The Preparation and Characterization of High-Performance and Thermally Stable Electroluminescent Poly(*p*-phenylene-vinylene-*b*-oligoethylene oxide)

Lu Zhu, Xiaozheng Tang

College of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai, 200240, China

Received 29 May 2006; accepted 20 September 2006 DOI 10.1002/app.25803 Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Two luminescent block copolymers (PPVPEO₂₀₀ and PPVPEO₆₀₀), composed of poly(p-phenylene-vinylene) (PPV) segments with three phenylene vinylene units and poly(ethylene oxide) (PEO) segments with molecular weight of 200 and 600, respectively, have been successfully synthesized. The structures of the copolymers were verified using FTIR, ¹H-NMR, and elemental analysis. Single-layer polymer light-emitting electrochemical cells (LEC) devices fabricated on the bases of thin films of PPVPEO₆₀₀ and on the bases of thin films of blends of PPVPEO₂₀₀ with additional PEO both demonstrated good electroluminescent (EL) performance with the onset voltage of 2.6 V

INTRODUCTION

Luminescent conjugated polymers have been paid considerable attention owing to their performances as the emissive medium in both polymer light-emitting diodes (LEDs) and polymer light-emitting elec-trochemical cells (LECs).^{1–4,8–18} Polymer LEDs are composed of conjugated polymers as the emissive medium sandwiched between two metal electrode, and polymer LECs consist of a polymer blend containing a luminescent conjugated polymer, an ionconductive polymer and an ionic salt sandwiched between an indium-tin oxide (ITO) electrode and a metal electrode.⁸ Turn-on voltages of polymer LECs and LEDs are as low as 3 V and they can be operated below 10 V.² The main advantage of polymer LEDs/LECs over other flat panel displays is their ease of fabrication because the conjugated polymer is soluble and can be deposited on a substrate from solution by simple processing techniques such as spin-coating or dip-coating.^{2,3} Among the conjugated polymers, poly(phenylene vinylene)s (PPVs) have proved to be the most promising luminescent poly-

Journal of Applied Polymer Science, Vol. 104, 1118–1125 (2007) © 2007 Wiley Periodicals, Inc.



and EL efficiency of 0.64 cd/A and 0.68 cd/A at 3.2 V, respectively. Thermal analysis shows that the decomposition temperature of PPVPEO₆₀₀ is about 305°C, which is higher than that of PPVPEO₂₀₀ and PEO. AFM studies of PPVPEO₆₀₀ thin films exhibits that the block copolymer self-assembles to form nanoscale network structures with pseudo-*cross*-linking points, thus accounting for its high thermal stability and good EL performance. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 1118–1125, 2007

Key words: luminescence; poly(*p*-phenylene vinylene); lightemitting electrochemical cell; block copolymers; self-assembly

mers and have been intensively investigated since the discovery of the electroluminescence (EL) phenomenon of the polymers.^{1,4} Luminescent polymers used to form light-emitting layers of LEDs/LECs are susceptible to water, oxygen, and other environmental elements present in ambient conditions. Since water and oxygen in the atmosphere are detrimental to the devices' lifetime, it is essential to protect the light-emitting layers from them.² To increase the longevity of the devices, various methods and techniques have been employed to protect the emissive layers, for example encapsulating them within protective layers of varying compositions.^{5,6} However, these types of seals are very expensive to fabricate and require extensive labor to assemble. In addition, the seals are large and heavy so that they severely limit the applications of the devices.^{5,7} However, to date, little attention has been paid to improve the stability of the emissive materials themselves.

Conventional polymer LEDs (metal/conjugated polymer/metal) are dual carrier devices. Electrons and holes are injected at the cathode and anode, respectively, into the undoped semiconducting polymer, and it is difficult to satisfy the conditions required for efficient, balanced injection for polymers with different band gaps and different ionization potentials. These restrictions are absent for polymer LECs, of which an electrochemical doping model

Correspondence to: X. Tang (zlcoco@sjtu.edu.com).

was proposed to account for the fundamental operating mechanism.9 Generally, there are still some drawbacks in polymer LECs, such as phase separation between the apolar luminescent polymer and the strong polar poly(ethylene oxide) (PEO), over oxidation of the luminescent polymer at higher bias voltages and slow response of its light-emission.8,15 An ideal emissive layer for polymer LECs would have interpenetrating network morphology: one network to provide the channels for ion transport and the other network to provide the pathways for transport of electronic charge carriers.¹⁰ To overcome the phase separation problem, the luminescent polymers with PEO side chain were synthesized to make the polymers possess ion-conductive property and the LECs based on them were demonstrated successfully.8,11,12 Many block copolymers were also prepared to improve the compatibility of two components of the polymer blend in LECs.^{1,8,13,14,16-18} However, the use of PEO in the polymer blends limits the thermal stabilities of the emissive layers of LECs owing to the low degradation temperature (T_d) of PEO,19 which may shorten the lifetime of the devices. So, it is necessary to use a single polymer containing both luminescent chains and ion-conductive chains as the emissive layer rather than a polymer blend in LECs. Crosslinked polymers usually have good mechanical and thermal stabilities,²⁰ but the insolubility of these materials limits their use in LECs owing to difficulties in fabricating devices. Generally, self-assembly of amphiphilic copolymers usually leads to well-ordered structures,^{21–23} in which stabilities were obtained²⁴; therefore, in this paper, a novel soluble block copolymer containing both luminescent segments and ion-conductive segments was synthesized, and the polymer could be self-assembled to form well-ordered nanoscale aggregation structures to obtain good stabilities and good EL performance. Poly(p-phenylene-vinylene-b-oligoethylene oxide) (PPVPEO) containing PPV chromophores and different PEO segments with different molecular weight (200 or 600), PPVPEO₂₀₀ or PPVPEO₆₀₀, were synthesized, respectively. LECs devices based on single polymer PPVPEO600 or a blend of PPVPEO200 and additional PEO are fabricated. EL performance of the devices and thermal stabilities of the polymers were studied. Furthermore, the aggregation structure of $PPVPEO_{600}$ thin films was investigated.

EXPERIMENTS

Materials

All solvents and materials were used as received unless otherwise noted. Sodium hydride was purchased from Rohm and Haas Co. Other chemicals were purchased from Sinopharm Chemical Reagent Co. Tetrahydrofuran was refluxed over a mixture of sodium and benzophenone and freshly distilled before use. PEO_{200} and PEO_{600} (average molecular weight of 200 and 600) were dried at 45°C under vacuum over P_2O_5 for a minimum of 3 days. All reactions were performed under a dry nitrogen atmosphere.

Synthesis of poly(ethylene oxide) bischloride (DCPEO $_{200}$ and DCPEO $_{600}$)

The poly(ethylene oxide) bischloride (DCPEO) was synthesized following the published procedure.²⁵

DCPEO₂₀₀, yield: 90%; ¹H-NMR (400 MHz, CDCl₃, δ /PPM): 3.77-3.75 (t, 4H, ClCH₂), 3.73-3.70 (t, 4H, ClCH₂CH₂), 3.69-3.60(s, 9.5H, OCH₂CH₂O). FTIR (KBr plate, γ , cm⁻¹): 670 (Cl—C), 1132 (C—O—C), 2875 (CH₂).

DCPEO₆₀₀, yield: 83%; ¹H-NMR (400 MHz, CDCl₃, δ /PPM): 3.76-3.74(t, 4H, ClCH₂), 3.73-3.70 (t, 4H, ClCH₂CH₂), 3.69-3.60(s, 55H, OCH₂CH₂O). FTIR (KBr plate, γ , cm⁻¹): 666 (Cl-C), 1130 (C-O-C), 2871 (CH₂).

Synthesis of poly(ethylene oxide) bis(4-aldehyde phenoxyl) (DHPEO $_{200}$ and DHPEO $_{600}$)

2.44 g (0.02 mol) of 4-hydroxybenzaldehyde were solved in 50 mL butanol into a flask equipped with mechanical stirrer, thermometer, dropping funnel, and refluxing. Under purged nitrogen, 0.85 g (0.021 mol) sodium hydroxide dissolved in 3 mL water were added into the reactor. Ten minutes later, 2.69 g/6.69 g (0.01 mol) of DCPEO₂₀₀/DCPEO₆₀₀ was added dropwise into the reactor. The reaction was refluxed with stirring for 30 h. At the end of the reaction, 0.5 mL of concentrated hydrochloric acid was added into the reaction system, and solid was filtrated out. The solid was washed several times with methanol. Then, the methanol solution was combined with filtrate and the mixture was concentrated by rotatory evaporator. The crude product was dried in a vacuum oven at 80°C for 24 h to remove solvents. Poly(ethylene oxide) bis(4-aldehyde phenoxyl) (DHPEO) obtained was brown.

DHPEO₂₀₀, yield: 67%; ¹H-NMR (400 MHz, CDCl₃, δ /PPM): 9.86 (s, 2H, CHO), 7.80(d, 4H, ArH), 6.99 (d, 4H, ArH), 4.20-4.18 (t, 4H, ArOCH₂), 3.87-3.85 (t, 4H, ArOCH₂CH₂), 3.73-3.61 (s, 9.2H, OCH₂CH₂O). FTIR (KBr plate, cm⁻¹): 1129 (C—O—C), 1680 (CH=O), 2871 (CH₂). Elem. Anal. Calcd for C₂₃H₂₈O_{7.5}: C, 65.08; H, 6.65. Found: C, 64.24; H, 6.36.

DHPEO₆₀₀, yield: 62%; ¹H-NMR (400 MHz, CDCl₃, δ /PPM): 9.86(s, 2H, CHO), 7.81 (d, 4H, ArH), 7.00 (d, 4H, ArH), 4.20-4.18 (t, 4H, ArOCH₂), 3.87-3.86 (t, 4H, ArOCH₂CH₂), 3.74-3.61(s, 9.2H, OCH₂CH₂O). FTIR (KBr plate, cm⁻¹): 1130 (C-O-C), 1677 (CH=O), 2871 (CH₂). Elem. Anal. Calcd for C₄₁H₆₄O_{16.5}: C, 59.98; H, 7.86. Found: C, 59.4; H, 7.25.

Synthesis of 1,4-bis(triphenylphosphoniomethyl) benzene dibromide (TPBrX)

5.28 g (0.02 mol) 1,4-bis(bromomethyl) benzene and 5.24 g (0.02 mol) triphenylphosphine were solved in *N*,*N*-dimethyl formamide (DMF) into a flask equipped with magnetic stirrer, thermometer, and refluxing. The reaction was continued with stirring for 2 h at 100°C. The white solid was collected by filtration and washed with DMF for several times. The crude product was recrystallized with chloroform. Yield: 76%. ¹H-NMR (400 MHz, CDCl₃): 7.77-7.59 (m, 30H, PPh), 6.91 (s, 4H, ArH), 5.34 (d, 4H, CH₂). Elem. Anal. Calcd for C₄₄H₃₈Br₂P₂: C, 67.02; H, 7.86. Found: C, 67.35%; H, 7.82.

Synthesis of copolymer PPVPEO₂₀₀ and PPVPEO₆₀₀

To a stirred solution of 1.58 g (0.066 mol) sodium hydride in tetrahydrofuran, a solution of 26.02 g (0.033 mol) TPBrX in tetrahydrofuran was added dropwise at ambient temperature under a nitrogen atmosphere. The mixture was stirred for 3 h under reflux, and then 12.73 g/24.63 g (0.03 mol) of DHPEO₂₀₀/DHPEO₆₀₀ was added dropwise into the reactor. The reaction was continued with stirring for 5 h and then cooled down to room temperature. 50 mL water was added in the reaction mixture. The resulting solution was saturated with sodium chloride and extracted with tetrahydrofuran (3 \times 10 mL). The organic extracts were dried over anhydrous sodium sulfate. The solvent was evaporated under vacuum. The polymer was subsequently isomerized into an all-trans configuration by refluxing for 6 h in chloroform in the presence of a catalytic amount of iodine. The obtained polymer was dried in vacuum at room temperature for 24 h.

PPVPEO₂₀₀ obtained was yellow in color. Yield: 54%. Elem. Anal. Calcd for $C_{62}H_{68}O_{11}$: C, 75.28; H, 6.93. Found: C, 74.63; H, 6.52.

PPVPEO₆₀₀ obtained was reddish brown in color. Yield: 43%. Elem. Anal. Calcd for $C_{98}H_{140}O_{30}$: C, 65.46; H, 7.85. Found: C, 63.88; H, 7.47.

Preparation of LECs

Single-layer LEC, indium-tin oxide (ITO)/PPVPEO₂₀₀ + PEO_{200,000} (LiClO₄)/Au was fabricated as follows: PPVPEO₂₀₀, PEO_{200,000} and LiClO₄ were dissolved in chloroform/acetonitrile (volume ratio of 1/1) with weight ratio of 1/1/1, and then the solution was spin-coated on glass/ITO substrate (the thickness of emitter was about 500 nm), followed by the thermal evapora-

tion of Au (200 nm) at 2×10^{-5} Torr. The area of the emissive layer is about 0.25 cm².

The fabrication of single-layer LEC, ITO/PPVPEO₆₀₀ (LiClO₄)/Au was similar with the above device except that PPVPEO₆₀₀ and LiClO₄ were solved in chloro-form/acetonitrile (volume ratio of 1/1) with weight ratio of 7/1.

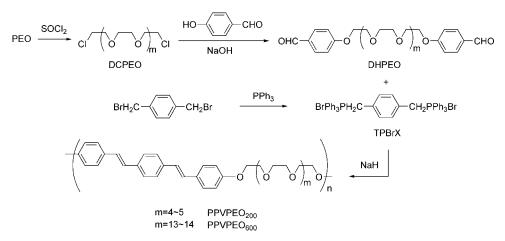
Measurement

NMR spectra were obtained with a Mercury 400 MHz spectrometer in CDCl₃. FTIR characterization was carried out on a Perkin-Elmer Paragon 1000 FTIR spectrometer by incorporating samples in KBr discs. Element analyses were achieved using Perkin-Elmer 2400-II. Gel permeation chromatography (GPC) measurement was carried out on a Perkin-Elmer 200 instrument using DMF as eluent, calibrated with polystyrene standards. Differential Scanning Calorimetry (DSC) and Thermal Gravimetric Analysis (TGA) for polymers were carried out under a nitrogen atmosphere using the Perkin-Elmer Pyris-1 and Perkin-Elmer TGA 7 instruments (heating rate: 10°C/min). Xray diffraction (XRD) patterns were recorded by using a Bruker D8 Advance instrument equipped with Cu Kα radiation performed at 40 kV and 40 mA. UV–vis absorption spectra were taken using a Perkin-Elmer Lambda 20 spectrophotometer. Photoluminescence (PL) spectra were measured using a Perkin-Elmer LS50B spectrophotometer. Electroluminescence (EL) analyses were carried out at room temperature in air atmosphere using a KGF-2 fluorometer. AFM images were obtained in both height and phase contrast mode using a Digital Instruments Multimode Nanoscope IIIa scanning force microscope in the tapping mode.

RESULTS AND DISCUSSION

Synthesis and characterization

Scheme 1 shows the synthetic route of the copolymers. The number-average molecular weights of PPVPEO₂₀₀ and PPVPEO₆₀₀ measured by GPC are 1465 with a polydispersity index of 1.97 and 2245 with a polydispersity index of 1.36, respectively. Polymer PPVPEO₆₀₀ are highly soluble in common organic solvents such as tetrahydrofuran (THF), chloroform, methylene chloride, and 1,2-dichloroethane. The polymer dissolution can be spin-coated onto various substrates giving highly transparent and homogeneous thin films. However, polymer PPVPEO₂₀₀ is only soluble in THF and chloroform, and can not give homogeneous thin films by spincoating. This may attribute to the low molecular weight and rigid backbone of PPVPEO₂₀₀ arising from the very short PEO segments compared to PPVPEO₆₀₀.



Scheme 1 The synthetic routes of PPVPEO₂₀₀ and PPVPEO₆₀₀.

The structure and purity of the copolymer PPVPEO₂₀₀ and PPVPEO₆₀₀ were comfirmed by spectroscopic methods. The FTIR spectrum of dialdehyde monomer showed a strong absorption peak of the carbonyl group at about 1685 cm^{-1} (Fig. 1). The abovementioned absorption peak no longer existed after the polymerization. Meanwhile, a new sharp absorption peak appeared at 965 cm⁻¹, which is ascribed to the out-of-plane bending mode of the C-H bond in the transvinylene groups. Shown in Figure 2 are the ¹H-NMR spectrum of PPVPEO₂₀₀ and $PPVPEO_{600}$ and the assignments of the peaks. From the figure, it was found that a peak at 9.86 ppm, assigned to the chemical shift of aldehydic protons of monomer, was no longer noticeable, while two sets of new doublet peaks appeared around 7.5-7.6 ppm, which could be assigned as the four vinylic protons' peaks. It is obvious that the ¹H-NMR analysis shows the agreement with the desired chemical structure, which is also in agreement with the results of elemental analysis. Based on the above analysis, it is confirmed that the copolymers, PPVPEO₂₀₀ and PPVPEO₆₀₀, have been synthesized.

Optical properties

The photophysical properties of PPVPEO₂₀₀ and PPVPEO₆₀₀ were investigated using UV–vis absorption and photoluminescence (PL) spectroscopies. The absorption and emission spectra of the two polymers, in chloroform and in the solid state, are depicted in Figure 3. Polymer PPVPEO₂₀₀ exhibited absorption maxima in dilute chloroform solution at 327 nm, and PPVPEO₆₀₀ exhibited maxima at 328 and 340 nm. However, the emission behavior in the solid state is different from that in solution significantly. The two copolymers exhibited blue fluorescence in solution, but in the thin films, transitions from blue emission to blue-green emission for the two polymers were observed when the films were

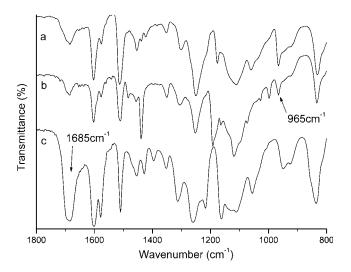


Figure 1 FTIR spectra of (a) PPVPEO₂₀₀, (b) PPVPEO₆₀₀, and (c) DHPEO₆₀₀.

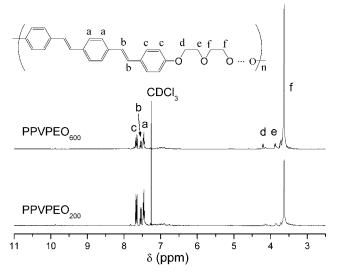


Figure 2 1 H-NMR spectra of polymer PPVPEO₂₀₀ and PPVPEO₆₀₀.

Journal of Applied Polymer Science DOI 10.1002/app

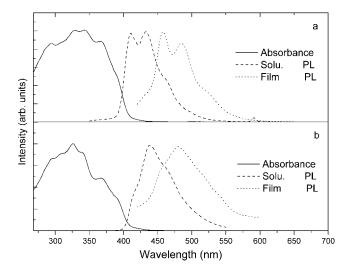


Figure 3 UV–vis absorption and PL spectra of (a) $PPVPEO_{600}$ and (b) $PPVPEO_{200}$.

irradiated with UV light. It is supposed that, owing to the different interactions from the very crowded and rigid backbone segments, the transitions could be caused by aggregation or excimer formation and eventually changes the conjugation properties of the polymers.²⁶ Furthermore, the optical band gaps are both 2.85 eV, which can be estimated from the absorption edges of the thin-film spectra.

Electroluminescent properties of LECs

Because PPVPEO₂₀₀ could not form a good enough film to act as the emissive layer of light emitting devices, we blend PPVPEO₂₀₀ and PEO_{200,000} (molecular weight of 200,000) together to form a homogeneous thin film. The single layer light-emitting electrochemical cells of ITO/PPVPEO₂₀₀ + PEO_{200,000}(LiClO₄)/Au and ITO/PPVPEO₆₀₀(LiClO₄)/Au were fabricated. Figure 4 represents typical results for current-voltage and brightness-voltage measurements. For both the two copolymers, the devices showed turn-on voltages as low as 2.6 V for both current and light emission, which is attractive for the commercial application of the devices. Furthermore, their brightness is approximately proportional to the injected current density. The maximum transfer efficiencies of current density to brightness (i.e., the ratio of brightness to current density) of the devices composed of PPVPEO₂₀₀ or $PPVPEO_{600}$ were 0.68 cd/A at 3.2 V and 0.64 cd/A at 3.2V, respectively. The above analysis shows that LECs based on PPVPEO₆₀₀ without additional PEO have the similar performance with that based on a blend of PPVPEO₂₀₀ and PEO_{200,000}.

Thermal properties

The TGA thermograms of $PPVPEO_{200}$, $PPVPEO_{600}$, and $PEO_{200,000}$ under a nitrogen atmosphere are

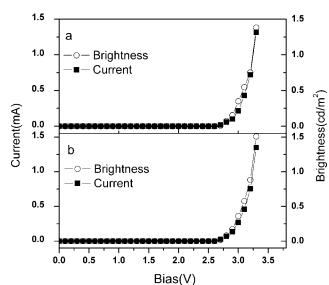


Figure 4 The current–voltage and brightness–voltage characteristics of LECs: (a) $ITO/PPVPEO_{200} + PEO_{200,000}$ (LiClO₄)/Au; (b) $ITO/PPVPEO_{600}$ (LiClO₄)/Au.

shown in Figure 5. The curves show $PEO_{200,000}$ degrades at about 260°C. However, both PPVPEO₂₀₀ and PPVPEO₆₀₀ are thermally stable up to about 305°C. Obviously, a high degradation temperature of the emissive layer is favorable for the longevity of the device operation. Therefore, LEC device based on PPVPEO₆₀₀ was more promising than the device based on blends of PPVPEO₂₀₀ and PEO_{200,000}. It was found that thermal degradation of both PPVPEO₂₀₀ and PPVPEO₆₀₀ take place in two stages with different weight loss ratio. From the weight ratio of PPV and PEO segments in both PPVPEO₆₀₀ and PPVPEO₂₀₀, it can be concluded that the first step involves degradation of the PEO segments, and the

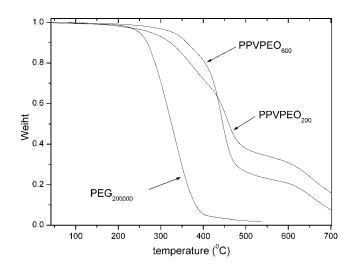


Figure 5 TGA curves of $PEO_{200,000}$, $PPVPEO_{200}$, and $PPVPEO_{600}$.

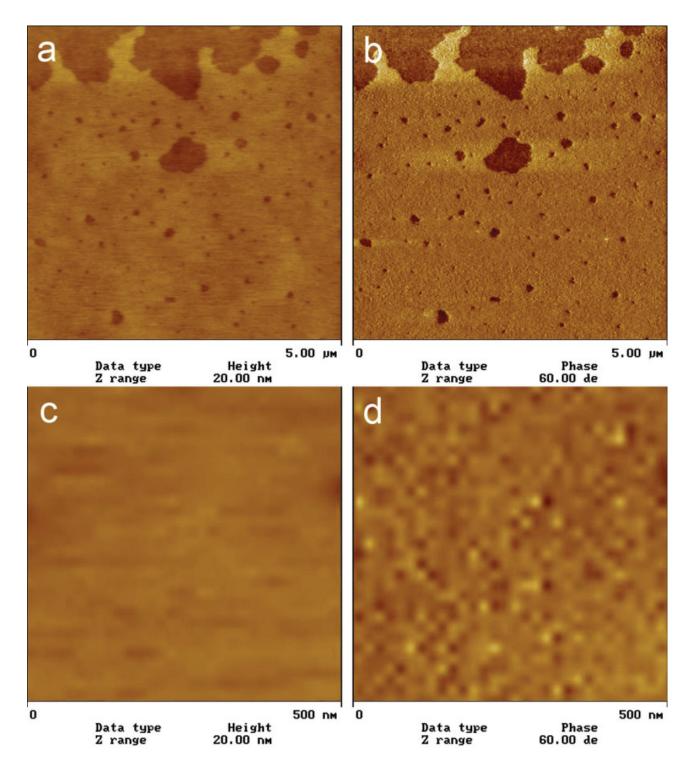


Figure 6 (a) AFM height and (b) phase images of the spin-coated PPVPEO₆₀₀ thin films and (c, d) the magnified height and phase images of a same area, respectively. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

second involves PPV segments degradation. It was noted that PPVPEO₆₀₀ was more thermally stable than PPVPEO₂₀₀. Degradation temperature of PPVPEO₆₀₀ is about 10°C higher than PPVPEO₂₀₀. This may attribute to the different aggregation structures of the two copolymers.

Aggregation structure of PPVPEO₆₀₀ thin film

The aggregation structure of thin films of copolymer $PPVPEO_{600}$ was investigated employing AFM microscopes to examine the topography and phase contrast feature of the surface of the film, which should

50

PEO₂₀₀₀₀₀ PPVPEO₆₀₀ -60 -40 -20 0 20 40 60 80 100 temperature (°C)

Figure 7 DSC plots of PEO_{200,000} and PPVPEO₆₀₀.

possess nanoscale feature sizes due to microphase separation. The PPVPEO₆₀₀ thin film was obtained by spin-coating from its chloroform/acetonitrile (volume ratio of 1/1) solution. Shown in Figure 6 are the height and phase images of a PPVPEO₆₀₀ thin film. In the height image [Fig. 6(a)], the top of the film appear flat, due to the expanded height scale of the image. The phase images [Fig. 6(b)] shows that many granular domains are present on the top of the film. Shown in Figures 6(c,d) are the magnified height and phase images of the film. The average diameter of the granules was around 20 nm and the average center to center distance of the granules domains was about 20 nm too. Previously studies revealed that the softer polymer domains exhibited darker contrast while the hard matrices appeared bright in the phase images.²¹ For the copolymers, the PPV segments are harder than the PEO segments. Additional, from the volume fraction of PPV and PEO and the ratio of the areas of the granules and the matrix, it can be concluded that the nanogranules are most likely the PPV domains and the continuous phase is the PEO domain.

DSC and XRD techniques were used to further study the aggregation structure of the PEO domains of the $PPVPEO_{600}$ thin film. Shown in Figure 7 are the DSC plots of PEO_{200,000} and PPVPEO₆₀₀. The endothermic peak of the plot of $PEO_{200,000}$ between $50^\circ C$ and $70^\circ C$ at heating scan corresponds to the crystalline PEO. Thus, in the DSC plot of $PPVPEO_{600}$, the absence of the above peak reveals that the PEO domains of PPVPEO₆₀₀ are amorphous. The XRD curve of PEO_{200,000} shows sharp reflection peaks at 19° (20) and 23.5° (20), which can be indexed to crystalline PEO (shown in Fig. 8). However, in the measurement of the sample of the $PPVPEO_{600}$ thin film, no sharp diffraction peaks but wide diffuse scattering peaks were observed, which further proves that the PEO domains of the PPVPEO₆₀₀ film are totally amorphous.

Figure 8 XRD curves of PEO_{200,000} and PPVPEO₆₀₀.

On the basis of the above discussions, we conclude that the suggested self-assembled structure of PPVPEO₆₀₀ thin films is that PPV nanogranules embedded in a matrix of amorphous PEO as shown in Figure 9. For self-assembly, organic solvents play an important role in increasing the solvent affinity of a block copolymer, behaving as a selective solvent for a block.¹⁸ Then, PEO blocks miscible with the solvent are exposed on the outer surface of aggregates, and the nonmiscible PPV blocks are located inside the aggregates. Thus these aggregations leads to the nanoscale network containing the luminescent domains and electrolyte matrix, which may account for the high EL efficiency of the LEC based on PPVPEO₆₀₀. Mobility of the soft PEO segments in the backbone of PPVPEO₆₀₀ is decreased by the rigid PPV segments, which cause PEO segments has not crystallized. Aggregations of the rigid PPV segments also perform as pseudo-cross-linking points to form a three dimensional network, which provides the polymer film with both good thermal stability and good

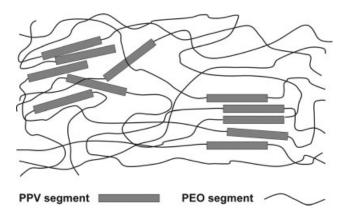
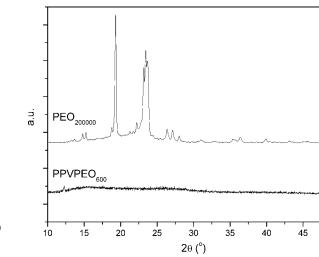


Figure 9 Suggested aggregation structure of the spincoated PPVPEO₆₀₀ thin film.





structural stability compared with the blend of $PPVPEO_{200}$ and $PEO_{200,000}$.

CONCLUSIONS

Luminescent poly(p-phenylene-vinylene-b-oligoethylene oxide) containing different length of PEO segments, PPVPEO₂₀₀ and PPVPEO₆₀₀, has been successfully synthesized, respectively. Single-layer LEC devices based on PPVPEO₆₀₀ or a blend of PPVPEO₂₀₀ and PEO_{200,000} are fabricated. Investigation of the PL, EL characterizations of the devices indicates that LEC based on PPVPEO₆₀₀ has almost the same performance with that based on a blend of PPVPEO₂₀₀ with PEO_{200,000}. However, TGA analysis shows that PPVPEO₆₀₀ is more thermally stable than PPVPEO₂₀₀ or PEO_{200,000}. AFM studies of PPVPEO₆₀₀ thin films exhibits that the block copolymer self-assembles to form nanoscale network structures with pseudocross-linking points, thus accounting for its high thermal stability and good EL performance.

References

- Wang, H.; Sun, Q.; Li, Y.; Liu, D.; Wang, X.; Li, X. React Funct Polym 2002, 52, 61.
- 2. Kwon, S. H.; Paik, S. Y.; Yoo, J. S. Synth Met 2002, 130, 55.
- Gustafuson, G.; Cao, Y.; Treacy, G. M.; Klavetter, F.; Colaneri, N.; Heeger, A. J. Nature 1992, 357, 477.
- Kraft, A.; Grimsdale, A. C.; Holms, A. B. Angew Chem Int Ed 1998, 37, 402
- 5. Kim, G. H.; Oh, J.; Yang, Y. S.; Do, L.-M.; Suh, K. S. Thin Solid Films 2004, 467, 1.

- Burrows, P. E.; Bulovic, V.; Forrest, S. R.; Sapochak, L. S.; Mccarty, D. M.; Thompson, M. E. Appl Phys Lett 1994, 65, 2922.
- Ghosh, A. P.; Gerenser, L. J.; Jarman, C. M.; Fornalik, J. E. Appl Phys Lett 2005, 86, 223503.
- 8. Sun, Q.; Wang, H.; Yang, C.; Wang, X.; Liu, D.; Li, Y. Thin Solid Films 2002, 417, 14.
- Pei, Q.; Yu, G.; Zhang, C.; Yang, Y.; Heeger, A. J. Science 1995, 269, 1086.
- 10. Pei, Q.; Yang, Y. J Am Chem Soc 118 (1996) 7416.
- 11. Morgado, J.; Cacialli, F.; Friend, R. H.; Chauh, B. S.; Rost, H.; Holmes, A. B. Macromolecules 2001, 34, 3094.
- 12. Stephan, O.; Collomb, V.; Vial, J.; Armand, M. Synth Met 2001, 113, 257.
- 13. Cho, C.-H.; Lee, Y.-S.; Nahm, K. S.; Y. B., Hahn; Yu, S.-C. Synth Met 2000, 114, 331.
- Benfaremo, N.; Sandman, D. J.; Tripathy, S.; Kumar, J.; Yang, K.; Rubner, M. F.; Lyons, C. Macromolecules 1998, 31, 3595.
- Li, Y.; Cao, Y.; Gao, J.; Wang, D.; Yu, G.; Heeger, A. J. Synth Met 1999, 99, 243.
- Yang, C.; He, G.; Wang, R.; Li, Y. Mol Cryst Liq Cryst 1999, 337, 473.
- 17. Sun, Q.; Wang, H.; Yang, C.; Li, Y. Synth Met 2002, 128, 161.
- 18. Sun, Q.; Wang, H.; Yang, C.; Li, Y. J Mater Chem 2003, 13, 800.
- Ma, C.-C. M.; Lee, C.-T.; Wu, H.-D. J Appl Polym Sci 1998, 69, 1129.
- Kim, Y.; Mayer, M. F.; Zimmerman, S. C. Angew Chem Int Ed 2003, 42, 1121.
- Lin, Z.; Kim, D. H.; Wu, X.; Boosahda, L.; Stone, D.; Larose, L.; Russell, T. P. Adv Mater 2002, 14, 1373.
- 22. Shimizu, T.; Masuda, M.; Minamikawa, H. Chem Rev 2005, 105, 1401.
- Choi, C.; Chae, S. Y.; Kim, T. H.; Kweon, J. K.; Cho, C. S.; Jang, M. K.; Nah, J. W. J Appl Polym Sci 2006, 99, 3520.
- 24. Armstrong, G.; Buggy, M. J Mater Sci 2005, 40, 547.
- 25. Pedersen, C. J. J Am Chem Soc 89 (19676) 7017.
- 26. Zheng, L.; Urian, R. C.; Liu, Y.; Jen, A. K.-Y.; Pu, L. Chem Mater 2000, 12, 13.