Stable Optical Emission from Annealed Poly (p-Phenylene Vinylene) Derivative Films Containing Oxadiazole

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The structure and optical properties of poly {[2-methoxy-5-(2-ethylhexyloxy)-p-phenylene vinylene]-alt-[2,5-diphenylene-1,3,4-oxadiazole vinylene]} (MEH-OPPV) are studied by examining and analyzing the photoluminescence, absorption, and Fourier transform infrared spectra of the MEH-OPPV films annealed at different temperatures. It is revealed that MEH-OPPV is of high thermal stability due to aryl-substituted oxadiazole groups introduced in the polymer backbone, which increases the conformational disorder to result in short conjugation lengths in MEH-OPPV. Because the interchain distance and the conjugation length are restricted by the large dihedral angle between the adjacent monomer units, the relaxation of the polymer chains cannot change the electron structures during thermal annealing. As a result, the optical properties of MEH-OPPV in the film are nearly unaffected by thermal annealing.

Key words: Conjugated polymers, photoluminescence (PL), thermal annealing

INTRODUCTION

Luminescence properties of poly(p-phenylene-vinylene) (PPV) and its derivatives have attracted a great deal of interest since the first light-emitting diodes (LEDs) based on PPV were reported in 1990 by Burroughs *et al.*[1] The external quantum efficiencies of polymer LEDs are still unsatisfactory, although much work has been performed to improve the device efficiency. A major factor responsible for low efficiencies is that the charge injection and transport in emissive layers are generally unbalanced. It has been found that the hole mobility in PPV and its simple derivatives is typically higher than electron mobility by two orders of magnitude.[2,3] An effective approach for improving electron transport is to incorporate the electron-transporting units into the main chain or as pendants attached to the backbone of PPV derivatives.[4–10] One of the most widely used electron transport moieties is oxadiazole-based compounds, which are generally used as electron injection or hole-blocking materials in LEDs, mainly because of their electron deficiency, high photoluminescence (PL) quantum yield, and good thermal and chemical stabilities.[11–13] The device stability and operating lifetime are two of the most important factors from a commercial point of view.[14] The degradation of conjugated polymers can lead to loss of light output and eventual failure of polymer LEDs.[15] Therefore, it is crucial to design and synthesize luminescent polymer with high thermal and optical stabilities.

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In our previous work, we have synthesized a PPV derivative containing aryl-substituted oxadiazole groups in the main chain, which can be used as an emissive layer in polymer LEDs.[16] Thermal annealing has previously been used as an efficient method to improve performance of optoelectronic devices based on conjugated polymers.[17,18] In this work, we have studied the optical properties of poly {[2-methoxy-5-(2-ethylhexyloxy)-p-phenylene vinylene]-alt-[2,5-diphenylene-1,3,4-oxadiazole vinylene]} (MEH-OPPV) films annealed at different temperatures. The experimental results show that MEH-OPPV is of high thermal stability attributed to aryl-substituted oxadiazole groups incorporated in the polymer main chain. Aryl-substituted oxadiazole groups disrupt the conformational order of MEH-OPPV to restrict the π-electron delocalization. Thermal annealing cannot change the conjugation lengths and interchain interaction of the polymer in the films; thus, the optical properties of MEH-OPPV are independent of annealing temperature.

EXPERIMENTS

The MEH-OPPV was synthesized via a Wittig condensation reaction.[16] The mass average molecular weight of the polymer was measured with gel permeation chromatography to be 16,400 g/mol. Figure 1a shows the chemical structure of MEH-OPPV. The MEH-OPPV was dissolved in tetrahydrofuran (THF) to form a solution with concentration of 2 mg/mL. The polymer films were prepared by spin coating the solution on glass substrates (5,000 rpm). The thickness of the polymer films is 80–100 nm. The spin-coating films were annealed 2 h in N_2 at 75°C, 100°C, and 150°C, respectively. At such temperatures, THF remaining in the films can further be volatilized because its boiling point is only 66°C. The electroluminescence (EL) device was fabricated as follows: MEH-OPPV film acting as an emitting layer was prepared by spin coating the solution on a patterned indium tin oxide (ITO) substrate with a sheet resistance of 50 Ω/cm. The thin aluminum layer was evaporated onto the polymer film (2×10^{-5} torr) to form a sandwich-structured single-layer device (Al/MEH-OPPV/ITO).

The PL and PL excitation (PLE) spectra of the polymer films were taken on a FluoroMax-2 fluorescence spectrophotometer using a xenon lamp as excitation source. The EL spectra of the device were measured on the FluoroMax-2 (France) fluorescence spectrophotometer with a direct current (DC) bias applied to the device. The absorption spectra of the polymer films were obtained on a Shimadzu (Japan) UV-3100 spectrophotometer. For measuring Fourier transform infrared (FTIR) spectra, MEH-OPPV films were prepared by drop coating the solution on KBr pellets and then the formed films were annealed 2 h at 125°C in air and N_2 atmospheres. The FTIR spectra of the samples were measured on a Bruker (Germany) IFS66V vacuum Fourier-transfer spectrometer. All the measurements were performed at room temperature.

RESULTS AND DISCUSSION

The normalized PL, PLE, and optical absorption spectra of the MEH-OPPV film and the EL spectrum of the device are displayed in Fig. 2. There exist two absorption bands with peak positions at 3.9 eV and 3.31 eV in the absorption spectrum, which have been regarded as n-π^* and π-π^* electron transitions, respectively.[16] The high intensity of n-π^* electron transition was attributed to the nonbonding electrons in the n orbital of nitrogen and oxygen atoms in oxadiazole groups. It can be seen from Fig. 2 that the peak position of the PLE spectrum of the MEH-OPPV film is also at 3.31 eV, indicating that the PL band of MEH-OPPV originates from π-π^* electron transitions. In addition, it can be seen from Fig. 2 that there is a shoulder near 2.75 eV in the PLE spectrum of the MEH-OPPV film that does not have a counterpart in the absorption curve. This indicates that there exist chromophores of relatively extensive conjugation in the film, which can emit light more effectively. The PL spectrum of the MEH-OPPV film with a peak position at 2.46 eV is similar to the EL spectrum of the device. This indicates that the excited states for emission in MEH-OPPV are the same for photoexcitation and electrical injection.[1,19] As a DC bias above the onset voltage is applied on the device, electrons are injected from the cathode to the π^*-band of MEH-OPPV and holes from the anode to π-band of MEH-OPPV. They encounter in the emitting layer to form excitons, which are trapped in the low-energy sites and then radiatively recombine to give out light.

Fig. 3 shows the PL spectra of the MEH-OPPV spin-coating films annealed in N_2 atmosphere at different temperatures. These PL spectra have the same peak position at 2.46 eV, identical to that of

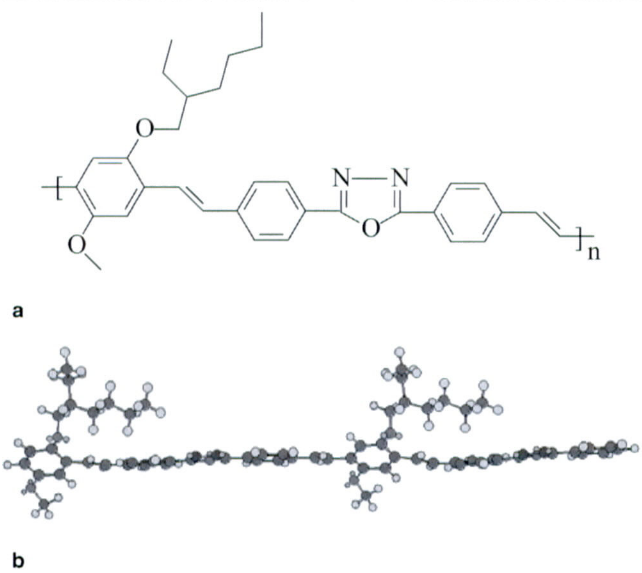

Fig. 1. (a) Chemical structure of MEH-OPPV and (b) stereo depictions of the lowest energy conformations of MEH-OPPV with two repeat units.

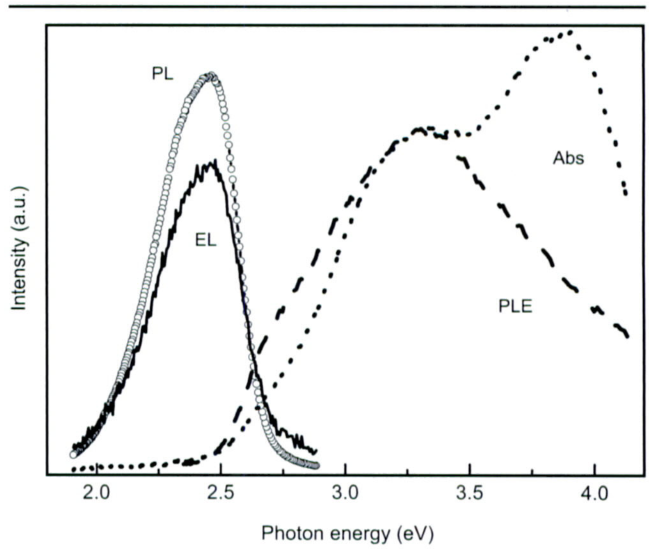

Fig. 2. PL, PLE, and absorption spectra of the MEH-OPPV spin-coating film and EL spectrum of the device with an applied DC bias of 8 V.

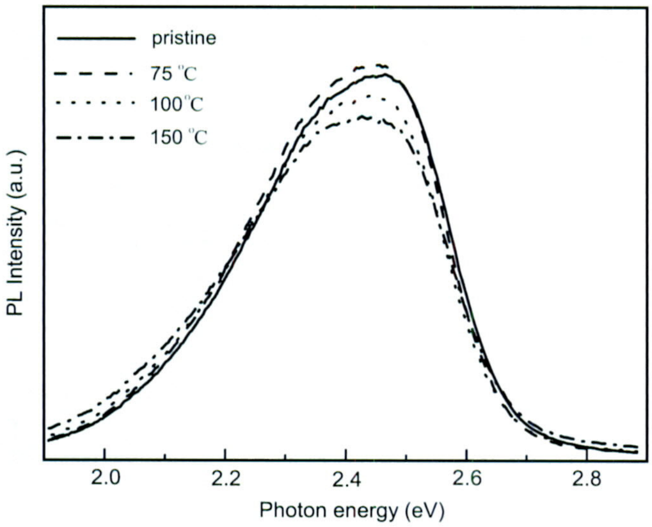

Fig. 3. PL spectra of the MEH-OPPV spin-coating films annealed in N_2 atmosphere at different temperatures.

unannealed (pristine) film except for a little change in PL intensity. This result is different from that observed in the annealed MEH-PPV films.[20,21] The PL peak positions of the annealed poly [2-methoxy-5-(2′-ethylhexyloxy)-p-phenylene vinylene] MEH-PPV films are redshifted markedly with increasing temperature, which is attributed to the lengthened conjugation segments and the enhanced interchain interaction caused by the relaxation of the polymer chains. MEH-OPPV becomes highly rigid as aryl-substituted oxadiazole groups are introduced in the backbone; as a result, the glass transition temperature of MEH-OPPV increases to reduce the relaxation ability. It has been disclosed that the glass transition temperature of the MEH-OPPV film is 143°C,[16] which is much higher than that of the MEH-PPV film (65°C).[21] On the other hand, aryl-substituted oxadiazole groups introduced into the polymer backbone destroy the planar conformation of the polymer. Figure 1b shows the stereo depiction of the lowest energy conformation of MEH-OPPV, taken by employing a conformational search using MM2 force field as implemented in ChemDraw Ultra 7.0. There is approximately a 35° dihedral angle between the adjacent monomer units in MEH-OPPV. The large dihedral angle increases the conformational disorder, which is expected to reduce the π-electron delocalization.[22–24] As a result, the emission from the MEH-OPPV is obviously blue shifted relative to that from the MEH-PPV. The chain relaxation cannot increase the conjugation lengths of MEH-OPPV in the films during thermal annealing due to the large dihedral angle. Consequently, the PL peak position of the annealed MEH-OPPV film is independent of annealing temperature. The above discussions can be further proved by examining the absorption and PLE spectra of the annealed MEH-OPPV films.

Figure 4a shows the absorption spectra of the MEH-OPPV spin-coating films annealed in N_2 atmosphere at 75°C, 100°C, and 150°C, respectively.

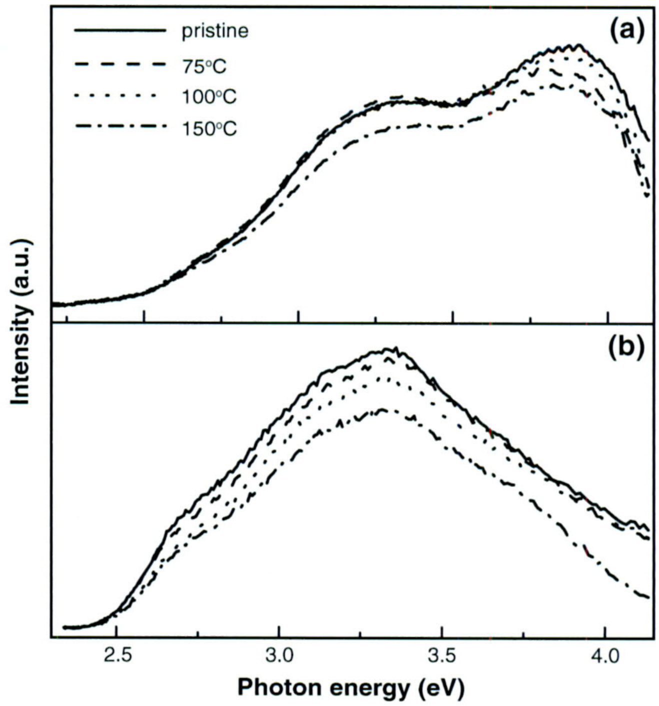

Fig. 4. (a) Optical absorption and (b) PLE spectra of the MEH-OPPV spin-coating films annealed in N_2 atmosphere at different temperatures.

For comparison, the absorption spectrum of the pristine film is also presented in Fig. 4a. It can be seen that the absorption peak positions of the annealed MEH-OPPV films have no shift with increasing temperature. The intensity of the 3.31 eV peak also remains unchanged, but that of the 3.9 eV peak slightly decreases with increasing temperature. It is noted that the absorption intensity of the film annealed at 150°C decreases relative to that of the pristine film. As the MEH-OPPV film is annealed at temperatures higher than its glass transition temperature, the polymer chains relax to a thermodynamically favorable conformation. In such cases, the absorption index of the film is expected to be changed. Correspondingly, we measured the PLE spectra of the MEH-OPPV films, as shown in Fig. 4b. It can be seen that the PLE spectra of the annealed films are completely identical in shape to those of the pristine film except for a little decrease in absolute intensity. These results indicate that the optical bandgaps of MEH-OPPV in the annealed films are same. Thermal annealing cannot change the electron structures of MEH-OPPV for the annealing temperature ranging from room temperature to 150°C. Polymer chain relaxation has very little impact on the conjugation lengths of MEH-OPPV, because there is no obvious difference for the optical properties of the MEH-OPPV film annealed at temperatures lower or higher than its glass transition temperature. The optical and electrical properties of the conjugated polymers in films strongly depend on the interchain interactions.[20] Because the interchain distance and the conjugation length are restricted by the large

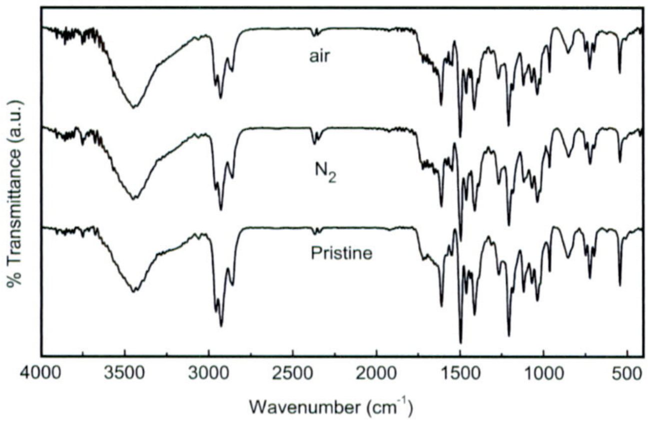

Fig. 5. FTIR spectra of the MEH-OPPV films before and after annealing at 125°C in air and N_2 atmospheres.

dihedral angle between the adjacent monomer units, the relaxation of the polymer chains cannot change the interchain interaction because the MEH-OPPV film is annealed at temperatures higher than its glass transition temperature.

To investigate the effect of thermal annealing on the chemical structure of MEH-OPPV, we measured the FTIR spectra of the MEH-OPPV films before and after annealing. Figure 5 shows the FTIR spectra of the pristine film and the MEH-OPPV films annealed at 125°C in air and N_2 atmospheres. Compared to the pristine film, there is no new absorption band appearing in the FTIR spectra of the annealed MEH-OPPV films, indicating that no new chemical bonds are formed in the polymer films during the annealing process. It can be seen from Fig. 5 that MEH-OPPV maintains thermal stability at 125°C in air and N_2 atmospheres. For the annealed MEH-PPV films, it has been found that a new absorption band ($\sim$1,720 cm^{-1}) appears in the FTIR spectra, which is characteristic of aromatic aldehyde.[25] The degradation of the emissive polymer will decrease the efficiencies of polymer LEDs and ultimately cause complete failure.[15] Compared to MEH-PPV, aryl-substituted oxadiazole groups are covalently incorporated in the backbone of MEH-OPPV, which enhance the thermal stability of the polymer. A luminescent polymer with high thermal stability is significant for application in optoelectronics.

CONCLUSIONS

By analyzing the PL, PLE, and optical absorption properties of the annealed MEH-OPPV films, it is revealed that MEH-OPPV is one of the thermally stable conjugated polymers for light emitting diodes. High thermal stability of MEH-OPPV is due to aryl-substituted oxadiazole groups incorporated in the backbone, which leads to highly rigid chains. Aryl-substituted oxadiazole groups also increase the conformational disorder to diminish the π-electron delocalization in MEH-OPPV. Since the interchain distance and the conjugation length are restricted by the large dihedral angle between the adjacent monomer units, the relaxation cannot change the electron structures of the polymer in the films. As a result, the PL properties of MEH-OPPV are independent of annealing temperature.

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