for cw PL measurements. For photoluminescence excitation measurements outside the range of the second harmonic of the Ti:sapphire laser (2.75–3.1 eV), a setup consisting of a tungsten lamp, two 0.25-m monochromators, and a photomultiplier tube was used. The transient PL spectra have been smoothed and all spectra are corrected for system responses.

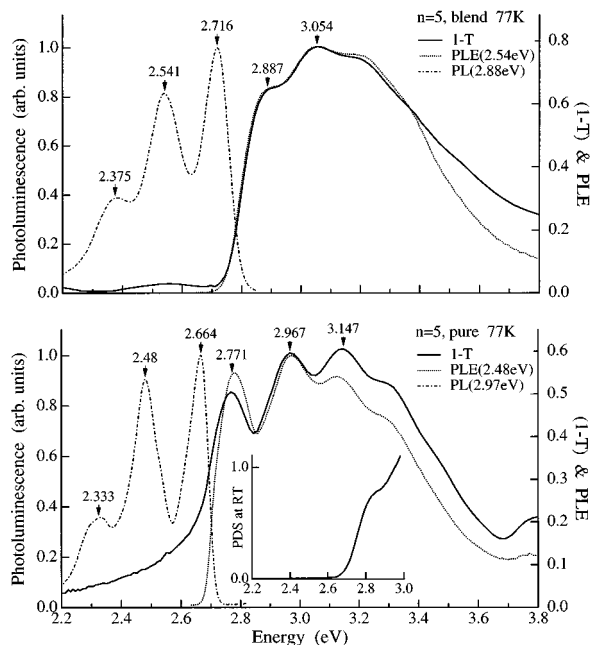


FIG. 2. Photoluminescence (left) and the complement of transmission ($1 - T$) and photoluminescence excitation (PLE) spectra (right) of thin films of an oligomer-PMMA blend (upper panel) and a concentrated oligomer film (lower panel) at 77 K. The PLE spectra have been scaled arbitrarily. The inset in the lower panel is the photothermal deflection spectrum of the pure film.

III. RESULTS

A. Basic properties

The optical spectra of the studied oligomers have been published previously.^{13,14} The absorption and PL spectra shift to lower energy with increasing oligomer length. The spectra have strong vibronic side bands and apparent Stokes shifts of approximately 0.15 eV. The effective Huang-Rhys factor of the PL spectra steadily decreases with increasing oligomer length, i.e., the relative oscillator strength of the zero-vibronic mode peak increases. For the absorption spectra the Huang-Rhys factor remains essentially constant.

The transient PL decays for blends of the $n = 3, 4$, and 5 oligomers are shown in Fig. 1 at both room temperature and 77 K. The weak structure in the decay curves is an artifact due to optical reflections. The PL lifetime of the oligomer-PMMA blends is exponential with a decay time of 1.1 ns. The PL decay is largely independent of both temperature and oligomer length.

B. Concentration effects

Figure 2 compares the optical absorption and emission spectra of an $n = 5$ oligomer when prepared as a dilute oligomer-PMMA blend (upper panel) and as a concentrated film (lower panel). The left curves show the PL spectra, the solid lines show the complement of the transmission ($1 - T$), and the dotted lines show the PL excitation spectra recorded at the peak of the first vibronic emission line. The spectra of the pure film have decreased linewidths; this is especially pronounced in the absorption spectrum. The apparent vibronic spacing increases from the blend (0.175 eV)

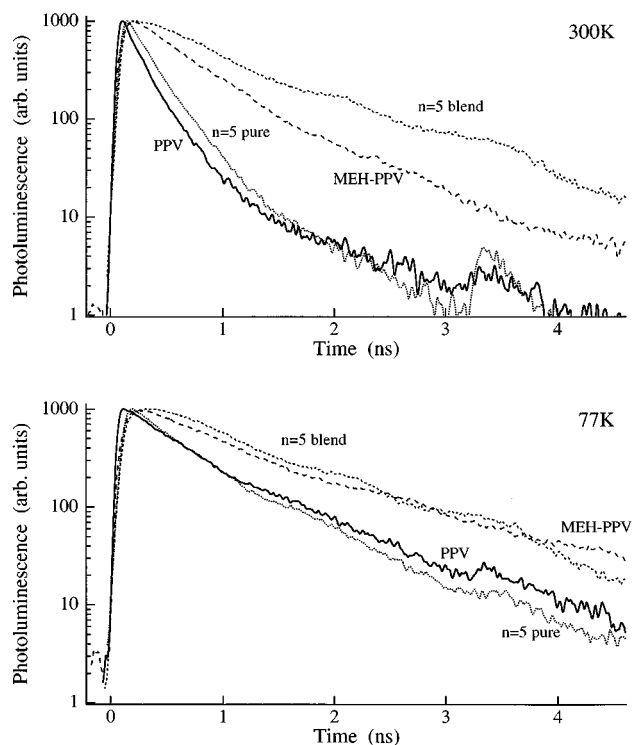


FIG. 3. Transient photoluminescence decay of a five-ring oligomer as a pure film and as a blend in PMMA, of MEH-PPV and of PPV, at 300 K (upper panel) and 77 K (lower panel). All curves are normalized to the same peak.

to the pure film (0.184 eV). There are several vibronic modes coupled to the electronic transition¹⁵ that are not resolved in these spectra and a redistribution of weight among the different contributing modes could cause the apparent peak shift. For the blend, the PL excitation spectrum is identical to the complement of the transmission except for photon energies below the absorption threshold and at very high photon energy. Below the absorption threshold, the transmission is modulated by interference effects in the thin film. At higher photon energies, the difference is due to reduced PL efficiency and/or to increased scattering. The pure film has a strong tail in the complement of the transmission for photon energies significantly below the absorption threshold that is not reproduced by the PL excitation spectrum. The photothermal deflection spectrum (PDS) of the pure oligomer films is shown in the inset of the lower panel. The photothermal deflection spectrum measures the heat produced by absorption and is therefore not sensitive to reflection or scattering. The absence of the low-energy tail in the PDS of the pure film indicates that the tail observed in the complement of the transmission spectrum of the concentrated film is due to a combination of reflection and scattering and does not correspond to absorption.

Figure 3 displays the transient PL decays of an $n = 5$ oligomer when prepared as a dilute oligomer-PMMA blend and as a concentrated film, MEH-PPV, and PPV at both 300 K (upper panel) and 77 K (lower panel). The behavior of the pure oligomer film and of the PPV film is similar. Unlike the exponential behavior of the oligomer-PMMA blends, they both exhibit a very fast initial decay followed by a much slower decrease. The initial decay is strongly temperature

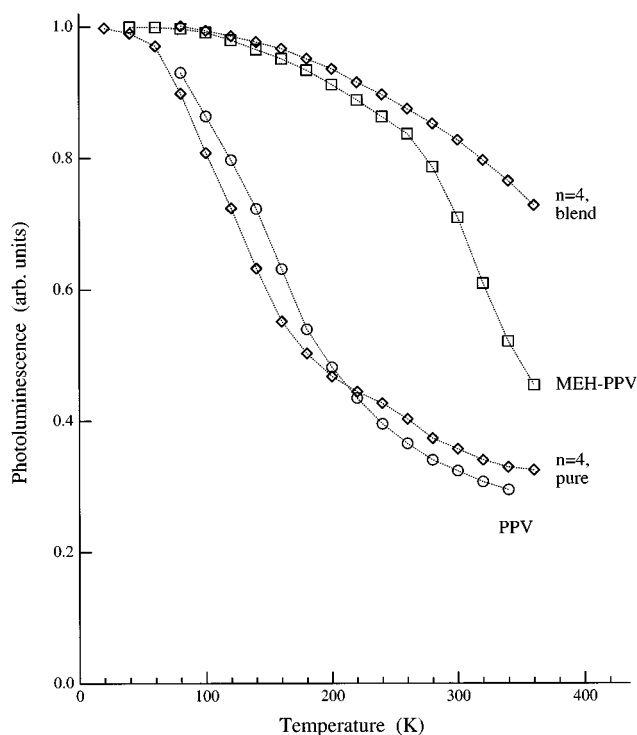


FIG. 4. Integrated photoluminescence intensity vs temperature for the $n=4$ oligomer as a pure film and as a blend, for MEH-PPV and for PPV.

dependent with a slope decay time of 0.23 and 0.47 ns at 200 and 77 K, respectively. The slope decay time at long times is roughly 1.4 ns, decreasing slightly at low temperature. The behavior of the MEH-PPV is intermediate between the dilute oligomer-PMMA blends and the concentrated oligomer and polymer films.

Figure 4 displays the temperature dependence of the spectrally integrated PL intensity of an $n=4$ oligomer when prepared as a dilute oligomer-PMMA blend and as a concentrated film, MEH-PPV, and PPV. The graphs are normalized to their intensity at 4 K;¹⁶ only the relative changes with temperature are significant. The smallest decrease in PL intensity with increasing temperature is observed for the oligomer blend. The PL efficiency decreases by less than 20% from 4 to 300 K. PPV and the concentrated oligomer film both exhibit a rapid decrease in PL efficiency above 60 K followed by a slower rate of decrease above 200 K. They both have about a 65% decrease in relative efficiency from 4 to 300 K. MEH-PPV exhibits features of both the oligomer blend and the concentrated film. Below 250 K, the change in PL efficiency is similar to that of the oligomer blend. Above 250 K, however, there is a sharp decrease in PL efficiency comparable to that seen in the pure films above 60 K.

C. Excitation energy dependence and redshift of the emission with time

Figure 5 shows the PL excitation spectra and a series of normalized PL spectra at different excitation energies for the $n=5$ oligomer both as a blend (upper panel) and as a pure film (lower panel), all at 77 K. The luminescence from the blend redshifts substantially as the excitation energy is de-

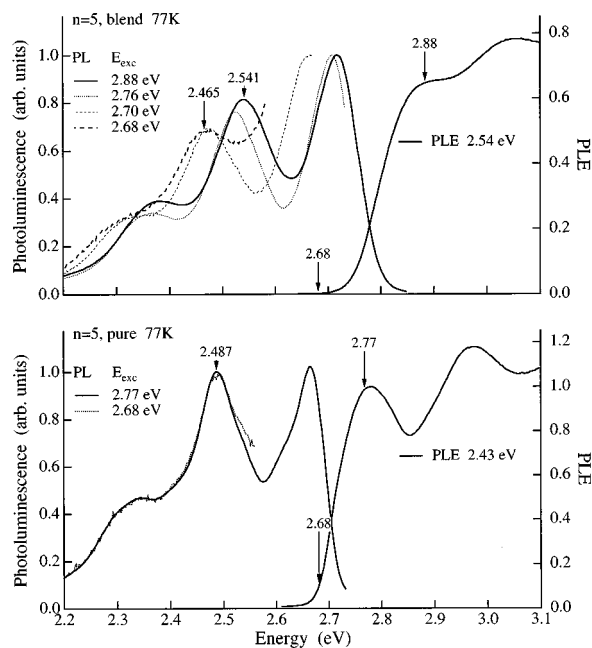


FIG. 5. Photoluminescence spectra of a blend (upper panel) and a pure film (lower panel) of a five-ring oligomer at various excitation energies at 77 K. The right curves show the photoluminescence excitation spectra for the indicated emission energies.

creased into the tail of the absorption. Changing the excitation energy from 2.88 eV (zero vibronic peak) to 2.68 eV (bottom of absorption edge) causes a shift of roughly 70 meV. No spectral shift is observed for the concentrated oligomer film.

The PL decay collected at the first vibronic peak emission energy of PPV oligomers dispersed in PMMA is exponential and independent of both temperature and oligomer length. As a function of emission energy, however, we observe non-exponential behavior. Figure 6 shows the transient PL decay of the $n=4$ oligomer in PMMA for three different emission energies at 77 K. There is a more rapid initial decay on the high-energy side (upper panel) of the first vibronic peak in emission and a slower initial decay for the luminescence on the low-energy side (lower panel). This nonexponential behavior corresponds to a redshift in the emission spectrum with time. Figure 7 shows PL spectra for four different emission time windows: 0.0–0.2, 0.2–0.5, 0.5–1.0, and 2.0–5.0 ns. The spectra are normalized to give the same intensity at the first vibronic peak. The first vibronic peak has redshifted by about 35 meV after a few nanoseconds. There is also a significant variation in the relative contribution of the vibronic sidebands. The spectra were computed by integrating time windows of a set of time decays measured at different emission energies.

IV. DISCUSSION

A. Radiative lifetime vs oligomer length

Knowledge of the fundamental radiative lifetime not only is important for estimating the PL efficiency from the observed PL decay time, but it is also directly related to the electronic structure of the organic molecule. The PL lifetime of the oligomer-PMMA blends with three to five phenylene-

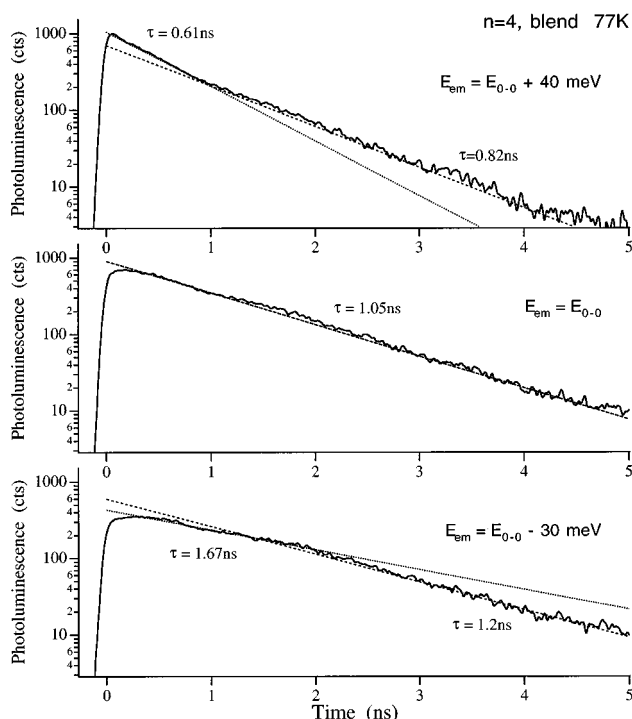


FIG. 6. Transient photoluminescence decay of a four-ring oligomer in PMMA at 77 K. The center panel shows the exponential decay with the emission collected at the first vibronic peak. The other panels show the effects of the transient redshift of the emission spectrum, when the emission is collected 40 meV above (upper panel) and 30 meV below (lower panel) the first vibronic emission line.

phenyl rings is exponential with a decay time of about 1.1 ns (Fig. 1). A decay time of 1.10 ns and a quantum efficiency of 94% was reported for the isopropyl-substituted three-ring oligomer in cyclohexane.¹⁷ Our measured lifetime is similar to these observations in related molecules where the PL efficiency was determined to be close to unity. This implies that the PL efficiency in the oligomer blends is also near unity and that the decay is determined by the intrinsic radiative lifetime of the oligomer molecule. For *trans*-stilbene, the radiative lifetime was indirectly determined to be approximately 1.5 ns in *n*-alkane solutions and followed a quadratic relation with the refractive index n .^{18,19} This leads to an estimate of 1.3 ns for blends in PMMA ($n \sim 1.5$). These results imply that the radiative lifetime is largely independent of oligomer length. By contrast there is a significant decrease of the absorption and emission energies of the oligomer molecules as the length of the molecule increases. The constant radiative lifetime coupled with the decrease in absorption and emission energies are facts that must be included in a description of the nature of the electronic states of the oligomer as a function of oligomer length.

B. Efficiency and quenching mechanisms

Because the PL efficiency of the emissive organic material gives an upper limit for the performance of LED's, investigating the causes of nonradiative quenching has been a major research interest.^{20–22} We argue that diffusion to

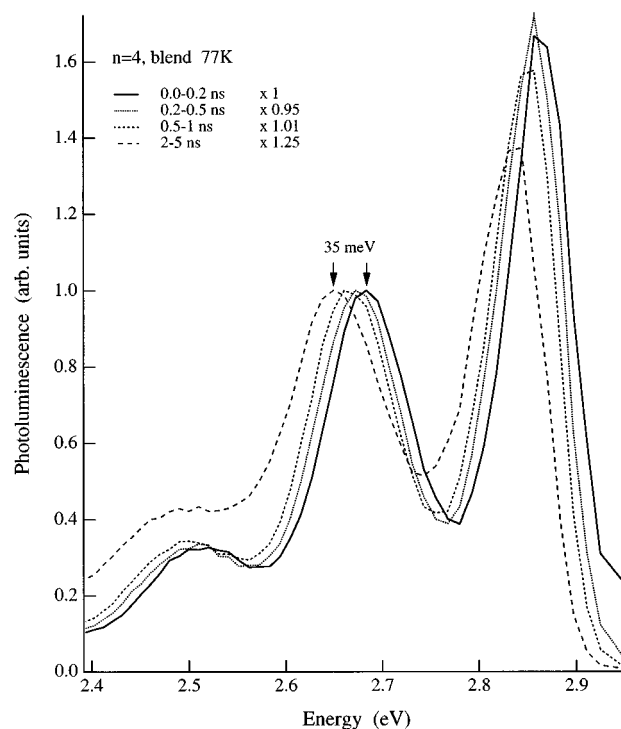


FIG. 7. Time-resolved photoluminescence spectra of a four-ring oligomer in PMMA at 77 K. The spectra were obtained by integrating the counts of a set of decay curves over the given time windows. The normalized factors for the time windows are indicated to the right of the legend.

impurity-related recombination centers is an important quenching mechanism in PPV-related materials.

Isolated oligomer molecules have high PL efficiency^{17,23} and an exponential PL decay independent of the oligomer length and nearly independent of temperature. In solid films of these molecules, high PL efficiency can be maintained only if there are few nonradiative recombination sites and/or if access to nonradiative sites is impeded. In concentrated spin-cast oligomer and PPV films, rapid, nonexponential PL decay is observed (Fig. 3) and the PL efficiency is strongly temperature dependent (Fig. 4). The rapid nonexponential decay and temperature-dependent PL efficiency are due to nonradiative recombination processes. Because isolated molecules do not act as nonradiative sites, quenching must arise from either an intrinsic intermolecular nonradiative process or from extrinsic nonradiative recombination centers. In vacuum evaporated five-ring PPV oligomer films, highly efficient PL with exponential decay times of 1.2 ns in both polycrystalline and amorphous films has been observed in our group.²⁴ This implies that intrinsic intermolecular nonradiative processes are not significant in these oligomers. The spin-cast films considered here contain significantly more impurities than the vacuum evaporated films; this suggests that the dominant nonradiative quenching mechanism we observe is impurity related.

The amorphous polymer MEH-PPV has properties of both the dilute blends and concentrated films. Below 250 K, its properties are similar to the oligomer blends. This implies that, at low temperatures, MEH-PPV can be viewed as a set of weakly interacting molecular units. At higher tempera-

tures, its PL decay and efficiency are similar to the concentrated films. This suggests that there is thermally activated diffusion to nonradiative sites. Since MEH-PPV consists of PPV chains with long side groups, the side chains may introduce an effective diffusion barrier between neighboring chains that is thermally overcome at higher temperatures. In analogy to the pure oligomer films, we suggest that diffusion to extrinsic impurities is the primary cause of the observed PL quenching.

C. Disorder and relaxation

In spite of significant progress in synthetic methods, conformational disorder continues to be a significant factor contributing to the properties of PPV-type materials. A comparison of the absorption spectra of conjugated polymers with that of related oligomers indicates that the polymers effectively consist of a set of segments of varying conjugation lengths. For PPV that is prepared by thermal conversion of a nonconjugated precursor, there is a smooth redshift of the absorption and PL spectra during conversion that is interpreted as the formation of longer conjugated segments. A similar argument is used to interpret the spectroscopic changes upon tensile drawing of thin films.²⁵

The effects of disorder are clearly evident in the PL properties of the oligomer blends. The PL spectra of the oligomer blends redshift upon lowering the excitation energy (Fig. 5) and in the time-resolved PL spectra, nonexponential decays are observed for emission energies on the flanks of the PL peaks (Fig. 6). These nonexponential decays correspond to a time-dependent spectral shift of the emission spectrum (Fig. 7). By contrast, the emission spectra of the concentrated oligomer films do not change with excitation energy (Fig. 5) or time. Since intermolecular diffusion is not important in the oligomer blends at 77 K, the observed excitation energy dependence of the PL spectra are due to site-specific disorder. A different molecular ensemble with different emission characteristics is excited as the excitation energy is changed. The time-dependent spectral shift seen in Fig. 7 implies either that there are small variations in the radiative lifetimes of the ensemble of disordered oligomer molecules or that there is a local relaxation of the excited molecules that takes place at the time scale of the PL decay. Intermolecular diffusion does occur in the concentrated oligomer films. The independence of the PL spectra on excitation energy observed in the concentrated oligomer films suggests that intermolecular diffu-

sion is faster than radiative recombination in these films so that emission occurs from the same low-energy molecular sites independent of the excitation energy. The PL shifts with excitation wavelength and with time seen in the oligomer blends is somewhat similar to that observed in pure PPV.²⁶ In PPV, these shifts have been attributed to diffusion, but disorder-induced variation in site energy and radiative lifetime may also play a role in determining the PL behavior of PPV.

V. SUMMARY

We presented measurements of the optical absorption and emission properties of poly(*p*-phenylene vinylene) and related materials focusing on the differences between molecules isolated by dispersion in an inert host and concentrated molecular films. Optical absorption spectra, PL spectra, and time-resolved PL spectra of dilute blends of PPV oligomers with between two and five phenylene-phenyl rings were compared with those of dense oligomer and polymer films. In dilute oligomer-PPMA blends with high PL efficiency, the PL decay is exponential, independent of both temperature and oligomer length. This implies that the fundamental radiative lifetime of PPV oligomers is essentially independent of oligomer length. By contrast, there is a substantial redshift of the absorption and emission energies as a function of oligomer length. Concentrated spin-cast oligomer films and polymers have a fast and strongly temperature-dependent PL decay that approaches that of the dilute oligomer results at low temperature. The difference in PL decay corresponds to changes in relative PL efficiency. The efficiency of the oligomer-PMMA blend is high and only weakly temperature dependent, whereas that of concentrated films is lower and strongly temperature dependent, decreasing by more than a factor of 3 from 10 to 350 K. The quenching of the PL efficiency in concentrated films is due to migration to extrinsic, impurity-related centers as opposed to an intrinsic intermolecular recombination process. The PL spectrum of a dilute oligomer blend redshifts substantially, both as the excitation energy is decreased and as the emission time increases. This spectral redshift is due to disorder-induced site-to-site variation and is not due to diffusion to lower-energy sites. In contrast, no spectral shift with excitation energy or emission time was observed for dense oligomer films.

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