

Synthesis and Electroluminescence Properties of a Novel Poly(paraphenylene vinylene)-Based Copolymer with Tri(ethylene oxide) Segments on the Backbone

HAIQIAO WANG,¹ LIAN DUAN,² YONG QIU,² XIAOGONG WANG,¹ DESHAN LIU¹

¹ Institute of Polymer Science, Department of Chemical Engineering, School of Material Science and Engineering, Tsinghua University, Beijing 100084, China

² Department of Chemistry, Tsinghua University, Beijing 100084, China

Received 26 January 2001; accepted 8 May 2001

ABSTRACT: A novel light-emitting copolymer [tri(ethylene oxide)-poly(paraphenylene vinylene) (TEO-PPV)] containing alternating rigid, conjugated distyrylbenzene [poly(paraphenylene vinylene) model oligomer] as light-emitting units and flexible tri(ethylene oxide) as ionic conductive units was synthesized. The polymer was characterized with Fourier transform infrared, ¹H-NMR, ultraviolet-visible spectroscopy, differential scanning calorimetry, and gel permeation chromatography. TEO-PPV has excellent solubility in conventional organic solvents such as tetrahydrofuran, chloroform, benzene, and toluene. The estimated lowest unoccupied molecular orbital, highest occupied molecular orbital, and band gap are 2.35, 5.29, and 2.94 eV, respectively. Single-layer and double-layer light-emitting diodes with indium tin oxide anodes and calcium cathodes were fabricated, and the photoluminescence (PL) and electroluminescence (EL) properties were investigated. The maximum EL emissive peak (475 nm) of the devices is essentially the same as that of PL. Anomalous current-voltage characteristics were observed in both devices. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2195–2200, 2002

Key words: poly(paraphenylene vinylene) (PPV)-like; tri(ethylene oxide); alternating copolymer; synthesis; electroluminescence; characterization; structure; properties

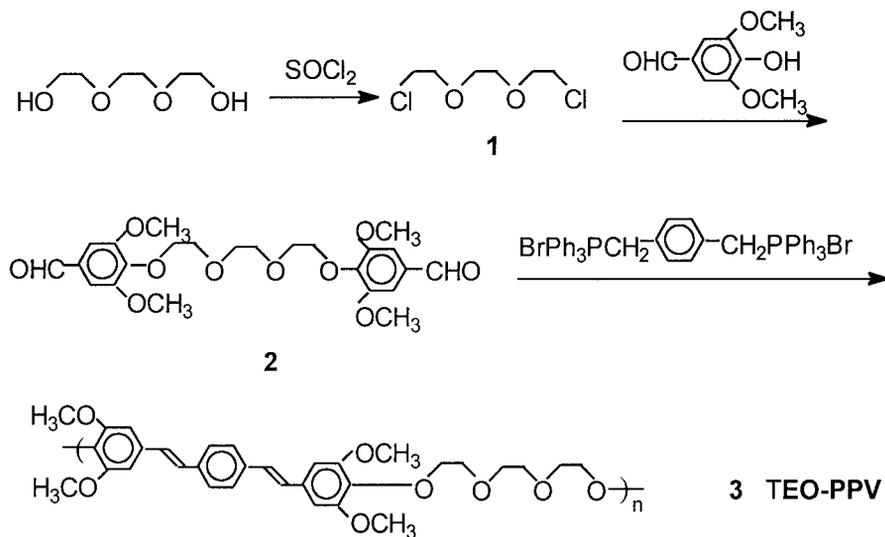
INTRODUCTION

Since the discovery of light emissions from poly(paraphenylene vinylene) (PPV) and analogous polymers, light-emitting diodes (LEDs) based on conjugated polymers as emissive layers have attracted wide research interest.^{1–3} Although a large number of polymers have been

synthesized and investigated, research for new polymers with high performance remains a major challenge in this area. Among light-emitting conjugated polymers, PPV and its derivatives are the most extensively studied luminescent polymer systems because of their high luminescence and the easy modification of their chemical structure for tailoring their electronic properties in many directions. Because of the long effective conjugation length of fully conjugated PPV, a blue-luminescent material is difficult to obtain. However, blue emitters are desirable for applications in full-color displays, but the number of available materials is still limited. To obtain blue-lumines-

Correspondence to: X. Wang (wxg-dce@mail.tsinghua.edu.cn).

Journal of Applied Polymer Science, Vol. 83, 2195–2200 (2002)
© 2002 John Wiley & Sons, Inc.
DOI 10.1002/app.10184



Scheme 1

cent PPV-based polymers, a number of PPV derivatives containing alternating π -conjugated chromophores and saturated aliphatic soft blocks or functional units have been synthesized recently.^{4–8} The well-defined short conjugated length of the phenylene vinylene segment gives a pure blue spectrum with a predictable emission wavelength, and the nonconjugated block provides good solubility, film-forming properties, and/or other functionality.

1995, Pei and coworkers^{9,10} reported a new approach with blends of poly(ethylene oxide) (PEO) or crown ether and lithium trifluoromethanesulfonate [Li(CF₃SO₃)] with a luminescent polymer for fabricating high-performance devices that they named *light-emitting electrochemical cells* (LECs). To overcome the phase separation between the apolar conjugated polymers and strong polar PEO, some luminescent polymers with a pendent ethylene oxide oligomer or crown ether attached to the main chain have been synthesized.^{11–13}

To develop polymers with better properties for fabricating LECs, we designed and synthesized a novel blue-luminescent PPV-based copolymer. The polymer contained alternating and well-defined rigid, conjugated and flexible, ionic conductive ethylene oxide segments in the main chain. The electroluminescence (EL) characteristics of single-layer and double-layer LED devices prepared from the polymer were investigated.

EXPERIMENTAL

Materials

The synthetic routes of the monomer and polymer are shown in Scheme 1.

1,8-Dichloro-3,6-dioxaoctane (1)

1 was synthesized according to the method proposed by Pedersen.¹⁴ The reaction yield was 90%.

bp: 84°C at 532 Pa (uncorrected). ¹H-NMR: (CDCl₃, δ): 3.74–3.78 (t, 4H, ClCH₂), 3.58–3.64 (t, 4H, ClCH₂CH₂), 3.66 (s, 4H, OCH₂CH₂O). Fourier transform infrared (FTIR; ν , cm⁻¹): 670 (Cl—C), 1130 (C—O—C), 2870 (CH₂).

1,8-Bis(2,6-dimethoxy-4-formylphenoxy)-3,6-dioxaoctane (2)

A mixture of 10 g (0.056 mol) of 4-hydroxy-3,5-dimethoxybenzaldehyde, 120 mL of ethylene glycol monomethyl ether, and 2.4 g (0.06 mol) of sodium hydroxide was stirred and heated to reflux under nitrogen for 30 min, and then a solution of 5.2 g (0.028 mol) of **1** diluted with 30 mL of ethylene glycol monomethyl ether was added dropwise. Refluxing was continued for 24 h. After cooling, the solvent was removed at a reduced pressure, and the residue was recrystallized two times from ethanol. The yield of **2** was 35%.

mp: 107–109°C. ¹H-NMR (CDCl₃, δ): 9.90 (s, 2H, CHO), 7.15 (s, 4H, ArH), 4.27 (t, 4H, ArOCH₂), 3.94 (s, 12H, CH₃), 3.85 (t, 12H,

ArOCH₂CH₂, 3.75 (s, 4H, OCH₂CH₂O). ELEM. ANAL. Calcd. for C₂₄H₃₀O₁₀: C, 60.25%; H, 6.28%. Found: C, 59.91%; H, 6.36%.

Polymerization

An equimolar amount of dialdehyde (0.002 mol) and 1,4-xylylenebis(triphenylphosphonium bromide) (0.002 mol) was dissolved in 40 mL of an anhydrous ethanol and chloroform mixture (3/1). Sodium ethoxide (10 mL freshly prepared by the dissolution of approximately 0.005 mol of cleaned sodium metal in 10 mL of anhydrous ethanol) was added dropwise at room temperature into the reaction system. The mixture was stirred for 24 h, and then 2% hydrochloric acid was added. A yellow solid was collected at the end of the condensation reaction and thoroughly washed with ethanol/water (3/1) to remove the byproducts triphenylphosphine oxide and NaCl. It was subsequently isomerized into an all-trans configuration by 4 h of refluxing in toluene in the presence of a catalytic amount of iodine. After removal of the toluene, the product was redissolved in 10 mL of chloroform and precipitated three times in *n*-hexane. The solid product was dried in a vacuum oven at 40°C for 2 days. The polymer obtained was yellow.

Yield: 60%. ELEM. ANAL. Calcd. for C₃₂H₃₆O₈: C, 70.07%; H, 6.57%. Found: C, 70.16%; H, 6.47%.

Characterization and Instrumentation

¹H-NMR spectra were obtained with a Bruker Spectrospin AM-500 spectrometer (Bruker Inc., Billerica, MA) in CDCl₃. FTIR characterization was performed on a Nicolet 560 spectrometer (Nicolet Instrument Corporation, Madison, WI), with KBr discs containing the polymer samples. Gel permeation chromatography (GPC) measurements were performed on a PL-GPC210 instrument (Polymer Laboratories, Shropshire, UK) with tetrahydrofuran (THF) as an eluent, calibrated with polystyrene standards. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) for the polymers were carried out under nitrogen with TA MDSC-2910 and TGA-2050 instruments (TA Instrument, Newcastle, DE) (heating rate = 10°C/min). Ultraviolet–visible (UV–vis) absorption spectra for both the chloroform solution and film were taken with a PerkinElmer Lambda Bio 40 spectrophotometer (PerkinElmer Corp., Shelton, CT). Photoluminescence (PL) spectra of the polymer in chloroform

solutions and net films were measured with PerkinElmer LS 50B and a Hitachi 850 fluorometers (Hitachi Co., Tokyo, Japan), respectively. EL analyses were performed at room temperature under an air atmosphere with a KGF-2 fluorometer (National Institute of Metrology, Beijing, China).

Cyclic voltammograms of the polymer films were recorded in a typical three-electrode cell with platinum wire electrodes as both the counter and working electrodes, and a saturated calomel electrode (SCE) was used as the reference electrode. Dried dichloromethane was used as the solvent with tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte.

Preparation of the LEDs

A single-layer LED—indium tin oxide (ITO)/tri(ethylene oxide)–poly(paraphenylene vinylene) (TEO–PPV)/Ca (Al)—was prepared by the spin coating of a chloroform solution of the polymer on a glass/ITO substrate (emitter thickness ~ 70 nm), followed by the thermal evaporation of Ca (40 nm) at 2 × 10⁻⁵ Torr. A layer of Al (100 nm) was deposited on the surface to protect the reactive Ca. For the preparation of a double-layer LED—ITO/TEO–PPV/2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD)/Ca (Al)—the top PBD layer was deposited on the polymer layer before Ca cathode deposition.

RESULTS AND DISCUSSION

Structure Characterization of TEO–PPV

The structure of TEO–PPV was identified with FTIR, ¹H-NMR, and elemental analysis. Figure 1 shows the FTIR spectra of the monomer (**2**) and TEO–PPV. A comparison of the FTIR spectrum of TEO–PPV with that of the starting monomer shows the disappearance of the band at 1700 cm⁻¹, which is the C=O stretching band for the aldehyde group present in the dialdehyde monomer. The appearance of a new band at 960 cm⁻¹ can be observed, and it implies the formation of a *trans*-vinylene group.⁴ The ¹H-NMR spectrum of TEO–PPV in CDCl₃ is also in agreement with that expected for the desired molecular structure.

The polymer TEO–PPV can be dissolved in conventional organic solvents, such as chloroform, dichloromethane, THF, benzene, and toluene. We

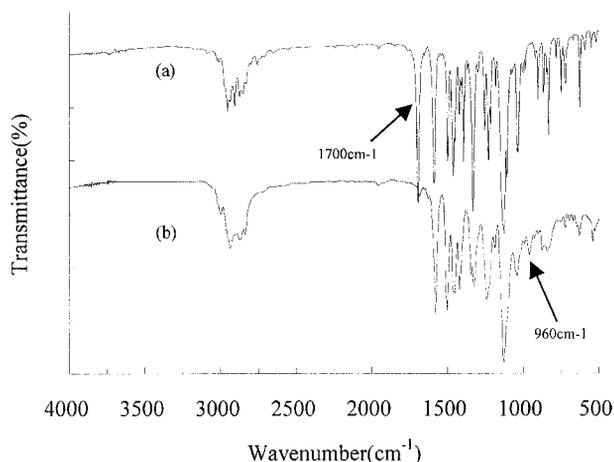


Figure 1 FTIR spectra of (a) monomer **2** and (b) copolymer **3**.

obtained polymer thin films of good quality by spin coating from a chloroform solution after filtration. The number-average and weight-average molecular weights of TEO-PPV are 2050 and 5153, respectively, relative to polystyrene standards. The polymer has a glass-transition temperature of about 51°C, and no melting or other phase transitions in the testing temperature range, 0–350°C, were observed. TGA analysis reveals that the polymer begins to decompose at about 380°C, indicating that TEO-PPV has good thermal stability.

Figure 2 shows the UV-vis absorption spectra and PL spectra (excited with 373 nm for a chloroform solution and 420 nm for a thin film) of a TEO-PPV chloroform solution and a TEO-PPV

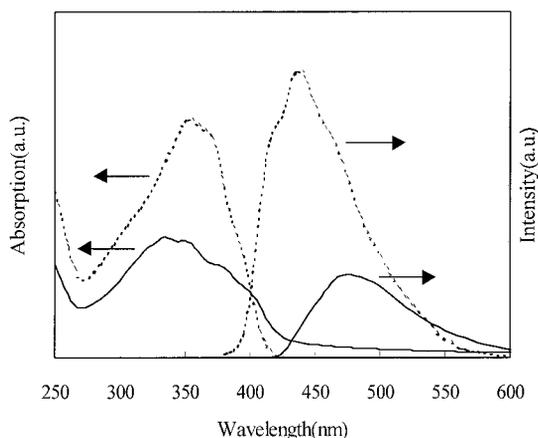


Figure 2 UV-vis and PL spectra of TEO-PPV in a chloroform solution (dotted line) and a net film (solid line).

thin film, respectively. The wavelength of the maximum absorption of TEO-PPV in the chloroform solution appears at about 354 nm, whereas that of the thin film shows a 9.5 nm redshift with respect to the solution. The band gap (E_g) between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), taken from the edge absorption of the thin-film spectrum, is about 2.94 eV. In comparison with the PPV copolymer (λ_{\max} at 375 nm, $E_g = 2.89$ eV) prepared by Yang et al.,⁴ E_g is larger and λ_{\max} is shorter for TEO-PPV. The PL maximum peaks of TEO-PPV in the chloroform solution and film appear at 438 and 476 nm, respectively. In comparison with the sample in the chloroform solution, the emission peak of the thin film exhibits a small redshift. This can be explained by an increase of the efficient conjugation length of the polymer in the aggregated state.

A cyclic voltammogram corresponding to the oxidation of TEO-PPV is shown in Figure 3. The maximum oxidation potential is about 1.5 V versus SCE, and the onset oxidation potential ($E_{\text{ox,on}}$) is about 0.89 V versus SCE. Because the oxidation process corresponds to the removal of charge from the HOMO band, $E_{\text{ox,on}}$ is closely related to the energy of the HOMO level of TEO-PPV. The two energy parameters that establish the positions of these LUMO and HOMO levels relative to vacuum are the electron affinity (EA) and ionization potential (IP), and these can be estimated from the two measured values, $E_{\text{ox,on}}$ and E_g . According to the literature,¹⁵ E_{HOMO} and E_{LUMO} can be calculated as follows:

$$E_{\text{HOMO}} = \text{IP} = eE_{\text{ox,on}} + 4.4 \text{ eV} = 5.29 \text{ eV} \quad (1)$$

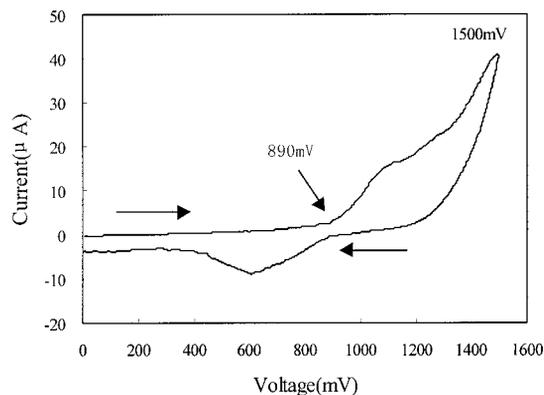


Figure 3 Cyclic voltammogram of PEO-PPV coated on ITO glass in 0.1M TBAPF₆ in dried dichloromethane with a Pt strip as the counter electrode and SCE as the reference electrode.

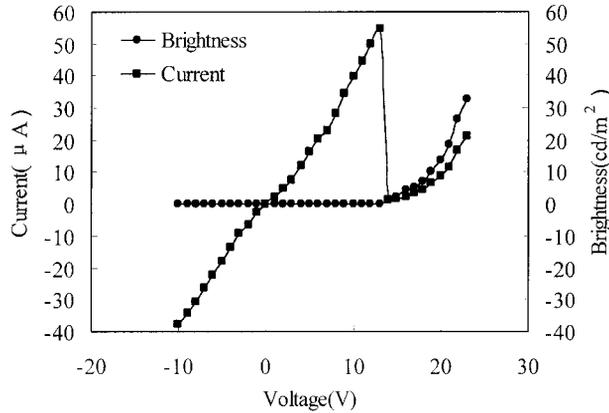


Figure 4 Current–voltage and brightness–voltage characteristics of a single-layer device.

$$E_{\text{LUMO}} = EA = IP - E_g = 5.29 - 2.94 = 2.35 \text{ eV} \quad (2)$$

EL Characteristics of Single-Layer and Double-Layer LEDs of TEO–PPV

The current–voltage and brightness–voltage characteristics of single-layer and double-layer devices are depicted in Figures 4 and 5, respectively. Anomalous current–voltage characteristics with negative differential resistance were observed in single-layer and double-layer devices, as observed by other groups in some light-emitting devices.^{16,17} We also noticed that the anomalous electrical characteristics could be reproduced qualitatively but not quantitatively, and there was no correlation between current and brightness in the region of anomalous electrical characteristics. Although further experiments are necessary to clarify that the phenomenon is not re-

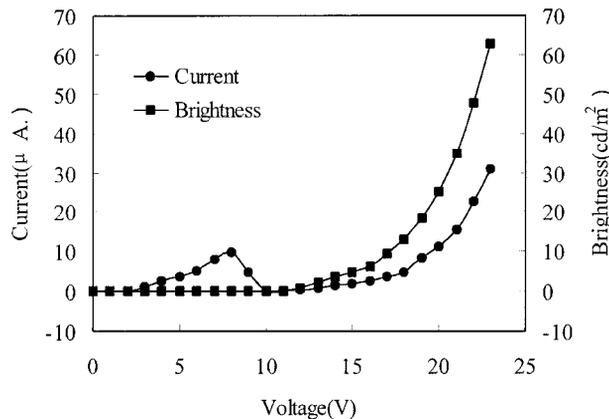


Figure 5 Current–voltage and brightness–voltage characteristics of a double-layer device.

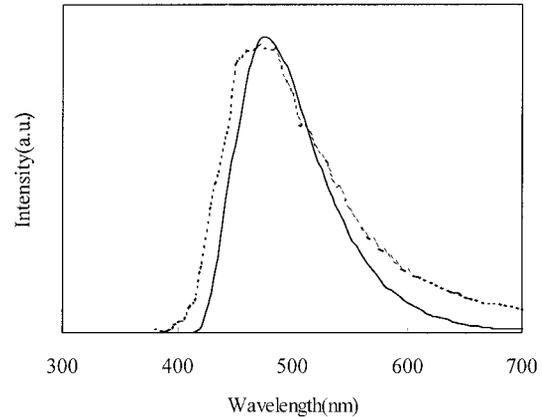


Figure 6 PL spectrum of film (solid line) and EL spectrum of ITO/TEO–PPV/Ca (dotted line).

lated to current leakage and is not dependent on the material, irreversible destruction of shorts can be ruled out as the dominant mechanism. In addition, we see that these anomalous electrical characteristics in the single-layer device are more evident than those in the double-layer device. Both devices showed some difference in the maximum current value in these regions of anomalous electrical characteristics.

The single-layer device shows a turn-on voltage at about 13 V. The brightness reaches the maximum 36 cd/m^2 at 23 V. The EL spectrum of the emission light is similar to the PL spectrum, as shown in Figure 6, indicating that they have similar relaxation processes. The double-layer device was fabricated by the introduction of a PBD electron-injection/transport layer. The bright blue light emission was observed. The turn-on voltage decreases to 11.5 V, and the maximum brightness increases to 63 cd/m^2 at 23 V. Problems such as the high hole-drift mobility of the polymer and the imbalance of charge injection existing in the single-layer device are avoided by the double-layer device, which shows higher efficiency. In the double-layer device, the PBD layer enhances electron injection from the cathode and blocks the transport of holes injected from the anode through the TEO–PPV layer, causing an increase in the probability of recombination with the emissive layer and eliminating the influence of the cathode. The shapes of the EL spectra of both devices were almost the same, which indicates that charge recombination and emission occurred in the polymer layer. Further studies on the optimization and fabrication of LECs based on TEO–PPV polymer will be reported in a future publication.

CONCLUSIONS

A novel luminescence copolymer (TEO-PPV) containing alternating rigid, conjugated PPV as light-emitting units and flexible tri(ethylene oxide) blocks as ionic conductive units was successfully synthesized. Excellent solubility in conventional organic solvents, good film-forming properties, and high thermal stability were found for this copolymer. Single-layer and double-layer LEDs with ITO anodes and Ca cathodes were fabricated, and blue emissions were obtained from both LED devices. Anomalous current-voltage characteristics with negative differential resistance were observed in both devices. The good luminescent properties combined with the ionic conductive function make TEO-PPV a good candidate as an emitter for novel LEC devices.

REFERENCES

- Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature* 1990, 347, 539.
- Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew Chem Int Ed Engl* 1998, 37, 402.
- Greenham, N. C.; Friend, R. H. *Solid State Phys* 1995, 49, 1.
- Yang, Z.; Sokolik, I.; Karasz, F. E. *Macromolecules* 1993, 26, 1188.
- Hay, M.; Klavetter, F. L. *J Am Chem Soc* 1995, 117, 7112.
- Zyung, T.; Hwang, D.-H.; Kang, I.-N.; Shim, H.-K.; Hwang, W.-Y.; Kim, J.-J. *Chem Mater* 1995, 7, 1499.
- Chang, E.-C.; Chen, S.-A. *J Appl Phys* 1999, 85, 2057.
- Lee, Y.-Z.; Chen, S.-A. *Synth Met* 1999, 105, 185.
- Pei, Q.; Klavetter, F. L. U.S. Pat. 08,268,763 (1994).
- Pei, Q.; Yu, G.; Zhang, C.; Yang, Y.; Heeger, A. J. *Science* 1995, 269, 1086.
- Pei, Q.; Yang, Y. *J Am Chem Soc* 1996, 118, 7416.
- Holzer, L.; Winkler, B.; Wenzl, F. P.; Tasch, S.; Dai, L.; Mau, A. W. H. *Synth Met* 1999, 100, 71.
- Morgado, J.; Cacialli, F.; Friend, R. H.; Chuah, B. S.; Moratti, S. C.; Holmes, A. B. *Synth Met* 2000, 111, 449.
- Pedersen, C. J. *J Am Chem Soc* 1967, 89, 7017.
- De Leeuw, D. M.; Simenon, M. M. J.; Brown, A. R.; Einerhand, R. E. F. *Synth Met* 1997, 87, 53.
- Berleb, S.; Brütting, W.; Schwoerer, M. *Synth Met* 1999, 102, 1034.
- Cimrová, V.; Neher, D. *Synth Met* 1996, 76, 125.