

Synthesis, Characterization, and Electro-optical Properties of a Soluble Conjugated Polymer Containing an Oxadiazole Unit in the Main Chain

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ABSTRACT: A novel copolymer, poly{[2,5-diphenylene-1,3,4-oxadiazole-vinylene]-alt-[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]} (MEH-OPP) containing a high-electron-affinity unit of aromatic oxadiazole in the main chain is synthesized through the Wittig condensation reaction. The obtained copolymer is easily soluble in conventional organic solvents. The structure of the copolymer was characterized by Fourier transform infrared, ¹H nuclear magnetic resonance, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and ultraviolet-visible and photoluminescence spectroscopy. The TGA result indicates that the copolymer has very high thermal stability (stable up to 310°C in nitrogen), while DSC investigation

demonstrates that the glass transition temperature (T_g) is 143°C, which might be a merit for the long-life operation of light-emitting devices. The absorption spectrum of film sample of the copolymer reveals two peaks at 310 and 370 nm, respectively, and the edge absorption corresponds to a band gap of 2.46 eV. A single-layer light-emitting diode device ITO/MEH-OPP/Al is successfully fabricated. The device emits visible yellowish-green light above the bias voltage of 4.0 V under ambient condition. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2618–2623, 2003

Key words: electroluminescence; light-emitting diode; copolymerization; Wittig condensation; conjugated polymers

INTRODUCTION

Following the first report¹ to use poly(*p*-phenylenevinylene) (PPV) in light-emitting diodes (LEDs), a number of π -conjugated polymers have been shown to exhibit application in the field of patterned light source and flat panel display. Much work has been done to develop novel luminescent polymeric materials, for example, PPV and its derivatives,^{1–5} poly(*p*-phenylene)s,^{6–8} polycarbazoles,^{9,10} polythiophenes,^{11–13} etc.

PPV and its derivatives are among the most extensively studied organic electroluminescent (EL) materials. By proper modification of the chemical structure, the fluorescent color of PPVs can span over visible color and further into the near-infrared region. However, most of PPVs used as light-emitting materials tend to be *p*-type polymers with much greater tendency for injecting and transporting holes than for electrons.³

Therefore, the imbalance of rates for electron and hole injection from the negative and positive contacts becomes the obstacle for improving the electroluminescent efficiency. The effective methods that have been developed thus far for improving the quantum efficiency by balancing injected electrons and holes are adding an electron transport layer in the device.^{14,15} However, the multilayer device always leads to an unfavorable increase in turn-on voltage, and requires careful selection of material and solvent to avoid damage of the emission layer in the process of spin-coating an electron transport layer.

Here, we report a novel copolymer, poly{[2,5-diphenylene-1,3,4-oxadiazole-vinylene]-alt-[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]} (MEH-OPP), in which the high electron affinity group of oxadiazole segment is introduced into the PPV main chain. The design is based on the following considerations: (1) the PPV backbone is a good hole-transporting electroluminescent material; (2) the branched alkoxy side group provides solubility and prevention from crystallization; and (3) the electron-deficient moiety, 2,5-diphenyl-1,3,4-oxadiazole, facilitates both electron injection and transport. Aromatic oxadiazole ring, incorporated into PPVs backbones, also has a potential advantage of dispersing the electron atmosphere density on the vinylene segment so as to decrease the opportunity to be oxidized by oxygen.¹⁶

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EXPERIMENTAL

Materials

Anhydrous toluene and tetrahydrofuran (THF) were obtained by distillation over sodium/benzophenone, and DMSO was distilled over calcium hydride. 2-Ethylhexyl bromine, potassium *tert*-butoxide, 2-nitropropane, and sodium ethoxide were used as received from Aldrich. All other commercial reagent-grade solvents and chemicals were used without further purification.

Synthesis

1-Methoxy-4-(2'-ethylhexyl) benzene (**1**) and 1,4-bis(chloromethyl)-2-methoxy-5-(2'-ethylhexyloxy)benzene (**2**)

Compounds **1** and **2** were synthesized according to procedure given in the literature.¹⁷

4-Methoxy phenol was reacted with 2-ethylhexyl bromine in the presence of sodium hydroxide to give compound **1**. And then **1** was refluxed with formaldehyde (37%) and hydrochloric acid in dioxane solution to give compound **2** as a white powder in 54% yield.

¹H-NMR (nuclear magnetic resonance) (CDCl₃): 6.95 (s, 2H, Ar—H), 4.62 (s, 4H, CH₂—Cl), 3.84 (t, 5H, —OCH₂— and —OCH₃), 0.9—1.5 (m, 15H, —C₇H₁₅).

Anal. Calcd. For C₁₆H₂₆O₂Cl₂: C, 61.26; H, 7.86. Found: C, 61.36; H, 7.96.

2-Methoxy-5-(2'-ethylhexyloxy)-1,4-formylbenzaldehyde (**3**)¹⁸

To a stirred solution of 3.33 g (0.01 mol) of **2** in 60 mL DMSO was added slowly 30 mL ethanol containing sodium ethoxide (2.70 g of purity 96%, 0.038 mol) and 2-nitropropane (3.40 g, 0.038 mol) under nitrogen atmosphere at room temperature. The reaction mixture gradually changed from yellow to black. After stirring for 24 h, the mixture was concentrated under the reduced pressure and washed with water and chloroform. The organic layer was concentrated and precipitated by adding cooled methanol. After the precipitate was filtered off, the solution was concentrated and redissolved in chloroform. And then the organic layer was dried with K₂CO₃. After removing the solvent, compound **3** was obtained as liquid in 74% yield.

¹H-NMR (300 MHz, CDCl₃, ppm) δ: 10.48 (m, 2H, —CHO), 7.31 (m, 2H, ArH), 4.64 (m, 2H, —OCH₂—), 3.87 (m, 3H, —OCH₃), 1.27–1.48 (m, 9H, —CH₂—, >CH—), 0.90–0.96 (m, 6H, —CH₃).

2,5-Dimethylphenyl-1,3,4-oxadiazole (**4**)

To a mixture of 33 g P₂O₅ dissolved in 16 mL of H₃PO₄ (85%, wt/wt) was added 8.0 g (0.6 mol) of 4-methyl

benzoic acid and 39.0 g (0.3 mol) of hydrazine sulfate. The reaction mixture was stirred at 134°C for 24 h, and then cooled and poured into 500 mL of water. The white precipitate was collected by filtration and washed with water. Recrystallization from anhydrous ethanol afforded white products in 90% yield.

IR (infrared) (KBr, cm⁻¹): 3025, 2929, 1610, 1575, 1550, 1495, 1400, 1305, 1260, 1200, 1180, 1062, 1015, 835, 825, 738; mp: 176–177°C.

¹H-NMR (300 MHz, CDCl₃) δ: 2.46 (s, 6H, —CH₃), 7.35 (d, 4H, ArH), 8.04 (d, 4H, ArH).

2,5-Bis(4'-chloromethyl phenyl)-1,3,4-oxadiazole (**5**)¹⁹

A 7.5 g (0.03 mol) sample of compound **4**, 5 mL of SO₂Cl₂, and a catalytic amount of benzoyl peroxide (BPO) as an initiator were added into 300 mL of anhydrous chlorobenzene. After refluxing for 3 h under nitrogen atmosphere, the reaction mixture was washed with dilute solution of NaHCO₃ and water successively, and then the organic layer was dried over anhydrous magnesium sulfate. After filtration, the solution was concentrated, and the resulting solid was recrystallized from anhydrous ethanol to yield 3.9 g of white crystals (40.8%).

IR (KBr, cm⁻¹): 3025, 2929, 1611, 1552, 1495, 1419, 1275, 1210, 1180, 1098, 1075, 1018, 850, 820, 718, 680, 642, 514; mp: 194–196°C.

¹H-NMR (300 MHz, CDCl₃) δ: 4.67 (s, 4H, —CH₂—), 7.58 (d, 4H, ArH), 8.17 (d, 4H, ArH).

Anal. Calcd. For C₁₇H₁₂N₂OCl₂: C, 60.19; H, 3.76; N, 8.78. Found: C, 60.66; H, 3.85; N, 8.82.

2,5-Bis[[4'-xylylene(triphenylphosphonium chloride)] phenyle]-1,3,4-oxadiazole (**6**).^{20,21}

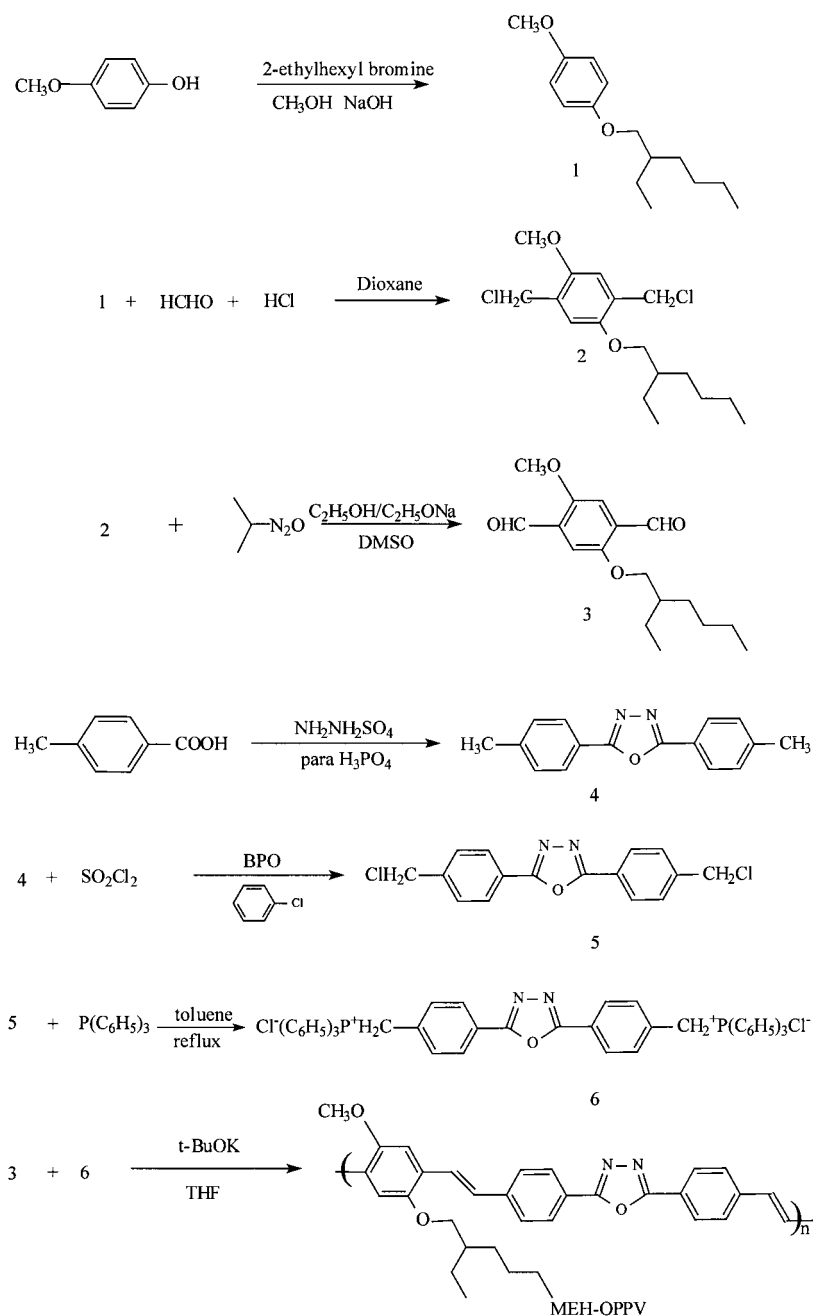
A solution of 1.597 g (5.0 mmol) of compound **5** and 2.62 g (10.0 mmol) of triphenylphosphine in 10 mL of anhydrous toluene was heated to reflux 24 h with stirring. The mixture was then cooled to room temperature. The precipitate was filtered and recrystallized in ethanol–ethyl acetate. After drying in a vacuum oven, a white solid powder was obtained 3.6 g (yield 85.4%).

IR (KBr, cm⁻¹): 3025, 2929, 1614, 1586, 1552, 1492, 1438, 1271, 1111, 1070, 1018, 997, 852, 751, 718, 689.

¹H-NMR (300 MHz, CDCl₃) δ: 5.93 (d, 4H, —CH₂—), 7.35–8.13 (m, 38H, ArH).

Polymerization: method A

To a solution containing 0.91 g (2.73 mmol) of monomer **2** and 0.09 g (0.28 mmol) of monomer **5** in 60 mL of anhydrous THF, a solution of potassium *tert*-butoxide (*t*-BuOK) (3.0 g of purity 95%, 26.8 mmol) in 30 mL of anhydrous THF was added dropwise at room temperature. Soon after the base was added, a light blue precipitate appeared, and then changed to orange. The



Scheme 1 Synthetic route to poly[[2,5-diphenylene-1,3,4-oxadiazole-vinylene]-alt-[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]] (MEH-OPP).

mixture was stirred for 10 h and then poured 200 mL of methanol. The copolymer powder was collected and dried under vacuum. The resulted copolymer could not dissolve in common organic solvents.

Polymerization: method B

Based on the Wittig condensation reaction, 1 g of compound 6 (3.4 mmol) and 2.87 g of compound 3 (3.4 mmol) were dissolved in a mixture of anhydrous THF (60 mL) in a 250 mL dried round-bottomed flask, which was equipped with a magnetic stirring bar and

capped with a rubber septum. A solution of potassium *tert*-butoxide (t-BuOK) (2.3 g of purity 95%, 20.4 mmol) in anhydrous tetrahydrofuran (THF) (30 mL) was added dropwise to the reaction flask via a syringe at room temperature under nitrogen atmosphere. The reaction mixture turned from yellow to orange with the addition of potassium *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 500 mL methanol and collected by filtration. Further purification was carried out by redissolving the polymer in chloroform

and precipitating in methanol twice. After drying under a vacuum oven for 24 h, an orange elastomer 0.68 g was obtained in 40% yield.

$^1\text{H-NMR}$ (300 MHz, CDCl_3) δ : 6.61–8.16 (m, 14H, ArH, $-\text{CH}=\text{CH}-$), 3.70 (m, 5H, $-\text{OCH}_3$, $-\text{CH}_2\text{O}-$), 0.68–1.60 (m, 15H, $-\text{C}_7\text{H}_{15}$).

FTIR (Fourier transform infrared (KBr, cm^{-1}): 3051 (aromatic C—H stretching), 2926 (s, $\nu_{\text{C-H}}$, CH_3), 2858 (s, $\nu_{\text{C-H}}$, CH_2), 1610, 1494 (m, ArH stretching), 1462 (m, $\delta_{\text{C-H}}$, CH_2), 1411, 1269, 1206, 1112, 1066 (s, C—O—C, stretching), 962 (*trans*-vinylene C—H, out-of-plane), 853 (*cis*-vinylene C—H), 747, 719, 691.

Measurements

IR spectra were recorded on a Bruker IFS66V vacuum Fourier-transfer spectrometer. $^1\text{H-NMR}$ spectra were collected on a Bruker DPX300 spectrometer. Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer for C and H determination. Thermogravimetric analysis (TGA) was conducted on a TA Instrument 2100 system with a TGA 2950 thermogravimetric analyzer under a heating rate of $20^\circ\text{C}/\text{min}$ and a nitrogen flow rate of 60 mL/min. Differential scanning calorimetry (DSC) was run on a Du Pont DSC 2910 module in conjunction with the Du Pont Thermal Analyst system. Ultraviolet-visible (UV-Vis) and fluorescence spectra were obtained on a Shimadzu UV-3100 spectrophotometer and a Perkin-Elmer 5050 luminescence spectrometer, respectively. In the fabrication of the single-layer LED device, indium tin oxide (ITO)-coated glass with a resistivity of $250 \Omega/\square$ was used as substrate. Uniform film of the copolymer was spin-coated onto ITO from a 1 wt % solution of copolymer in THF to obtain a film of about 100 nm thick (measured by an ALPHA STEP 500 profilometer). The film was dried in a vacuum oven at 30°C for 24 h before device fabrication. 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 . All the processes except the evaporation of the top electrode were done under ambient atmosphere. Electrical and optical characterization was also carried out under ambient atmosphere. Current–voltage measurements were carried out using a 2650 digital source-measure unit.

RESULTS AND DISCUSSION

Monomer and polymer synthesis

There have been a few approaches for introducing aromatic oxadiazole moieties into the polymer side chain to form a fully conjugated polymer.^{22–24}

In case of our experiment, in order to introduce the oxadiazole ring into the main chain, Wittig condensa-

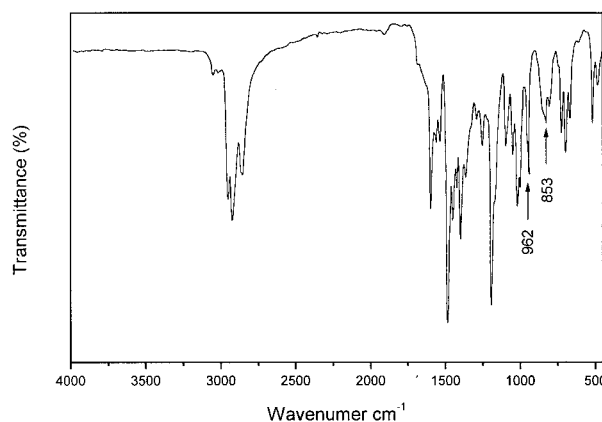


Figure 1 FTIR spectra of MEH-OPP film.

tion reaction was used to obtain alternating copolymer by using terephthalaldehyde (**3**) and triphenylphosphonium chloride (**6**) monomers as shown in Scheme 1. The obtained copolymer can be dissolved in common organic solvent. The IR spectrum of the copolymer film showed the presence of both *cis*- $\text{CH}=\text{CH}$ (853 cm^{-1}) and *trans*- $\text{CH}=\text{CH}$ (962 cm^{-1}) absorption in medium intensity in Figure 1. The 2,5-Dimethylphenyl-1,3,4-oxadiazole (**4**) was synthesized from 4-methyl benzoic acid through one step reaction. This method not only gives a high yield but also avoids multistep synthesis.¹⁹

Synthesis of a random-type copolymer with same repeat units as the alternating copolymer (MEH-OPP) was also done by dehydrohalogenation reaction utilizing *t*-BuOK reagent with compound **2** and compound **5** as monomers. It was found, however, that the dehydrohalogenation reaction only gave insoluble precipitate. This was considered to be due to the large difference in the reactivity of the two monomers toward the *t*-BuOK reagent, resulting in a block-type copolymer, which was not soluble in the polymerization medium.

Thermal analysis of the copolymer

Thermal stability of copolymer is important for device longevity. Figure 2 displays the TGA chart of MEH-OPP. The TGA analysis reveals that the copolymer is stable in nitrogen up to 310°C , and no weight loss was observed at lower temperature. Between 310 and 600°C , there is about 60% weight loss, which is a result of the decomposition of the polymer. Thus, the polymer is quite stable in nitrogen. The glass transition (T_g) of the polymer was determined by DSC in nitrogen atmosphere at a heating rate of $20 \text{ min}/^\circ\text{C}$. Figure 3 shows that the glass-transition temperature of the copolymer was around 143°C . This result indicates that the polymer possesses a relative high T_g due to the oxadiazole rigid structure, which is favorable for the lifetime of LED

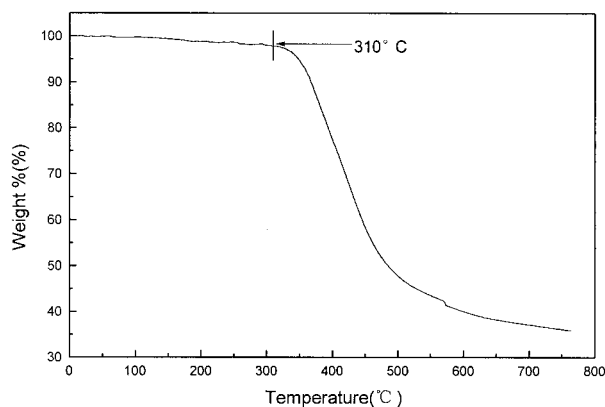


Figure 2 TGA thermograms of MEH-OPPV (heat from 20 to 80°C at 20°C/min).

device since active emissive polymers and charge injecting/transporting materials with high glass transition temperature might exhibit longer device lifetime.²⁵

UV-visible and photoluminescence spectra

The UV-visible absorption and photoluminescence (PL) spectra of the copolymer are depicted in Figure 4. The UV-visible absorption spectra of the copolymer in both solution and solid film show two peaks at 323 and 369 nm and 310 and 377 nm, respectively. The longer wavelength peak is attributed to the electron transition of $\pi-\pi^*$ along the conjugated polymer main chain, whereas the shorter wavelength peak originates from the $n-\pi^*$ electron transition of the aromatic side chain. The $\pi-\pi^*$ absorption peak is red shifted by 8 nm from solution to film, which is due to a reduction of disorder or an increase in effective conjugation length of conjugated polymer, which implies that the conformation of the solid-state copolymer is in a rather ordered state. The absorption edge for the film sample is measured to be 506 nm, from which the $\pi-\pi^*$ band gap energy is estimated to be 2.46 eV.

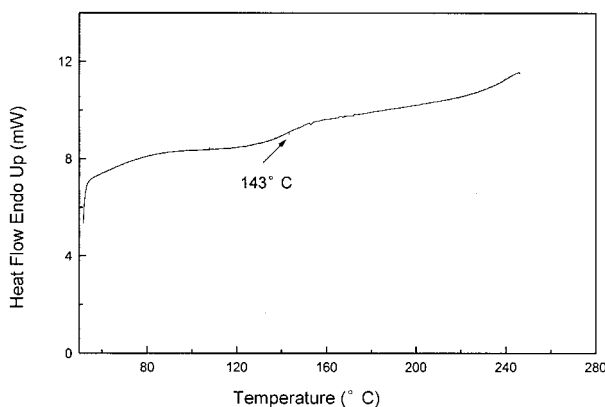


Figure 3 DSC of MEH-OPPV (heat from 50 to 250°C at 10°C/min).

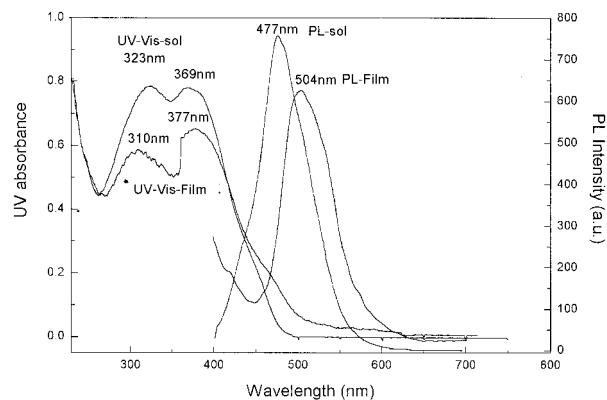


Figure 4 UV-visible absorption and PL (excited at 386 nm) spectra of MEH-OPPV in THF and film states at room temperature.

The emission spectra of the copolymer in solution and in solid films are quite different. The maximum emission peaks are 477 nm for solution and 504 nm for film (excited at 386 nm), which corresponds to yellowish-green light. In comparison with its solution emission peak, the maximum emission peak in the solid film shifted about 27 nm toward longer wavelength. The red shift of the emission band of the film samples may be due to the intrachain and/or interchain excimers generated in the polymer.

LED device and electroluminescent behavior

An ITO/MEH-OPPV/Al single-layer light-emitting diode was successfully fabricated. Under a forward bias (ITO wired positively), the single-layer diode began to emit visible yellowish-green light at about 4 V. The current-voltage (I-V) curve of the LED device, displayed in Figure 5, shows typical diode characteristics. When the forward bias was increased, the current increased rapidly after 6 V. The EL emission

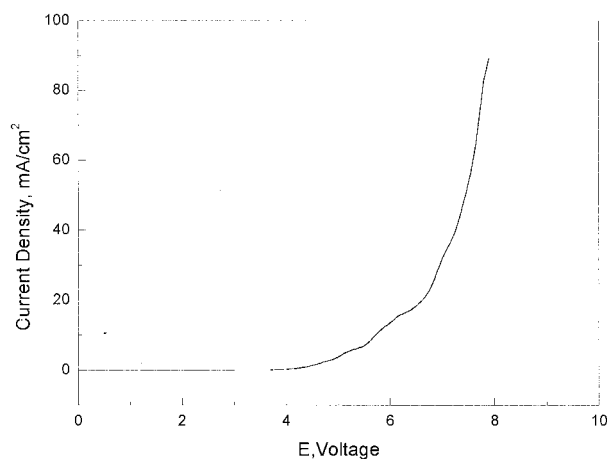


Figure 5 Characteristics of current density vs. drive voltage of an ITO/MEH-OPPV/Al device.

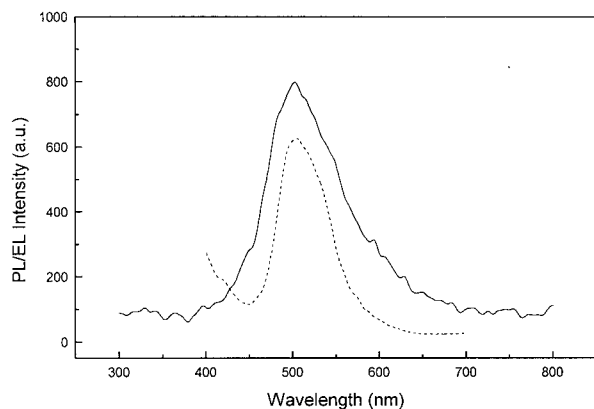


Figure 6 PL spectra of MEH-OPPV film (dash) and EL spectra of the ITO/MEH-OPPV/Al device (solid).

spectrum of the LED device as shown in Figure 5 was very similar to the PL spectrum, indicating that same excitation was involved in both cases.

These results demonstrate that the synthesized copolymer may be a potential active material for use in LEDs. Because the fabrication and characterization of the LED devices were conducted under ambient conditions, better EL performance may be expected if the processes are carried out in more strict conditions. More detailed study on EL properties of the new copolymer is in progress.

CONCLUSION

Herein we report a facile synthetic route to a new conjugated copolymer, poly{[2,5-diphenylene-1,3,4-oxadiazole-vinylene]-alt-[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]} (MEH-OPPV), in which an electrodeficient aromatic oxadiazole moiety is introduced into the PPV backbone to enhance the electron affinity. The copolymer can readily dissolve in common organic solvents, which makes it processable. The absorption and fluorescent emission spectra of the copolymer indicate that it is a yellowish-green luminescent material with a band gap of 2.46 eV. We successfully fabricated a single-layer light-emitting di-

ode device, ITO/MEH-OPPV/Al, which emits visible yellowish-green light above the bias voltage 4.0 V (Figure 6).

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