Optical emission from the aggregated state in poly [2-methoxy-5-(2′-ethyl-hexyloxy)-*p*-phenylene vinylene]

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(Received 1 September 2005; accepted 21 November 2005; published 8 February 2006)

We report the photoluminescence characteristics of solid solutions of poly[2-methox-5-(2′-ethyl-hexyloxy)-*p*-phenylene vinylene] (MEH-PPV) with different concentrations in polystyrene. Reduction in the distances between the MEH-PPV chains with increased MEH-PPV concentrations makes the conjugation segments aggregated in the solid solution. Absorption by the conjugation segments in the aggregated state leads to a redshift absorption edge. By comparing the photoluminescence and absorption spectra of the solid solutions with those of the 100% MEH-PPV film, it is shown that the emission from the 100% MEH-PPV film originates from the radiative recombination of excitons in the aggregated state. © *2006 American Vacuum Society.*

[DOI: 10.1116/1.2155531]

I. INTRODUCTION

Conjugated polymers have attracted increasing interest because of their potential applications in many fields, such as light-emitting diodes (LEDs),[1] lasers,[2,3] light-emitting electrochemical cells (LECs),[4] plastic solar cells,[5,6] field effect transistors,[6,7] and biological and chemical sensors.[8] Poly(*p*-phenylene vinylene) (PPV) and its derivatives are typically nondegenerate ground-state conjugated polymers, in which the lowest energy excited states have been identified as bound neutral excitons.[9] It has been documented that the interchain interaction and possible interchain species play important roles in the photophysics of the conjugated polymers.[10–27]Here, an interchain interaction refers to the interaction between the conjugation segments since the conjugated polymer chains consist of many segments with different conjugation lengths. It is generally believed that the strong interchain interactions favor the formation of weakly emissive interchain species in the conjugated polymers. Controlling the interchain interactions is an important way to optimize the performances of optoelectronic devices based on conjugated polymers. In many conjugated polymers such as poly(2,5-hexyloxy-*p*-phenylene cyanovinylene) (CN-PPV),[11] ladder-type poly(*p*-phenylene) (L-PPP),[12] and poly (*p*-pyridyl vinylene) (PPyV),[13] the redshifts of their photoluminescence (PL) peaks from the films compared with those from the diluted solutions have been attributed to the presence of the interchain species. However, the excited states responsible for emission in the poly[2-methoxy-5-(2′-ethyl-hexyloxy)-*p*-phenylene vinylene] (MEH-PPV) film are still controversial.[11–13,19–23,25] The redshifts of the PL peaks in the MEH-PPV films in comparison with that of the MEH-PPV solutions have been attributed to various causes including the intrachain excitons in more extended polymer chains,[19] strong polarization interaction of the excited state with the environment,[23] or the interchain species.[25] It is of both scientific and commercial interests (electronics and optoelectronics) to clarify the excited states in the conjugated polymers.

In this work, we study the PL properties of MEH-PPV of different concentrations in an inert polymer, polystyrene (PS). Our results show that the conjugation segments aggregate in the solid solution when the concentration of MEH-PPV is increased. By analyzing the PL and absorption spectra of the solid solutions and the MEH-PPV film, it can be shown that the emission from the MEH-PPV film originates from the radiative recombination of the excitons in the aggregated state. Hence, controlling the interchain interaction is an effective way to modify the electrical and optical properties of the MEH-PPV films.

II. SAMPLE PREPARATION AND EXPERIMENTS

MEH-PPV was synthesized via the improved Gilch reaction.[28] Using gel permeation chromatography, its mass average molecular weight (M_w) was measured to be 5×10^5 g/mol. The inert polymer PS was purified by redeposition. Figure 1 shows the chemical structures of both MEH-PPV and PS. To prepare the solid solutions, MEH-PPV and PS were dissolved in tetrahydrofuran (THF) separately and then blended with different proportions. The ratios

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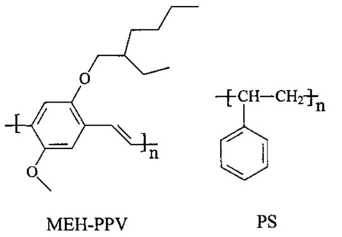

FIG. 1. Chemical structures of MEH-PPV and PS.

of MEH-PPV to PS by weight were 1/1000, 1/100, 1/50, 1/20, 1/10, 1/5, and 1/1, respectively. The solid solutions of MEH-PPV/PS were prepared by drop-coating the blended solutions on glass substrates. Pure PS and MEH-PPV films were also deposited in a similar manner onto glass substrates, respectively. The PL and PL excitation (PLE) spectra were obtained using the FluoroMax-2 fluorescence spectrophotometer. The absorption spectra of the samples were acquired by a Shimadzu UV-3100 spectrophotometer. All the experiments were performed at room temperature.

III. RESULTS AND DISCUSSION

Figure 2 displays the normalized PL spectra acquired from the PS film and the solid solutions of MEH-PPV/PS with different MEH-PPV concentrations using excitation from the 450 nm line of a Xe lamp. It can be seen that no PL exists for PS under the 450 nm excitation. The PL of the MEH-PPV/PS solid solutions is very pronounced and all the PL spectra can be deconvoluted using Gaussians into three subbands with peak positions being at ~555, 590, and 630 nm, respectively. As shown in Fig. 2, the intensity of the 555 nm subband relative to the 590 nm one diminishes with increasing MEH-PPV concentration in the solid solution. The 555 nm subband finally disappears in the PL spectrum of the 100% MEH-PPV film without PS. The intensities of the 590 and 630 nm subbands gradually increase and are finally dominant in the PL spectrum of the 100% MEH-PPV film without PS. The presence of these distinct subbands in the PL spectra indicates that there are different excited states in the solid solutions.

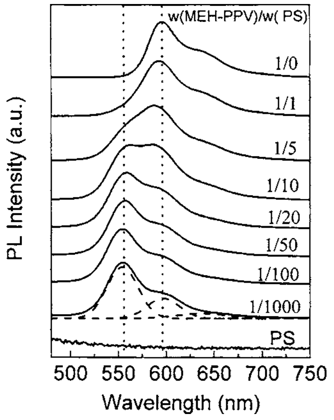

FIG. 2. Normalized PL spectra of the solid solutions of MEH-PPV/PS, with the dashed lines showing the Gaussian subbands of the diluted solid solution with a ratio of MEH-PPV to PS by weight being 1:1000.

Since the MEH-PPV chains are separated by the inert PS in the diluted solid solution with the ratio of MEH-PPV to PS by weight being 1 to 1000, the conjugation segments form a separated state and thus the emission mainly originates from optical transitions of the excitons in the separated states. It has been previously discovered that photoexcitation of a separated conjugated polymer chromophore can produce intrachain excitons.[20] Therefore, the 555 nm subband is characteristic of the intrachain exciton. With increasing MEH-PPV concentration in the solid solution, the distances between the MEH-PPV chains decrease so that the conjugation segments in the different chains come together to form an aggregated state. Using a combination characterization of both third-harmonic generation and near-field scanning optical microscopy, Schaller *et al.*[21] found that a limited number of aggregation domains form in the MEH-PPV film. This indicates that the aggregates can occur in solution. The higher the MEH-PPV concentration in the solid solution, the larger the amount of the conjugation segments in the aggregated state and the higher the relative intensity of the 590 nm subband. Thus, the 590 nm subband can be identified to be related to the excitons in the aggregated state. The optical and electrical properties of the conjugated polymers in the aggregated state strongly depend on the interchain interactions which are affected by film preparation parameters such as the spin-coating speed, thermal annealing, as well as concentration and solvent of the solution.[19,23,29]

It can be observed that the linewidth of the 555 nm subband is almost equal to that of the 590 nm subband. It has been shown that the two types of excitons have the same PL decay times (~300 ps).[20,29–32] It has been noted that the radiative lifetime of the excited state depends on the degree of conjugation of the polymer.[32,33] It is reasonable to consider that the π electrons in the excitons in the aggregated state cannot be delocalized to cross the aggregated conjugation segments. It has been found further that the linewidth of the 630 nm subband is broader than that of the 590 nm subband. In addition, based on the time-resolved PL spectra, the PL decay time measured at an emission wavelength of 640 nm exceeds 600 ps for the MEH-PPV solution and is much longer than that of the intrachain exciton.[30] The 630 nm subband in the MEH-PPV has been identified to be related to the interchain species,[19,23,29,30] but its nature and origin are debatable. Moreover, it can be seen from Fig. 2 that the relative intensity of the 630 nm subband goes up with increased MEH-PPV concentration in the solid solutions, and the intensity of the 630 nm subband is about 0.3 of the 590 nm subband value for all the solid solutions. Therefore, we suggest that the interchain species are in concomitance with the aggregated state in MEH-PPV. Blocking the aggregation of the conjugation segments can prevent the formation of the interchain species.

To study the effects of the aggregated state on the optical properties of the MEH-PPV in the solid solutions, we mea-

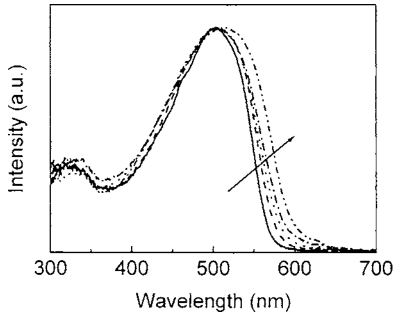

FIG. 3. Normalized absorption spectra of the solid solutions of MEH-PPV/PS, with the arrow showing the ratios of MEH-PPV to PS by weight changing from 1/1000 to 1/50, to 1/10, to 1/5, and finally, to 1/1.

sured the absorption spectra of the solid solutions. As shown in Fig. 3, the absorption peaks of the MEH-PPV/PS solid solutions are all at 500 nm, but the absorption edges are redshifted with increasing MEH-PPV concentration. The optical energy gap of the polymer is reduced, giving rise to redshifted absorption if the lengths of the conjugation segments in the MEH-PPV are increased. Correspondingly, the emission peak of the intrachain excitons will be redshifted. Figure 2 shows that the peak position of the 555 nm subband does not exhibit the redshift, but its intensity compared with that of the 590 nm subband is decreased with increasing MEH-PPV concentration in the solid solutions. The results indicate that the lengths of the conjugation segments do not increase, but the number of the intrachain exciton responsible for light emission is reduced in the solid solutions with increasing MEH-PPV concentration. As discussed above, there are more conjugation segments in the aggregated state in the solid solution with higher MEH-PPV concentration and owing to the interchain interaction, the energy bands of the aggregated segments widen to reduce their optical energy gaps.[26] As a result, the absorption by the conjugation segments in the aggregated state causes the redshifted absorption spectra. The results indicate that the aggregated state exists in the ground state in the MEH-PPV.

Figure 4 depicts the normalized PLE spectra of the MEH-PPV/PS (1/1000 by weight) solid solution taken at monitoring emission wavelengths of 555, 590, and 630 nm, respectively. Aside from a difference in the absolute intensity, these curves are identical. Similarly, the PLE spectra acquired from the 100% MEH-PPV film are also identical (see the inset of Fig. 4). These phenomena are in agreement with those reported by Gettinger *et al.*[34] The PLE spectra being independent of the monitoring emission wavelength imply that the PL subbands in the MEH-PPV originate from the same photoexcitation. As a conjugation segment is excited by a photon with an energy above the threshold, the intrachain exciton that is created can migrate to the conjugation segment in the aggregated state, from which emission occurs. In other words, the excitons in the aggregated state and the interchain species originate from the energy transfer from the intrachain excitons since the excitation energy is higher than the threshold of the conjugation segments of the MEH-PPV in the separated state.

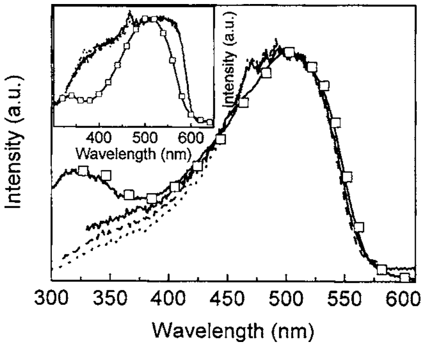

FIG. 4. Normalized absorption spectrum (-□-) and PLE spectra of the diluted solid solution of the MEH-PPV/PS (1/1000 by weight), with the inset showing the normalized absorption (-□-) and PLE spectra of the 100% MEH-PPV film. The PLE spectra were measured under monitoring emission wavelengths at 555 (dotted line), 590 (dash line), and 630 nm (solid line), respectively.

For comparison, Fig. 4 shows the normalized absorption spectra of the MEH-PPV/PS (1/1000 by weight) solid solution. The PLE spectra are identical in shape to the absorption spectrum for such diluted solid solution. In contrast, the PLE spectra of the 100% MEH-PPV film are no longer similar in shape to the absorption spectrum (see the inset of Fig. 4). As discussed above, the conjugation segments of the MEH-PPV in the diluted solid solution are in the separated state, whereas there are many conjugation segments in the aggregated state in the 100% MEH-PPV film. The obvious difference between the PLE and absorption spectra of the 100% MEH-PPV film stems from the aggregation of the conjugation segments. The aggregation of the polymer chains favors Förster energy transfer for the excited states. It has been reported that the energy migration of the excited states in conjugated polymers via Förster transfer takes place rapidly, typically in just a few picoseconds.[18,35,36] Due to the rapid energy transfer, the excitons can easily migrate to low-energy sites including quenchers, allowing a single quencher site to extinguish the emission from hundreds of chromophores in the conjugated polymer.[37,38] Thus, prevention of the aggregation of the conjugation segments is crucial to the enhancement of the performance of light-emitting diodes based on conjugated polymers.

To investigate the variation in the PLE spectra of the MEH-PPV/PS solid solutions with different MEH-PPV concentrations, we measured the PLE spectra using a monitoring emission wavelength of 630 nm. The results are shown in Fig 5. It can be seen that the PLE bands of the solid solutions become broad with increasing MEH-PPV concentration. As the concentration of MEH-PPV in the solid solution is increased, there are more conjugation segments of MEH-PPV in the aggregated state to make the average electron bands wider. Moreover, the difference in shape between the PLE and absorption spectra is obviously increased with increasing MEH-PPV concentration. It suggests that the excitation energies in the system are more inhomogeneous because of more conjugation segments in the aggregated state.

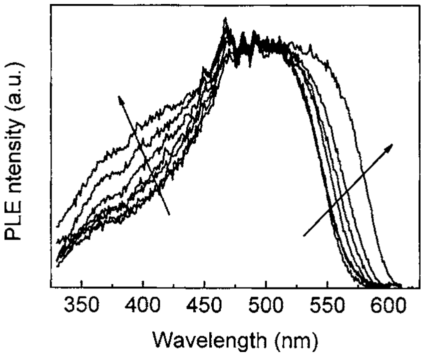

FIG. 5. Normalized PLE spectra of the solid solutions of MEH-PPV/PS measured under a monitoring emission wavelength of 630 nm, with the arrow showing the ratios of MEH-PPV to PS by weight changing from 1/1000 to 1/100, to 1/50, to 1/20, to 1/10, to 1/5, and finally, to 1/1.

IV. CONCLUSION

We have studied the luminescence properties of the MEH-PPV/PS solid solutions with different concentrations. As the concentrations of MEH-PPV in the solid solutions increase, the conjugation segments form the aggregated state both in the excited state and the ground state. Absorption by the conjugation segments in the aggregated state leads to the redshift absorption edges of the solid solutions. The 590 nm PL subband in the 100% MEH-PPV film originates from the radiative recombination of the excitons in the aggregated state whose electronic and optical properties depend on the interchain interaction.

ACKNOWLEDGMENTS

This work was supported by Grant Nos. 10225416 and 60476038 from the National Natural Science Foundations of China and the LAPEM. Partial support was also from Jiangsu Planned Projects for Postdoctoral Research Funds, Major State Basic Research Project No. G001CB3095 of China, Hong Kong Research Grants Council (RGC) Competitive Earmarked Research Grants (CERG) No. CityU 1137/03E, and City University of Hong Kong Strategic Research Grant (SRG) No. 7001642.

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