

Synthesis and Characterization of Poly(1,4-phenylenevinylene) Derivatives Containing Liquid Crystalline Oxadiazole Groups

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ABSTRACT: Two novel poly(1,4-phenylenevinylene) (PPV) derivatives containing liquid crystalline oxadiazole side chains were prepared by a dehydrochlorination process. The homopolymer poly(2-methoxy-5-((2-methoxy-phenyl)-5-hexyloxy-phenyloxy-1,3,4-oxadiazole)-1,4-phenylenevinylene) (HO-PE₆) is insoluble in common solvents, whereas the copolymer poly(2-methoxy-5-((2-methoxy-phenyl)-5-hexyloxy-phenyloxy-1,3,4-oxadiazole)-(2-methoxy-5-(2'-ethylhexyloxy))-1,4-phenylenevinylene) (CO-PE₆) is soluble in common solvents such as chloroform, THF, and *p*-xylene. The molecular structure of CO-PE₆ was confirmed by FTIR, ¹H-NMR, UV-vis spectroscopy, and polarized light microscopy. CO-PE₆ showed a maximum emission at 556 nm in chloroform and at 564 nm in

solid film, when excited at 450 nm. The maximum electroluminescence emission of the device indium-tin oxide (ITO)CO-PE₆/Al is at 555 nm. The turn-on voltage of LEDs based on CO-PE₆ and MEH-PPV is 6.5 and 8.5 V, respectively. The electron mobility of CO-PE₆ is higher than that of MEH-PPV based on the results of current-voltage and electrochemical behavior of both MEH-PPV and CO-PE₆. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 396–403, 2004

Key words: light-emitting polymers; poly(*p*-phenylenevinylene) derivatives; electron transport; 1,3,4-oxadiazole group; electrochemistry

INTRODUCTION

The observation of electroluminescence (EL) in a poly(*p*-phenylenevinylene) (PPV)-based diode was first reported in 1990 by the Cambridge group.¹ Ever since, the field has attracted a great deal of interest in the search for highly efficient electroluminescent polymers,² the optimization of device structure to maximize their efficiencies, across the full visible range.^{3,4} To optimize the device efficiency of polymeric light-emitting diodes (LEDs), three crucial contributions have been identified: charge injection, transport, and recombination. An unbalanced injection results in an excess of one carrier type and thus in current flow that does not contribute to light emission. Furthermore, it can also result in an enhanced nonradiative recombination because of the interactions of excitons with

these carriers. An unbalanced charge transport on the other hand gives rise to confinements of EL emission to a region close to one of the injecting electrodes where enhancement of nonradiative decay rate is expected.³ Many attempts have been made to improve the yield of exciton formation in the electroluminescent polymer layer of an LED, including chemical modification of PPVs,^{4,5} use of different electrodes,⁶ and use of electron- and hole-transporting layers to balance the injection of the electron/hole.⁷ It has been recognized that the electron mobility in PPV is significantly lower than that of the hole and thus improving the electron mobility of PPV and its derivatives is one of the key methods to improve the devices' performance.

It is well known that 1,3,4-oxadiazole derivatives are electron-deficient compounds, which thus show relatively high electron mobility. 2-(4-Biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) is widely used as an electron-transport layer in LEDs. Incorporation of 1,3,4-oxadiazole as pendants to the polymer backbone and to the main chain has been reported in the literature. Peng et al.⁸ reported, concerning the PPV derivative containing the oxadiazole groups both in the side chains and in the main chain, that devices based on it showed an improved external efficiency compared to that of PPV. Jin et al.⁹ incorporated 1,3,4-

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oxadiazole moieties as pendant groups to the conjugated polymer main chain and EL efficiency is improved.

The introduction of molecular orientation that promotes a large overlap of wave function of the π -orbital among π -conjugated molecules is one of the promising approaches to the attainment of high charge mobility. Tokuhisa et al.¹⁰ reported the high electron mobility in a novel liquid crystalline (LC) oxadiazole, in which the electron mobility in its LC film was much higher than that in the isotropic glassy film. Inspired by their work, we are particularly interested in preparing novel PPV derivatives in which LC oxadiazole is attached to the backbone through a flexible spacer. Introduction of a spacer might decrease the interaction between the main chain and oxadiazole and thus could induce the orientation of oxadiazole groups to further enhance the electron mobility in the conjugated polymers.

We report here the synthesis and characterization of a new soluble statistical copolymer bearing an aromatic 1,3,4-oxadiazole side chain [e.g., poly(2-methoxy-5-((2-methoxy-phenyl)-5-hexyloxy-phenyloxy-1,3,4-oxadiazole))-1,4-phenylenevinylene)-*co*-(2-methoxy-5-(2'-ethylhexyloxy))-1,4-phenylenevinylene (CO-PE₆)].

EXPERIMENTAL

Measurements

¹H-NMR spectra were recorded with a Varian Unity 400 spectrometer (400 MHz; Varian Associates, Palo Alto, CA), using deuterated chloroform (CDCl₃) as solvent and tetramethylsilane (TMS) as an internal chemical shift reference. FTIR spectra were recorded with a Bio-Rad FTS-7 spectrometer (Bio-Rad, Hercules, CA); the samples were pressed tablets with KBr. The molecular weight of the polymer was estimated from gel permeation chromatography (Waters GPC 410; Waters Chromatography Division/Millipore, Milford, MA) in tetrahydrofuran (THF) using polystyrene as calibration standards. UV-vis spectra were measured with a Shimadzu UV-3100 UV-vis spectrometer (Shimadzu, Kyoto, Japan). The photoluminescence (PL) spectrum was measured with a Shimadzu RF-5301 PC spectrometer.

Synthesis

1-Bromo-(6-(4-methoxy)/phenoxy)hexane (A₆)

A mixture of 6.2 g of *p*-hydroxyanisole (0.05 mol), 50 mL of 1,6-dibromohexane (0.30 mol), 30 g of anhydrous potassium carbonate, 0.3 g of KI, and 200 mL of dry acetone was heated under reflux for 24 h in a nitrogen atmosphere. After cooling to room temperature, the mixture was filtered to remove salts and

concentrated by evaporating acetone. The remaining mixture was poured into 200 mL methanol. The product was precipitated out immediately, filtered, and dried to give A₆ as a white solid (9.44 g, 65.8% yield). m.p.: 55–56°C.

¹H-NMR (400 MHz, CDCl₃) (ppm, from TMS): 1.49–1.51 (broad, 4H, –C–C–CH₂–CH₂–C–C–), 1.75–1.79 (m, 2H, Br–C–CH₂–C–C–C–C–), 1.87–1.91 (m, 2H, –C–C–C–C–CH₂–C–O–), 3.41–3.44 (t, 2H, –CH₂Br), 3.76 (s, 3H, –OCH₃), 3.89–3.92 (t, 2H, –OCH₂–C–), 6.83 (s, 4H, Ar–H, *o*-to, –O–).

1-[(4-Methoxy)phenoxy]-6-4-[(ethyl benzoate)oxy]hexane (B₆)

A mixture of A₆ (0.02 mol), *p*-hydroxyanisole (0.02 mol), 30 g of anhydrous potassium carbonate, 0.3 g of KI, and 200 mL of dry acetone was heated under reflux for 24 h in a nitrogen atmosphere. After cooling to room temperature, the mixture was filtered to remove salts and concentrated by evaporating acetone. The remaining mixture was poured into 200 mL of methanol. A white residue was precipitated out immediately, which was filtered and dried to give B₆ (95% yield). m.p.: 97–98°C.

¹H-NMR (400 MHz, CDCl₃) (ppm, from TMS): 1.36–1.39 (t, 3H, –C–CH₃–), 1.54–1.58 (m, 4H, –C–C–CH₂–CH₂–C–C–), 1.78–1.83 (m, 4H, –C–CH₂–C–C–CH₂–C–), 3.76 (s, 3H, –O–CH₃), 3.90–3.93 (t, 2H, –O–CH₂–C–), 4.00–4.03 (t, 2H, –C–CH₂–O–), 4.33–4.35 (d, 2H, –O–CH₂–CH₃), 6.83 (d, 4H, Ar–H, *o*-to, –O–), 6.89–6.90 (d, 2H, Ar–H, *o*-to, –O–CH₃), 7.97–7.99 (d, 2H, Ar–H, *o*-to, –COOC₂H₅).

{4-[6-(Methoxy)phenoxy]hexoxy}benzoyl hydrazine (C₆)

A mixture of B₆ (0.0415 mol), 30 mL (excess) of hydrazine monohydrate, and 100 mL of methanol was heated under reflux for 48 h. After the completion of the reaction, the mixture was cooled and a white solid was obtained (78.3% yield). m.p.: 156–157.5°C.

¹H-NMR (400 MHz, CDCl₃) (ppm, from TMS): 1.53 (m, 4H, –C–CH₂CH₂–C–), 1.79–1.83 (m, 4H, –CH₂–C–C–CH₂–), 3.76 (s, 3H, –Ar–O–CH₃), 3.90–3.93 (t, 2H, H₃CO–Ar–O–CH₂), 3.99–4.02 (t, 2H, H₂NHNOC–Ar–OCH₂), 4.12 (broad, 2H, NH₂) 6.83 (s, 4H, Ar–H, *o*-to, –O–CH₂–, O–CH₃), 6.90–6.93 (d, 2H, Ar–H, *o*-to, –O–CH₂), 7.3 (s, H, –NHNH₂), 7.68–7.70 (d, 2H, Ar–H, *o*-to–, CONHNH₂).

N-(4-(6-Methoxy-phenoxy)hexoxybenzoyl)-*N'*-(4-methoxybenzoyl)hydrazine (D₆)

A mixture of 0.896 g of C₆ (0.0028 mol), 5.04 g (excess) of fresh *p*-methoxy-benzoyl chloride, 60 mL of pyridine was treated at 0–5°C for 8 h. The reaction mixture

was poured into cold water. The product was precipitated out immediately and dried under vacuum (87% yield). m.p.: 116–117°C.

$^1\text{H-NMR}$ (400 MHz, CDCl_3) (ppm, from TMS): 1.54–1.56 (m, 4H, $-\text{C}-\text{CH}_2\text{CH}_2-\text{C}-$), 1.79–1.82 (m, 2H, $-\text{C}-\text{CH}_2-\text{C}-\text{C}-\text{C}-$), 1.84–1.87 (m, 2H, $-\text{C}-\text{C}-\text{C}-\text{CH}_2-\text{C}-$), 3.76 (s, 3H, $-\text{O}-\text{CH}_3$), 3.89 (s, 3H, $-\text{O}-\text{CH}_3$), 3.91–3.93 (t, 2H, $-\text{O}-\text{CH}_2-\text{C}-$), 4.04–4.06 (t, 2H, $-\text{C}-\text{CH}_2-\text{O}-$), 6.83–6.84 (d, 4H, Ar—H, *o*-to, $-\text{O}-\text{CH}_3$, $-\text{O}-\text{CH}_3$), 6.97–7.04 (d, 4H, Ar—H, *o*-to, $-\text{OCH}_2$), 8.03–8.11 (d, 4H, Ar—H, *o*-to, $-\text{CONH-HNOC}-$), 9.42 (s, 2H, $-\text{CONHHNOC}-$). FTIR (KBr, cm^{-1}): 3298 cm^{-1} ($\nu_{\text{N-H}}$), 1680 cm^{-1} ($\nu_{\text{C=O}}$), 1645 cm^{-1} ($\delta_{\text{N-H}}$).

2-[4-(Methoxy)phenyl]-5-[[4-(6-methoxy)phenoxy]hexoxy]phenyl-1,3,4-oxadiazole (E_6)

D_6 (0.002 mol) was heated slowly for 30 min in 100 mL of POCl_3 . The color of the mixture turned deeply with gas production. Under a nitrogen atmosphere, the mixture was heated under reflux for 24 h. After POCl_3 was distilled off, the reaction mixture was cooled to room temperature and then poured into 400 mL of cold water. The precipitate was collected by filtration and washed with methanol; the obtained crude product was further purified by column chromatography (basic Al_2O_3 , cyclohexane/ethyl acetate = 1:1.2). A light yellow solid was obtained (84% yield). m.p.: 122–123°C.

$^1\text{H-NMR}$ (400 MHz, CDCl_3) (ppm, from TMS): 1.54–1.57 (m, 4H, $-\text{C}-\text{CH}_2\text{CH}_2-\text{C}-$), 1.79–1.81 (m, 2H, $-\text{C}-\text{CH}_2-\text{C}-\text{C}-\text{C}-$), 1.82–1.84 (m, 2H, $-\text{C}-\text{C}-\text{C}-\text{CH}_2-\text{C}-$), 3.76 (s, 3H, $-\text{O}-\text{CH}_3$), 3.89 (s, 3H, $-\text{O}-\text{CH}_3$), 3.90–3.93 (t, 2H, $-\text{O}-\text{CH}_2-\text{C}-$), 4.04–4.06 (t, 2H, $-\text{C}-\text{CH}_2-\text{O}-$), 6.83–6.85 (d, 2H, Ar—H, *o*-to, $-\text{O}-\text{CH}_3$), 6.97–6.99 (d, 2H, Ar—H, *o*-to, $\text{CH}_3-\text{O}-$), 7.00–7.04 (d, 4H, Ar—H, *o*-to, $-\text{O}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{O}-$), 8.03–8.11 (d, 4H, Ar—H, *o*-to, $-\text{CNONC}-\text{Aromatic}$). ANAL. calcd for $\text{C}_{28}\text{H}_{30}\text{O}_5\text{N}_2$ (474): C, 70.8%; H, 6.33%. Found: C, 69.9%; H, 6.39%. FTIR (KBr, cm^{-1}): 1607 cm^{-1} (aromatic $\nu_{\text{C=N}}$). UV-vis absorption $\lambda_{\text{max}} = 284$ nm (measured in CDCl_3). PL $\lambda_{\text{max}} = 357,373$ nm (measured in CDCl_3).

1,4-Dibromomethyl-2-methoxy-5-(2-(4-methoxy)phenyl)-5-(4-hexoxy)phenyl-1,3,4-oxadiazole benzene (BE_6)

In a flat flask, the mixture of 2.03 g of E_6 (0.0043 mol), 0.897 g of paraformaldehyde (0.03 mol), and 3 mL of 36% HBr was dissolved in 40 mL of 1,4-dioxane. The mixture was heated and stirred at 70°C for 6 h under a N_2 atmosphere. After being cooled to ambient temperature, the mixture was diluted with chloroform followed by extraction with water and NaHCO_3 (aq).

The chloroform solution was dried with MgSO_4 followed by removal of the chloroform. The yellow solution was poured into a large amount of methanol and a yellow precipitate appeared. The product was filtered and recrystallized from hexane. m.p.: 124–125°C; yield: 50%.

$^1\text{H-NMR}$ (400 MHz, CDCl_3) (ppm, from TMS): 1.54–1.57 (m, 4H, $-\text{C}-\text{CH}_2\text{CH}_2-\text{C}-$), 1.79–1.81 (m, 2H, $-\text{C}-\text{CH}_2-\text{C}-\text{C}-\text{C}-$), 1.82–1.84 (m, 2H, $-\text{C}-\text{C}-\text{C}-\text{CH}_2-\text{C}-$), 3.76 (s, 3H, $-\text{O}-\text{CH}_3$), 3.89 (s, 3H, $-\text{O}-\text{CH}_3$), 4.04–4.06 (t, 4H, $-\text{C}-\text{CH}_2-\text{O}-$), 4.60–4.61 (s, 4H, $\text{Br}-\text{CH}_2-\text{Ar}-\text{CH}_2-\text{Br}$), 6.83–6.85 (d, 2H, Ar—H, *o*-to, $-\text{O}-\text{CH}_3$), 6.97–6.99 (d, 2H, Ar—H, *o*-to, $\text{CH}_3-\text{O}-$), 7.00–7.04 (d, 4H, Ar—H, *o*-to, $-\text{O}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{O}-$), 8.03–8.11 (d, 4H, Ar—H, *o*-to, $-\text{CNONC}-\text{Aromatic}$).

2-Methoxy-5-(2-ethylhexyl-oxy)benzene (M_1)

According to the Chen and Wunderlich,¹¹ M_1 (a kind of yellow liquid) was synthesized. Yield: 83%.

$^1\text{H-NMR}$ (CDCl_3), $\delta = 0.92$ –1.00 (t, 6H, $-\text{CH}_2-\text{CH}_3$), 1.30–1.68 (m, 8H, $-\text{CH}_2-\text{CH}_2-\text{CH}_3$), 1.68–1.69 (t, 1H, $-\text{CH}_2-\text{CH}-(\text{CH}_2)_2-$), 3.75–3.77 (s, 3H, $-\text{OCH}_3$), 3.77–3.79 (s, 2H, $-\text{OCH}_2-$), 6.84 (s, 4H, Ar—H).

1,4-Dibromo-2-methoxy-5-(2-ethylhexyl-oxy)xylene (M_2)

M_2 was synthesized by the same way with BE_6 . Yield: 80%; m.p.: 81–82°C.

$^1\text{H-NMR}$ (CDCl_3), $\delta = 0.92$ –1.00 (t, 6H, $-\text{CH}_2-\text{CH}_3$), 1.30–1.68 (m, 8H, $-\text{CH}_2-\text{CH}_2-\text{CH}_3$), 1.68–1.69 (t, 1H, $-\text{CH}_2-\text{CH}-(\text{CH}_2)_2-$), 3.75–3.77 (s, 3H, $-\text{OCH}_3$), 3.77–3.79 (s, 2H, $-\text{OCH}_2-$), 4.51 (s, 4H, Ar— CH_2-Br), 6.84 (s, 2H, Ar—H).

Poly(2-methoxy-5((2-methoxy-phenyl)-5-hexyloxy-phenyloxy-1,3,4-oxadiazole)-1,4-phenylenevinylene) (HO-PE_6)

To a three-neck flask equipped with a thermometer and a stirrer, 0.66 g BE_6 (0.001 mol) and 1.12 g potassium *tert*-butoxide (0.01 mol) were placed in 18 mL solution consisting of 10 mL xylene, 5 mL *tert*-butoxide, and 3 mL *o*-dichlorobenzene. The mixture was refluxed for 4 h at 70°C under a nitrogen atmosphere. During the reaction, the viscosity of the medium increased and the color changed from yellow to red. After being cooled to room temperature, the mixture was poured into a large amount of hexane, and the polymer was collected by filtration. The polymer was purified by being dissolved into chloroform and precipitated in hexane, collected, and dried for 1 day under vacuum. Unfortunately, the HO-PE_6 could not dissolve in any common organic solvents.

FTIR (KBr, cm^{-1}): 2941, 2856 ($-\text{CH}_2-$, $\nu_{\text{C-H}}$); 1604 ($-\text{C}=\text{N}-$, $\nu_{\text{C-N}}$); 995 ($-\text{CH}=\text{CH}-$ in the polymer backbone, $\nu_{\text{CH}=\text{CH}}$).

Poly(2-methoxy-5((2-methoxy-phenyl)-5-hexyloxy-phenyloxy-1,3,4-oxadiazole))-co-(2-methoxy-5-(2'-ethylhexyloxy))-1,4-phenylenevinylene (CO-PE₆)

Copolymer CO-PE₆ was synthesized by copolymerization of BE₆ and M₂ in the mixture of xylene, *o*-dichlorobenzene, and THF using potassium *tert*-butoxide as strong base.

¹H-NMR (400 MHz, CDCl₃) (ppm, from TMS): 0.91 (d, 6H, $-\text{CH}_3$), 1.35, 1.49–1.53, 1.825 (broad, 16H, $-\text{C}-\text{CH}_2-\text{C}-$, 1H, $-\text{CH}_2-\text{CH}-(\text{CH}_2)_2-$), 3.71–3.79 (broad, 9H, $-\text{O}-\text{CH}_3$), 3.88–3.96 (m, 6H, $-\text{O}-\text{CH}_2-\text{C}-$), 6.86–6.90 (broad, 6H, Ar-H, *o*-to, $-\text{O}-\text{CH}_3$), 7.19–7.22 (s, 4H, Ar-H, *o*-to, $-\text{O}-\text{CH}_2-\text{C}-$), 7.45–7.50 (d, 2H, $-\text{CH}=\text{CH}-$), 7.932 (broad, 4H, Ar-H, *o*-to, $-\text{CNONC}$ -Aromatic). According to the integral areas of the proton peaks at $\delta = 7.93$ and 7.45, the molar percentage of the oxadiazole group in the copolymer could be calculated, which is 16.7%.

Poly(2-methoxy-5-(2'-ethylhexyloxy))-1,4-phenylenevinylene (MEH-PPV)

¹H-NMR (CDCl₃), $\delta = 0.89$ – 1.02 (t, 6H, $-\text{CH}_2-\text{CH}_3$), 1.22–1.36 (m, 4H, $-\text{CH}_2-\text{CH}_2-\text{CH}_3$), 1.47–1.56 (b, 4H, $-\text{CH}_2-\text{CH}_2-\text{CH}_3$), 1.82–1.87 (t, 1H, $-\text{CH}_2-\text{CH}-(\text{CH}_2)_2-$), 3.95 (s, 3H, $-\text{OCH}_3$), 4.09 (s, 2H, $-\text{O}-\text{CH}_2-$), 7.19 (d, 2H, Ar-H), 7.47–7.51 (d, 2H, $-\text{CH}=\text{CH}-$).

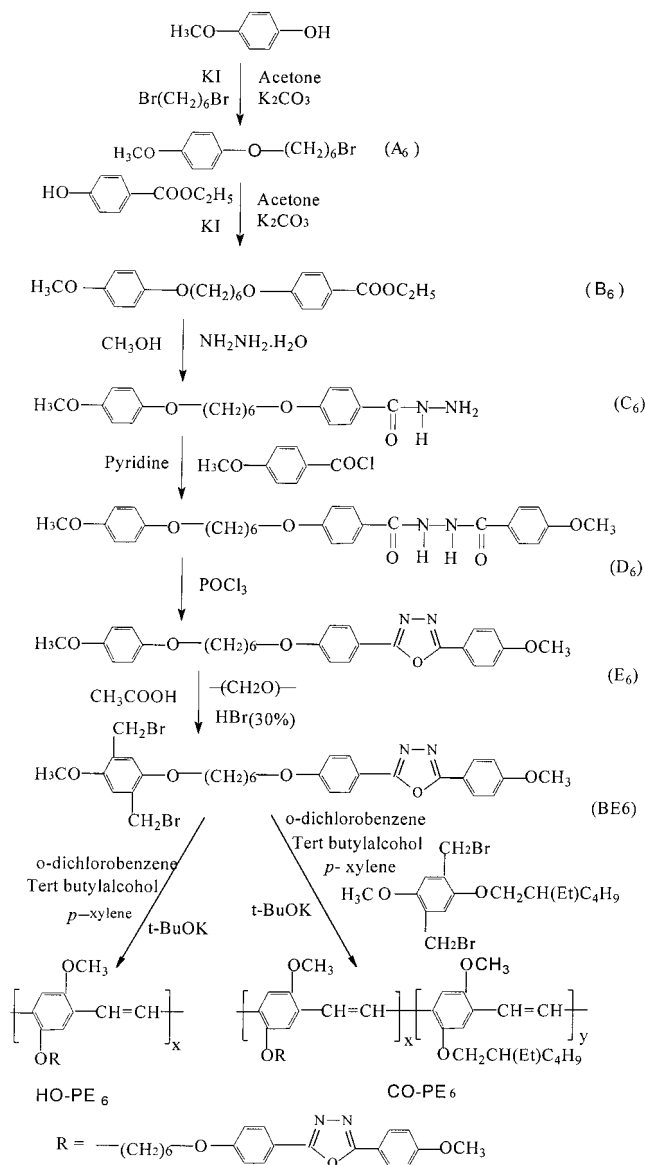
Fabrication of LED

Aluminum (Al) and indium–tin oxide (ITO) were used as the electron and hole injection electrode, respectively. The films of the polymers were spin-coated onto the ITO-coated glass substrate at room temperature. The thickness of the films was about 150 nm depending on the concentration and the spin rate. The deposition rates were controlled by the quartz oscillating thickness monitor to be 0.1 nm/s. The emitting area was $2 \times 2 \text{ mm}^2$.

RESULTS AND DISCUSSION

Synthesis and characterization of monomer E₆

The synthetic strategy, which is given in Scheme 1, consists of five steps to the desired liquid crystalline oxadiazole derivative. The first two steps progressed according to the typical method of the Williamson reaction. 1,3,4-Oxadiazole derivative E₆ was prepared by dehydrative cyclization of the mixed hydrazide (D₆). The peak at $\delta \approx 9.42$ ppm in the ¹H-NMR spectrum of D₆ was assigned to the proton of the N–H



Scheme 1 Synthetic route of novel PPV derivatives with 1,3,4-oxadiazole side group.

group and the bands at 1690 and 1645 cm^{-1} in its IR spectrum were assigned to the stretching vibration of $-\text{C}=\text{O}$ groups, whereas that at 3243 cm^{-1} was attributed to the stretching vibration of the N–H group. For E₆, no proton peak was observed at $\delta \approx 9.42$ ppm in its ¹H-NMR spectrum and a new band at 1609 cm^{-1} coming from the stretching vibration of the $-\text{C}=\text{N}-$ group attributed to the formation of 1,3,4-oxadiazole rings was observed. FTIR and ¹H-NMR spectroscopy as well as elemental analysis confirmed the structure of E₆. The ¹H-NMR spectrum of E₆ is given in Figure 1. The DSC results of E₆ in the heating and cooling cycles showed that it melted at 122°C, and upon cooling from its isotropic phase, a schlieren texture began to appear at 115.8°C and then crystallized at 93.7°C. The polarized optical microphotograph of E₆ at its

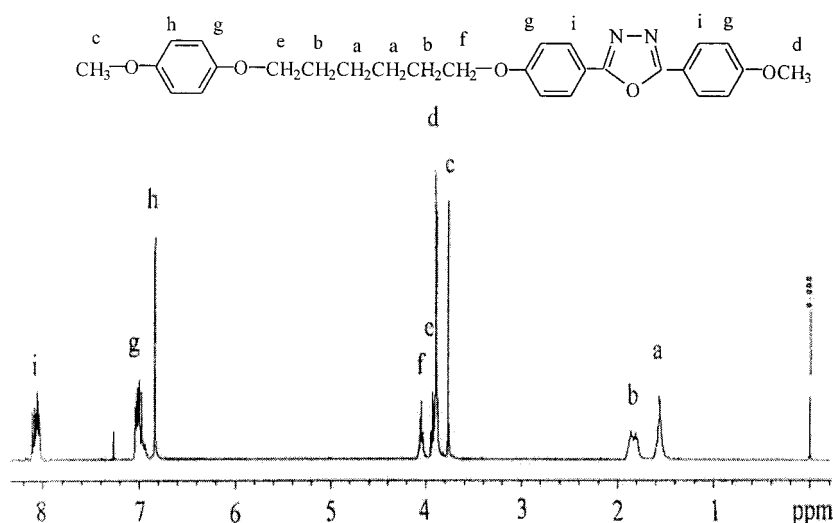


Figure 1 $^1\text{H-NMR}$ spectrum of E_6 .

liquid crystalline phase showing schilerene texture is given in Figure 2.

Synthesis of polymers

Monomer E_6 was first treated with formaldehyde and HBr in acetic acid to give dibromomethyl derivative BE_6 . The polymers were prepared by polymerization of BE_6 and/or M_2 through dehydrobromination at 70°C in the mixture of *p*-xylene, *o*-dichlorobenzene, and THF in the presence of potassium *tert*-butoxide. The rate of polymerization increased with the increase of polarity of the solvent, suggesting an anionic mechanism.¹² Homopolymer $HO-PE_6$ is insoluble in common organic solvents, whereas copolymer $CO-PE_6$ is soluble in ordinary solvents such as chloroform, THF, *p*-xylene, and so on. The proposed molecular structure of $CO-PE_6$ was characterized by FTIR and $^1\text{H-NMR}$

spectroscopy. The double peaks at $\delta = 7.45\text{--}7.50$ ppm are attributed to the protons of *trans*- $\text{CH}=\text{CH}$ -groups in the polymer backbone. According to the integral areas of the protons at $\delta = 7.93$ and $7.45\text{--}7.50$ ppm, the molar percentage of oxadiazole groups in the copolymer could be measured to be 16.7%. The number-average molecular weight of the $CO-PE_6$ was determined to be $M_n = 1.26 \times 10^4$ by GPC, relative to polystyrene standards, with a polydispersity index of 1.51. MEH-PPV was synthesized for comparison in the same conditions. No liquid crystalline behavior of the polymers was observed based on the results of DSC and polarized optical microscopy.

Optical properties of $CO-PE_6$

UV-vis and PL spectra of E_6 , $CO-PE_6$, and MEH-PPV in chloroform are given in Figure 3. The two absorption bands centered at 299 and 487 nm are assigned to the absorptions of oxadiazole group and the highly $\pi-\pi^*$ transitions of *trans*-configuration of the conjugated PPV backbone, respectively. The PL spectrum of $CO-PE_6$ excited at 450 nm shows an emission maximum at 556 nm. Both the shape and emission maximum of the photoluminescence of $CO-PE_6$ are similar to that of MEH-PPV. The maximum emission of $CO-PE_6$ red-shifted from 556 nm in chloroform to 564 nm in solid (Fig. 5). The red shift of the maximum emission of MEH-PPV is 39 nm (from 555 nm in chloroform to 594 nm in solid).

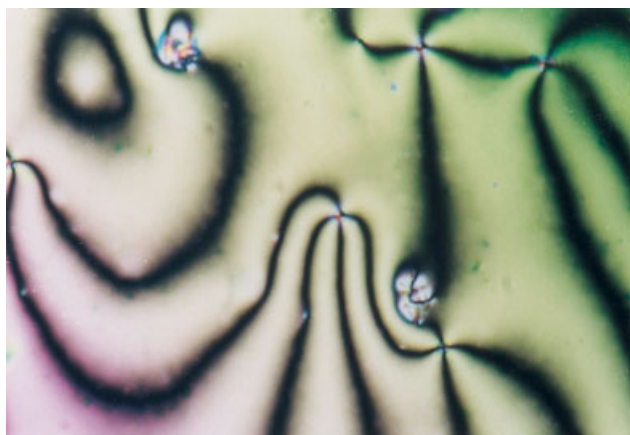


Figure 2 Polarized optical microphotograph of E_6 at 102°C in the course of cooling ($\times 200$).

Electrochemical behavior and energy level parameters

Cyclic voltammetry (CV) was conducted using a BAS 100B/W electrochemical workstation under nitrogen

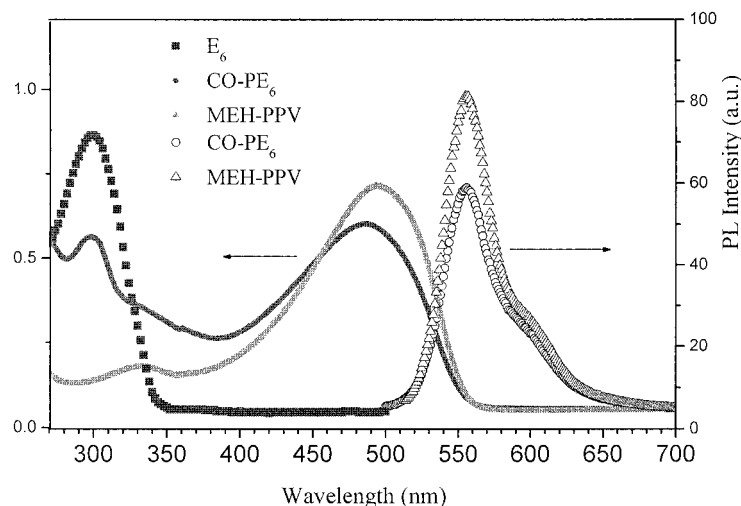


Figure 3 UV-visible spectra of E_6 , $CO-PE_6$, and $MEH-PPV$ and PL spectra of $MEH-PPV$ and $CO-PE_6$ in chloroform.

atmosphere. The cyclic voltammetry curves of $MEH-PPV$ and $CO-PE_6$, which were measured in a three-electrode compartment cell with 0.1M tetrabutylammonium perchlorate in dimethylformamide solution, using a silver/silver ion (Ag/Ag^+) reference electrode, a platinum wire as a counter electrode, and another platinum wire as a working electrode, are shown in Figure 4. The energy level parameters that establish the positions of the frontier orbital, that is, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) relative to vacuum level, are the ionization potential (IP) and electron affinity (EA). Extensive previous studies have illustrated that the energy parameters IP and EA are related to the measured redox potential by $IP = E_{ox} + 4.5$ eV and $EA = E_{red} + 4.5$ eV,^{13,14} where E_{ox} and E_{red} are the oxidation and reduction potentials in volts versus the normal hydrogen electrode potential, whereas IP and EA are in electronvolts. The energy gap E_g is the separation between the HOMO and LUMO levels; thus, $E_g = IP - EA$. The energy level parameters, HOMO, LUMO, and E_g of $MEH-PPV$ and $CO-PE_6$ are listed in Table I. There are some differences between the optical energy gap E_g^{opt} , which was obtained from the optical absorption, and the electrochemical gap E_g^{el} . This systematic error by different methods is estimated to be less than 0.5 eV.

Electroluminescence properties

Polymer LEDs were fabricated using $MEH-PPV$ and $CO-PE_6$ as emitting layers, and their electroluminescence properties were investigated. The thickness of emitting layers for the devices studied was about 150 nm by controlling polymer concentration as well as deposition rates. The current-voltage curves of the two devices are shown in Figure 5. The turn-on voltage of the single-layer LEDs, ITO/ $MEH-PPV$ /Al (De-

vice A) and ITO/ $CO-PE_6$ /Al (Device B), is 8.5 and 6.5 V, respectively. It can be seen that the current of Device B was higher than that of Device A at the same

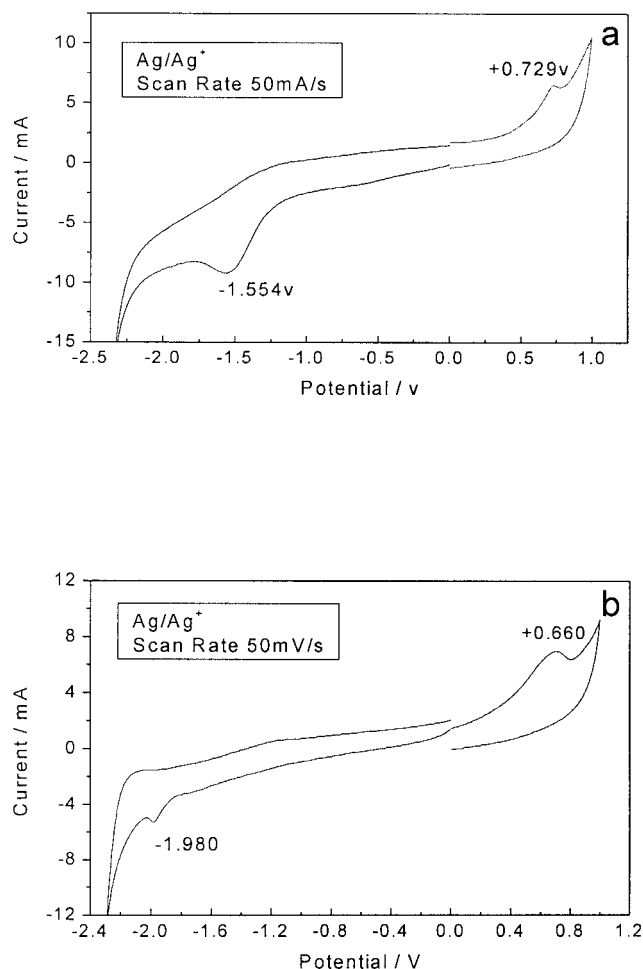


Figure 4 Cyclic voltammetry curves of (a) $MEH-PPV$ and (b) $CO-PE_6$ in DMF solution.

TABLE I
Energy Level Parameters of MEH-PPV and CO-PE₆

Sample	E_{ox} (V)	E_{red} (V)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{g}^{el} (eV)	$E_{\text{g}}^{\text{opt}}$ (eV)
CO-PE ₆	+0.660	-1.980	-5.16	-2.52	2.64	2.56
MEH-PPV	+0.729	-1.554	-5.23	-2.95	2.28	2.53

voltage, which indicated that CO-PE₆ was facilitated for the transportation of electrons. There is no large difference between the injection processes of the two devices from the HOMO and LUMO levels of MEH-PPV and CO-PE₆, and again the thickness of the two devices is about the same (150 nm). The turn-on voltage of Device B is 2 V lower than that of Device A, and its current increased sharply with the increase of voltage, which means the CO-PE₆ should have higher electron mobility than that of MEH-PPV. The introduction of LC-oxadiazole improved the electron-transport ability of the electroluminescent material and thus might result in the improved quantum efficiency of the device.

The electroluminescence spectrum of ITO/CO-PE₆/Al and the PL spectrum of CO-PE₆ in solid are given in Figure 6. The EL spectrum of CO-PE₆ is much the same as its corresponding PL spectrum except that the EL peak was broader.

CONCLUSIONS

A soluble conjugated copolymer CO-PE₆ containing PPV backbone and 1,3,4-oxadiazole side chains was

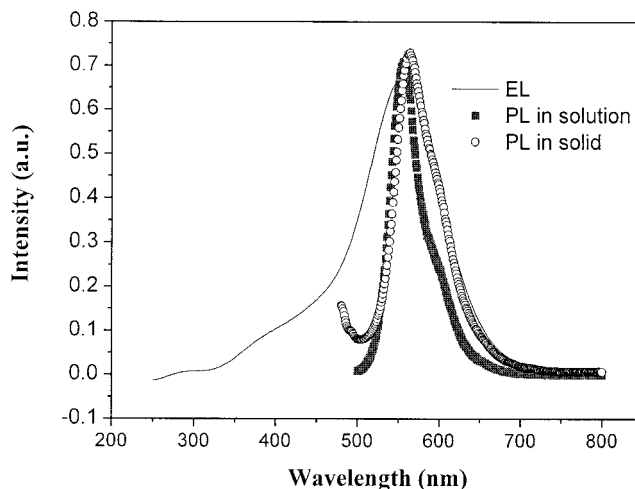


Figure 6 Electroluminescence spectrum of ITO/CO-PE₆/Al (solid line), PL spectra of CO-PE₆ in solution (CHCl₃; dashed line) and in solid state (CHCl₃; dotted line).

designed and synthesized. The UV-vis absorption spectrum of CO-PE₆ in chloroform shows two peaks: 299 and 487 nm, corresponding to the absorption of the liquid crystalline oxadiazole group and the π - π^* transitions of the *trans* -CH=CH- group in the conjugated PPV chain, respectively. Its maximum PL emission centered at 556 nm. The EL emission of CO-PE₆ is at 555 nm. The turn-on voltage of LED based on CO-PE₆ was lower than that of MEH-PPV, and the electron mobility in CO-PE₆ might be higher than that in MEH-PPV from the results of CV and current-

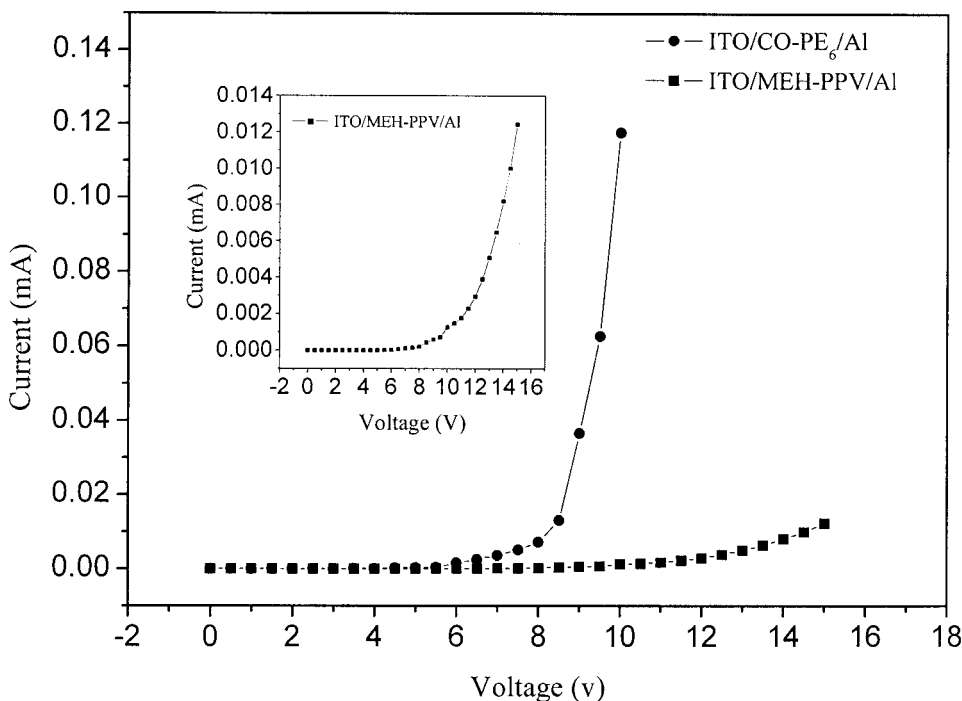


Figure 5 Current-voltage curves of device ITO/CO-PE₆/Al and ITO/MEH-PPV/Al.

voltage curves of the devices that have almost the same thickness.

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