Synthesis and Characterization of Novel Soluble Alternating Copoly(phenylene vinylene) Derivative for Light-Emitting Electrochemical Cell

Dong Xiang, Qundong Shen, Suyang Zhang, Xiqun Jiang

Department of Polymer Science & Engineering, College of Chemistry & Chemical Engineering, Nanjing University, Nanjing 210093, People's Republic of China

ABSTRACT: A novel alternating copolymer, poly{[2,5-di(2-(2-ethoxy ethoxy)ethoxy)-1,4-phenylene vinylene]-alt-1,4-[phenylene vinylene]}, has been synthesized through the Wittig condensation as electroluminescent material. In this copolymer, one component is phenylene vinylene with flexible oligo(ethylene oxide) side chain that facilitates ion transportation and phase miscibility between nonpolar and polar part of composite luminescent layer, and another is a rigid phenylene vinylene moiety to improve luminescent quantum efficiency and tune color. The copolymer shows good solubility and thermal stability for device fabrication compared to poly(phpeylene vinylene)(PPV). The band gap value of copolymer is between those of corresponding homopolymers, which indicates that alternating copolymerization is a suitable way to obtain luminescent polymer with desired band gap. The maximum wavelength of photoluminescence of copolymer is 539 nm (yellowish-green). The HOMO and LUMO energy levels obtained by cyclic voltammetry measurement indicate that the electron injection ability of copolymer has been greatly improved compared with that of the PPV. A more balanced carrier injection and higher quantum efficiency are proved by electroluminescent properties of corresponding light-emitting devices. The turn-on voltage of LEC device (ITO/copolymer + PEO + LiClO$_4$/Al) is found to be 2.3 V, with current comparative to LED (ITO/copolymer/Al) at 9.5 V. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 1350–1356, 2003

Key words: light-emitting diodes (LED)s; copolymerization; luminescence; cyclic voltammetry; light-emitting electrochemical cells (LEC)

INTRODUCTION

Light-emitting electrochemical cell (LEC) is an electrochemically driven light-emitting device utilizing a composite of a luminescent semiconductor and a solid-state ionic conductor as the active electroluminescent (EL) layer sandwiched between two contacts. Pei et al. first described such devices containing a blend of conjugated luminescent poly(phenylene vinylene) (PPV)[1] or its derivative, MEH-PPV,[2] with polymer electrolyte made of poly(ethylene oxide) (PEO) and lithium salt as the active layer. The operating mechanism of LEC can be described as an electrochemical redox of the conjugated polymer and the accompanying redistribution of ions from the solid-state electrolyte, which cause a p-type doping near the anode and an n-type doping near the cathode. The combination of electrons injected from the n-type side of the junction and holes injected from the p-type side of the junction emits light.[3] Because of the Ohmic contacts between the metal electrodes and the doped regions of the polymer, and the improved injection balance between electron and hole of carrier, LEC offers a number of potential advantages such as relative high quantum efficiency, dual light emission, and low turn-on voltage for electroluminescence over an undoped light-emitting diode (LED) made with the same semiconducting polymer.

Due to the nonpolar character of a conventional light-emitting component (PPV and MEH-PPV) and the polar character of a polymer electrolyte (PEO), these two components within the EL layer may separate into two phases. One phase of semiconducting polymer enables electron transport of the injected electron and the hole, and another phase of the solid-state electrolyte enables ion transport. In such a case, the slower response rate of LEC with respect to LED was found and was ascribed to slow diffusion of ion to semiconducting phase. Addition of a surfactant to obtain a nanometer-length scale-separated light-emitting layer ensures a maximum interfacial area and rapid effective transport of ions into the semiconducting polymer.[4] However, the physical loss of surfactant molecules by migration is inevitable and detrimental to maintenance of the original properties of the device.

To address the problems related to dispersion stability, PPV homopolymers with an oligo(ethylene oxide) side chain covalently attached to the aromatic ring of backbone have been reported.[5–6] The response time of such an LEC was drastically reduced from a second to a microsecond range, which demonstrates that the phases miscibility of the blends and ionic conductivity are crucial for performance of LEC.[7]

Although flexible oligo(ethylene oxide) side chains decrease the persistence length of PPV, the decrease of the photo-luminescent (PL) quantum efficient will occur due to the reduction of main chain stiffness.[8] To improve the intrinsic rigidity of the conjugated polymer, we design a PPV-based alternating copolymer. In this copolymer, one component is 2,5-di(2-(2-ethoxy ethoxy)ethoxy)-1,4-phenylene vinylene (DTEO-PV) with a flexible oligo(ethylene oxide) side chain to facilitate ion transportation and phase miscibility between the nonpolar and polar parts of the composite, and another is a rigid 1,4-phenylene vinylene to improve the luminescent quantum efficiency and chemically tune color.[9] On the basis of this structure, a good solubility can also be expected, which will make it easy for device fabrication. Here we report the synthetic details of this copolymer and its thermal stability, electrochemical property, and PL/EL behaviors.

EXPERIMENTAL

Materials

Anhydrous toluene and tetrahydrofuran were obtained by distillation over sodium/benzophenone. Commercial *tert*-butyl alcohol was dried by refluxing it with sodium until about two-thirds of the metal was dissolved, and then distilled. All other commercial reagent-grade solvents and chemicals were used without further purification.

Measurements

IR spectra were recorded on a Bruker IFS66V vacuum Fourier-transfer spectrometer. ^{1}H-NMR spectra were collected on a Bruker DPX300 spectrometer. Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer for C and H determination. Mass spectra were collected by an LCQ Finningan MAJ electrospray mass spectrometer. Thermogravimetric analysis (TGA) was conducted on a TA Instrument 2100 system with a TGA 2950 thermogravimetric analyzer under a heating rate of 10°C/min and a nitrogen flow rate of 60 mL/min. Ultraviolet-visible (UV-Vis) and fluorescence spectra were obtained on a Shimadzu UV-3100 spectrophotometer and a Perkin-Elmer 5050 luminescence spectrometer, respectively. Gel permeation chromatography (GPC) analysis was conducted on a Waters GPC 244 system using poly-styrene standards and THF as an eluent at a flow rate of 1 mL/min. Cyclic voltammetry (CV) was performed on an EG & G Princeton Model 273 potentiostat/galvanostat system with a three-electrode cell using a working platinum electrode coated with a film of copolymer and solid electrolyte blend, a Pt wire counter electrode, and a Ag wire reference electrode at a scan rate of 20 mV/s. The solid electrolyte was a 20 wt % blend of LiClO$_4$ in PEO.

Fabrication and characterization of EL devices

Two types of EL devices were fabricated. The first is an LED with an ITO/copolymer/Al structure. Copolymer was spin-coated (1800 rpm) on ITO from a 1 wt % solution of copolymer in chloroform to obtain a film of about 70 nm thick (measured by ALPHA STEP 500 surface profiler). The second type of device was an LEC with an ITO/ copolymer + PEO + LiClO$_4$ /Al structure. The polymer blend layer was spin-coated (1800 rpm) on ITO from a solution of 92 mg of copolymer, 95 mg of PEO, and 19 mg of LiClO$_4$ in 10 mL of DMF to obtain a film of about 50 nm thick. Cleaning of the ITO includes ultrasonication and extraction steps in CHCl$_3$ and ethanol. Sheet resistance of ITO is about 30 Ω/square. The aluminum contact (about 500 nm in thickness) was deposited onto the active layer by vacuum evaporation (5×10^{-6} Torr). The active area of the electroluminescent devices was approximately 24 mm^2.

Current–voltage measurements were carried out using a 2650 digital source-measure unit. Simultaneously, the luminance was detected by using a model UBD-1/4 degree luminance meter. All measurements were performed under ambient atmospheric conditions.

Synthesis

2-(2-ethoxyethoxy) ethyl chloride (1)

A mixture of the dry pyridine (1.76 mol), 2-(2-Ethoxyethoxy) ethanol (1.6 mol), and petroleum ether (200 mL) was cooled to 0°C, and the thionyl chloride (2.08 mol) was added with stirring at such a rate that the temperature did not rise above 5°C/min.[10] After completion of the addition, the reaction mixture was then allowed to warm to room temperature and thereafter heated to reflux until the evolution of gas ceased. When cold, the mixture separated into two phases and the organic layer was collected. After evaporation of the petroleum ether and thionyl chloride, the light brown residue was washed with dilute sodium hydroxide and sodium chloride solutions (10%) successively, and dried with anhydrous magnesium sulfate. The colorless liquid product **1** (154.4 g, yield 60%) was then obtained by distillation of the residue under re-

duced pressure. ^{1}H-NMR (CCl$_4$) δ (ppm): 1.00 (3H, —CH$_3$, t), 3.52 (2H, —CH$_2$—Cl, t), 3.28–3.52 (8H, —CH$_2$—CH$_2$CH$_2$OCH$_2$—, m); IR (KBr) ν_{max}(cm^{-1}): 2960 (s), 2850 (s), 1420 (m), 1376 (m), 1298 (s), 1046 (m), 670 (m).

1,4-di[2-(2-ethoxy ethoxy)ethoxy]benzene (2)

To a mixture of hydroquinone (0.12 mol), potassium hydroxide (0.3 mol), PEO (0.016 mol, M_W = 750), and anhydrous ethanol (100 mL) was added dropwise **1** (0.26 mol) under vigorous stirring.[11] With the temperature raised slightly and plenty of solid salt precipitating, the mixture darkened into black brown color. After adding all of **1**, the mixture was then stirred and heated at 74°C for 24 h and cooled. The dark brown precipitation was filtered and washed by anhydrous ethanol several times until it turned white. After removal of ethanol, the filtrate was dissolved in ether (200 mL), washed with dilute solution of sodium hydroxide and brine successively, and dried with anhydrous CaCl$_2$. Elimination of the ether afforded a yellow brown solid. The crude product was finally purified by column chromatography using silica gel-60 and several mixtures of petroleum ether/acetic ester as eluents to yield a white solid compound **2** (24.2 g, yield 67%). ^{1}H-NMR (CCl$_4$) δ (ppm): 1.02–1.25 (6 H, CH$_3$, t), 3.23–4.00 (20 H, —OCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_2$—, m), 6.64–6.68 (4 H, —C$_6$H$_4$—, s); IR (KBr) ν_{max}(cm^{-1}): 2950 (s), 2900 (s), 2840 (s), 1498 (s), 1446 (s), 1368 (m), 1344 (m), 1278 (m), 1225 (s), 1102 (s), 1060 (s), 930 (m), 822 (m), 754 (m); m.p. 33–34°C.

2,5-bis(chloro-methyl)-1,4-di[2-(2-ethoxy ethoxy)-ethoxy]benzene (3)

To a stirred solution of **2** (0.04 mol) in 60 mL of dioxane and 20 mL of concentrated hydrochloric acid, cooled to 2°C, 24 mL of 37% formalin solution was added. A stream of hydrogen chloride gas was bubbled through the mixture for 30 min, and then the temperature was increased to 56°C. After 2 h, another 16 mL of formalin solution was added at 2°C. The temperature was again raised and reaction was allowed to proceed for 20 h at 56°C. The mixture was saturated with hydrogen chloride throughout.[12]The solvents were then completely removed to give a light yellow liquid residue, which was dissolved in 80 mL of ether and washed with a dilute solution of NaHCO$_3$ and brine successively. Elimination of the solvent afforded a yellow solid. The crude product was finally purified by column chromatography using silica gel-60 and several mixtures of petroleum ether/acetic ester as eluents to yield a light yellow solid compound **3** (10 g, yield 56%). ^{1}H-NMR (CDCl$_3$) δ (ppm): 1.24 (6 H, CH$_3$–t), 3.52–3.90 (16 H, —CH$_2$OCH$_2$CH$_2$OCH$_2$—, m), 4.18 (4 H, —CH$_2$OC$_6$H$_2$, m), 4.65 (4 H,

—CH$_2$Cl, s), 6.96 (2 H, —C$_6$H$_2$—, s); IR (KBr) ν_{max}(cm^{-1}): 2950 (s), 2850 (s), 1504 (s), 1440 (m), 1410 (s), 1370 (m), 1346 (m), 1310 (m), 1256 (m), 1210 (s), 1175 (m), 1100 (s), 1054 (s), 946 (m), 865 (m), 738 (m), 700 (m), 628 (m); Anal. Calcd for C$_{20}$H$_{32}$Cl$_2$O$_6$: C, 54.67%; H, 7.34%; Cl, 16.14%. Found: C, 54.45%; H, 7.46%; Cl, 16.34%; m.p. 39–39.5°C.

1,4-di[2-(2-ethoxy ethoxy)ethoxy]-2, 5-xylenebis(triphenylphosnium chloride) (4)

A mixture of **3** (9.51 mmol) and triphenylphosphine (19.2 mmol) in 80 mL of anhydrous toluene was heated at reflux temperature with stirring for 22 h.[13,14] The mixture was then cooled to room temperature. The precipitation was collected by filtration and washed with cold anhydrous toluene several times. After drying in a vacuum oven, a white solid powder **4** was obtained (7.7 g) in 84% yield; m.p.: 245–246°C ; ^{1}H-NMR (CDCl$_3$) δ (ppm): 1.18 (6 H, CH$_3$—, t), 3.20–3.58 (20 H, —CH$_2$OCH$_2$CH$_2$OCH$_2$—CH$_2$O—, m), 6.55 (4 H, —CH$_2$OC$_6$H$_2$, d), 7.45–7.73 (32 H, —C$_6$H$_2$—, (C$_6$H$_5$)$_3$P—, m); IR (KBr) ν_{max}(cm^{-1}): 3400 (m), 3000 (m), 2800–2950 (s), 1580 (w), 1500 (m), 1480 (m), 1425 (s), 1390 (m), 1340 (m), 1310 (m), 1220 (s), 1100 (s), 1050 (s), 990 (m), 940 (s), 860 (m), 830 (m), 740 (s), 730 (m), 690 (s), 630 (w), 490–510 (s); ESR-MAS: (C$_6$H$_5$)$_3$-P$^+$CH$_2$C$_{20}$H$_{30}$O$_6$C$^+$H$_2$P(C$_6$H$_5$)$_3$ (M^{2+}, 446.5).

Poly{[2,5-di(2-(2-ethoxy ethoxy)ethoxy)-1,4-phenylene vinylene]-alt-1,4-[phenylene vinylene]} (5)

Based on the Wittig condensation reaction,[15] **4** (3.46 mmol) and terephthalaldehyde (3.46 mmol) were dissolved in a mixture of anhydrous *tert*-butanol (10 mL) and tetrahydrofuran (20 mL) in a 100-mL dried round-bottomed flask, which was equipped with a magnetic stirring bar and capped with a rubber septum. A solution of *tert*-butoxide (8.3 mmol) in anhydrous tetrahydrofuran (16 mL) and *tert*-butanol (8 mL) was added dropwise to the reaction flask via a syringe at room temperature. The reaction mixture turned from yellow to orange with the addition of *tert*-butoxide. The reaction mixture was stirred for another 10 h at room temperature after completion of the addition. The resulting polymer was precipitated out from methanol and collected by filtration. Further purification was carried out by dissolving the polymer into chloroform and precipitating in methanol twice. After drying under a vacuum oven for 24 h, an orange elastomer **5** (1.07 g) was obtained in 66% yield. ^{1}H-NMR (CDCl$_3$) δ (ppm): 1.23 (CH$_3$—, m) 3.55–4.27 (—CH$_2$CH$_2$OCH$_2$CH$_2$O—CH$_2$—, m), 7.28 (CDCl$_3$, s), 7.12–7.17 (—HC=CH—, m), 7.49–7.62 (—C$_6$H$_2$—, m). FTIR (film on NaCl plate) ν_{max}(cm^{-1}) 3051 (w), 2972–2928 (m), 2867 (s), 1597 (w), 1514 (m), 1493 (m), 1422
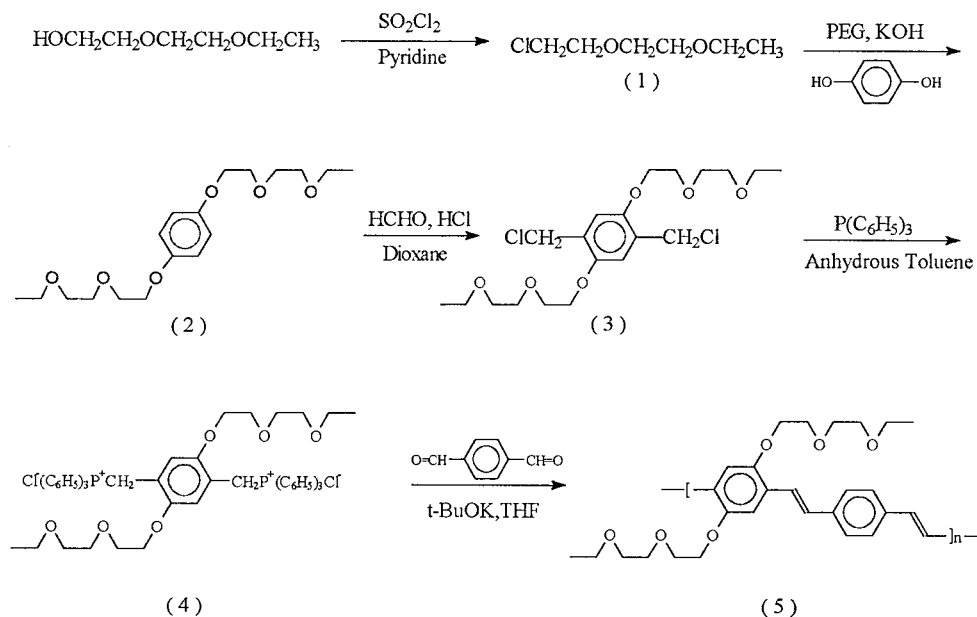
Scheme 1 Synthetic route to poly{[2,5-di(2-(2-ethoxy ethoxy)ethoxy)-1,4-(phenylene vinylene)]-alt-1,4-[phenylene vinylene]}.

(m), 1349 (w), 1260 (w), 1210 (s), 1112 (s), 962 (m), 856 (w). Anal. Calcd. for $(C_{28}H_{36}O_6)_n$: C, 71.46%; H, 8.14%; O, 20.40%; Found: C, 67.35; H, 8.25; O, 24.40.

RESULTS AND DISCUSSION

Sample preparation and identification

Scheme 1 shows the synthesis route of alternating copolymer **5**. The key intermediates to synthesis of the targeted copolymer are compounds **2** and **3**, which exhibit good solubility in common solvents and poor ability of crystallization due to the introduction of flexible side groups. Purification by conventional method of recrystallization was unsuccessful and gave low yield. We thus adapted column chromatography separation with a mixed solvent of petroleum/acetic ester as an eluent and obtained a satisfying result.

The Gilch dehydrohalogenation polymerization has been widely applied to the preparation of soluble PPVs.[16,17] Generally, a random PPV copolymer was obtained by this method.[18] This one-step route shows great advantages over various precursor routes. However, gelation or microgel emerged in this route implies that some structural defect will be introduced into the materials.[19] We proposed that an interchain substitution by-reaction between the carbonionic intermediate arising from chain propagation of anion polymerization and —CHCl— groups in the nonfully conjugated polymer chains leads to generation of multianions and eventual gelation. We found that poly[2,5-di (2-(2-ethoxy ethoxy) ethoxy)-1,4-phenylene vinylene] (DTEO-PPV) homopolymer obtained by the Gilch method was only partial dissolved in chloroform, which can be ascribed to the existence of microgel. Besides the Gilch route, the PPV copolymer can also be synthesized by Wittig condensation[20–22] and the Heck route.[23] To avoid gelation in the polymerization, we take the Wittig reaction between the appropriate dialdehyde and 1,4-xylylene bis(triphenylphosphonium chloride) derivative to prepare the alternating copolymer. The copolymer **5** shows good solubility in some common solvents such as $CHCl_3$, DMF, and THF. The GPC analysis reveals that the value of the number-average molecular weight (M_n) and weight-average molecular weight (M_w) is 7,840 and 16,400, respectively. These results indicate that the introduction of long oligo(ethylene oxide) side chains significantly improve the solubility of the polymer.
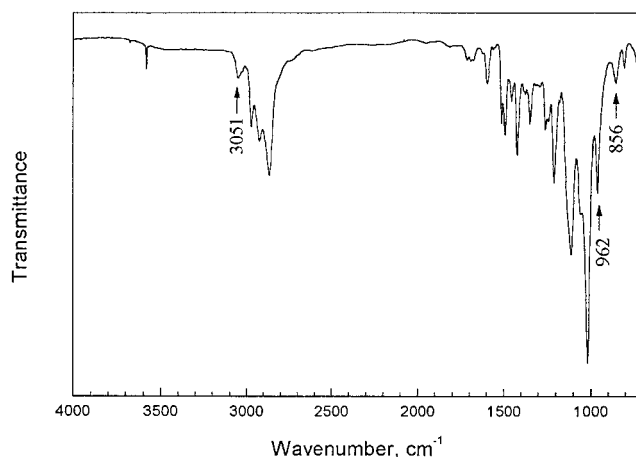
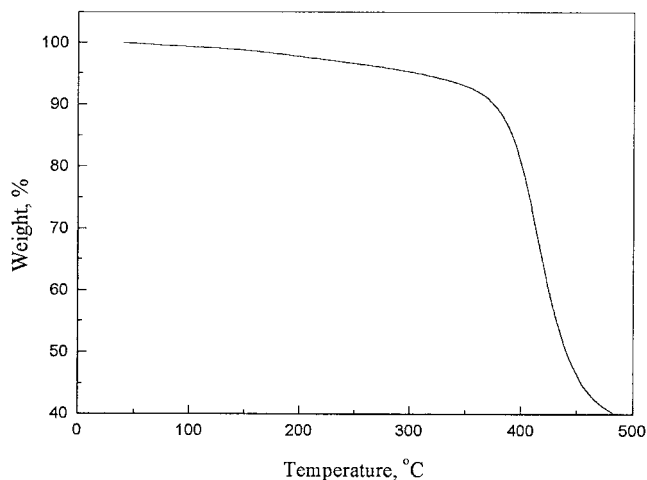**Figure 1** FTIR spectrum of copolymer 5 cast on a NaCl plate.

The IR spectrum of copolymer **5** (Fig. 1) shows the presence of olefins. The peak at 3051 cm^{-1} corresponds to the C—H stretching vibration mode of olefin, and the peaks at 962 and 856 cm^{-1} are attributed to the C—H bending vibrations of the *trans-* and *cis*-olefins, respectively. Compared with the corresponding NMR spectrum of the monomer, resonance of protons on the newly formed vinylene groups shows a new peak at about 7.15 ppm.
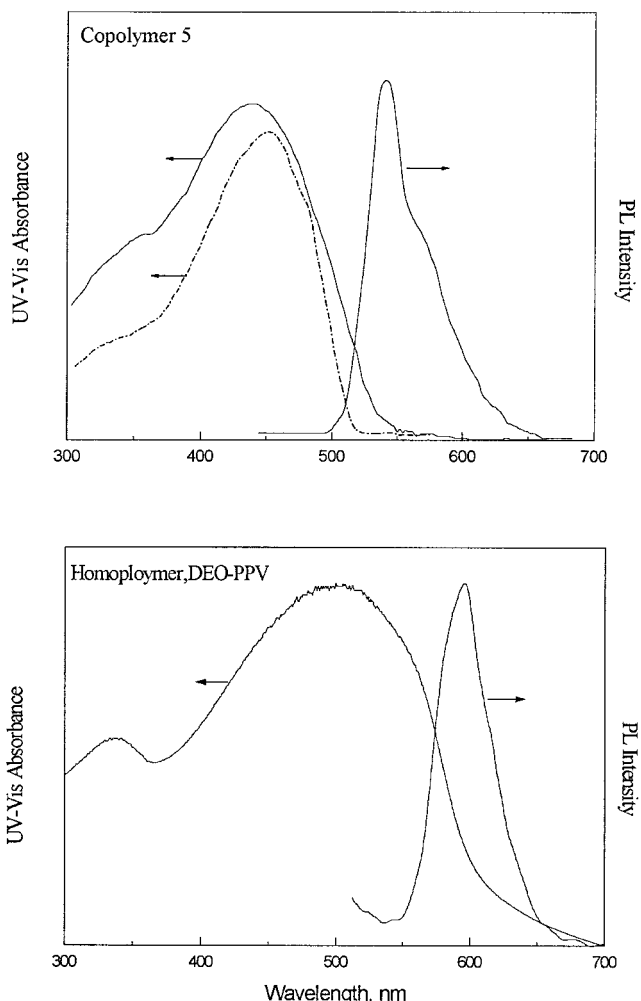
Thermal analysis

Thermogravimetric analysis is shown in Figure 2. The copolymer exhibits an onset of degradation at 365°C, and no distinct weight loss was observed at lower temperature. This onset temperature is higher than that of dialkoxy-substituted PPVs such as MEH-PPV or BEH-PPV (both onsets at 340°C).[24] The maximum rate of weight loss takes place at temperature above 400°C. The result of TGA reveals that the copolymer is quite stable in nitrogen atmosphere, which may be favorable for long-life operation when it used as light-emitting devices.

Optical properties

UV-Vis absorption and photo-luminescent (PL) spectra for DTEO-PPV homopolymer and copolymer are depicted in Figure 3. The electron absorption spectra of DTEO-PPV homopolymer in the solid state shows two peaks at about 337 and 500 nm, respectively. The longer wavelength is attributed to the electron transition of $\pi-\pi^*$ along the conjugated main chain, while the shorter one originates from the n–π^* electron transition of the aromatic side chains. The edge absorption at 605 nm corresponds to an optical band gap (E_{opt}) of 2.05 eV, which is lower than the band gap of parent PPV (2.49 eV).[25] In addition, the band gap of DTEO-

**Figure 3** UV-Vis absorption and PL spectra of PPV in solid state (solid line) or chloroform solution (dash line).

PPV homopolymer is slightly different from that of dimethoxy-substituted PPV (E_{opt} = 2.03 eV)[11] and MEH-PPV (2.1 eV).[26] This means that the band gap of PPV was influenced by alkoxyl substituents and was essentially independent of the species of the alkoxyl substituent.[6] The red shift of the DTEO-PPV homopolymer should be ascribed to the electron-donating effect of the alkoxyl-substituent. On the other hand, the copolymer in the solid state shows maximum absorption of $\pi-\pi^*$ transition at 436 nm; a shoulder peak of n–π^* transition at 358 nm also was observed. The edge absorption at 534 nm corresponds to an optical band gap (E_{opt}) of 2.32 eV. This band gap value of copolymer is between that of corresponding DTEO-PPV and PPV, which indicate that alternating copolymerization is a suitable way to obtain luminescent polymer with desired band gap.

It can also be found that the edge absorption of the copolymer in chloroform solution was at 512 nm, corresponding to E_{opt} of 2.42 eV. Reduction of the band gap and narrowing the absorption peak from solution

Figure 2 TGA curve of copolymer at a heating rate of 10°C/min under flowing nitrogen.
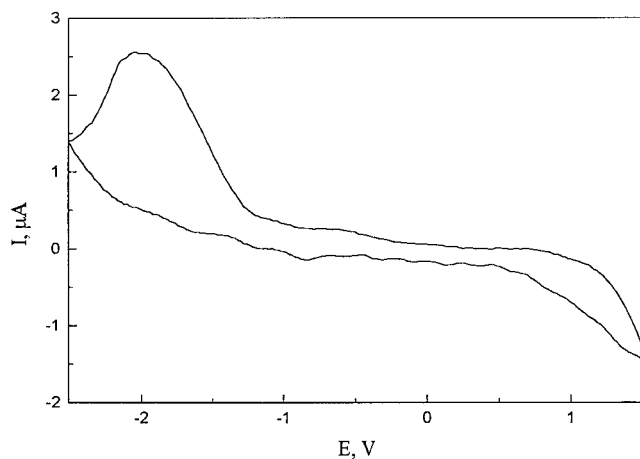
Figure 4 Cyclic voltammogram of copolymer 5/PEO/LiClO$_4$ coated on a Pt working microelectrodes at a scan rate of 20 mV/s; Pt and Ag wires as counter and reference electrodes, respectively.

to film are due to a reduction of the disorder or an increase in the effective conjugation length of the conjugated polymer, which implies that the conformation of the solid-state copolymer is in a rather ordered state.

The emission spectrum of copolymer obtained by excitation at 425 nm in Figure 3 shows the maximum emission wavelength is 539 nm, which corresponds to yellow-green light.

Electrochemical properties

Figure 4 depicts the cyclic voltammogram of copolymer **5,** through which we can investigate the redox behavior of polymer and estimate the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the material. The p-doping and n-doping processes occur under the positive and negative scans. Accompanying the doping process, there was an obvious color change in the polymer film, i.e., orange in the neutral state and dark brown under the doped state. But no obvious reversible doping and dedoping process was observed. The onset potentials of the reduction and oxidation are −1.17 V and 1.12 V vs. Ag, respectively. According to the standard normal potential (0.39 eV) of ferrocene/ferrocenium (FOC) in this system and the vacuum energy level (4.8 eV) of it, the HOMO and LUMO energy level can be estimated to be 5.53 and 3.24 eV, respectively.[27,28] The former value is slightly lower than that of PPV (5.4 eV), which means that the copolymer has worse hole injection ability than PPV. The latter value is much lower than the PPV (2.12 eV), which indicates that the electron injection ability of copolymer has been greatly improved compared with that of the PPV. From this preliminary result, a more balanced injection of hole and electron and a better

quantum efficiency can be expected when this novel copolymer is used as the emission material for a single-layer LED. The energy gap from HOMO and LUMO energy level is 2.29 eV, which is in accordance with the band gap obtained by electronic spectra.

Electroluminescent behavior

The current–voltage and luminance–voltage curves of the LED (ITO/copolymer **5**/Al) are displayed in Figure 5. The I/EL-V characteristics of the device show a typical diode character. The turn-on voltage of light (6 V) is significantly lower than the 15 V for the PPV, indicating a greatly improved injection balance between hole and electron. Comparing the current–voltage curve with the luminance–voltage curve, one can notice that, the turn-on voltage of light (6 V) is not in the same place as that of current (ca. 4 V). This means that an imbalanced injection of opposite charges still exists and the electron injection is less efficient than hole injection.[29] This result is consistent with that from the electrochemical studies.

We have also investigated the electroluminescent properties of the LEC device with a structure of ITO/copolymer **5** + PEO + LiClO$_4$/Al. The turn-on voltage (2.3 V) of this device is significantly lower than that of the corresponding LED, with a current of 1.8 mA comparative to that of the latter at a voltage of 9.5 V. This shows a better charge injection and EL efficiency in the LEC device than corresponding LED. In fact, the current injection is so high that we did not obtain the I/EL-V curve of the device due to its quick damage in the air. It is apparent that necessary encapsulation and inert gas protection should be utilized in the future studies of this device. It is worthy to point out that the novel copolymer can be blended with the solid electrolyte without difficulties. This provides it a good promise in the application of LEC devices.
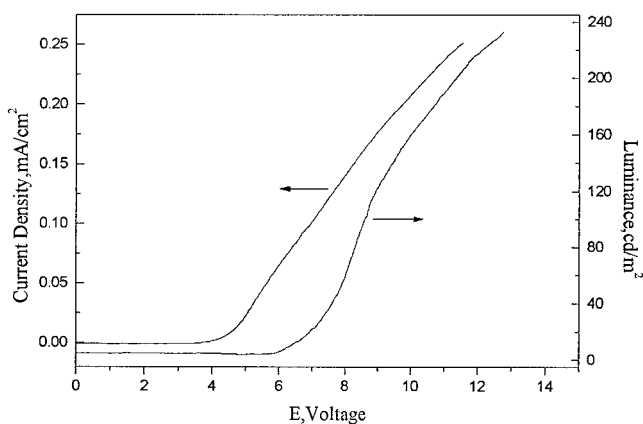
Figure 5 Current density and light output vs. drive voltage for LED of ITO/copolymer 5/Al.

CONCLUSION

A novel alternating copolymer, poly{[2,5-di (2-(2-ethoxy ethoxy)ethoxy)-1,4-phenylene vinylene]-alt-1,4-[phenylene vinylene]}, has been synthesized through the Wittig condensation. Incorporation of a flexible oligo(ethylene oxide) moiety as a side chain to PPV backbone improved the solubility of PPV in comment solvents and the high-quality copolymer films can be fabricated by spin-coating techniques. TGA analysis shows that the copolymer has quite good thermal stability, which could be valuable for longer device operation when it is used as emission material. The absorption and fluorescent emission spectra of the copolymer indicate that it is a yellowish-green emitting material with a band gap of 2.32 eV. The HOMO and LUMO energy levels obtained by cyclic voltammetry measurement indicate that the electron injection ability of copolymer has been greatly improved compared with that of the PPV. A more balanced carrier injection and higher quantum efficiency are proved by electroluminescent properties of corresponding light-emitting devices. A single-layer LED device with a stable metal (Al) as cathode was successfully fabricated. The threshold voltage of the device is about 6 V. In addition, the turn-on voltage of LEC device (ITO/copolymer + PEO + $LiClO_4$/Al) is found to be 2.3 V, with current comparative to LED (ITO/copolymer/Al) at 9.5 V.

References

1. Pei, Q.; Yang, Y.; Yu, G.; Zhang, C.; Heeger, A. J. J Am Chem Soc 1996, 118, 3922.
2. Pei, Q.; Yu, G.; Zhang, C.; Yang, Y.; Heeger, A. J. Science 1995, 269, 1086.
3. Smith, D. L. J Appl Phys 1997, 81, 2869.
4. Cao, Y.; Yu, G.; Heeger, A. J.; Yang, C. Y. Appl Phys Lett 1996, 68, 3218.
5. Chuah, B. S.; Hwang, D.-H.; Kim, S. T.; Moratti, S. C.; Holmes, A. B.; De Mello, J. C.; Friend, R. H. Synth Met 1997, 91, 279.
6. Winkler, B.; Dai, L.; Mau, A. W.-H. Chem Mater 1999, 11, 704.
7. Holzer, L.; Wenzl, F. P.; Tasch, S.; Leising, G.; Winkler, B.; Dai, L.; Mau, A. W. H. Appl Phys Lett 1999, 75, 2014.
8. Gettinger, C. L.; Heeger, A. J.; Drake, J. M.; Pine, D. J. J Chem Phys 1994, 101, 1673.
9. Burn, P. L.; Holmes, A. B.; Kraft, A.; Bradley, D. D. C.; Brown, A. R.; Friend, R. H.; Gymer, R. W. Nature 1992, 356, 47.
10. Ames, D. E.; Bowman, R. E. J Chem Soc 1950, 1, 406.
11. Lenz, R. W.; Han, C.; Lux, M. Polymer 1989, 30, 1041.
12. Garay, R. O.; Mayer, B.; Karasz, F. E.; Lenz, R.W. J Polym Sci Part A Polym Chem 1995, 33, 525.
13. Wang, B.; Wasielewski, M. R. J Am Chem Soc 1997, 119, 12.
14. Fieser, L. F.; Haddadin, M. J. J Am Chem Soc 1964, 86, 2392.
15. Pang, Y.; Li, J.; Hu, B.; Karasz, F. E. Macromolecules 1999, 32, 3946.
16. Wudl, F.; Hoger, S.; Zhang, C.; Pakbaz, K.; Heeger, A. J. Polym Prepr 1993, 34, 197.
17. Wudl, F.; Srdanov, G. U.S. Pat. 5189136 (1993).
18. Burn, P. L.; Kraft, A.; Baigent, D. R.; Bradley, D. D. C.; Brown, A. R.; Friend, R. H.; Gymer, R. W.; Holms, A. B.; Jackson, R. W. J Am Chem Soc 1993, 115, 10117.
19. Hsieh, B. R.; Yu, Y.; Vanlaeken, A. C.; Lee, H. Macromolecules 1997, 30, 8094.
20. Yang, Z.; Sokolik, I.; Karasz, F. E. Macromolecules 1993, 26, 1188.
21. Brandon, K. L.; Bentley, P. G.; Bradley, D. D. C.; Dunmur, D. A. Synth Met 1997, 91, 305.
22. Chen, Z.-K.; Meng, H.; Lai, Y.-H.; Huang, W. Macromolecules 1999, 32, 4351.
23. Pasco, S. T.; Lahti, P. M.; Karasz, F. E. Macromolecules 1999, 32, 6933.
24. Wudl, F.; Hoger, S. U.S. Pat. 5679757 (1997).
25. Burn, P. L.; Bradley, D. D. C.; Friend, R. H.; Halliday, D. A.; Holmes, A. B.; Jackson, R. W.; Kraft, A. J Chem Soc Perkin Trans I 1992, 3225.
26. Parker, I. D. J Appl Phys 1994, 75, 1656.
27. Bredas, J. L.; Silbey, R.; Boudreaux, D. S.; Chance, R. R. J Am Chem Soc 1983, 105, 6555.
28. Gebhardt, V.; Bacher, A.; Thelakkat, M.; Stalmach, U.; Meier, H.; Schmidt, H.-W.; Haarer, D. Adv Mater 1999, 11, 119.
29. Pei, Q.; Yang, Y. Adv Mater 1995, 7, 559.