Emission Properties of Composite Semiconducting Polymer Nanoparticles

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Received 21 May 2009; accepted 13 December 2009
DOI 10.1002/app.31976

ABSTRACT: A series of composite polymer nanoparticles was prepared from poly(*N*-vinylcarbazole) (PVK) and poly(2,5-bistriethoxy-*p*-phenylene vinylene-*alt*-phenylene vinylene) (BTEO–PPV-*alt*-PPV). The nanoparticle sizes were measured to be in the range of 50–80 nm with transmission electron microscopy. The photoluminescence intensity of PVK decreased with the content of BTEO–PPV-*alt*-PPV increasing in the composite polymer nanoparticles because the excited states in PVK were quenched by BTEO–PPV-*alt*-PPV. The emission from BTEO–PPV-*alt*-PPV was enhanced in the composite polymer nanoparticles because of energy transfer from PVK to BTEO–PPV-*alt*-PPV for excitation at the absorption maximum of PVK. The energy-transfer efficiency was markedly improved in the composite polymer nanoparticles versus the composite polymer films according to emission spectral analyses. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 3340–3344, 2010

Key words: conjugated polymers; fluorescence; luminescence; nanocomposites; photophysics

INTRODUCTION

Semiconducting polymer nanoparticles have attracted much attention because of their novel electronic and optical properties.[1–7] High-performance photoelectronic devices, such as light-emitting diodes and thin-film transistors, have been prepared with semiconducting polymer nanoparticles as active layers.[8,9] Conjugated polymer nanoparticles have also been applied in biochemical assays based on fluorescence resonance energy transfer.[10] A novel class of monodisperse conjugated polymer nanoparticles has been readily prepared by facile reprecipitation.[11] The optical properties of such polymer nanoparticles have been discovered to depend on the sizes of the nanoparticles, which can be controlled by the aging time because of aggregation-driven growth. Electrogenerated chemiluminescence has been observed from single conjugated polymer nanoparticles, and this allows the study of the dynamics of the oxidation process and the heterogeneous electron-transfer kinetics at the single particle level.[12] Doping techniques based on resonance energy transfer have been proved to be effective ways of improving the luminescence efficiency and tuning the emission color of organic light-emitting diodes.[13,14] It is important to obtain tunable emission polymer nanoparticles with high luminescence efficiencies for application in nano-optoelectronic devices. Tunable emissions from semiconducting polymer nanoparticles via doping techniques have been reported in a few publications.[15,16] The energy-transfer process in nanostructures is obviously different from that in films. Enhanced resonance energy transfer has been found in poly(*N*-vinylcarbazole) (PVK) nanostructures doped with poly[2-methoxy-5-(2′-ethyl hexyloxy)-*p*-phenylene vinylene] (MEH–PPV) or tris(8-hydroxyquinoline) aluminum.[17,18]

Reprecipitation is a facile and simple method for preparing semiconducting polymer nanoparticles. Semiconducting polymers are dissolved in an organic solvent that is miscible with water, and this precursor solution is injected rapidly into water to form a stable aqueous suspension of polymer nanoparticles.[19] In this study, we prepared a series of poly(2,5-bistriethoxy-*p*-phenylene vinylene-*alt*-phenylene vinylene) (BTEO–PPV-*alt*-PPV/PVK) nanoparticles with different contents of BTEO–PPV-*alt*-PPV via the reprecipitation method. The emission color of the composite polymer nanoparticles changed from blue to green with the dopant concentration increasing. The enhanced photoluminescence (PL) emission from BTEO–PPV-*alt*-PPV in the composite polymer nanoparticles was observed for excitation at the maximum absorption of PVK. Because there was an overlap between the emission spectrum of the PVK nanoparticles and the absorption spectrum of the BTEO–PPV-*alt*-PPV nanoparticles, resonance energy transfer from PVK to BTEO–PPV-*alt*-PPV occurred

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Contract grant sponsor: National Natural Science Foundations of China; contract grant number: 50801013.

Journal of Applied Polymer Science, Vol. 117, 3340–3344 (2010)

in the composite polymer nanoparticles and contributed to the enhanced PL emission from BTEO–PPV-*alt*-PPV. The energy-transfer efficiency in the composite polymer nanoparticles was two times that in the composite films according to PL spectral analyses. The reasons for this enhanced energy transfer in the composite polymer nanoparticles are discussed in this article according to the spectral analyses.

EXPERIMENTAL

PVK (Acros Organics, Geel, Belgium) was used as received without any purification. The weight-average molecular weight of PVK was 90,000 g/mol. BTEO–PPV-*alt*-PPV was synthesized via a Wittig condensation reaction.[20] The weight-average molecular weight of the polymer was measured with gel permeation chromatography to be approximately 5×10^5 g/mol. The chemical structures of PVK and BTEO–PPV-*alt*-PPV are shown in Figure 1. The two kinds of polymers were dissolved in distilled tetrahydrofuran (THF) to prepare solutions with a concentration of 1 mg/mL, and then the two polymer solutions were blended with different volume proportions. The weight ratios of BTEO–PPV-*alt*-PPV to PVK in the blend solutions were 1/100, 2/100, 5/100, 10/100, 20/100, and 50/100, respectively. Polymer nanoparticles were prepared via the reprecipitation method. In a typical process of nanoparticle preparation, 100 μL of the polymer solution was rapidly injected into 10 mL of water with vigorous stirring for 20 min, and then the nanoparticle aqueous suspension was treated with sonication for 10 min. Polymer films were spin-coated onto clean glass substrates. The PL and photoluminescence excitation (PLE) spectra of the nanoparticle aqueous suspensions, THF solutions, and films were taken on a FluoroMax-2 fluorescence spectrophotometer (Jobin Yvon, Longjumeau Cedex, France). The nanoparticle aqueous suspensions and THF solutions were added to quartz cuvettes (1 cm × 1 cm) for measuring the PL and PLE spectra. The absorption spectra were acquired on a Shimadzu UV-3100 spectrophotometer (Kyoto, Japan). The morphologies of the nanoparticles were characterized by field-emission transmission electron microscopy (TEM; G2 20 S-TWIN, FEI Tecnai, Hillsboro, Oregon). All the experiments were performed at room temperature.

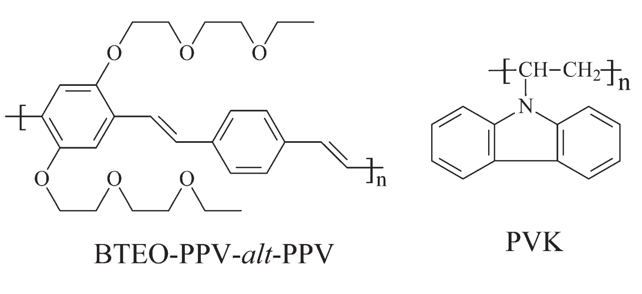

Figure 1 Chemical structures of BTEO–PPV-*alt*-PPV and PVK.

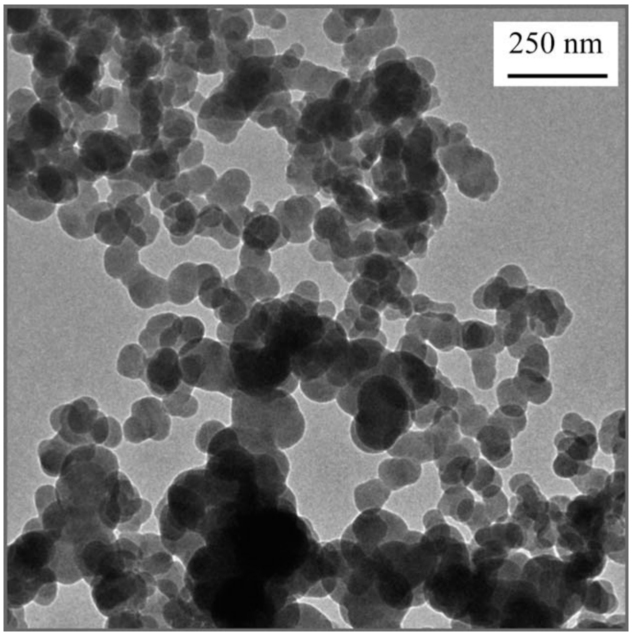

Figure 2 TEM images of the PVK nanoparticles.

RESULTS AND DISCUSSION

Figure 2 shows the morphologies of the PVK nanoparticles obtained from the aqueous suspension. The colloidal polymer nanoparticles adhere to one another after water volatilizes. The nanoparticle sizes are in the range of 50–80 nm. We have found that such a polymer nanoparticle morphology is common for many polymer nanoparticle films prepared freshly from aqueous suspensions.

The absorption and PL spectra of the PVK and BTEO–PPV-*alt*-PPV nanoparticles are shown in Figure 3. The absorption spectrum of the PVK nanoparticles has two peaks at 330 and 345 nm. The PL

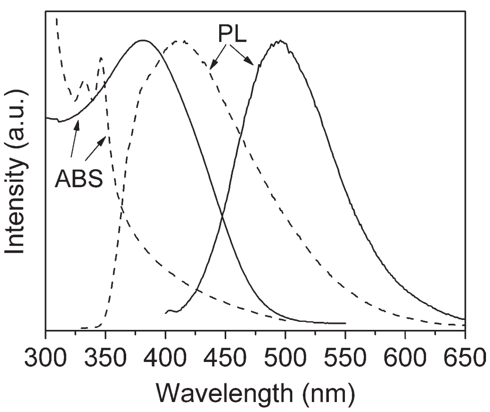

Figure 3 Absorption and PL spectra of (—) the BTEO–PPV-*alt*-PPV nanoparticles and (– – –) the PVK nanoparticles.

spectrum of the PVK nanoparticles has a peak at 410 nm, whereas the PL peak of the BTEO–PPV-*alt*-PPV nanoparticles is at 500 nm. In comparison with the film, the PL spectrum of the BTEO–PPV-*alt*-PPV nanoparticles shows a little blueshift.[21] Normally, the conformation of the polymer chains depends on the solvent. For example, the hydrodynamic radius of the MEH–PPV chains is larger in chlorobenzene than in THF.[22] The polymer chains are coiled in a poor solvent to reduce the conjugation length, and this contributes to a steady blueshift in the PL spectrum. In the nanoparticles, the polymer chains are coiled and collapsed to reduce the conjugation length. The density of the polymer in the colloidal nanoparticles is usually lower than that in the films. Therefore, the interchain interaction will be weakened in the nanoparticles. The reduced conjugation length and the weakened interchain interaction can increase the band gap of the polymer and bring the PL spectra of the conjugated polymer nanoparticles to a blueshift. The absorption maximum of the BTEO–PPV-*alt*-PPV nanoparticles is at 380 nm, and this partially overlaps with the PL spectrum of the PVK nanoparticles. This provides a prerequisite for effectively energy transfer from PVK to BTEO–PPV-*alt*-PPV in the composite nanoparticles.

Figure 4 shows the PL spectra of the polymer nanoparticles photoexcited at 345 nm. There are two PL peaks at 410 and 500 nm in the PL spectra of the composite polymer nanoparticles, which are connected to the excitations in PVK and BTEO–PPV-*alt*-PPV, respectively. The intensity of the emission from PVK is reduced, whereas the emission from BTEO–PPV-*alt*-PPV is increased with the content of BTEO–PPV-*alt*-PPV increasing in the composite polymer nanoparticles. The emission from the BTEO–PPV-*alt*-PPV nanoparticles without PVK is much weaker with photoexcitation at 345 nm, which is the absorption maximum of PVK. The PL intensity of the BTEO–PPV-*alt*-PPV/PVK nanoparticles (50/100 w/w) is nearly 4.5 times that of the BTEO–PPV-*alt*-PPV nanoparticles without PVK. The results indicate that there might be excitation energy transfer from PVK to BTEO–PPV-*alt*-PPV in the composite polymer nanoparticles. It can be proved by the measurement and analysis of the PLE spectra of the samples.

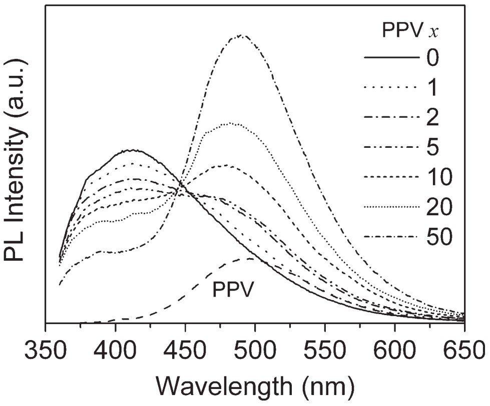

Figure 4 PL spectra of (– – –) the BTEO–PPV-*alt*-PPV nanoparticles and the BTEO–PPV-*alt*-PPV/PVK nanoparticles (excitation at 345 nm). *x* refers to the weight ratio of BTEO–PPV-*alt*-PPV (*x*) to PVK (100).

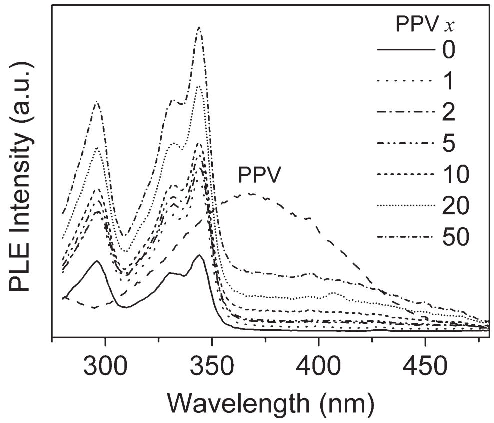

Figure 5 PLE spectra of (– – –) the BTEO–PPV-*alt*-PPV and the BTEO–PPV-*alt*-PPV/PVK nanoparticles measured at a monitoring emission wavelength of 500 nm. *x* refers to the weight ratio of BTEO–PPV-*alt*-PPV (*x*) to PVK (100).

Figure 5 shows the PLE spectra of the polymer nanoparticles measured at the monitoring emission wavelength of 500 nm, which is mainly the emission from BTEO–PPV-*alt*-PPV. The structured PLE spectrum of the PVK nanoparticles has two peaks at 330 and 345 nm, which correspond to $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_1$ transitions, respectively.[23] The BTEO–PPV-*alt*-PPV nanoparticles have a wide PLE spectrum with a peak at approximately 370 nm, which is due to the $\pi \rightarrow \pi^*$ transition. The PLE intensity of the PVK nanoparticles without BTEO–PPV-*alt*-PPV is very low. With increasing content of BTEO–PPV-*alt*-PPV, the PLE intensities of the composite polymer nanoparticles at 345 and 370 nm are increased. The increased PLE intensity at 370 nm is attributable to the increased direct absorption of BTEO–PPV-*alt*-PPV in the composite polymer nanoparticles. Although the content of PVK is decreased, the PLE intensities of the composite polymer nanoparticles at 345 nm are markedly increased. The increased PLE intensity at 345 nm indicates that the photoexcitation of PVK contributes to the emission from BTEO–PPV-*alt*-PPV. As the composite polymer nanoparticles are photoexcited at the absorption maximum of PVK, intrachain excimers are formed in PVK. The resonance energy transfer from PVK to BTEO–PPV-*alt*-PPV occurs before the radiative transitions of the intrachain excimers in PVK take place. As a result, the enhanced emission from BTEO–PPV-*alt*-PPV is observed.

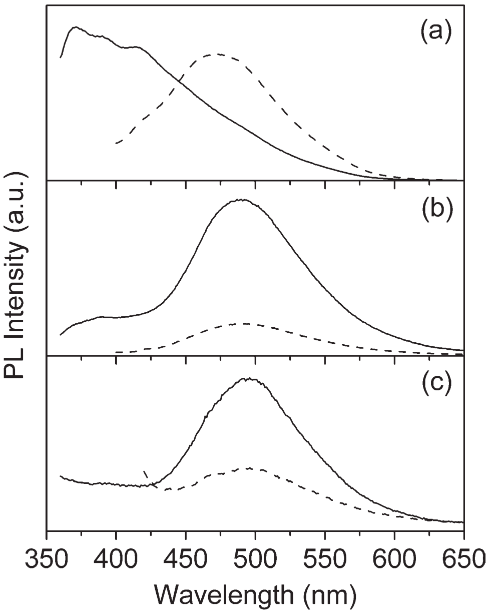

Figure 6 PL spectra of BTEO–PPV-*alt*-PPV/PVK (50/100 w/w): (a) a THF solution, (b) nanoparticles, and (c) a film photoexcited at (—) 345 and (– – –) 380 nm.

Figure 6 shows the PL spectra of the BTEO–PPV-*alt*-PPV/PVK (50/100 w/w) THF solution, nanoparticles, and film photoexcited at 345 and 380 nm. The THF solution was prepared by the addition of 100 μL of the composite polymer solution (1 mg/mL) to 10 mL of THF. The PL spectrum with a single peak at 480 nm was obtained when the composite polymer solution was photoexcited at 380 nm. Such an emission originates from the radiative transitions of the excited states in BTEO–PPV-*alt*-PPV because the 380-nm light cannot be absorbed by PVK. A strong PL emission from PVK can be detected and the PL peak of BTEO–PPV-*alt*-PPV cannot be observed in the PL spectrum when the solution is photoexcited at 345 nm because the low emission from BTEO–PPV-*alt*-PPV is concealed in the PL spectrum of PVK. In a diluted THF solution, the chains of BTEO–PPV-*alt*-PPV and PVK are extended and separated by a lot of solvent molecules. Because the distance between BTEO–PPV-*alt*-PPV and PVK is very large, the resonance energy transfer can be greatly restrained. However, in the composite polymer nanoparticles, the energy transfer from PVK to BTEO–PPV-*alt*-PPV can be easily realized. It can be clearly seen from Figure 6(b) that the PL intensity at 500 nm of the composite polymer nanoparticles photoexcited at 345 nm is higher than that of the particles photoexcited at 380 nm. According to the absorption spectra in Figure 3, both BTEO–PPV-*alt*-PPV and PVK can absorb 345-nm light, whereas only BTEO–PPV-*alt*-PPV can absorb 380-nm light. Therefore, when the sample is photoexcited at 380 nm, the excited states are formed only in BTEO–PPV-*alt*-PPV. In that case, the emission from the composite polymer nanoparticles is due to the direct photoexcitation of BTEO–PPV-*alt*-PPV. The PLE results in Figure 4 indicate that the absorption in PVK contributes to the emission from BTEO–PPV-*alt*-PPV in the composite polymer nanoparticles. When the composite polymer nanoparticles are photoexcited at 345 nm, the excited states are formed in the two polymers. The energies of the excited states in PVK can be transferred to BTEO–PPV-*alt*-PPV through dipole–dipole interactions, and then a strong emission from BTEO–PPV-*alt*-PPV can be observed.

The energy-transfer efficiency is obviously improved in the composite polymer nanoparticles with respect to the BTEO–PPV-*alt*-PPV/PVK films. This can be proved by a comparison of the PL spectra of the composite polymer nanoparticles with those of the composite polymer films with the same dopant concentration. Figure 6(c) shows that the PL intensity of the composite polymer film photoexcited at 345 nm is only 2.4 times that of the film photoexcited at 380 nm. According to Figure 6(b), the PL intensity of the composite polymer nanoparticles photoexcited at 345 nm is 4.86 times that of the nanoparticles photoexcited at 380 nm. The results indicate that the energy-transfer efficiency in the composite polymer nanoparticles is more than two times that in the composite polymer films.

Enhanced energy transfers from PVK to other acceptors, such as tris(8-hydroxyquinoline) aluminum and MEH–PPV, have also been found in nanowires and nanoparticles.[17,18] In most composite polymer films, microscale and nanoscale phase separations usually take place because of a positive enthalpy change increasing the mixture free energy. The phase separations heavily affect the energy transfer of the excitations in polymer semiconductors. In fact, the aggregation of the acceptors (BTEO–PPV-*alt*-PPV) decreases the effective dopant concentration in the composite polymer films. Thus, the energies of the excited states in the donors (PVK) cannot effectively transfer to the acceptors, and this results in low energy-transfer efficiency in the composite polymer films. During the process of preparing composite polymer nanoparticles, a composite polymer solution is divided into many little droplets by a shearing force as a THF solution is injected into water with vigorous stirring. Simultaneously, THF molecules diffuse into water, and the polymer chains are exposed to a poor solvent (water); then, the polymer chains in the droplets become coiled and aggregate to form nanoparticles. The polymer chains of BTEO–PPV-*alt*-PPV are uniformly distributed in the composite polymer nanoparticles. It can be calculated that the chain lengths of PVK and BTEO–PPV-*alt*-PPV are several hundreds of nanometers according to their molecular weights. During the process of forming the composite polymer nanoparticles, the polymer chains of PVK and BTEO–PPV-*alt*-PPV are coiled and entangle one another. The effective contact of the two kinds of polymer chains contributes to the efficient energy transfer in the composite polymer nanoparticles.

The emissions from the conjugated polymer nanoparticles have been proved to be redshifted with the nanoparticle size increasing because of π–π orbital overlap of the closely stacked/aggregated polymer backbones in the nanoparticles.[11] The effects of the nanoparticle sizes on the emission properties of the composite polymer nanoparticles containing donors and acceptors are more complicated. The average distance between the donor and the acceptor is increased in the large composite polymer nanoparticles, and the energy-transfer efficiency should be reduced because the resonance energy transfer intensively depends on the distance between the donor and the acceptor. On the other hand, the energy-transfer efficiency can be obviously increased with an increase in the polymer densities in the composite polymer nanoparticles because the donors and the acceptors are very close to each other. An increase in the polymer density in the composite polymer nanoparticles can be achieved by an increase in the hydrophobicity of the semiconducting polymer or a reduction of the temperature used for preparing the nanoparticles. In this case, the semiconducting polymer chains become more coiled and aggregate more tightly in the composite polymer nanoparticles in the aqueous suspensions, and this results in high energy-transfer efficiency.

CONCLUSIONS

We prepared a series of BTEO–PPV-*alt*-PPV/PVK nanoparticles, and by measuring and analyzing their PL and PLE spectra, we found that the excitation energies in PVK could effectively transfer to BTEO–PPV-*alt*-PPV in the composite polymer nanoparticles. The energy-transfer efficiency in the composite polymer nanoparticles was higher than that in the composite polymer films with the same dopant concentration. The uniform distribution and the effective contact of the two polymer chains contributed to the enhanced energy transfer in the composite polymer nanoparticles.

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