

Synthesis and Characterization of Novel Phenyl-Substituted Poly(*p*-phenylene vinylene) Derivatives

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ABSTRACT: Two novel phenyl-substituted poly(*p*-phenylene vinylene) derivatives, poly{2-[3',4'-(2"-ethylhexyloxy)(3",7"-dimethyloctyloxy)benzene]-1,4-phenylenevinylene} (EDP-PPV) and poly{2-[3',4'-(2"-ethylhexyloxy)(3",7"-dimethyloctyloxy)benzene]-5-methoxy-1,4-phenylenevinylene} (EDMP-PPV), and their copolymer, poly{2-[3',4'-(2"-ethylhexyloxy)(3",7"-dimethyloctyloxy)benzene]-1,4-phenylenevinylene-co-2-[3',4'-(2"-ethylhexyloxy)(3",7"-dimethyloctyloxy)benzene]-5-methoxy-1,4-phenylenevinylene} (EDP-co-EDMP-PPV; 4:1, 1:1, and 1:4), were successfully synthesized according to the Gilch route. The structures and properties of the monomers and the resulting conjugated polymers were characterized with ¹H-NMR, ¹³C-NMR, elemental analysis, gel permeation chromatography, thermogravimetric analysis, ultraviolet-visible absorption spectroscopy, and photoluminescence and electroluminescence (EL) spectroscopy.

The EL polymers possessed excellent solubility in common solvents and good thermal stability with a 5% weight loss temperature of more than 380°C. The weight-average molecular weights and polydispersity indices of EDP-PPV, EDMP-PPV, and EDP-co-EDMP-PPV were 1.40–2.58 × 10⁵, and 1.19–1.52, respectively. Double-layer light-emitting diodes with the configuration of indium tin oxide/polymer/tris(8-hydroxyquinoline)aluminum/Al devices were fabricated, and EDP-co-EDMP-PPV (1:1) showed the highest EL performance and exhibited a maximum luminance of 1050 cd/m² at 19.5 V. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1259–1266, 2005

Key words: conjugated polymers; light-emitting diodes (LED); luminescence

INTRODUCTION

Since the discovery of electroluminescence (EL) in poly(*p*-phenylene vinylene) (PPV) in 1990,¹ polymer light-emitting diodes (PLEDs) have attracted wide research interest because of the many advantages over inorganic and organic small-molecule-based light-emitting diodes (LEDs), such as low cost, flexibility, wide viewing angles, fast switching times, easy processability, ease of forming large areas, and easy design of the molecular structure for EL polymers.^{2–6} Research for new π -conjugated polymers with higher performance remains one of the major challenges in the area, although a large number of light-emitting polymers have been synthesized and investigated, and the performance of PLEDs has been improved greatly in recent years. Among the many kinds of conjugated polymers, PPV and its derivatives are still

the leading candidates, mainly because of their good processability, structural diversity, thermal stability, and high luminescence efficiencies.^{7,8}

In designing PPV derivatives, we consider the achievement of high efficiency and luminance in PLEDs important for preventing a self-quenching process due to the formation of excimers in the solid state, which is closely related to the EL performance. Recently, various bulky side groups such as alkoxy, alkylsilyl, phenyl, and fluorenyl groups have been substituted onto PPV main chains, and they can suppress the intermolecular interactions that lead to the formation of excimers to some extent and tune the emission colors.^{9–12} Most recently, there has been increasing interest in phenyl-substituted PPV derivatives as luminescent polymers because of their higher fluorescence efficiency and enhanced photostability.^{13–15}

To develop polymers with better performance for fabricating PLEDs, we report the synthesis and characterization of two novel phenyl-substituted poly(*p*-phenylenevinylene) derivatives, poly{2-[3',4'-(2"-ethylhexyloxy)(3",7"-dimethyloctyloxy)benzene]-1,4-phenylenevinylene} (EDP-PPV) and poly{2-[3',4'-(2"-ethylhexyloxy)(3",7"-dimethyloctyloxy)benzene]-5-methoxy-1,4-phenylenevinylene} (EDMP-PPV), and their copolymer, poly{2-[3',4'-(2"-

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ethylhexyloxy)(3'',7''-dimethyloctyloxy)benzene]-1,4-phenylene-vinylene-co-2-[3',4'-(2''-ethylhexyloxy)(3'',7''-dimethyloctyloxy)benzene]-5-methoxy-1,4-phenylenevinylene} (EDP-co-EDMP-PPV; 4:1, 1:1, and 1:4). Different dialkoxy-branched long chains in the side chains were added to improve solubility in common organic solvents and to fine-tune the emission colors. The copolymers with EDP-PPV and EDMP-PPV were synthesized to tune the optical properties and improve the luminescence properties of PPV derivatives by intramolecular energy transfer between different band gaps of the two components.

EXPERIMENTAL

Measurements

¹H- and ¹³C-NMR spectra were recorded with a Bruker AM-300 spectrometer (Karlsruhe, Germany), and the chemical shifts (ppm) were recorded. Elemental analysis was performed with a Flash EA 1112 elemental analyzer (Thermo Electron SPA, Italy). The molecular weights and polydispersities of the polymers were determined by gel permeation chromatography (GPC) analysis with respect to polystyrene calibration [a Waters 515 HPLC pump, a Waters 2414 differential refractometer, and three Waters Styragel columns (HT2, HT3, and HT4) (Waters, Milford, MA)] with tetrahydrofuran (THF) as an eluent at a flow rate of 1.0 mL/min at 35°C. Thermogravimetric analysis (TGA) was conducted on a PerkinElmer 7 thermogravimetric analyzer (Perkin Elmer Cetus Instruments, Norwalk, CT) with a heating rate of 20°C/min under a nitrogen atmosphere. Differential scanning calorimetry (DSC) analysis was performed on a 2920 MDSC instrument (TA Instruments (New Castle, DE)) under a nitrogen atmosphere at a heating rate of 10°C/min. The ultraviolet-visible (UV-vis) spectra were recorded on a Hitachi UV-3010 spectrometer (Hitachi, Japan). The photoluminescence (PL) spectra were obtained with a Hitachi F-4500 fluorescence spectrophotometer (Hitachi, Japan).

LEDs were fabricated with these polymers as emissive materials, with tris(8-hydroxyquinoline)aluminum (Alq₃) as an electron-transport layer, and with aluminum as a cathode. The polymer film was spin-coated onto indium tin oxide (ITO) substrates (sheet resistance = 30 Ω/□) from a chloroform solution (8 mg/mL). The thickness of the polymer films was about 50 nm, and the active area of the EL devices was 5 mm². EL spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer with the LED devices forward-biased. Current-voltage (I-V) characteristics were measured with a Hewlett-Packard 4140B semiconductor parameter analyzer (Hewlett-Packard Company, Palo Alto, CA). All the measurements were

performed under the ambient atmosphere at room temperature.

Materials

Diethyl ether and THF were distilled over sodium and benzophenone. Chloroform and methanol were dried by distillation over CaH₂. 2-Bromo-5-methoxyterephthalic acid diethyl ester, 2-bromoterephthalic acid diethyl ester, and 3,4-dihydroxybromobenzene were prepared according to literature procedures.^{14,16,17} All other solvents and reagents were analytical-grade quality, were purchased commercially, and were used without further purification.

Synthesis

3,4-(3',7'-Dimethyloctyloxy)hydroxybromobenzene (1)

To a stirred solution of 3,4-dihydroxybromobenzene (10.00 g, 52.91 mmol) and NaOH (2.12 g, 52.91 mmol) in ethanol (100 mL) under argon was added dropwise 3,7-dimethyloctylbromide (11.69 g, 52.91 mmol). The reaction mixture was refluxed for 24 h and cooled to room temperature. Then, the solid residue was removed by filtration, and ethanol in the filtrate was removed by evaporation. The chloroform and water were added, and two phases were separated; the water phase was extracted twice with chloroform. The resulting organic phases were combined and washed three times with water. The organic extracts were dried over magnesium sulfate, evaporated, and purified with column chromatography (silica gel; petroleum ether as an eluent) to yield 8.76 g (50%) of **1** as a colorless oil.

¹H-NMR (300 MHz, CDCl₃, δ, ppm): 0.87–0.95 (m, 9H, CH₃), 1.15–1.35 (m, 6H, CH₂), 1.54–1.63 [m, 3H, CH₂, CH(CH₃)₂], 1.89 (m, 1H, CH₂CH), 4.02 (t, 2H, OCH₂), 5.62–5.72 (d, 1H, OH), 6.67–6.80 (m, 1H, ArH), 6.91–7.06 (m, 2H, ArH). ANAL. Calcd for C₁₆H₂₅BrO₂: C, 58.36%; H, 7.65%. Found: C, 58.25%; H, 7.51%.

3,4-(2'-Ethylhexyloxy)(3',7'-dimethyloctyloxy)bromobenzene (2)

2 was synthesized according to the procedure described for **1** with **1** (8.00 g, 24.32 mmol), 2-ethylhexylbromide (4.93 g, 25.53 mmol), and NaOH (1.02 g, 25.53 mmol). A colorless oil (7.88 g) of **2** was obtained in a 74% yield.

¹H-NMR (300 MHz, CDCl₃, δ, ppm): 0.86–0.95 (m, 15H, CH₃), 1.15–1.34 (m, 14H, CH₂), 1.40–1.57 [m, 3H, CH₂, CH(CH₃)₂], 1.80–1.88 (m, 2H, CH₂CH), 3.82–3.84 (d, 2H, OCH₂), 3.96–3.99 (d, 2H, OCH₂), 6.72–6.75 (t, 3H, ArH), 6.98–6.99 (t, 2H, ArH). ANAL. Calcd for

$C_{24}H_{41}O_2$: C, 65.29%; H, 9.36%. Found: C, 64.96%; H, 9.32%.

3,4-(2'-Ethylhexyloxy)(3',7'-dimethyloctyloxy)benzene-2-boronic acid (**3**)

To a stirred solution of dried diethyl ether (100 mL) and *n*-butyllithium (*n*-BuLi; 21.0 mL, 1.6M in hexane, 32.10 mmol) under argon was added dropwise a solution of **2** (12.87 g, 29.18 mmol) in dried diethyl ether (25 mL) at -78°C . The reaction solution was kept at -78°C for 3 h, and tributyl borate (8.05 g, 35.02 mmol) was added dropwise. The solution was kept stirring for 1 h at -78°C and then was allowed to warm slowly to room temperature overnight before the reaction was quenched with the addition of 1.0M HCl. The two phases were separated, and the water phase was extracted twice with diethyl ether. The combined organic extracts were washed three times with water, dried over magnesium sulfate, evaporated, and purified with column chromatography [silica gel; the by-products were eluted with petroleum ether, and the products were eluted with petroleum ether/ethyl acetate (5/1)] to yield 8.92 g (75%) of **3** as a colorless oil.

$^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ , ppm): 0.87–0.99 (m, 15H, CH_3), 1.16–1.35 (m, 14H, CH_2), 1.42–1.59 [m, 3H, CH_2 , $\text{CH}(\text{CH}_3)_2$], 1.84–1.89 (m, 2H, CH_2CH), 3.80–4.12 (m, 4H, OCH_2), 6.82–7.02 (m, 1H, ArH), 7.19–7.731 (m, 1H, ArH), 7.70–7.84 (ds, 1H, ArH).

2-[3',4'-(2"-Ethylhexyloxy)(3",7"-dimethyloctyloxy)benzene]terephthalic acid diethyl ester (**4a**)

To a stirred mixture of 2-bromoterephthalic acid diethyl ester (2.70 g, 8.96 mmol), K_2CO_3 (2.47 g, 17.87 mmol), toluene (30 mL), and water (30 mL) under argon were added **3** (4.00 g, 9.85 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (0.1045 g, 89.60 μmol). The reaction mixture was kept stirring for 24 h at 90°C and was cooled to room temperature. The two phases were separated, and the water phase was extracted twice with ethyl acetate. The organic phases were combined and washed three times with water. The organic extracts were dried over magnesium sulfate, evaporated, and purified with column chromatography [silica gel; chloroform/petroleum ether (1/3) as an eluent] to yield 3.77 g (72%) of **4a** as a colorless oil.

$^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ , ppm): 0.85–0.96 (m, 15H, CH_3), 1.05–1.33 (m, 14H, CH_2), 1.39–1.55 [m, 9H, CH_2 , $\text{CH}(\text{CH}_3)_2$, CH_2CH_3], 1.82–1.88 (m, 2H, CH_2CH), 3.86–4.06 (m, 4H, OCH_2), 4.09–4.16 (q, 2H, CH_2CH_3), 4.40–4.43 (q, 2H, CH_2CH_3), 6.84 (s, 1H, ArH), 6.86 (s, 1H, ArH), 6.90–6.92 (d, 1H, ArH), 7.76–7.78 (d, 1H, ArH), 8.01–8.10 (m, 2H, ArH). ANAL. Calcd for $\text{C}_{36}\text{H}_{54}\text{O}_6$: C, 74.19%; H, 9.34%. Found: C, 74.05%; H, 9.28%.

2-[3',4'-(2"-Ethylhexyloxy)(3",7"-dimethyloctyloxy)benzene]-5-methoxyterephthalic acid diethyl ester (**4b**)

4b was synthesized according to the procedure described for **4a** with **3** (4.83 g, 11.90 mmol), 2-bromo-5-methoxyterephthalic acid diethyl ester (3.58 g, 10.82 mmol), K_2CO_3 (2.98 g, 21.63 mmol), toluene (30 mL), water (30 mL), and $\text{Pd}(\text{PPh}_3)_4$ (0.1250 g, 108.20, μmol). A colorless oil (5.05 g) of **4b** was obtained in a 76% yield.

$^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ , ppm): 0.85–0.96 (m, 15H, CH_3), 1.04–1.33 (m, 14H, CH_2), 1.36–1.53 [m, 9H, CH_2 , $\text{CH}(\text{CH}_3)_2$, CH_2CH_3], 1.84–1.90 (m, 2H, CH_2CH), 3.97 (s, 3H, OCH_3), 3.85–4.05 (m, 4H, OCH_2), 4.08–4.12 (q, 2H, CH_2CH_3), 4.36–4.41 (q, 2H, CH_2CH_3), 6.79 (s, 1H, ArH), 6.81 (s, 1H, ArH), 6.88–6.90 (d, 1H, ArH), 7.72 (s, 1H, ArH), 7.64–7.81 (m, 1H, ArH). ANAL. Calcd for $\text{C}_{37}\text{H}_{56}\text{O}_7$: C, 72.51%; H, 9.21%. Found: C, 72.21%; H, 9.11%.

2-[3',4'-(2"-Ethylhexyloxy)(3",7"-dimethyloctyloxy)benzene]-1,4-bis(hydroxymethyl)benzene (**5a**)

To a stirred mixture of LiAlH_4 (0.51 g, 6.39 mmol) in dried THF (35 mL) was added dropwise a solution of **4a** (3.72 g, 6.39 mmol) in dried THF (8 mL), and the mixture was refluxed overnight. The reaction mixture was cooled to room temperature, and 1.0M HCl, water, and chloroform were added successively. The two phases were separated, and the water phase was extracted twice with chloroform. The combined organic extracts were washed three times with water, dried over magnesium sulfate, and evaporated to yield 2.61 g (82%) of **5a** as a colorless oil, which was used in the next step without further purification.

$^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ , ppm): 0.85–0.97 (m, 15H, CH_3), 1.16–1.33 (m, 14H, CH_2), 1.47–1.54 [m, 3H, CH_2 , $\text{CH}(\text{CH}_3)_2$], 1.85–1.88 (m, 2H, CH_2CH), 3.86–4.08 (m, 4H, OCH_2), 4.62 (s, 2H, CH_2OH), 4.71 (s, 2H, CH_2OH), 6.85 (s, 1H, ArH), 6.87 (s, 1H, ArH), 6.90–6.93 (d, 1H, ArH), 7.26–7.28 (d, 1H, ArH), 7.34–7.35 (d, 1H, ArH), 7.50–7.52 (d, 1H, ArH). ANAL. Calcd for $\text{C}_{32}\text{H}_{50}\text{O}_4$: C, 77.06%; H, 10.10%. Found: C, 77.04%; H, 10.12%.

2-[3',4'-(2"-Ethylhexyloxy)(3",7"-dimethyloctyloxy)benzene]-5-methoxy-1,4-bis(hydroxymethyl)benzene (**5b**)

5b was synthesized according to the procedure described for **5a** with **4b** (4.98 g, 8.14 mmol) and LiAlH_4 (0.65 g, 17.09 mmol). A colorless solid (3.68 g) of **5b** was obtained in an 86% yield.

mp: $60\text{--}62^\circ\text{C}$. $^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ , ppm): 0.86–0.98 (m, 15H, CH_3), 1.16–1.37 (m, 14H, CH_2), 1.53–1.56 [m, 3H, CH_2 , $\text{CH}(\text{CH}_3)_2$], 1.79–1.85 (m, 2H,

CH₂CH), 3.94 (s, 3H, OCH₃), 3.86–4.07 (m, 4H, OCH₂), 4.65–4.69 (d, 2H, CH₂OH), 4.70–4.72 (d, 2H, CH₂OH), 6.80–6.92 (m, 3H, ArH), 7.11 (s, 1H, ArH), 7.20 (s, 1H, ArH). ANAL. Calcd for C₃₃H₅₂O₅: C, 74.96%; H, 9.91%. Found: C, 74.82%; H, 9.89%.

2-[3',4'-(2"-Ethylhexyloxy)(3",7"-dimethyloctyloxy)benzene]-1,4-bis(bromomethyl)benzene (**6a**)

To a stirred solution of **5a** (2.55 g, 5.12 mmol) and triphenyl phosphine (3.76 g, 14.34 mmol) in dried THF (45 mL) under argon at 0°C was added carbon tetrabromide (4.76 g, 14.34 mmol) in portions. The reaction mixture was kept stirring overnight at room temperature, and then chloroform and water were added after most THF was evaporated. The two phases were separated, and the water phase was extracted twice with chloroform. The combined organic extracts were dried over magnesium sulfate, evaporated, purified with column chromatography [silica gel; ethyl acetate/petroleum ester (1/50) as an eluent] to yield 2.26 g (71%) of **6a** as a colorless oil.

¹H-NMR (300 MHz, CDCl₃, δ, ppm): 0.85–0.98 (m, 15H, CH₃), 1.15–1.35 (m, 14H, CH₂), 1.48–1.54 [m, 3H, CH₂, CH(CH₃)₂], 1.81–1.89 (m, 2H, CH₂CH), 3.91–4.09 (m, 4H, OCH₂), 4.46 (s, 2H, CH₂Br), 4.49 (s, 2H, CH₂Br), 6.91–6.96 (q, 2H, ArH), 7.04 (d, 1H, ArH), 7.30 (s, 1H, ArH), 7.36–7.38 (q, 1H, ArH), 7.48–7.50 (d, 1H, ArH). ¹³C-NMR (300 MHz, CDCl₃, δ, ppm): 11.20, 14.15, 19.69, 22.64, 22.75, 23.95, 24.79, 28.02, 29.10, 29.91, 30.61, 32.14, 32.83, 37.45, 39.31, 39.43, 67.55, 71.87, 113.39, 114.36, 121.19, 121.29, 128.29, 129.48, 130.99, 131.60, 132.11, 135.52, 138.02, 142.54, 148.83, 149.05. ANAL. Calcd for C₃₂H₄₈Br₂O₂: C, 61.54%; H, 7.75%. Found: C, 61.40%; H, 7.76%.

2-[3',4'-(2"-Ethylhexyloxy)(3",7"-dimethyloctyloxy)benzene]-5-methoxy-1,4-bis(bromomethyl)benzene (**6b**)

6b was synthesized according to the procedure described for **6a** with **5b** (3.66 g, 6.93 mmol), triphenyl phosphine (5.09 g, 19.41 mmol), and carbon tetrabromide (6.44 g, 19.41 mmol). A colorless oil (3.08 g) of **6b** was obtained in a 68% yield.

¹H-NMR (300 MHz, CDCl₃, δ, ppm): 0.85–0.97 (m, 15H, CH₃), 1.15–1.33 (m, 14H, CH₂), 1.46–1.55 [m, 3H, CH₂, CH(CH₃)₂], 1.80–1.87 (m, 2H, CH₂CH), 3.95 (s, 3H, OCH₃), 3.89–4.08 (m, 4H, OCH₂), 4.45–4.46 (d, 2H, CH₂Br), 4.53–4.55 (d, 2H, CH₂Br), 6.82–6.96 (m, 3H, ArH), 7.13 (s, 1H, ArH), 7.24 (s, 1H, ArH). ¹³C-NMR (300 MHz, CDCl₃, δ, ppm): 11.19, 14.15, 19.69, 22.64, 22.74, 23.94, 24.78, 28.03, 28.34, 29.10, 29.90, 29.91, 30.61, 32.72, 37.44, 39.31, 39.43, 55.70, 55.89, 67.59, 71.87, 111.58, 112.88, 113.45, 113.60, 114.60, 114.63, 121.26, 121.35, 121.44, 126.62, 128.32, 131.17,

131.95, 132.79, 134.69, 136.94, 148.57, 148.77, 149.09, 156.67. ANAL. Calcd for C₃₃H₅₀Br₂O₃: C, 60.55%; H, 7.70%. Found: C, 59.17%; H, 7.42%.

EDP-PPV

To a stirred solution of **6a** (0.41 g, 0.66 mmol) in dried THF (60 mL) under argon at room temperature was added dropwise potassium *tert*-butoxide (3.90 mL, 1.0M in THF, 3.90 mmol). The mixture was stirred overnight at room temperature. The viscous mixture was added dropwise to stirred methanol. The crude polymer was collected by filtration, washed with methanol, and stirred with two portions of a mixture of methanol and water (1/1) for 1 h. The polymer was filtered off, washed with methanol, dried under a high vacuum, and dissolved in chloroform with stirring at room temperature overnight. The solution was filtered, and the polymer was precipitated by dropwise addition to methanol. The precipitated polymer was collected, washed with methanol, and dried under a high vacuum. Then, the polymer was again dissolved in chloroform, filtered, precipitated, and dried under a high vacuum to yield 205 mg (68%) of EDP-PPV as a bright yellow solid.

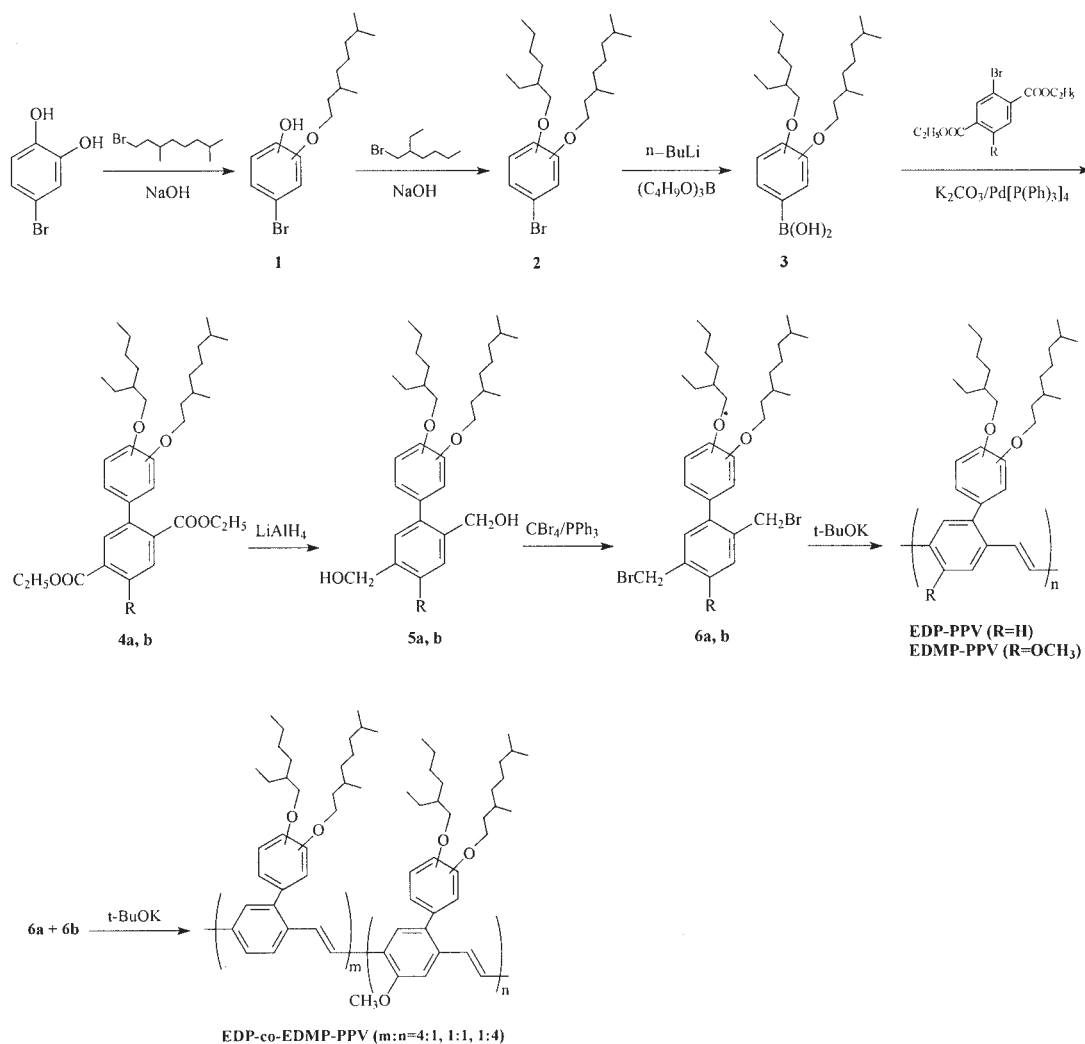
¹H-NMR (300 MHz, CDCl₃, δ, ppm): 0.84–0.97 (m, 15H, CH₃), 1.12–1.35 (m, 14H, CH₂), 1.42–1.56 [m, 3H, CH₂, CH(CH₃)₂], 1.82 (br, 2H, CH₂CH), 3.83–4.07 (br, 4H, OCH₂), 6.65–7.66 (br, 8H, ArH, CH=CH). ANAL. Calcd for (C₃₂H₄₆O₂)_n: C, 83.06%; H, 10.02%. Found: C, 82.72%; H, 9.96%.

EDMP-PPV and EDP-*co*-EDMP-PPV (4:1, 1:1, and 1:4) were synthesized according to the procedure described for EDP-PPV. The composition ratios of the copolymer are the initial monomer molar ratios used during the polymerization process.

RESULTS AND DISCUSSION

Syntheses and characterization

The monomers and the corresponding polymers were prepared according to Scheme 1. 3,4-Dihydroxybromobenzene was used as a starting material for the synthesis of **1** through alkylation with 3,7-dimethyloctyl bromide in the presence of NaOH. Evidently, the long alkyl group could be introduced to the 3- or 4-position of 3,4-dihydroxybromobenzene, and the molar ratio was 1:2, which was calculated by a comparison of the areas for the peaks at 5.62 and 5.72 ppm in the ¹H-NMR spectra. Then, the alkylation of **1** with 2-ethylhexyl bromide in the presence of NaOH produced **2**. Compound **3** was obtained through the reaction of **2** with *n*-BuLi to yield the lithium salt and through a subsequent conversion to the borate ester with tributyl borate, which was in turn hydrolyzed with hydrochloric acid to produce the corresponding



Scheme 1 Syntheses of the monomers and the resulting polymers.

aryl boronic acid. Palladium-catalyzed cross-coupling, known as Suzuki coupling,¹⁸ between the resulting aryl boronic acid and the substituted terephthalic acid diethyl esters in toluene produced **4a** and **4b** in 72–76% yields. The reduction of **4a** and **4b** with LiAlH₄ yielded **5a** and **5b**, respectively. Then, the bromination of the resulting hydroxyl groups of **5a** and **5b** with an excess of triphenyl phosphine and carbon tetrabromide yielded the monomers **6a** and **6b**, respectively.

The structures of the monomers were confirmed by ¹H- and ¹³C-NMR spectroscopy and elemental analyses. The homopolymerization of **6a** and **6b** and the copolymerization of **6a** and **6b** were easily performed by the Gich route to the corresponding polymers with an excess of potassium *tert*-butoxide in THF at room temperature overnight under an argon atmosphere.¹⁹ The use of excess strong alkali was very important to ensure the formation of the fully eliminated structure. During the polymerization, the reaction mixture became progressively viscous and remained homogenous without any formation of gel portions, showing a strong fluorescent light.

The resulting EL polymers were easily dissolved in common organic solvents such as chloroform, toluene, and xylene at room temperature.

The structures of these polymers were identified with ¹H-NMR spectroscopy and elemental analyses. The benzylic proton peaks at about 4.5 ppm for the monomers disappeared during the polymerization, and new vinylic proton peaks appeared at about 6.7–7.2 ppm along with phenyl proton peaks, which confirmed the polymerization reaction. In addition, all the other peaks showed good correspondence with the resulting polymers.

Table I summarizes the polymerization results, molecular weights, and thermal data for these polymers. The weight-average molecular weights and polydispersity indices were 1.40–2.58 × 10⁵ and 1.19–1.52, respectively. The TGA data for the polymers revealed a relatively high thermal stability, with 5% loss weight temperatures of 383–396°C. TGA curves of the polymers are shown in Figure 1. DSC curves showed glass-transition temperatures (*T_g*'s) of approximately 206–223°C. The high thermal stability of the EL polymers

TABLE I
Polymerization Results, Molecular Weights, and Thermal Data for the Polymers

Polymer	Yield (%)	M_n ($\times 10^{-5}$) ^b	M_w ($\times 10^{-5}$) ^b	PDI	TGA (°C) ^c	T_g (°C) ^d
EDP-PPV	68	0.94	1.40	1.48	396	223
EDMP-PPV	61	1.55	2.12	1.37	389	214
EDP-PPV-co-EDMP-PPV (4:1) ^a	58	1.13	1.71	1.52	390	218
EDP-PPV-co-EDMP-PPV (1:1) ^a	56	2.17	2.58	1.19	383	206
EDP-PPV-co-EDMP-PPV (1:4) ^a	60	1.99	2.49	1.25	388	209

M_w = weight-average molecular weight; M_n = number-average molecular weight; PDI = polydispersity index.

^a Initial monomer feed ratios.

^b Determined by GPC in THF on the basis of polystyrene standards.

^c Temperature at 5% weight loss under nitrogen.

^d Determined by DSC at a heating rate of 5°C/min under nitrogen.

was closely related to the performance of the LEDs and prevented morphological changes, deformation, and degradation of the emitting layer by current-induced heat during the operation of the EL devices.²⁰

Optical and EL properties

Figure 2 shows the optical absorption and PL spectra of EDP-PPV, EDMP-PPV, and EDP-co-EDMP-PPV (4:1, 1:1, and 1:4) in the solid state. The maximum absorptions of EDP-PPV, EDMP-PPV, and EDP-co-EDMP-PPV [4:1, 1:1, and 1:4; Fig. 2(a)], corresponding to the π - π^* transitions, were observed at approximately 426, 466, 438, 454, and 456 nm, respectively. The absorption edge of the absorption spectra for EDP-PPV, EDMP-PPV, and EDP-co-EDMP-PPV (4:1, 1:1, and 1:4) were 509, 547, 527, 536, and 544 nm, respectively, corresponding to the optical band gaps of 2.44, 2.27, 2.36, 2.32, and 2.29 eV. As shown in Figure 2(b), the maximum emission peaks of EDP-PPV, EDMP-PPV, and EDP-co-EDMP-PPV (4:1, 1:1,

and 1:4) occurred at approximately 510, 548, 531, 539, and 542 nm, respectively. In addition, the PL spectra of each polymer in the solid state showed one shoulder longer than the maximum peak, and this was mostly attributed to a 0-1 intrachain singlet transition. No emission peak from the EDP-PPV units of EDP-co-

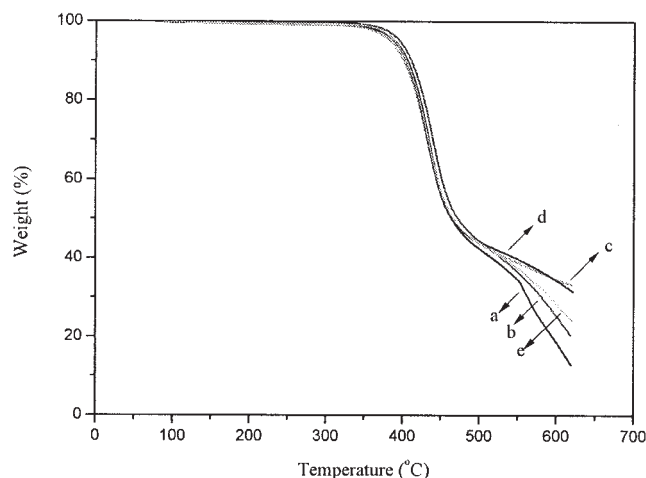


Figure 1 TGA thermograms of the resulting polymers: (a) EDMP-PPV, (b) EDP-PPV, (c) EDP-co-EDMP-PPV (1:1), (d) EDP-co-EDMP-PPV (1:4), and (e) EDP-co-EDMP-PPV (4:1).

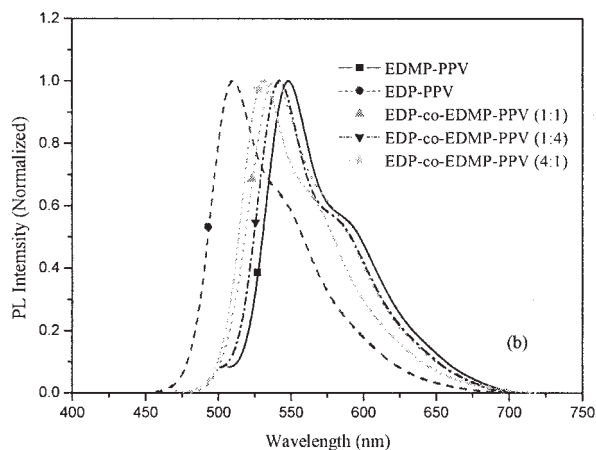
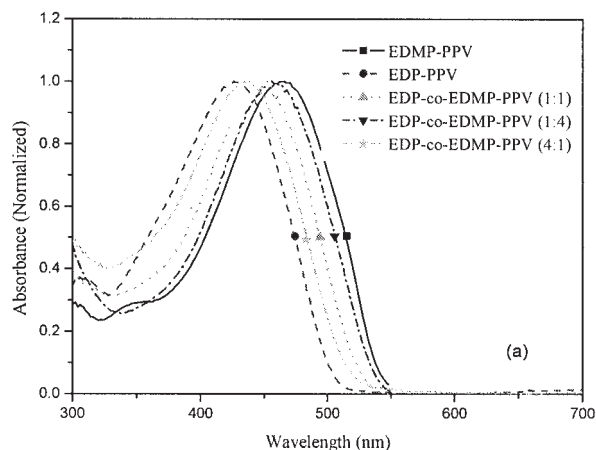


Figure 2 (a) UV-vis absorption and (b) PL spectra of EDP-PPV, EDMP-PPV, and EDP-co-EDMP-PPV (4:1, 1:1, and 1:4) in the solid state.

EDMP-PPV (4:1, 1:1, and 1:4) was observed, and this indicated that efficient energy transfer occurred from a wider band gap of EDP-PPV to a smaller band gap of EDMP-PPV components.

Double LEDs with the configuration of ITO/polymer/Alq₃/Al devices were fabricated to investigate the EL properties of the resulting polymers. Figure 3 shows the EL spectra of ITO/polymer/Alq₃/Al devices; the PLEDs of the novel phenyl-substituted PPV derivatives emitted green to orange light. The EL spectrum peaks of EDP-PPV, EDMP-PPV, and EDP-co-EDMP-PPV (4:1, 1:1, and 1:4) were almost identical to those of the PL spectra, as shown in Figure 2(b). The results indicated that the PL and EL processes experienced the same excited state.

Figure 4 shows I-V and luminance-voltage (L-V) characteristics of the ITO/polymer/Alq₃/Al devices. The current density increased exponentially with the increasing forward bias voltage; this was a typical diode characteristic [Fig. 4(a)]. The current density of EDP-PPV was less than that of EDMP-PPV at the same applied voltage, and this was probably due to the lowest unoccupied molecular orbital (LUMO) of EDP-PPV being higher than that of EDMP-PPV. When the concentration of EDMP-PPV of EDP-co-EDMP-PPV increased, the electron could be transferred to the LUMO of EDP-PPV by way of that of EDMP-PPV, and so the current density in the PLEDs showed a noticeable increase. The turn-on voltages of EDP-PPV, EDMP-PPV, and EDP-co-EDMP-PPV (4:1, 1:1, and 1:4) were approximately 9.5, 6.5, 8.5, 9, and 7.5 V, respectively. The maximum luminance values of EDP-PPV and EDMP-PPV were approximately 320 cd/m² at 25 V and 830 cd/m² at 16.5 V, respectively. In comparison with the two homopolymers, the copolymer EDP-co-EDMP-PPV (1:1) possessed the highest EL performance and exhibited a maximum luminance of 1050 cd/m² at 19.5 V. The maximum luminance of EDP-co-EDMP-PPV (1:1) was about 12 times higher than that

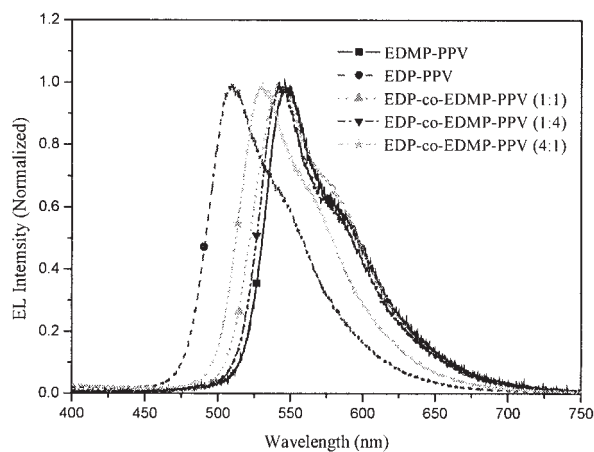


Figure 3 EL spectra of the ITO/polymer/Alq₃/Al devices.

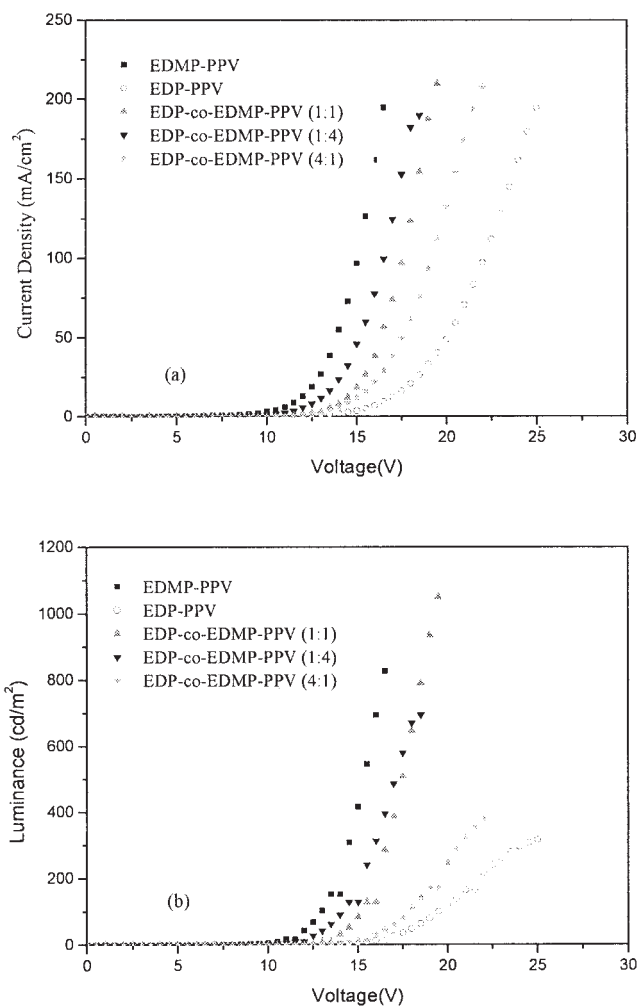


Figure 4 (a) I-V and (b) L-V characteristics of the ITO/polymer/Alq₃/Al devices.

of poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV) devices reported earlier.²¹ On the basis of these results, this copolymer system may be the most promising material of the three polymers for large-area flat-panel displays.

CONCLUSIONS

A series of new phenyl-substituted PPV derivatives, EDP-PPV, EDMP-PPV, and EDP-co-EDMP-PPV (4:1, 1:1, and 1:4), were successfully synthesized according to the Gilch route. The resulting polymers possessed excellent solubility in common organic solvents, good thermal stability, and high molecular weights. Double-layer LEDs with the configuration of ITO/polymer/Alq₃/Al devices were fabricated, and they emitted green to orange light. The turn-on voltages of EDP-PPV, EDMP-PPV, and EDP-co-EDMP-PPV (4:1, 1:1, and 1:4) were approximately 9.5, 6.5, 8.5, 9, and 7.5 V, respectively. EDP-co-EDMP-PPV (1:1) had the highest EL performance and exhibited a maximum lumi-

nance of 1050 cd/m² at 19.5 V. The resulting EL polymers may have potential applications in large-area flat-panel displays.

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. Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Bredas, J. L.; Logdlund, M.; Salaneck, W. R. *Nature* 1999, 397, 121.
3. Cao, Y.; Parker, I. D.; Yu, G.; Zhang, C.; Heeger, A. J. *Nature* 1999, 397, 414.
4. Gustafsson, G.; Cao, Y.; Treacy, G. M.; Klavetter, F.; Colaneri, N.; Heeger, A. J. *Nature* 1992, 357, 477.
5. Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew Chem Int Ed* 1998, 37, 402.
6. Mitschke, M.; Bauerle, P. *J Mater Chem* 2000, 10, 1471.
7. Spreitzer, H.; Becker, H.; Kluge, E.; Kreuder, W.; Schenk, H.; Demandt, R.; Schoo, H. *Adv Mater* 1998, 10, 1340.
8. Janietz, S.; Bradley, D. D. C.; Grell, M.; Inbasekaran, M.; Woo, E. *Appl Phys Lett* 1998, 73, 2453.
9. Chu, H. Y.; Hwang, D.-H.; Do, L.-M.; Chang, J.-H.; Shim, H.-K.; Holmes, A. B.; Zyung, T. *Synth Met* 1999, 101, 216.
10. Hsieh, B. R.; Yu, Y.; Forsythe, E. W.; Schaaf, G. M.; Feld, W. A. *J Am Chem Soc* 1998, 120, 231.
11. Lee, S. H.; Jang, B.-B.; Tsutsui, T. *Chem Lett* 2000, 1184.
12. Peng, Z.; Zhang, J.; Xu, B. *Macromolecules* 1999, 32, 5162.
13. Johansson, D. M.; Srdanov, G.; Yu, G.; Theander, M.; Inganäs, O.; Andersson, M. R. *Macromolecules* 2000, 33, 2525.
14. Johansson, D. M.; Wang, X.-J.; Johansson, T.; Inganäs, O.; Yu, G.; Srdanov, G.; Andersson, M. R. *Macromolecules* 2002, 35, 4997.
15. Becker, H.; Spreitzer, H.; Kreuder, W.; Kluge, E.; Schenk, H.; Parker, I.; Cao, Y. *Adv Mater* 2000, 12, 42.
16. Kim, K.; Hong, Y.-R.; Lee, S.-W.; Jin, J.-I.; Park, Y.; Sohn, B.-H.; Kim, W.-H.; Park, J.-K. *J Mater Chem* 2001, 11, 3023.
17. Stewart, D.; McHattie, G. S.; Imrie, C. *J Mater Chem* 1998, 8, 47.
18. Martin, A. R.; Yang, Y. *Acta Chem Scand* 1993, 47, 221.
19. Gilch, H. G.; Wheelwright, W. L. *J Polym Sci Part A-1: Polym Chem* 1966, 4, 1337.
20. Tokito, S.; Tanaka, H.; Noda, K.; Okada, A.; Taga, Y. *Appl Phys Lett* 1997, 70, 929.
21. Jin, S.-H.; Kang, S.-Y.; Kim, M.-Y.; Chan, Y.-U.; Kim, J. Y.; Lee, K.; Gal, Y.-S. *Macromolecules* 2003, 36, 3841.