

Effect of Thermal Annealing in Atmosphere on Photoluminescence of BTEO–PPV Films

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ABSTRACT: The photoluminescence (PL) spectra of poly[2,5-bis-(tri-ethoxy)-1,4-phenylene vinylene] (BTEO–PPV) films are blue-shifted with increasing thermal annealing temperature. It is known from the UV–vis absorption spectra that thermal annealing decreases the conjugation length of the polymer. For BTEO–PPV films, unlike with MEH–PPV films, the symmetric triethoxy side groups further block aggregation of the polymer chains. The absorption Fourier transfer infrared spectra showed that thermal

annealing in atmosphere destroyed the chain structure of BTEO–PPV film by thermal oxidation to form aldehyde groups, which resulted in low PL efficiency of the annealed films. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2477–2480, 2006

Key words: PPV and its derivatives; photoluminescence; thermal annealing; conjugated polymers; luminescence; thin films

INTRODUCTION

Polymer light-emitting diodes (PLEDs) have become an exciting technology for application in flat-panel displays because of their good properties such as low cost, high external efficiency, and full color, as well as mechanical flexibility.^{1,2} The luminescence efficiency and lifetime of PLEDs have been improved in the laboratory to reach display requirement, but their stability is still a main reason to limit their commercial application. The structure of PLEDs is one or more layers of polymers sandwiched by two electrodes. When a dc voltage is applied, electrons and holes are injected from cathode and anode and meet in the luminescence layer to form excitons, and then luminescence is realized by the radiative recombination of the excitons. Because of the imbalance injection of electrons and holes, as well as the nonradiative recombination of the excitons, a part of the electric energy was transferred into heat energy to make the device temperature enhanced. Under a high temperature, conjugated polymer can be oxidized by oxygen left in the polymer films during fabricating the devices. Thermal oxidation breaks polymer chains to decrease the conjugation length of polymers. In addition, carbonyl groups act as nonradiative centers to lower the luminescence efficiency of PLEDs.^{3,4} To improve the performance and lifetime of PLEDs, it is important to

understand the heat oxidation mechanism of conjugated polymers and to find the methods for improving their thermal stability.

It has been reported that the conformational states in MEH–PPV films can be changed and device performance is improved by thermal annealing.^{5–7} In addition, thermal annealing in vacuum is a method to modify the light-emitting color of PLEDs to some degree. For annealed MEH–PPV films, the polymer chains relax to aggregate, resulting in an increase of the interchain exciton. For adjusting the light-emitting color, various functional groups are incorporated into poly(1,4-phenylene vinylene), either in side groups or in the main chains. BTEO–PPV with symmetric triethoxy side groups, which we used in the present study, can emit greenish-yellow light. In this study, we investigated the effects of thermal annealing in atmosphere on the optical properties and chain structures of BTEO–PPV with PL, UV–vis absorption, and Fourier transform infrared (FTIR) spectra.

EXPERIMENTAL

BTEO–PPV was dissolved in tetrahydrofuran (THF; 2 mg/mL), and the polymer films were prepared by spin-coating or drop-coating the solution on cleaned glass substrates. The two kinds of films were annealed in atmosphere for 2 h at 50°C, 75°C, 100°C, and 125°C, respectively. The PL spectra of the polymer films were measured with a FluoroMax-2 fluorescence spectrophotometer using a xenon lamp as the excitation source. The UV–vis absorption spectra of the polymer films were determined on a Shimadzu UV-3100 spec-

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trophotometer. The BTEO-PPV films were made by drop-coating the solution on KBr pellets and then unannealed or annealed at 75°C and 125°C, respectively, for measuring the FTIR spectra using a Bruker IFS66V vacuum Fourier-transfer spectrometer.

RESULTS AND DISCUSSION

Figure 1 shows the normalized PL spectra of the spin-coated BTEO-PPV films annealed at different temperatures in atmosphere. As can be seen, varying the annealing temperature was able to distinctly change the PL spectra of the films. For the unannealed BTEO-PPV film (pristine film), a PL spectrum with a green peak (545 nm) and a yellow shoulder (575 nm) was observed. The energy difference between the peak and the shoulder was about 0.12 eV, consistent with that of MEH-PPV.^{8,9} In the PL spectrum of the MEH-PPV film, the emission peak and the shoulder came from the radiative recombination of intrachain and interchain excitons, respectively.⁵⁻⁹ Because BTEO-PPV has the same backbone structure as MEH-PPV, the energy differences between the intrachain and intrachain excitons in the two kinds of PPV derivatives will be similar to each other. For the PL spectrum of the BTEO-PPV film, it was reasonable to consider that the peak at 545 nm originated from intrachain excitons and the shoulder at 575 nm from interchain excitons.

Conjugated polymer chains had coiled conformations in THF.⁷ Some of the BTEO-PPV chains were locked with the coiled conformations as the solvent volatilized quickly during spin coating. At same time, a part of the BTEO-PPV chains also were extended by the centrifugal force.⁹ It has been indicated that chain conformation plays an important role in the photo-

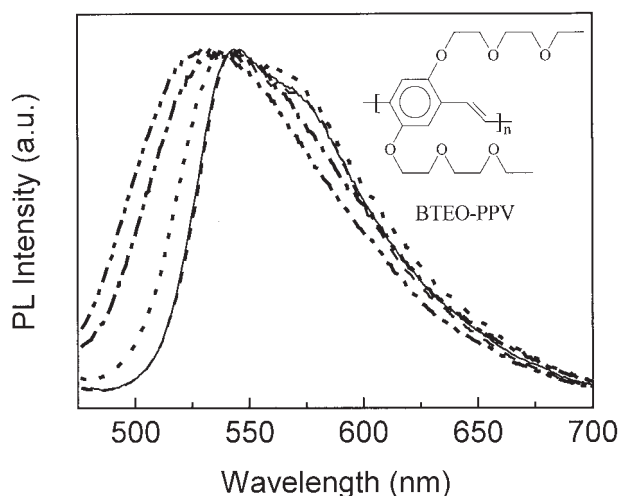


Figure 1 PL spectra of the spin-coated BTEO-PPV films annealed at different temperatures: pristine (thin solid), 50°C (dash), 75°C (dot), 100°C (dash dot), 125°C (dash dot dot). The inset is the chemical structure of BTEO-PPV.

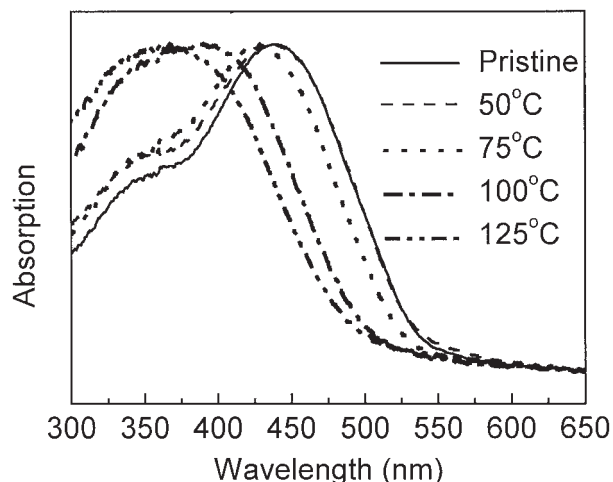


Figure 2 UV-vis absorption spectra of the spin-coated BTEO-PPV films annealed at different temperatures.

physics of conjugated polymers.¹⁰ As shown in Figure 1, the PL spectrum of the film annealed at 50°C was mostly identical with that of the pristine film. So BTEO-PPV can be maintained stably under such a temperature. When the annealing temperature was greater than 50°C, the PL peaks of the annealed films were blue-shifted. For example, the PL peak was at 530 nm for the film annealed at 125°C for 2 h. At an annealing temperature higher than 50°C, the polymer chains were able to relax and became coiled tightly, and also BTEO-PPV could be oxidized by thermal annealing to break the polymer chains, so the conjugated length was reduced in order to increase the energy band gap of BTEO-PPV. As a result, the PL peaks of the annealed films were blue-shifted, as were the corresponding absorption spectra, which is discussed later. Figure 1 also shows that the shoulder intensities of the PL spectra of the films decreased as the annealing temperature increased. This indicates that thermal relaxation cannot improve the aggregation of polymer chains. For the annealed MEH-PPV film, the shoulder intensity of the PL spectrum was enhanced, which was attributed to the increased interchain interaction because of the relaxation of the MEH-PPV chains.^{5,7} BTEO-PPV has symmetric triethoxy side groups, different from MEH-PPV, so it can be said that the symmetric triethoxy side groups blocked further aggregation of the polymer chains and limited the increase in interchain excitons in annealed BTEO-PPV films.

Figure 2 shows the UV-vis absorption spectra of the spin-coated BTEO-PPV films annealed at different temperatures in atmosphere. The coiled conformation and the chemical defects of the polymer chains widened the distribution of the conjugated segments.¹¹ The excitation energies of the conjugated polymers were strongly dependent on conjugation length;

TABLE I
Stokes Shift Data of Spin-Coating BTEO-PPV Films
Annealed at Different Temperatures

Temperature	Absorption peak (eV)	PL peak (eV)	Stokes shift (eV)
Pristine	2.82	2.27	0.55
50°C	2.82	2.27	0.55
75°C	2.91	2.30	0.61
100°C	3.18	2.31	0.87
125°C	3.39	2.34	1.05

shorter segments had higher excitation energies,¹² so BTEO-PPV showed wide absorption (as shown in Fig. 2). For a film annealed at 50°C, the absorption spectrum was not changed markedly because the polymer chains could hardly relax, and then the conformations of the polymer chains were not obviously changed. With the annealing temperature increasing above 50°C, the main peak and the edge of the absorption spectra moved toward the shorter wavelength (blue shift). The main absorption peak was at 365 nm for the film annealed at 125°C for 2 h, which was blue-shifted about 70 nm compared with that of the pristine film (435 nm). The blue shift of the absorption spectra indicates that the conjugation length of BTEO-PPV was reduced. There were two reasons for this result: first, thermal relaxation made the polymer chains coil more tightly, and, second, thermal oxidation made the polymer chains break (explained later).

It has been reported that exciton energy can transfer rapidly from a shorter segment to a longer segment in conjugated polymers.¹³⁻¹⁵ Normally, emissions come from the radiative recombination of excitons on long segments with low energies in conjugated polymers. So an energy difference develops between the absorption and the emission of conjugated polymers. Stokes shift is determined as the energy difference between the peaks of the absorption and emission spectra of luminescence polymers. The apparent Stokes shifts of the unannealed and annealed spin-coated BTEO-PPV films at different temperatures are summarized in Table I. The Stokes shifts of the annealed films increased with an increasing annealing temperature. A large Stokes shift has been correlated with low luminescence efficiency in conjugated polymers.¹⁶ In our experiments, we found that the intensity of the PL spectra of the films decreased with increasing annealing temperature. This was indicated by the experiments and analysis that the luminescence efficiency of the annealed films was lower than that of the pristine film.

By further analyzing the data in Table I, it can be seen that the energies of the absorption and PL peaks increased with increasing annealing temperature and that the former increased more quickly than the latter did. For the film annealed at 125°C, compared with the pristine film, the energy of the absorption peak in-

creased about 0.57 eV, but the energy of the PL peak increased only about 0.07 eV. As the spin-coated BTEO-PPV films were annealed at higher temperatures, the polymer chains became coiled more tightly because of relaxation and more polymer chains were broken by oxidation, which induced the distribution of conjugation length toward short segments. So the energy of the absorption peak was raised with increasing annealing temperature. Because the emission of the luminescence polymer mainly came from excitons on the long conjugation segments, the energy of the emission peak increased slightly. From the above results and discussion, it was shown that the analyses of changes in polymer chain conformation induced by thermal annealing were correct. Also, the results provided evidence of the mechanism of the Stokes effect in luminescent polymers.

As shown in Figure 3, the PL peak of the unannealed drop-coated film was at about 555 nm. It was red-shifted 10 nm compared with that of the unannealed spin-coated film. The conjugation length of BTEO-PPV in the drop-coated film was longer than that in the spin-coated film because the polymer chains had time to relax into a thermodynamically favorable conformation during drop coating.⁹ A comparison of the PL spectra of the pristine spin-coated and drop-coated films (as shown in Figs. 1 and 3, respectively) showed that the intensity of the emission from interchain excitons in the latter was higher than that in the former. Spin coating leads polymer chains to a highly disordered state; in contrast, drop coating allows the polymer chains to form aggregates as the solvent evaporates slowly.¹⁷ There were more aggregates in the drop-coated films than in the spin-coated films, so more interchain excitons were produced in

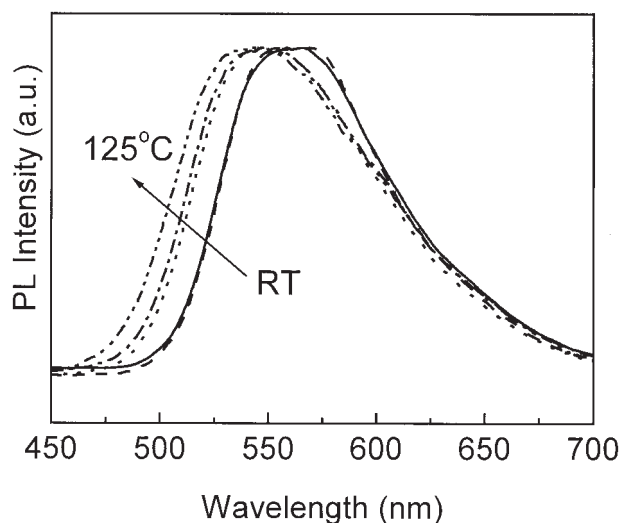


Figure 3 PL spectra of the drop-coated BTEO-PPV films annealed at different temperatures (annealing temperatures were unannealed, 50°C, 75°C, 100°C, and 125°C).

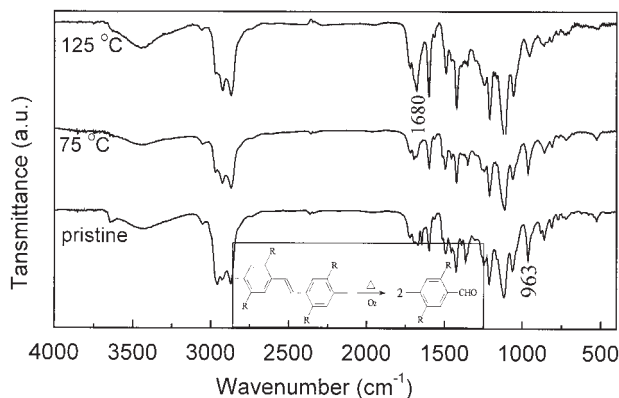


Figure 4 FTIR spectra of unannealed and annealed BTEO-PPV films at 75°C and 125°C, respectively. The inset shows the oxidation reaction of the polymer.

the drop-coated films under photoexcitation. Although the chain conformations of BTEO-PPV in the drop-coated and spin-coated films were different, similar changes in the chain conformations and chemical structures of the polymer occurred in both kinds of films during thermal annealing, so the PL peak of the annealed drop-coated film was blue-shifted. For a drop-coated film annealed at 125°C for 2 h, the PL peak was at 540 nm.

The FTIR spectrum was an effective method to study molecular structure. For investigating the effects of annealing on the chemical structure of BTEO-PPV, we measured the FTIR spectra of the unannealed and annealed drop-coated BTEO-PPV films at 75°C and 125°C, respectively, in atmosphere for 2 h (as shown in Fig. 4). For the films annealed at a high annealing temperature, such as 125°C, compared with the pristine film, the intensity of the absorption peak at 963 cm^{-1} (trans-CH double-bond out-of-plane wag) was decreased. The reduced intensity of the trans-CH out-of-plane wag shows that the conjugation length of BTEO-PPV was decreased.¹⁹ The absorption peak at 1680 cm^{-1} , identified as the carbonyl C=O stretch mode of aromatic aldehyde, increasing with annealing temperature, indicates an increase in the number of aromatic aldehydes.^{4,18,19} From this investigation, it can be estimated that the oxidation reaction occurred in the polymer films during annealing at high temperature, as described in the inset of Figure 4. The aromatic aldehydes with high electron affinity were capable of dissociating excitons and quenching the PL acutely to lower the PL efficiency of the BTEO-PPV films.¹⁸

CONCLUSIONS

The experiment results indicated that the structures and optical properties of BTEO-PPV film were distinctly affected by thermal annealing at temperatures higher than 50°C. During thermal annealing the polymer chains became tightly coiled. In contrast, thermal annealing brought the polymer chains to oxidation to form aromatic aldehydes and to destroy the conjugation of the polymer chains. As a result, the conjugated segments of the polymer were shortened, resulting in the blue-shifting PL peak of the annealed film. Because of the increase in aromatic aldehydes with high electron affinity, the nonradiative recombination of excitons was increased, and so the PL efficiency of the annealed BTEO-PPV films was reduced. Interestingly, different from MEH-PPV film, the symmetric triethoxy side groups in BTEO-PPV blocked further aggregation of chains and limited the increase in the interchain exciton in the annealed films.

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