Fluorescence from Conjugated Polymer Aggregates in Dilute Poor Solution

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Received: September 30, 1998; In Final Form: January 19, 1999

We examine a PPV derivative, viz. poly(2,5-dioctyloxy *p*-phenylene vinylene) (DOO−PPV) in poor solution. The solubility of DOO−PPV in toluene solution exhibits dramatic variation when cooled below room temperature. The fluorescence exhibits a characteristic red-shift emission spectrum during the cooling process. This fluorescence spectrum and the accompanying red-shift absorption spectrum suggest that the polymer forms dimer-like aggregates in dilute poor solution. The reduction in solubility also introduces a quenching effect. In comparing the photophysics of the film and the solutions, we can see that the films are comprised of individual polymer and interchain aggregates, but the fluorescence exhibits only the behavior of aggregates. At low temperature, additional light-emitting species result in spectral dynamics over several nanoseconds in the films. This indicates multiple emission species in polymer films.

1. Introduction

Light-emitting polymers, poly(*p*-phenylenevinylene) (PPV) and its derivatives, in the thin film phase attract great interest because of their electro-luminescence applications.[1,2] The luminescent properties of these phenylenevinylene polymers are very similar to those of aromatic dyes with one major difference: most dyes operate only in dilute solution. On the contrary, the polymers exhibit high fluorescence yields even in thin films. They show negligible concentration quenching, and hence exhibit superior performance.[3] Compared to those in dilute solution, the fluorescence of phenylenevinylene polymers exhibits a red-shift spectrum in thin film form. It is generally assumed that fluorescent species in polymer films are similar to those in dilute solutions, which both involve intrachain excitons.[4] This red-shift spectrum can be ascribed to an increase in effective conjugation length in solid films.[5] However, further investigation suggests another mechanism: the fluorescence of films appears to arise from interchain species rather than from intrachain species.[6−13] In particular, it is discovered that for CN−PPV, the film exhibits high fluorescence yield.[14,15] Accordingly, the fluorescence lifetime is longer in thin film phase than in a dilute solution.[6] Furthermore, the emission of the CN−PPV films is from interchain species, rather than from the intrachain excitons in dilute solution.[6,7] These results call for further investigation of the photophysical properties of CN−PPV aggregate states, with the goal of achieving higher fluorescence yields in thin film phase.[7,16−17] It is believed that the interchain emission is a special property of CN−PPV. Nevertheless, the absorption and fluorescence of oligo-phenylenevinylene films exhibit behaviors different from that of those in solutions.[8,9] For some oligomers, the behaviors in the condensed phase are found to be typical of dimer-like H aggregates, with parallel molecular alignment. Since phenylenevinylene oligomers exhibit aggregate effects in the condensed phase, it may be expected that interchain interactions also play important roles in its polymer counterpart.

In this paper, we present the photophysical studies of a symmetrically substituted PPV derivative, viz. poly(2,5 dioctyloxy *p*-phenylenevinylene), (DOO−PPV), in three different states: good solution, poor solution, and thin film. In some cases, such as with CN−PPV and PPyV,[13] there are sharp differences between intrachain and interchain emissions, which are observed in CW as well as in time-resolved fluorescence spectra. On the other hand, DOO−PPV exhibits only small differences in fluorescence spectra and dynamics between the thin films and solutions. It is difficult to directly compare the differences in these two phases. We show here that DOO−PPV forms interchain species in poor solution, even under dilute condition. From absorption and fluorescence spectra, these interchain species are identified as dimer-like aggregates. Furthermore, the film is compromised of both intrachain and aggregate species, while film emissions come mainly from the dimer-like aggregates. Even with similarity in PL spectrum, the fluorescence dynamics in poor solution exhibit different behaviors from those of films. This indicates that the aggregates suffer additional quenching in film, thereby reducing fluorescence efficiency. The low-temperature fluorescence of films exhibits wavelength-dependent dynamics on a nanosecond time scale. With longer delay time, an excimer-like emission spectrum appears. This implies the multiplicity of emission species in film.

2. Experimental Section

DOO−PPV is prepared following the procedure similar to that used by Holmes and co-workers[18] and Wudl and co-

10.1021/jp983921t CCC: $18.00
Published on Web 03/16/1999

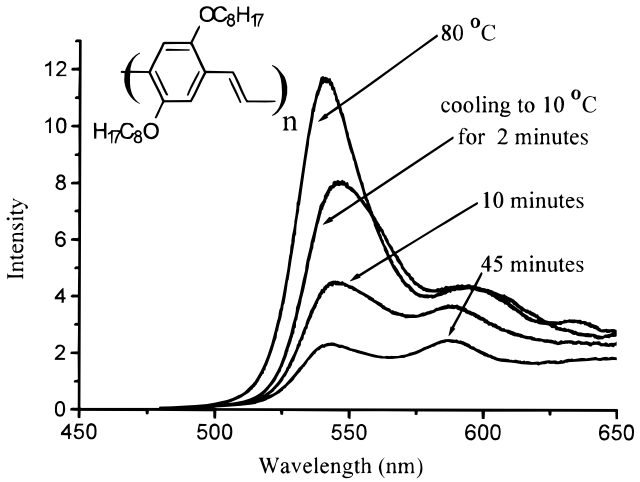

Figure 1. Fluorescence spectra in toluene at 80 °C, and after cooling to 10 °C after various time periods. The concentration is about 2×10^{-6} M monomer unit, which is 1/30 of that in Figure 2.

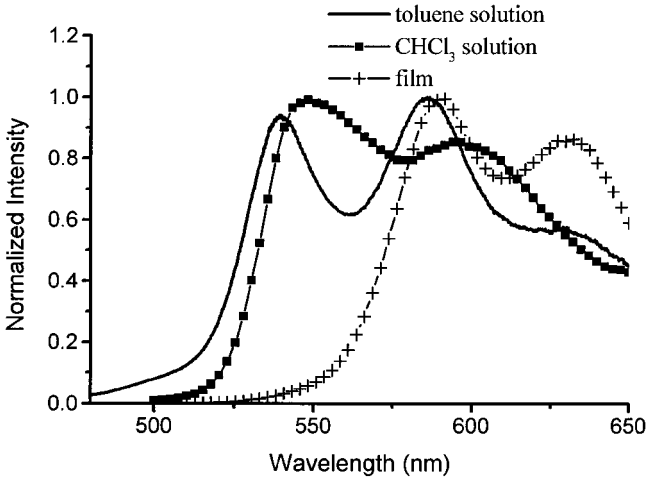

Figure 2. Fluorescence spectrum of DOO−PPV in toluene after cooling to 10 °C for 30 min. The spectra in the chloroform solution and in thin films are shown for comparison.

workers.[19] Using gel permeation chromatography (GPC), the molecular weight of DOO−PPV in chloroform solution is determined to be about 2 000 000. At room temperature, DOO−PPV cannot dissolve well in toluene. The dilute toluene solution is formed by mixing toluene with a few drops of chloroform solution. After nitrogen bubbling for a few minutes, the mixture is then placed in a hot-water bath to allow the polymer to be completely dissolved in toluene. To prepare the film, the polymer is dissolved in chloroform and then dip-coated or spin-coated on a glass substrate.

The absorption spectrum is recorded on a Hitachi U-3200 spectrophotometer under ambient conditions. DOO−PPV's fluorescence during the cooling of toluene is recorded on a Hitachi F-4010 fluorescence spectrophotometer. The steady-state fluorescence spectrum is recorded by a LN CCD based system. PL quantum yield is measured by a SPEX Fluorolog-3 fluorescence spectrometer with front-face collection method. Time-resolved fluorescence is recorded on a time-correlated single-photon counting apparatus with a time resolution of about 80 ps. The excitation power used is less than 0.3 mW (~4 pJ per pulse). The solution sample is exposed to nitrogen bubbling before the experiment. The polymer film is placed in a closed cycle cryostat under dynamic vacuum (better than 10^{-5} mbar) for various temperature experiments.

3. Results and Discussion

The solubility of polymer in a solution depends on its solvent and temperature.[20] At room temperature, DOO−PPV can be well dissolved in chloroform. In dilute chloroform solution, the fluorescence spectrum of DOO−PPV exhibits a peak at 550 nm, and a shoulder at 595 nm. However, the spectrum of the thin film shows two peaks, one at 585 nm and the other at 630 nm. They exhibit different vibration separations. The solubility of DOO−PPV in toluene exhibits dramatic variations near room temperature. As the temperature is raised slightly above room temperature, (~50 °C), the toluene becomes a good solvent. When the solution is maintained at room temperature for several hours, DOO−PPV forms fiber-like sediments. Eventually, most DOO−PPV accumulates at the bottom, and the upper part of the vessel contains a clear yellowish solution. Accordingly, the absorption and PL spectra of DOO−PPV in toluene exhibit temperature-dependent behaviors. This dramatic temperature-dependent behavior is very similar to that of the previously reported dMON−PPV in benzene.[21] Figure 1 shows the fluorescence spectrum of DOO−PPV in toluene solution during the cooling process from ~80 to 10 °C for various time periods. The polymer in toluene solution is very dilute, with absorbance less than 0.03 for a 1 cm optical pass. The concentration of the polymer is about 2×10^{-6} M monomer units, which corresponds to the average distance between polymers > 1 μm. At 80 °C, the fluorescence resembles that in chloroform solution. After cooling to 10 °C for 2 min, the spectrum exhibits a red-shift. This behavior can be ascribed simply to the temperature dependence of the solvent dielectric constant. After maintaining the solution at 10 °C for a longer time, the peak near 550 nm reduces, while a new peak of nearby 587 nm arises. This newly formed peak is similar to the peak in thin films. Eventually, the peak near 550 nm disappears completely, while the newly formed peak at 587 nm dominates. Figure 2 shows the typical fluorescence spectrum of DOO−PPV in toluene after cooling to 10 °C for 30 min. The fluorescence spectra in chloroform solution and thin film are shown for comparison. The fluorescence spectrum in toluene solution shows dual peaks. The relative ratio of the peaks depends not only on the cooling period, but also on the polymer concentration. At higher concentration, the fluorescence at 550 nm decreases more quickly and completely. These temperature- and concentration-dependent behaviors strongly suggest the red-emission fluorescence in forming of aggregations.

The results in Figures 1 and 2 show that aggregations form in dilute solution with small temperature differences, and thus it is reasonable to directly compare the spectra without further concern of environmental differences. The two noteworthy features are as follows: (1) During cooling of poor solution, the reducing rate of the peak near 550 nm is not related to the rate of growth of the peak near 587 nm; we will discuss this phenomenon in a later paragraph. (2) The aggregation has a characteristic fluorescence spectrum. There are several possible consequences when polymers form aggregations: (i) Interchain aggregate states (dimer or excimer) are formed.[6−13] (ii) Aggregations can influence the "stiffness" of the polymer backbone, and lengthen the ordered conjugation length.[5] Possibility (i) is supported by the following considerations. Possibility (ii) implies that the interchain interaction influences the polymer structures, and subsequently increases the conjugated length of the intrachain excitons. Possibility (ii) appears less likely on the basis of the characteristic fluorescence spectrum presented in Figure 1. During the the cooling process, the fluorescence spectrum

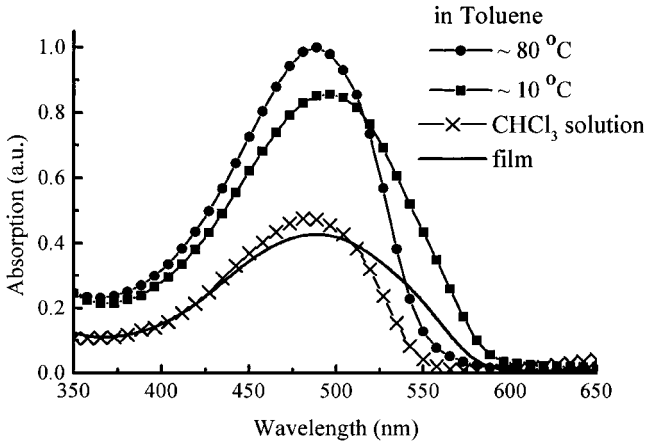

Figure 3. Absorption spectra in toluene at 80 and 10 °C. The spectra in chloroform solution and in thin films are shown for comparison.

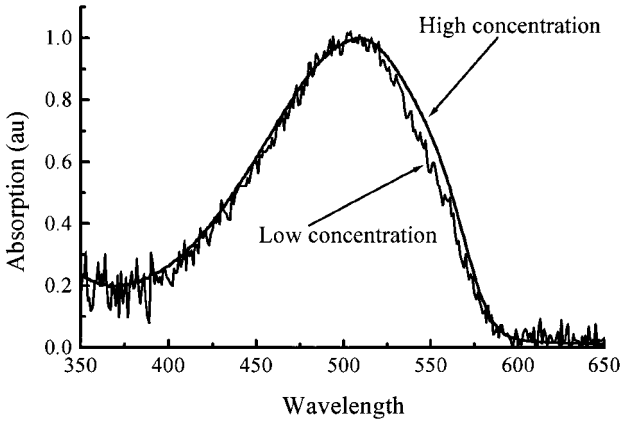

Figure 4. Absorption spectra in toluene with concentrations different by a factor of 30 after the same cooling time.

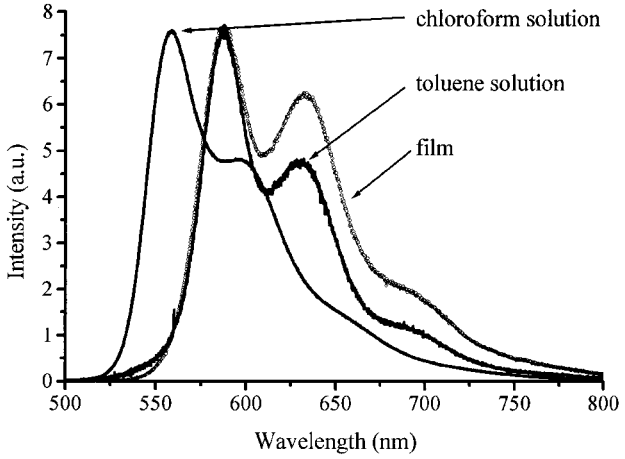

Figure 5. Fluorescence spectra of DOO−PPV in chloroform solution, toluene solution, and film, recorded by the CCD-based system. The spectrum in toluene results from the subtraction of different concentrations of aggregates.

does not exhibit a multiple red-shift. To estimate the correspondent change of ordered conjugation length, we compare the spectra of polymer and oxy-hexyl substituent oligomer with the three phenyl-ring. The fluorescence peak of the oligomer occurs at 460 nm. We assume that the conjugation chain length dependence of the fluorescence peak of this series of oligomers is the same as that of the oxy-propyl substituent, (POP)n. According to size dependence of the $S_0 \leftrightarrow S_1$ transition in (POP)n, the shift in fluorescence from 550 to 587 nm in DOO−PPV can be related to the change of repeating chain units from 7 to 9−10 units. Since this is not the long-chain limit case, it is expected to have a finite energy difference for different effective chain units. Since the experiments were performed under dilute conditions, negligible energy transfer occurred. Thus, the fluorescence from different conjugated lengths should have appeared at various concentrations or cooling time periods. But the spectrum of Figure 1 shows the opposite. Hence, we conclude that the rise of the newly formed 587 nm fluorescence peak is most likely from interchain aggregates. More supporting evidence comes from comparing the fluorescence spectra between the single polymer and aggregate. This will be discussed in a later paragraph.

The intermolecular species, i.e., aggregate, can be divided into dimer and excimer, according to the existence of a ground-state interaction; i.e., change in the shape of the absorption spectrum.[22] Figure 3 shows the absorption spectra in toluene at high temperature (~80 °C), as well as at low temperature (~10 °C). The absorption spectra in chloroform solution and in films are both shown for comparison. Similar to the fluorescence spectrum, the absorption spectrum in toluene solution at 80 °C exhibits nearly the same shape as that in chloroform solution. Compared to the spectrum at 80 °C, the absorption spectrum at 10 °C is broadened and red-shifted. The results indicate that the polymer in toluene solution forms dimer-like aggregates. After further comparison between the 10 °C spectrum and the film absorption spectrum, it appears that these two species are nearly identical on the low-frequency side. The spectrum of films is broader on the high-frequency side, but it matches well with the corresponding portion of the spectrum in chloroform solution. The comparison of the absorption spectra suggests that the film is comprised of single polymers and aggregates.

Figure 4 compares the absorption spectra in toluene solution with two concentrations different by more than 1 order of magnitude after the same amount of cooling time. These spectra are almost identical in shape, except with a difference on the low energy side. The concentration-dependent absorption behavior further confirms the formation of dimer-like aggregates in the toluene solution.

Figure 5 shows the fluorescence spectra of single polymer, dilute aggregate, and film forms of DOO−PPV, as recorded by the CCD-based system. A fluorescence spectrum in chloroform solution is used to represent the single-polymer spectrum. The aggregate spectrum is recorded by the following method. After cooling for several hours, most of the polymers in the toluene solution form fiber-like aggregates, and gather at the bottom of the cell. However, some polymers remain dissolved in solution. The lower part of the cell has a larger amount of aggregates than the upper part, but it has the same concentration of dissolved polymers. The fluorescence spectrum of the toluene solution is taken by subtracting the spectrum of the lower part from that of upper part in the cell, which can be used to represent the net fluorescence spectrum of dilute aggregates in toluene. The fluorescence in toluene solution exhibits a spectrum almost identical to that in chloroform solution, except with a 900 cm^{-1} difference. The aggregate spectrum has much smaller Huang−Rhys parameters[23] than the single polymer spectrum.[24] This is an additional supporting evidence which rule out lengthening the effective conjugation length in poor solution. The expectation of a monotonically decrease of the Huang−Rhys parameter within a longer conjugation length system[25,26] contradicts the fluorescence spectra shown here. In comparing the fluorescence spectrum of films with solutions, we see clear evidence that the fluorescence in films has the same origin as that in dilute

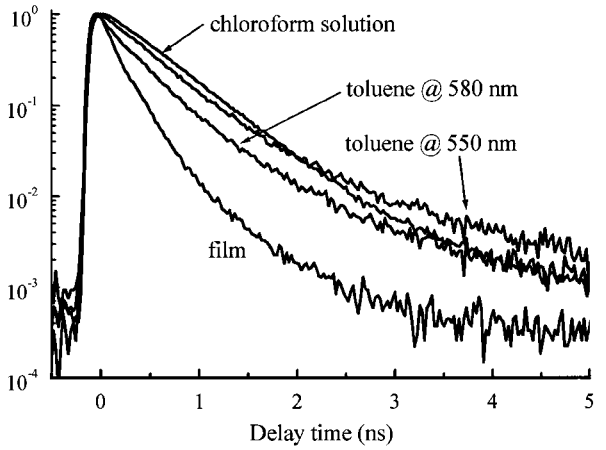

Figure 6. Time-resolved fluorescence of DOO−PPV at various conditions, in good solution (chloroform solution), poor solution (toluene solution), and film.

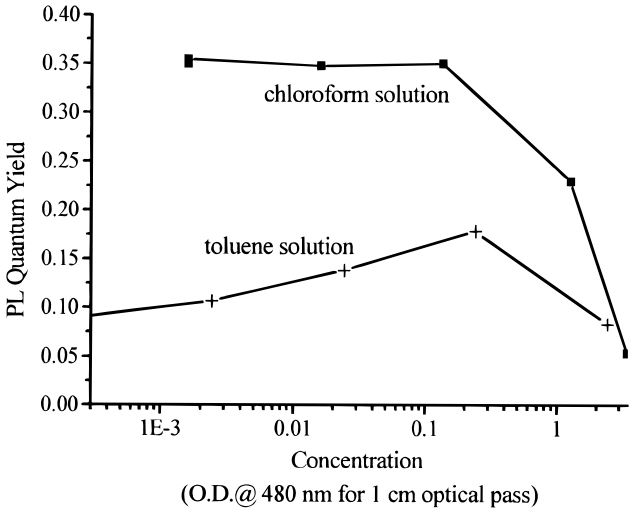

Figure 7. Fluorescence quantum yields, QE, of DOO−PPV in chloroform and toluene solutions with various concentrations at room temperature. At low concentration, the QE in toluene solution decreases as dilution, but that in chloroform solution remains the same.

aggregates (toluene solution), rather than that of single polymer chains (chloroform solution). Moreover, the fluorescence in films exhibits additional red emission, compared to that of dilute aggregate. This can be due to additional red-emission species in films, or alternatively, the large Huang−Rhys parameter in film. However, the fluorescence at low temperature has spectral dynamics which support the multi-emission species in film.

Figure 6 shows room-temperature time-resolved fluorescence spectra of DOO−PPV in films and in chloroform and toluene solutions, monitored at 550 and 580 nm. The fluorescence dynamics in chloroform solution, in toluene at 80 °C, and in films exhibit negligible wavelength-dependent dynamics. However, after cooling to 10 °C for 10 min, the fluorescence decay dynamics in toluene at 550 nm exhibit behaviors different from that at 580 nm. The decay dynamics at 550 nm is similar to that of chloroform solution, but the 580 nm peak exhibits a faster relaxation. The different decay time indicates that the fluorescence comes from different emissive species. Note that the time-resolved fluorescence spectrum at these two wavelengths does not represent the decay dynamics of a single polymer and interchain aggregate in toluene solution, respectively. Since the fluorescence spectrum of each component has a width, the peaks at 550 and 580 nm each have a certain contribution from the other. Therefore, the decay dynamics at 550 nm only represent a major component from the individual polymer, and a minor effect from the aggregates. Moreover, the fast decay dynamics in films show that additional nonradiative relaxation is introduced when aggregates condensed in the form of a film.

The absorption spectrum indicates that film comprises both intrachain as well as interchain states. But because of the efficient energy transfers from intrachain to interchain states, the films only exhibit fluorescence from the interchain aggregate states. The characteristic fluorescence lifetimes in chloroform solution and in films are 0.50 and 0.23 ns, respectively. At 10 °C, the fluorescence lifetimes of DOO−PPV in toluene at 550 and 580 nm, are 0.47 and 0.39 ns, respectively. In toluene, the decay dynamics at 550 nm is very similar to that of in chloroform. This indicates that they are of the same origin, both from the intrachain excitation. The presumption that the aggregate state in toluene is the same as that in films suggests the same natural fluorescence decay time. However, the decay dynamics of that in films are twice as fast as that of aggregates in toluene. This indicates that increasing the density of aggregate in the films will enhance the relaxation rate. Accordingly, the additional red-emission in the films also supports the increase of relaxation rate to form some new species in films.

During cooling of poor solution, the reduction rate of the peak near 550 nm is not related to the rate of growth of the peak near 587 nm. This rate dependence indicates that, while DOO−PPV becomes insoluble in toluene solution, effects other than formation of fluorescent aggregates influence the fluorescence intensity. To elucidate this property, we perform the concentration-dependent experiments. Figure 7 shows the fluorescence quantum yields (QE) of DOO−PPV in chloroform and toluene solutions, with various concentrations at room temperature. At high concentration, both suffer concentration quench in reducing the QE. However, the behaviors at low concentration are different. The fluorescence spectrum of the chloroform solution remains the same as the reducing concentration. The QE, 0.35, remains the same, regardless of dilution. Nevertheless, at low concentration, toluene solution exhibits more single polymer spectrum, but less fluorescence yield. The maximum yield occurs in the concentration of absorbance at 480 nm $\sim$ 0.3. The QE, 0.17, is about half the value of that of a single polymer in good solution. By reducing the concentration, the QE is further reduced to below 0.1. Hence, the concentration-dependent behavior in toluene solution cannot be simply explained by two species, i.e., a single polymer and aggregate. In particular, the fluorescence quantum yield at extreme dilute concentration of toluene solution is much less than that of chloroform solution. We attribute this to single chain distortion in poor solution.

The reduction of the 550 nm peak is due not only to the formation of aggregates, but also to the single polymer distortion. Although the intensity decreases, the time-resolved fluorescence at 550 nm shows no corresponding change in the decay dynamics. This indicates that the reduction of fluorescence at 550 nm is from the diminishing number of light-emitting chromophore units, rather than from additional nonradiative relaxation. A "solubility-induced steric effect", i.e., the conformational change due to the interaction between the polymer and solvent, is proposed to explain this effect. At high temperature, the polymer dissolves in toluene quite well. At lower temperature, the potential between polymer and solvent is raised. Thus, the polymer tends to form aggregates to reduce the overall surface exposed to solvent. However, when the polymer concentration is extremely low, a single polymer chain can stay in the poor solvent for minutes without forming aggregates. Therefore, the polymer distorts its backbone to

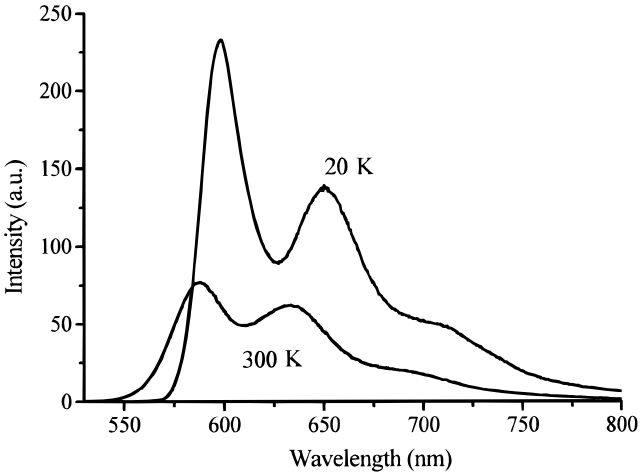

Figure 8. Fluorescence spectra of films at room and low temperature, 20 K.

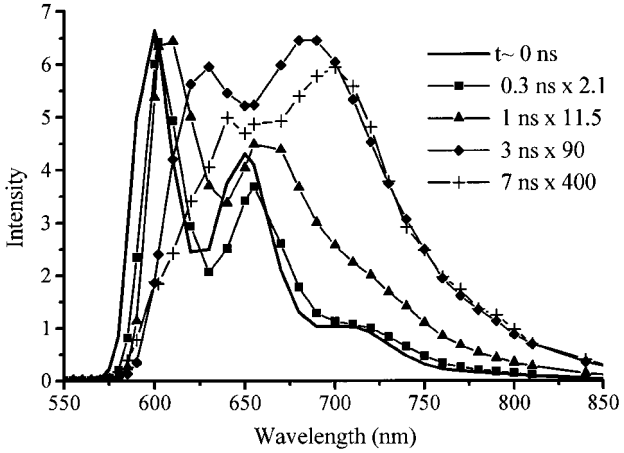

Figure 9. Spectral dynamics of films at 20 K. The spectrum at 0 ns resembles the cw spectra, but is slightly blue-shifted. After 7 ns, the fluorescence spectra are featureless. The intensity at various delay times is scaled up with respect to the 0 ns data. The scaling factors are shown in the figure.

reduce the potential. This distortion reduces the number of light-emitting excitons without influencing the measured fluorescence lifetime.[9,27]

Low-temperature spectroscopy provides additional insight on the fluorescence species of films. Figure 8 shows the fluorescence spectra of films at 20 and 300 K. The fluorescence spectrum at 20 K exhibits a red-shift behavior, which is similar to that of MEH−PPV.[28] The fluorescence peak at 587 nm shifts to 600 nm, whereas the 630 nm peak shifts to 645 nm. The fluorescence decay dynamics at 20 K is shown in Figure 9. Since the fluorescence lifetime of films exhibits almost no wavelength dependence at room temperature, it demonstrates strong nonradiative relaxation at ambient conditions. At low temperature, we examine fluorescence spectral dynamics on a nanosecond time scale, and we observe a continuous red-shift as time progresses. The 0−1 ns spectrum indicates that there is a distribution of states that emit light in films. However, the shape of the spectra after 3 ns bears little resemblance to the cw spectra. The spectrum at 7 ns is almost featureless. The similarity to the fluorescence spectrum in CN−PPV films indicates the presence of additional excimer-like emission species in DOO−PPV film.[29] At room temperature the nonradiative process dominates the decay of excimer-like species. Thus, no spectral dynamics can be observed at room temperature.

The fluorescence yields as well as the luminescent properties of films, depend on the preparation condition.[30,31] Since DOO−PPV tends to form aggregates, it is not easy to block the interaction between polymers. Hence, the upper limit of the fluorescence yield of film is set by the dilute aggregates. Because of additional effect existence in poor solution, i.e., single polymer distortions, it would not be straightforward to derive the quantum yield of aggregates. Further investigations on the fluorescence yield of dilute aggregates as well as on the origin of the additional relaxation channels, should be helpful for optimizing the properties of light emitting polymer films.

4. Conclusion

In summary, the photophysical properties of a symmetrically substituted PPV derivative, viz. poly(2,5 dioctyloxy *p*-phenylenevinylene) (DOO−PPV), in various states: good solution, poor solution, and thin films are investigated. The solubility of DOO−PPV in toluene exhibits drastic variations at temperatures between 10 and 80 °C. As the temperature is lowered, the solubility decreases and consequently the polymer forms aggregates, even in dilute condition. In addition, this reduction in solubility introduces a quenching effect. The absorption spectra indicate that films are comprised of individual polymers and aggregates, but the fluorescence in films arises only from the aggregated regions due to fast energy transfer. In films, the aggregates suffer additional quenching, which reduces up to half of the fluorescence. In addition, at low temperature, the fluorescence dynamics of films exhibit a wavelength-dependent behavior. The absence of spectral dynamics of films at room temperature can be attributed to the strong nonradiative relaxation under ambient conditions. Further understanding of the origin of this quenching effect would be helpful to improve the fluorescence performance of polymer films.

Acknowledgment. We thank Prof. L. J. Rothberg for the helpful discussions. One of the authors, W. S. Fann acknowledges the inspiration of Professor Brian Kohler. This research was supported by the National Science Council, Taiwan, R.O.C.

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