Synthesis and Properties of a Soluble Conjugated Polymer, Poly(2-methoxy-5-n-butoxy-p-phenylene vinylene)

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ABSTRACT: The synthesis of poly(2-methoxy-5-n-butoxy-p-phenylene vinylene) (MBPPV) via a dehydrochlorination of 2-methoxy-5-n-butoxy-α,α'-dichloro-p-xylene is described. The soluble polymer was characterized by elemental analysis, Fourier transform infrared (FTIR), ^{1}H nuclear magnetic resonance (NMR), and UV-visible spectroscopy. The energy gap (E_g) of the polymer was 2.53 eV determined by cyclic voltammogram. Light-emitting diode (LED) and light-emitting electrochemical cell (LEC) with the polymer were fabricated. The LED displayed unipolar I-V dependence with the turn-on voltage at 4.2 V. I-V curve of the LEC with poly(ethylene oxide) (PEO, Mw 2×10^4) displayed mirror symmetry with the turn-on voltage at 2.7 V, but to the device with PEO (Mw 5×10^6) no mirror symmetry was observed, the turn-on voltages at +2.7 V, −11.5 V. The emission maximum of the polymer in chloroform was at $\lambda = 550$ nm, whereas the emission maxima of the LED at 5.2 V and the LEC at 4.8 V were at $\lambda = 566$, 569 nm, respectively. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 2180–2185, 2000

Key words: conjugated polymer; photoluminescence; electroluminescence; light emitting diodes; light emitting cells

INTRODUCTION

Since the Cambridge group[1] first fabricated a green light-emitting diode (LED) using poly(p-phenylenevinylene) (PPV), a number of different conjugated polymers emitting in various portions of the visible spectrum have been reported, such as PPV derivatives,[2–4] poly(p-phenylene) derivatives,[5,6] and polythiophenes.[7] The approach to polymer formation has involved either polymers that are insoluble in their final form and are prepared via processible precursor polymers, or materials that are soluble in their conjugated forms.[8] In recent times much of the emphasis has rested on the soluble polymers because of their relative ease of processing into single-layer devices and their high luminescence yields.[9–13] Now most of PPV derivatives are prepared via a processible precursor route.[4] The process includes two steps: first, a soluble precursor polymer is prepared, and then it is converted to conjugated polymer in vacuum at high temperature. The conjugated polymer synthesized this way is insoluble. Because the soluble conjugated polymers have so many advantages, researchers have been trying to find methods to synthesize soluble PPV derivatives. Poly(2-methoxy-5-n-butoxy-p-phenylene vinylene) (MBPPV)[14] had been prepared in the form of thin film from its water-soluble sulfonium-salt precursor polymer, but the resulting final form was insoluble and the electrical

conductivity of the I_2 and $FeCl_3$ doped polymer was discussed instead of its properties in LED or light-emitting electrochemical cells (LEC).

Progress in the field of polymer LED has been rapid since 1990[1] because of its important advantages over inorganic semiconductors for LED, such as low cost, easy processing, mechanical properties, the choice of geometry, and so on. In 1995, Pei et al.[15] prepared LEC, which offered a new approach to light-emitting devices fabricated from semiconducting polymer. LECs possess some good qualities over LEDs.[16] Conventional metal/polymer/metal LEDs are dual carrier devices in which electrons and holes are injected at the cathode and anode, respectively, into the undoped semiconducting polymer. To minimize the potential barriers at the polymer/metal interfaces and to optimize carrier injection, the cathode and the anode should be chosen with work functions matching the bottom of the conduction band (π^*) and the top of the valance band (π) of the semiconducting polymer, respectively. It is difficult, therefore, to satisfy the conditions required for efficient, balanced injection for polymers with different band gaps and with different ionization potentials. Polymer LECs avoid this problem by utilizing a polymer blend containing a semiconducting luminescent polymer and a solid-state electrolyte. At voltages above the energy gap of the semiconducting polymer, electrochemical redox and the accompanying redistribution of ions from the solid electrolyte cause p-type doping near the anode and n-type doping near the cathode; a p-i-n junction is created in situ. Light emission occurs in the insulating (i) region between the n- and p-doped layers.

We report here the synthesis of soluble MBPPV and the fabrication of a single-layer LED and LECs by using MBPPV and the blend of MBPPV and poly(ethylene) oxide (PEO) as active layers. The properties of the prepared LED and LECs were discussed.

EXPERIMENTAL

Materials

All reagents used in this work were commercial products of high quality employed as received. Potassium tert-butoxide was prepared according to the literature.[17]

Measurements

Elemental analysis was performed by an Elemental Analyzer model 1106. Fourier transform infrared (FTIR) spectra were recorded on a Bruker IFS66v Spectrometer. ^{1}H NMR spectra were obtained on a Varian-Unity 400 MHz instrument. Ultraviolet (UV)-Vis spectrum was measured with a Shimadzu UV-3100 UV-Vis spectrophotometer. Photoluminescence (PL) and electroluminescence (EL) spectra were measured with a Shimadzu RF-5301 PC spectrofluorometer.

Synthesis of 2-methoxy-5-n-butoxy benzene(1)

We dissolved 4-methoxyphenol (0.02 mol) and n-butyl bromide (0.02 mol) in ethyl alcohol (50 mL). Finely ground potassium hydroxide (0.02 mol) was added to the solution. The mixture was refluxed for 20 hours. Then it was poured into plenty of water after cooled to room temperature. The crude product was precipitated out and then recrystallized from isopropanol, dried in a vacuum at 50°C, to give pure product as white crystals. Yield: 90%.

[1]H nuclear magnetic resonance (NMR) ($CDCl_3$), $\delta = 0.92–1.00$ (t, 3H, —CH_2—CH_3), 1.40–1.55 (m, 2H, —CH_2—CH_3), 1.68–1.78 (m, 2H, —CH_2—CH_2—CH_3), 3.66 (s, 3H, —OCH_3), 3.75–3.90 (t, 2H, —OCH_2—), 6.76 (s, 4H, Ar—H).

Synthesis of 2-methoxy 5-n-butoxy-α,α'-dichloro-p-xylene(2)

We placed 1 (0.02 mol), concentrated HCl (3 mL), and 1,4-dioxane (25 mL) in a three-necked flask equipped with a thermometer, stirrer, and a glass frit. The flask was heated to 65°C, formaldehyde (36%, 5 mL) was added dropwise for 1.5 hours, and HCl gas was bubbled through the frit for 4 hours. After that, concentrated HCl (10 mL) was added into the flask and the crude product began to precipitate from solution. Upon cooling, the crude product was isolated, neutralized, and recrystallized from hexane. Yield: 85%.

^{1}H NMR ($CDCl_3$), $\delta = 0.90–1.06$ (t, 3H, —CH_2—CH_3), 1.40–1.56 (m, 2H, —CH_2—CH_3), 1.64–1.80 (m, 2H, —CH_2—CH_2—CH_3), 3.84 (s, 3H, —OCH_3), 3.90–4.06 (t, 2H, —OCH_2—), 4.63 (s, 4H, —CH_2Cl), 6.91 (s, 2H, Ar—H).

Polymerization of 2

We placed 2 (0.02 mol), potassium tert-butoxide (0.05 mol), tert-butylalcohol (5 mL), and xylene (10 mL) in a three-necked flask equipped with a thermometer, stirrer, and reflux. The mixture was kept at 95°C for 1.5 hours in a nitrogen atmosphere. Following the start of the reaction,

the viscosity of the medium increased and the color changed from fluorescent yellow to red. After the prescribed time, the mixture was cooled to room temperature and filtered. The red solution was poured into plenty of methanol and red precipitate came out from solution. Then the product was filtered, washed with water, and dried in a vacuum at 60°C. Yield: 45%.

FTIR (KBr): 3055, 2954, 2918, 2864, 1672, 1620, 1500, 1460, 1406, 1346, 1200, 1066, 1032, 964, 860, 688, 580, 464 cm^{-1}.

^{1}H NMR (CDCl$_3$), δ = 1.04 (broad, 3H), 1.56 (broad, 2H), 1.86 (broad, 2H), 3.95 (broad, 3H), 4.09 (broad, 2H), 7.18 (broad, 2H), 7.47–7.52 (broad, 2H). (C$_{13}$H$_{16}$O$_2$)$_n$ (204.29) Calc. C 76.47 H 7.84. Found C 74.44 H 7.67.

Cyclic Voltammetry Test

Cyclic voltammetry experiments were carried out in a three-electrode compartment cell with a total volume of electrolyte solution (0.1 M Bu$_4$NClO$_4$ in acetonitrile), using the saturated calomel electrode (SCE) as reference, a platinum wire as counter electrode, and a platinum disc (effective area 0.5 cm^2) as a working electrode, on which the thin polymer was coated by dipping. The experiment was performed using an HPD-1A Model Potentiometer under nitrogen atmosphere.

Fabrication of LED

Aluminum (Al) and indium-tin-oxide (ITO) were used as the electron injection and hole injection electrodes respectively. The film of MBPPV was spin coated onto the ITO-coated glass substrate at room temperature. The thickness of the film was about 150 nm, depending on the concentration in dichloromethane and the spin rate. Al electrode was deposited at pressure around 1×10^{-6} Torr, and its deposition rate was controlled by a quartz oscillating thickness monitor to be 0.1 nm/s. The thickness of Al was 250 nm. The emitting area was 2×2 mm^2.

Fabrication of LECs

Al and ITO were used as the back and forward electrodes, respectively. Thin film of the blend of MBPPV, PEO, and Bu$_4$NClO$_4$ (1 : 1 : 0.5 by weight) was used as the active light-emitting layer between ITO and Al electrodes. The composite polymer film was spin cast from dichloromethane solution onto the ITO substrate and then dried by air. The thickness of the polymer layer was 150 nm. The Al layer (250 nm) was evaporated onto the polymer film at pressure around 1×10^{-6} Torr and used as backelectrode. The active area of the device was 2×2 mm^2.

RESULTS AND DISCUSSION

Synthesis and Characterization of MBPPV

The synthetic strategy, consisting of three steps, to obtain the desired polymer from simple starting materials is outlined in Scheme 1. According to our procedure, the yield of the first two steps were all more than 80% and the reaction condition were moderate. The key point of the third step is the controlling of the reaction temperature. If it is too low, the conjugated polymer will not be obtained.

IR spectrum of MBPPV is shown in Figure 1. The valence bands of the aliphatic C—H groups are seen between 3000 and 2800 cm^{-1}. The aromatic ring vibrations and deformation vibrations of the side chains appear in the fingerprint region between 1620 and 1300 cm^{-1}. The strong band at 1200 cm^{-1} is attributed to the asymmetric C—O—C vibration. For arylene alkylethers, this band is normally found at 1250 cm^{-1}.[18] For poly(2,5-dibutoxy-p-phenylene), this band was also found at 1200 cm^{-1}.[19] The weak band at 1066 cm^{-1} is attributed to the asymmetric O—C—C vibration. The strong band at 1032 cm^{-1} is attributed to the symmetric C—O—C vibration. The out-of-plane vibration of the aromatic hydrogen shows a strong absorption at 860 cm^{-1}. It should be noticed that there are two weak bands at 3055 and 1672 cm^{-1}, which are attributed to C—H and C=C stretching vibrations of an olefin, separately. A strong absorption corresponding to an out-of-plane C—H binding vibration of a *trans*-1,2-disubstituted olefin is observed at 964 cm^{-1},
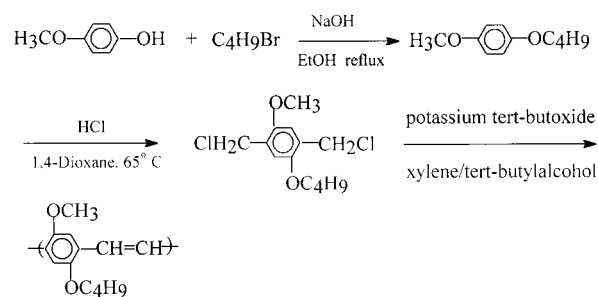
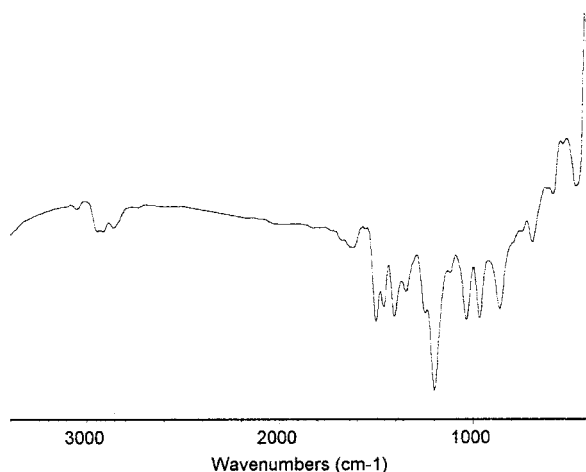**Scheme 1** Synthetic route to MBPPV.

Figure 1   Infrared spectrum of MBPPV.

which indicates that the synthesized polymer is a polymer with *trans*-structure.

In the case of intrinsically insoluble PPV, IR spectroscopy has been conventionally the typical tool for structure analysis. Because the polymer MBPPV synthesized this way is soluble, other methods are available as well. Further support for the structure is obtained by ^{1}H NMR spectrum, as shown in Figure 2. Chemical shifts at δ = 1.04, 1.56, 1.86, and 4.09 ppm are attributed to the absorption of protons of —CH_2—CH_3, —CH_2—CH_2—CH_3, —CH_2—CH_2—CH_3, and —OCH_2—, respectively. Chemical shift at δ = 3.95 ppm belongs to that of —OCH_3. The absorption of protons of Ar—H is seen at δ = 7.18 ppm. One doublet peak is observed at $\delta \approx 7.5$ ppm

(J = 22.4 Hz), which is assignable to the absorption of protons of *trans*-olefin.

Optical and Electrical Properties

The UV-Vis and fluorescence spectra of the conjugated polymer MBPPV in chloroform are given in Figure 3, which show a maximum absorption at 478 nm and a maximum emission at 550 nm. Photoluminescence spectrum has a narrow half width 45 nm.

The cyclic voltammogram of a MBPPV coated Pt wire was measured in a one-compartment, three-electrode cell with a Pt wire counter electrode and an SCE reference at a scan rate of 50 mVs^{-1}. On sweeping the polymer cathodically and anodically, a reduction peak at −1.92 V and oxidation peak at +1.09 V were observed, as shown in Figure 4. The values of reduction onset and oxidation onset were −1.82 V and 0.71 V, respectively, from which the electrochemical band gap Eg 2.53 eV was obtained.

The current-voltage curves of the LED and the LECs are depicted in Figure 5, showing a typical characteristic that with the increase of forward bias the currents of LED and LECs both increase rapidly after 4.2 V and 2.7 V, respectively. With the increase of backward bias, no current of LED was observed from curve a. Curve b is roughly mirror symmetry relative to 0 V, whereas for curve c there is no mirror symmetry relative to 0 V. The current of LEC with PEO (Mw 5 × 10^6) could be seen until the LEC was biased at −11.5 V, which is possibly caused by the PEO with higher molecular weight used in this device. Yu et
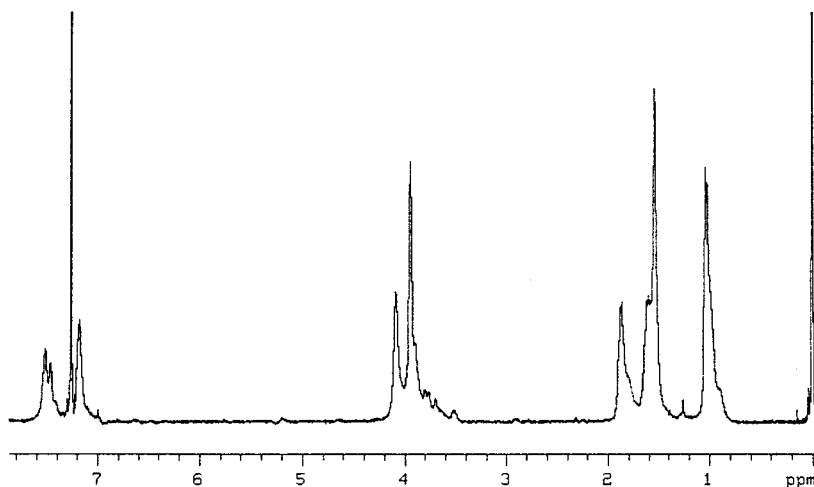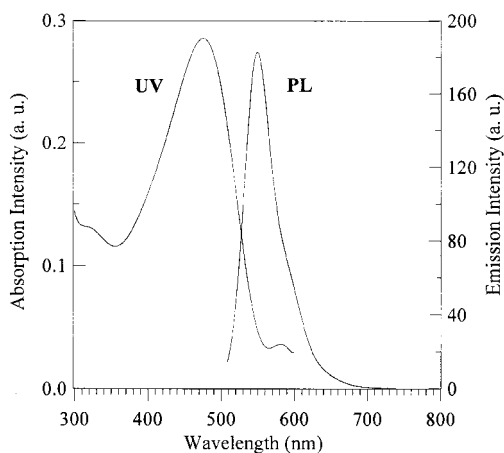

Figure 2 ^{1}H NMR spectrum of MBPPV.

Figure 3 Absorption and PL spectra of MBPPV, in CHCl$_3$.

Figure 5 Current-voltage curves of LED (a), LECs with (b) PEO Mw 2×10^4, and (c) PEO Mw 5×10^6.

CONCLUSIONS

It has been shown that the soluble conjugated polymer MBPPV can be prepared via a dehydrochlorination route, induced by potassium tert-butoxide in xylene and tert-butylalcohol. This synthetic approach is simple in contrast to the precursor route and the polymer prepared this way is soluble, which is very important for the fabrication of LEDs and LECs.

The energy gap Eg of MBPPV (2.53 eV) was obtained from cyclic voltammetry experiments. The PL spectrum of MBPPV showed maximum emission at 550 nm in chloroform, whereas the EL spectra of the LED and LEC were similar with emission peaks at 566 nm and 569 nm, respectively. The current voltage characteristics of the single layer LED and the LEC with PEO (Mw 2 $\times$ 10^4) were typical. The LED showed unipolar I-V dependence with the turn-on voltage at 4.2 V. The LEC with PEO (Mw 2×10^4) displayed mirror symmetry relative to 0 V with the turn-on

al.[16] found that the pristine LECs with crown ether only displayed unipolar I-V dependence. The ionic conductivity in the crown ether electrolyte is negligible at room temperature. In the composite polymer film of the LEC, the molecular chains of the PEO with higher molecular weight will be easily bent and exhibit some attributes of crown ether, so the performance of the LEC with the higher molecular weight PEO (Mw 5×10^6) is between that of the LEC with crown ether and that of the LEC with the lower molecular weight PEO (Mw 2×10^4). The mechanism will be reported later.

The EL spectra of the single-layer LED at 5.2 V and the LEC at 4.8 V are illustrated in Figure 6. The emission peaks of the EL spectra are 566 nm and 569 nm, respectively. The two EL spectra have the similar spectral shape with the half width 56 nm, which are narrower than that of MEHPPV (about 100 nm).[15]
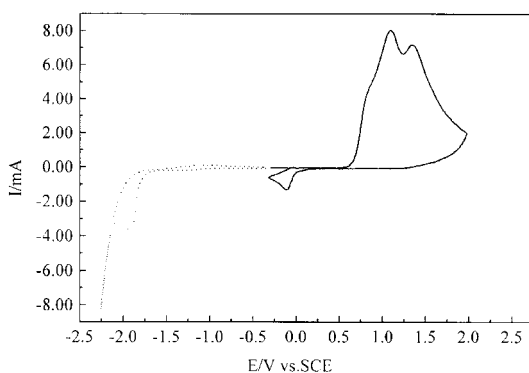

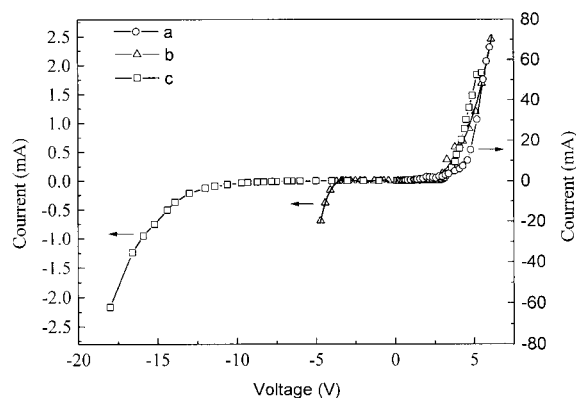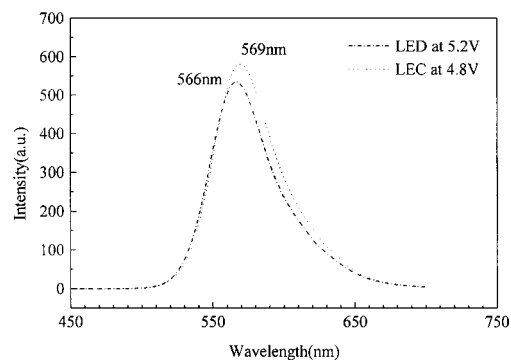**Figure 4** Cyclic voltammogram of MBPPV film.

Figure 6 EL spectra of LED at 4.2 V and LEC with PEO Mw 5×10^6 at 3.8 V.

voltage at 2.7 V. It is noteworthy that the performance of the LEC with PEO (Mw 5×10^6) was different from that of the LEC with PEO (Mw 2×10^4), the forward turn-on voltage at $+2.7$ V, the backward turn-on voltage at -12.0 V. The ionic conductivity in PEO with different molecular weight may be different, which will influence the current voltage characteristics of LECs. The detailed influence of PEO to the performance of LEC will be studied later.

REFERENCES

1. 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.

2. Hay, M.; Klavetter, F. L. J Am Chem Soc 1995, 117, 7112.

3. Kim, H. K.; Ryu, M. K.; Lee, S. M. Macromolecules 1997, 30, 1236.

4. Hsieh, B. R.; Wan, W. C.; Yu, Y.; Gao, Y.; Goodwin, T. E.; Gonzalez, S. A.; Feld, W. A. Macromolecules 1998, 31, 631.

5. Vahlenkamp, T.; Wegner, G. Macromol Chem Phys 1994, 195, 1993.

6. Remmers, M.; Schulze, M.; Wegner, G. Macromol Rapid Commun 1996, 17, 239.

7. Dyreklev, P.; Berggren, M.; Inganas, O.; Andersson, M. R.; Wennerstrom, O.; Hjertberg, T. Adv Mater 1995, 7, 43.

8. Burn, P. L.; Grice, A. W.; Tajbakhsh, A.; Bradley, D. D. C.; Thomas, A. C. Adv Mater 1997, 9, 1171.

9. Staring, E. G. J.; Demandt, R. C. J. E.; Braun, D.; Rikken, G. L. J.; Kessner, Y. A. R. R.; Venhuizen, T. H. J.; Wynberg, H.; Hoeve, W. T.; Spoelstra, K. J. Adv Mater 1994, 6, 934.

10. Lee, J. K.; Schrock, R. R.; Baigent, D. R.; Friend, R. H. Macromolecules 1995, 28, 1996.

11. Hilberer, A.; Brouwer, H. J.; van der Scheer, B. J.; Wildeman, J.; Hadziioannou, G. Macromolecules 1995, 28, 4525.

12. Kim, D. U.; Tsutsui, T.; Saito, S. Chem Lett 1995, 587.

13. Kim, S. T.; Hwang, D. H.; Li, X. C.; Gruner, J.; Friend, R. H.; Holmes, A. B.; Shim, H. K. Adv Mater 1996, 8, 979.

14. Jin, J.-I.; Park, C.-K.; Shim, H.-K. Polymer 1994, 35, 480.

15. Pei, Q.; Yu, G.; Zhang, C.; Yang, Y.; Heeger, A. J. Science 1995, 269, 1086.

16. Yu, G.; Cao, Y.; Andersson, M.; Gao, J.; Heeger, A. J. Adv Mater 1998, 10, 385.

17. Baumgarten, H. E. Organic Syntheses, Coll. 5, 361; John Wiley & Sons, Inc: New York, 1973.

18. Hesse, M.; Meier, H.; Zeeh, B. Spektroskopische Methoden in der organischen Chemie, 2nd ed.; Thieme, Stuttgart, 1984.

19. Vahlenkamp, T.; Wegner, G. Macromol Chem Phys 1994, 195, 1933.