

Color-Tunable Electroluminescent Polymers by Substituent on the Poly(*p*-phenylenevinylene) Derivatives for Light-Emitting Diodes

Sung-Ho Jin,* Seung-Yun Kang, and In-Suk Yeom

Department of Chemistry Education, Pusan National University, Pusan 609-735, Korea

Jin Young Kim, Sung Heum Park, and Kwanghee Lee

Department of Physics, Pusan National University, Pusan 609-735, Korea

Yeong-Soon Gal

Polymer Chemistry Lab, Kyungil University, Hayang 712-701, Korea

Hyun-Nam Cho

Korea Institute of Science and Technology, P.O. Box 131, Seoul 130-650 Korea

Received June 4, 2002. Revised Manuscript Received September 25, 2002

Color tunable electroluminescent polymers, poly[2-{4'-[(3'',7''-dimethyloctyl)oxy]phenoxy}-1,4-phenylenevinylene] (*p*-DMOP-PPV), poly[2-{3'-[(3'',7''-dimethyloctyl)oxy]phenoxy}-1,4-phenylenevinylene] (*m*-DMOP-PPV), poly[2-{2'-[(3'',7''-dimethyloctyl)oxy]phenoxy}-1,4-phenylenevinylene] (*o*-DMOP-PPV), and poly[2-{4'-[(3'',7''-dimethyloctyl)oxy]phenoxy}-1,4-phenylenevinylene]-*co*-2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] (*p*-DMOP-PPV-*co*-MEH-PPV) were synthesized by the Gilch polymerization, and their electrooptical properties were characterized. The emission colors can be tuned by moving the bulky substituents from the para to the ortho position in the phenoxy side group along the π -conjugated polymer backbone. External photoluminescent (PL) quantum efficiencies of the present polymers are four or five times larger than that of MEH-PPV. Light-emitting diodes (LED) with the ITO/PEDOT/polymer/Al configuration were fabricated by using those polymers. The turn-on voltage of the *p*-DMOP-PPV-*co*-MEH-PPV (3:7) was found to be 1.8 V and it is lower than those of *o*-, *m*-, and *p*-DMOP-PPV and MEH-PPV. The LED performance of the *p*-DMOP-PPV-*co*-MEH-PPV was found to be improved with various feed ratios of MEH-PPV content as compared with the devices using pure *p*-DMOP-PPV or MEH-PPV. The maximum brightness and luminance efficiency of the present polymers were 7000 cd/m² and 1.0 cd/A at 10 V, respectively.

Introduction

Electroluminescent (EL) is the emission of light from the films of certain materials sandwiched between two electrodes due to the stimulation by an electric current or voltage. Since the first report on EL in poly(*p*-phenylenevinylene, PPV),¹ various types of π -conjugated polymers have been extensively investigated as light-emitting materials,^{2–5} including polyfluorenes,^{6–8} poly-

phenylenes,^{9,10} and polythiophenes.^{11,12} Among them, two classes of polymers, PPV derivatives and poly-(dialkylfluorene) derivatives, have emerged as leading candidate materials for the polymer LEDs.^{13,14} The attractiveness of using those π -conjugated polymers over organic fluorescent dyes for the organic LED is the fact that the more stable and resilient films can be easily processed onto the large area electrode surface by means of spin-coating because of the solubility of the emitting

* To whom correspondence should be addressed. E-mail: shjin@pusan.ac.kr. Fax: +82-51-581-2348.

(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) Choi, S. K.; Gal, Y. S.; Jin, S. H.; Kim, H. K. *Chem. Rev.* **2000**, *100*, 1645.

(3) Gal, Y. S.; Lee, W. C.; Lee, S. S.; Bae, J. S.; Kim, B. S.; Jang, S. H.; Jin, S. H.; Park, J. W. *Korea Polym. J.* **2000**, *8*, 131.

(4) Gal, Y. S.; Lee, W. C.; Kim, S. Y.; Park, J. W.; Jin, S. H.; Koh, K. N.; Kim, S. H. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 3151.

(5) Holdcroft, S. *Adv. Mater.* **2001**, *13*, 1753.

(6) Ohmori, Y.; Uchida, M.; Muro, K.; Yoshino, K. *Jpn. J. Appl. Phys.* **1991**, *30* (12B), L1943.

(7) Pei, Q.; Yang, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7416.

(8) Neher, D. *Macromol. Chem., Rapid Commun.* **2001**, *22*, 1365.

(9) Grem, G.; Leditzky, G.; Ullrich, B.; Leising, G. *Adv. Mater.* **1992**, *4*, 436.

(10) Yang, Y.; Pei, Q.; Heeger, A. J. *J. Appl. Phys.* **1996**, *79* (2), 934.

(11) Ohmori, Y.; Uchida, M.; Muro, K.; Yoshino, K. *Jpn. J. Appl. Phys.* **1991**, *30*, L1938.

(12) Berggren, M.; Inganäs, O.; Gustafsson, G.; Rasmussen, J. R.; Andersson, M. R.; Hjertberg, T.; Wennerström, O. *Nature* **1994**, *372*, 444.

(13) Spreitzer, H.; Becker, H.; Kluge, E.; Kreuder, W.; Schenk, H.; Demandt, R.; Schöo, H. *Adv. Mater.* **1998**, *10*, 1340.

(14) Janietz, S.; Bradley, D. D. C.; Grell, M.; Inbasekaran, M.; Woo, E. *Appl. Phys. Lett.* **1998**, *73*, 2453.

polymers in common organic solvents. The other advantage is the color tunability as obtained by changing the molecular structure of the emitting polymers by introducing the substituents into the polymer backbone.¹⁵ To realize the full color LED device, it is necessary to develop pure red, green, and blue emission colors. There are several points to be considered during the design of emitting polymers for the LED application such as processibility, purity, thermal and oxidative stability, color of emission, luminescence efficiency, and balance of injected charge carriers, and so on. However, the major drawbacks of these polymers are the difficulty of purification, the low external quantum efficiency, and the lack of operation stability during the device operation. To overcome those drawbacks of emitting polymers, the flexible side chains are introduced along the polymer backbone in order to interfere with the interaction between the polymer chains, which results in the formation of amorphous morphology. Through the fine-tuning of their molecular architecture via introduction of the substituents into the polymer backbone¹⁵ or polymerization methods,¹⁶ these emitting polymers have achieved ease of processibility, high purity, and tunability of emission colors. These advanced emitting polymers exhibited high molecular weight, efficiency, brightness, and long-term operation in the polymer-based LEDs. In our previous work, we have synthesized interesting PPV derivatives which showed a high performance for the polymer-based LED,^{17–19} and we also fabricated color-tunable blending systems between emitting polymers and oxadiazole polymer as an electron transport polymer for LEDs.²⁰

In this paper, we report synthesis and characterization of the color-tunable PPV derivatives and their copolymers as obtained by the molecular design for improving the device characteristics. To improve the EL characteristics and control the emission colors, 3,7-dimethyloctyloxy groups were introduced into the ortho-, meta-, and para-positions of the phenyloxy PPV backbone. Those polymers were synthesized by the Gilch polymerization method to get high molecular weight, easy purification, narrow polydispersity, and good thermal stability.

Experimental Section

Synthesis of 2-(4'-Methoxyphenoxy)-1,4-dimethylbenzene (1a). To a 250-mL three-necked flask fitted with reflux condenser, oil bubbler, and magnetic stirrer bar, 4-methoxyphenol (20 g, 0.16 mol) and KOH (6.44 g, 0.115 mol) were added at room temperature while stirring. The mixture was heated to 120 °C and allowed to reflux for 3 h. Subsequently, the mixture was heated to 150 °C with stirring under reduced pressure until the resulting water was removed, and then it was cooled to room temperature. To the above flask 2-bromo-

p-xylene (25.17 g, 0.136 mol), catalytic amounts of Cu, and small amount of 4-methoxyphenol were added. The mixture was stirred at 200 °C for 3 h. After confirming disappearance of the starting material, 4-methoxyphenol, by TLC, the mixture was cooled to room temperature. The reaction mixture was poured into excess water and extracted with ether. The combined organic layers were washed several times further with water, dried over anhydrous MgSO₄, and filtered. The solvent was removed by evaporation under reduced pressure. The product was purified by chromatography on silica gel using hexane as an eluent to give 2-(4-methoxyphenoxy)-1,4-dimethylbenzene (**1a**) (21.4 g, 65%).

¹H NMR (CDCl₃): δ 2.26, 2.27 (s, 6H, 2CH₃ on aromatic ring), 3.81 (s, 3H, OCH₃), 6.65–7.15 (m, 7H, aromatic protons).

C₁₅H₁₆O₂: Calcd. C 78.92, H 7.06; found C 78.80, H 7.12.

2-(3'-Methoxyphenoxy)-1,4-dimethylbenzene (**1b**) and 2-(2'-methoxyphenoxy)-1,4-dimethylbenzene (**1c**) were synthesized in a method similar to that for **1a** and gave 30% and 64% yield, respectively.

Synthesis of 4-(2',5'-Dimethylphenoxy)phenol (2a). In a 500-mL three-necked flask, 2-(4'-methoxyphenoxy)-1,4-dimethylbenzene (**1a**) (20 g, 87.7 mmol) was dissolved in 200 mL of methylene chloride and AlCl₃ (56.11 g, 0.42 mol) was added at 0 °C with stirring. In the flask, methyl sulfide (32.7 g, 0.53 mol) was added slowly and stirred at 0 °C for 2 h. After confirming disappearance of the starting material, 2-(4'-methoxyphenoxy)-1,4-dimethylbenzene (**1a**), by TLC, the mixture was poured slowly into a cold mixture of aqueous NH₄Cl and ice water. Then the reaction mixture was poured into excess water and extracted with ether. The combined organic layers were washed several times further with water, dried over anhydrous MgSO₄, and filtered. The solvent was removed by evaporation under reduced pressure. The product was purified by chromatography on silica gel using hexane/ethyl acetate (10:1) as an eluent to give 4-(2',5'-dimethylphenoxy)phenol (**2a**) (14 g, 97%).

¹H NMR (CDCl₃): δ 2.15, 2.21 (s, 6H, 2CH₃ on aromatic ring), 5.15 (s, 1H, –OH), 6.6–7.20 (m, 7H, aromatic protons).

C₁₄H₁₄O₂: Calcd. C 78.48, H 6.59; found C 78.32, H 6.51.

3-(2',5'-Dimethylphenoxy)phenol (**2b**) and 2-(2',5'-dimethylphenoxy)phenol (**2c**) were prepared by the same procedure as that used for the preparation of **2a** and gave 96% and 97% yield, respectively.

Synthesis of 2-{4'-[(3'',7''-Dimethyloctyl)oxy]phenoxy}-1,4-dimethyl benzene (3a). In a 500-mL three-necked flask, 4-(2',5'-dimethylphenoxy)phenol (**2a**) (14 g, 65 mmol), KOH (4.03 g, 72 mmol), 1-bromo-3,7-dimethyloctane (17.4 g, 78 mmol), and catalytic amounts of KI were dissolved in 150 mL of methanol and heated to reflux for 24 h with magnetic stirring. After confirming disappearance of the starting material, 4-(2',5'-dimethylphenoxy)phenol (**2a**), by TLC, the mixture was cooled to room temperature. The reaction mixture was poured into excess water and extracted with ether. The combined organic layers were washed several times further with water, dried over anhydrous MgSO₄, and filtered. The solvent was removed by evaporation under reduced pressure. The product was purified by chromatography on silica gel using hexane as an eluent and then the crude product was further purified by vacuum distillation to give 2-{4'-[(3'',7''-dimethyloctyl)oxy]phenoxy}-1,4-dimethyl benzene (**3a**) (17 g, 74%).

¹H NMR (CDCl₃): δ 0.82–0.98 (m, 9H, 3CH₃), 1.16–1.36 (m, 6H, (CH₂)₃), 1.46–1.91 (m, 4H, 2CH₂–, 2.25 (s, 6H, 2CH₃ on aromatic ring), 4.02 (t, 2H, OCH₂), 6.60–7.13 (m, 7H, aromatic protons).

C₂₄H₃₄O₂: Calcd. C 81.31, H 9.67; found C 81.07, H 9.52.

The synthesis of 2-{3'-[(3'',7''-dimethyloctyl)oxy]phenoxy}-1,4-dimethyl benzene (**3b**) and 2-{2'-[(3'',7''-dimethyloctyl)oxy]phenoxy}-1,4-dimethyl benzene (**3c**) were prepared as described in synthesis of **3a** and the yields were 77% and 70%, respectively.

Synthesis of 1,4-Bis(bromomethyl)-2-{4'[(3'',7''-dimethyloctyl)oxy]phenoxy}benzene (4a). To a 500-mL three-necked flask, 2-{4'-[(3'',7''-dimethyloctyl)oxy]phenoxy}-1,4-dimethyl benzene (**3a**) (17 g, 48 mmol), N-bromosuccinimide

(15) Robitaille, L.; Leclerc, M.; Callender, C. L. *Macromolecules* **1993**, *5*, 1755.

(16) Gilch, H. G.; Wheelwright, W. L. *J. Polym. Sci., Part A: Polym. Chem.* **1966**, *4*, 1337.

(17) Lee, J. H.; Yu, H. S.; Kim, W.; Gal, Y. S.; Park, J. H.; Jin, S. H. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4185.

(18) Jin, S. H.; Jung, J. E.; Park, D. K.; Jeon, B. C.; Kwon, S. K.; Kim, Y. H.; Moon, D. K.; Kim, S. H.; Gal, Y. S. *Eur. Polym. J.* **2001**, *37*, 921.

(19) Jin, S. H.; Jang, M. S.; Suh, H. S.; Cho, H. N.; Lee, J. H.; Gal, Y. S. *Chem. Mater.* **2002**, *14*, 643.

(20) Jin, S. H.; Kim, W. H.; Song, I. S.; Kwon, S. K.; Lee, K. S.; Han, E. M. *Thin Solid Films* **2000**, *363* (12), 255.

(NBS) (18.8, 105 mmol), catalytic amounts of benzoyl peroxide, and 200 mL of CCl_4 were added. The mixture was refluxed and stirred until the appearance of white solid on top of the solution. After confirming disappearance of the starting material, 2-{4'-[(3'',7''-dimethyloctyl)oxy]phenoxy}-1,4-dimethylbenzene (**3a**), by TLC, the mixture was cooled to room temperature. The succinimide was filtered off, and the mother liquor was poured into excess water and extracted with chloroform. The combined organic layers were washed several times further with water, dried over anhydrous MgSO_4 , and filtered. The solvent was removed by evaporation under reduced pressure. The product was purified by chromatography on silica gel using hexane as an eluent to give 6 g (25%) of 1,4-bis(bromomethyl)-2-{4'[(3'',7''-dimethyloctyl)oxy]phenoxy}benzene (**4a**).

^1H NMR (CDCl_3): δ 0.85–0.97 (m, 9H, 3 CH_3), 1.17–1.34 (m, 6H, (CH_2)₃), 1.42–1.92 (m, 4H, 2CH, $-\text{CH}_2-$), 3.99 (t, 2H, OCH_2), 4.33, 4.61 (s, 4H, 2- CH_2Br), 6.72–7.39 (m, 7H, aromatic protons). ^{13}C NMR (CDCl_3 , δ ppm): 19.7, 22.6, 24.7, 27.8, 28.0, 29.9, 32.6, 36.3, 37.3, 39.2, 66.8, 115.7, 117.1, 121.0, 123.2, 127.9, 131.5, 139.9, 149.3, 155.9, 156.7.

$\text{C}_{24}\text{H}_{32}\text{O}_2\text{Br}_2$: Calcd. C 56.2; H 6.30; found: C 56.44; H 6.342.

The other monomers, 1,4-bis(bromomethyl)-2-{3'-[(3'',7''-dimethyloctyl)oxy]phenoxy}benzene (**4b**) and 1,4-bis(bromomethyl)-2-{2'-[(3'',7''-dimethyloctyl)oxy]phenoxy}benzene (**4c**), were synthesized in a method similar to that for **4a** and gave 26% and 20% yield, respectively.

Synthesis of Poly[2-{4'-[(3'',7''-dimethyloctyl)oxy]phenoxy}-1,4-phenylenevinylene] (p-DMOP-PPV). To a 100-mL Schlenk flask dried with stream of hot air and flushed with N_2 , monomer (**4a**) (0.2 g, 0.39 mmol) was added and then it was dried and flushed with N_2 again, and dissolved in 30 mL of dry THF. The solution was cooled in an ice bath under N_2 atmosphere. A solution of potassium *tert*-butoxide in THF (2.34 mL, 1.0 M) was then added at a rate of 4.68 mL/hr via syringe pump. After complete addition of the base, the reaction mixture was stirred at room temperature for 3 h. Some of 4-(*tert*-butyl)benzyl bromide was added to the reaction mixture and further stirred for 1 h. The color of the reaction mixture changed from colorless to greenish, then to yellow/orange, and also the viscosity was increased. The reaction mixture was poured into 300 mL of methanol to precipitate the polymer. The collected polymer was further purified by Soxhlet extraction with methanol to remove the low molecular weight oligomer and inorganic impurities. The resulting polymer was redissolved in chloroform. The solvent moieties were evaporated with a rotary evaporator and again reprecipitated into 300 mL of methanol. The precipitated polymer was collected by suction filtration and dried in a vacuum oven to yield of polymer (**5a**) (0.081 g, 60%).

^1H NMR (CDCl_3): δ 0.87–0.94 (m, 9H, 3 CH_3), 1.17–1.33 (m, 6H, (CH_2)₃), 1.57 (br, 4H, 2CH, $-\text{CH}_2-$), 3.97 (br, 2H, $-\text{OCH}_2$), 6.81–7.57 (br, 9H, aromatic protons and vinylic protons).

$(\text{C}_{24}\text{H}_{30}\text{O})_n$: Calcd. C 82.24, H 8.63; found C 80.80, H 7.12.

The poly[2-{3'-[(3'',7''-dimethyloctyl)oxy]phenoxy}-1,4-phenylenevinylene] (*m*-DMOP-PPV) (**4b**), poly[2-{2'-[(3'',7''-dimethyloctyl)oxy]phenoxy}-1,4-phenylenevinylene], (*o*-DMOP-PPV) (**4c**), and *p*-DMOP-PPV-*co*-MEH-PPV with various feed ratio of 1,4-bis(chloromethyl)-2-[(2'-ethylhexyl)oxy]-5-methoxybenzene²¹ were synthesized and purified in a similar method for *p*-DMOP-PPV.

Characterization. ^1H - and ^{13}C -NMR spectra were recorded on a Bruker AM-300 spectrometer. FT-IR spectra of the polymers were obtained with a Bomem Michelson series FT-IR spectrometer. UV-visible absorption spectra were obtained using a Shimadzu UV-3100 spectrometer. Thermal analysis (TGA) was performed under nitrogen atmosphere at a heating rate of 10 $^\circ\text{C}/\text{min}$ with a DuPont 9900 thermogravimetric analyzer. The molecular weight and polydispersity of the polymer in THF solution were determined by gel permeation chromatography (GPC) analysis relative to polystyrene stan-

dards. Electrochemical measurements of the present polymers were performed using cyclic voltammetry (CV) at room temperature in a three-electrodes cell with Pt as the counter electrode and Ag/AgCl reference electrode with 0.1 M tetraethylammonium tetra fluoroborate in acetonitrile as the electrolyte. Emission spectra were made with dilute solution ($\sim 10^{-6}$ M) on a Perkin-Elmer LS-50 fluorometer utilizing a lock-in amplifier system with a chopping frequency of 150 Hz.

For the absorption and PL spectra of the thin films, each material was dissolved in chlorobenzene (CB) with a concentration of 0.5 wt %, and spin-coated on a pre-cleaned fused silica with a thickness around 80 nm. Absorption spectra of the thin films were recorded by a Varian 5E UV-Vis-NIR spectrophotometer. Solid-state emission measurements were performed on the films, which were mounted to fused silica substrates with an angle of 45 $^\circ$ to the excitation beam direction. Those three DMOP-PPV derivatives and the *p*-DMOP-PPV-*co*-MEH-PPV copolymers films were excited at 450 nm, whereas the excitation wavelength of the pure MEH-PPV film was set to 480 nm using a xenon lamp combined with a monochromator. An Oriel InstaSpec IV CCD detection system in combination with a typical integrating sphere method²² was used for the PL and EL spectra measurements together with the external PL quantum efficiencies.

The typical device configuration is an ITO/PEDOT/polymer/Al device. For the preparation of polymer LEDs, the glass substrates electrode coated with indium tin oxide (ITO) was thoroughly cleaned by successive washes with acetone, isopropyl alcohol, and ethyl alcohol in an ultrasonic bath, dried with nitrogen gas, and heated for drying. To build up the buffer layer, the PEDOT:PSS layer was deposited onto the ITO-coated substrate. The polymer film was prepared by the spin-coating of the polymer solution containing 1.0–0.5 wt % in chlorobenzene. The respective layer thickness was defined by using an appropriate spinning speed and concentration of the polymer solution. Uniform and pinhole-free films with a thickness range from 80 to 120 nm were easily obtained from the resulting polymer solution. The aluminum electrode (about 100 nm) was deposited by vacuum evaporation at a pressure less than 10^{-6} Torr, yielding active areas of 4 mm². Current density–voltage (*J*–*V*) and luminance–voltage (*L*–*V*) characteristics of all the devices were measured using a Keithley 236 source measure unit equipped with a calibrated photomultiplier tube. All the processes and measurements were carried out in air at room temperature.

Results and Discussion

Scheme 1 outlines the synthesis of the monomers and the corresponding polymers. Monomers (**4a–4c**) containing 3,7-dimethyloctyloxy substituents linked with the ortho-, meta-, and para-positions of 2-phenoxy-1,4-bis(bromomethyl)benzene were synthesized by 5 steps according to Scheme 1. The methoxyphenoxy group was introduced into the 1,4-dimethylbenzene skeleton by means of an Ullmann-type coupling reaction in copper catalyst.²³ The yield of Ullmann-type coupling reaction between 3-methoxyphenol and 2-bromo-*p*-xylene was relatively low, which was due to the immiscibility of potassium salt of 3-methoxyphenol and 2-bromo-*p*-xylene. Demethylation of **1a–1c** was performed in the presence of methyl sulfide and aluminum chloride²⁴ to give 4-(2',5'-dimethyl phenoxy)phenol in almost quantitative yields. To improve the processibility and color tuning of the present polymers, the bulky alkoxy side chain, 3,7-dimethyloctyloxy group, is introduced at the

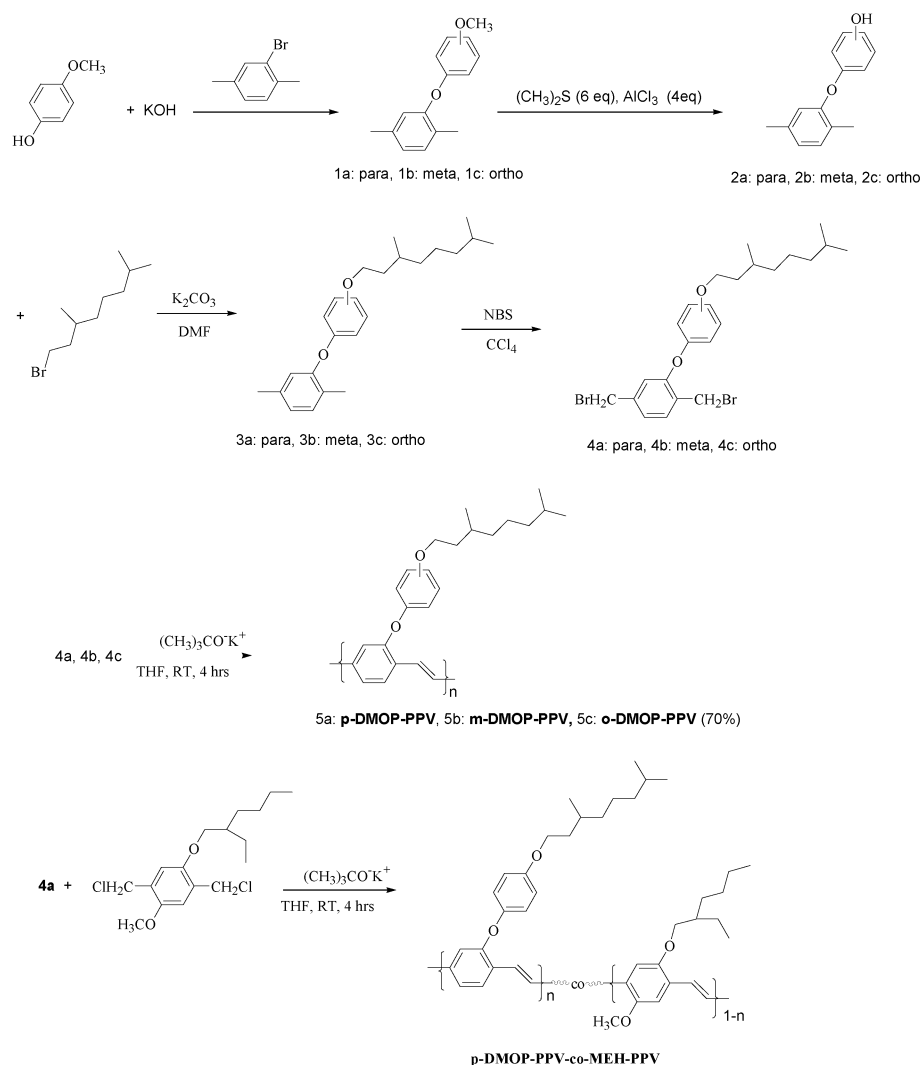
(22) John, C.; Mello, C.; Winmann, F.; Friend, R. H. *Adv. Mater.* **1997**, 9 (3), 230.

(23) Lindley, J. *Tetrahedron* **1984**, 40, 1433.

(24) Node, M.; Nishide, K.; Sai, M.; Ichikawa, K.; Fuji, K.; Fujita, E. *Chem. Lett.* **1979**, 97.

(21) Wudl, F.; Srdanov, G. U.S. Patent 5189136, 1993.

Scheme 1. Synthetic Scheme of Monomers and Polymers



ortho-, meta-, and para-positions of the phenoxy side group by the Williamson ether synthesis method. The newly designed monomers were obtained via bromination of compound **3** in the presence of AIBN and easily purified by column chromatography using hexane as an eluent. The structure and purity of the intermediates and monomers were proven by ^1H - and ^{13}C NMR spectroscopies and elemental analyses. The polymerization of bis(bromomethyl)benzene derivatives was performed with a large excess of potassium *tert*-butoxide in cooled dry THF under nitrogen atmosphere. The addition rate of excess base is very important to control the molecular weight of the present polymers. During the polymerization, the viscosity of the reaction mixture was increased with the homogeneous solution without any precipitation showing a fluorescent light. Most PPV derivatives with phenyl substituent are limited in their application, because of their poor solubility and gelation during the polymerization. Recently, many research groups developed the soluble phenyl PPV derivatives by introducing the alkyl substituents into the phenyl ring.^{12,25} Our present synthetic strategy of the monomers is the introduction of a 3,7-dimethyloctyloxy group

into the different position of the phenoxy side ring. The resulting polymers are expected to have the increased processibility for the device fabrication and tuning of the emission colors by steric hindrance between the 3,7-dimethyloctyloxyphenoxy substituents and vinylic protons along the π -conjugated polymer backbone. As shifting the substituents from the para- to the ortho-position in the phenoxy side ring along the π -conjugated polymer backbone, the effective conjugation length is more shortened than that of meta or para position. To increase the molecular weight and improve the device performance, a copolymerization was carried out with various initial monomer concentrations of 1,4-bis(chloromethyl)-2-[(2'-ethylhexyloxy)-5-methoxybenzene] according to the similar method of homopolymerization. The resulting copolymers, *p*-DMOP-PPV-*co*-MEH-PPV with various monomer feed ratios, showed higher molecular weight and good solubility behavior in common organic solvents than those of *o*-, *m*-, and *p*-DMOP-PPV. Table 1 summarizes the polymerization results and molecular weights of the homopolymers and copolymers. The average molecular weights (*M_w*) and polydispersity values of the present polymers were in the range of $11.5\text{--}72.9 \times 10^4$ and 2.24–4.28, respectively. *p*-DMOP-PPV-*co*-MEH-PPV showed higher molecular weight

(25) Johansson, D. M.; Srdanov, G.; Yu, G.; Theander, M.; Inganäs, O.; Andersson, M. R. *Macromolecules* **2000**, *33*, 2525.

Table 1. Polymerization Yield, Weight Average Molecular Weight (M_w), and Polydispersity

polymer	yield (%)	$M_w \times 10^{-4,a}$	M_w/M_n^a
<i>o</i> -DMOP-PPV	70	24.2	2.81
<i>m</i> -DMOP-PPV	74	25.3	2.93
<i>p</i> -DMOP-PPV	65	11.5	2.46
<i>p</i> -DMOP-PPV- <i>co</i> -MEH-PPV (7:3) ^b	71	72.9	4.28
<i>p</i> -DMOP-PPV- <i>co</i> -MEH-PPV (5:5) ^b	66	26.1	3.65
<i>p</i> -DMOP-PPV- <i>co</i> -MEH-PPV (3:7) ^b	70	30.6	2.24

^a M_w and PDI of the polymers were determined by GPC using polystyrene standards. ^b Initial monomer feed ratios.

when compared to that of *o*-, *m*-, and *p*-DMOP-PPV, which was attributed to the higher solubility behavior during the polymerization reaction in common organic solvents than those of *o*-, *m*-, and *p*-DMOP-PPV. The structure and thermal stability of the polymers were identified by ¹H NMR, UV-visible spectroscopy, and TGA thermogram, respectively. Bromobenzyl proton peaks of the monomers showed two peaks at 4.33 and 4.61 ppm, which were attributed to the asymmetric molecular structure by the introduction of one substituent, 3,7-dimethyloctyloxyphenoxy side group, into the 1,4-bis(bromomethyl)benzene unit. The benzylic proton peaks at 4.33 and 4.61 ppm disappeared during the polymerization and the new vinylic proton peaks were observed in 6.8–7.2 ppm together with the phenyl proton peaks. All other peaks showed good correspondence with the resulting polymers. The TGA thermograms of the present polymers revealed a high thermal stability up to 400 °C. The durability of the LEDs is closely related to the thermal stability of the emitting materials.²⁶ The high thermal stability of the present polymers prevents morphological change of the emitting layer caused by Joule heat due to the applied electric fields of LED.

Figure 1 shows optical absorption spectra of the homopolymers (Figure 1a) and copolymers (Figure 1b) in solid state. Homopolymers with the ortho-, meta-, and para- positions of the 3,7-dimethyloctyloxy substituent in the phenoxy side group show almost the same absorption maxima at about 451, 455, and 464 nm. However, the band gap of the *o*-, *m*-, and *p*-DMOP-PPV, taken from the absorption edge spectrum, exhibited quite a different range of 2.41, 2.37, and 2.31 eV, respectively. As the 3,7-dimethyloctyloxy group is linked from the para to the ortho position of the phenoxy side group, the effective conjugation length is more shortened by steric hindrance between the 3,7-dimethyloctyloxyphenoxy side group and vinylic protons, because of the distortion in the coplanarity of the polymer backbones. The maximum absorption spectra of the copolymers are more red-shifted than those of *o*-, *m*- and *p*-DMOP-PPV.

Figure 2 shows the emission spectra of the present polymers and the MEH-PPV thin films under excitation at the absorption maximum wavelength of each polymer. The emission peaks of the *o*-, *m*-, and *p*-DMOP-PPV (Figure 2a) are broader, and the peaks were observed at 549, 560, and 585 nm with vibronic peaks at about 518, 530, and 539 nm and one shoulder at longer than 580 nm in *o*-DMOP-PPV. As the MEH-PPV content increases, the emission peaks of the copolymers (Figure 2b) are red-shifted from 549 to 600 nm. Such a

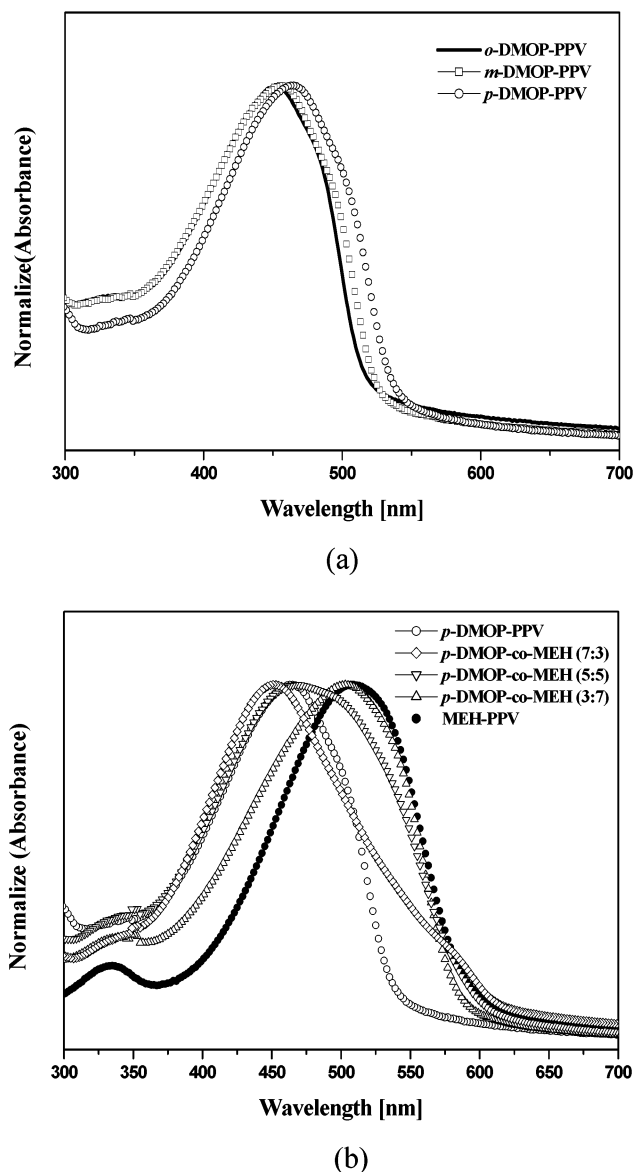


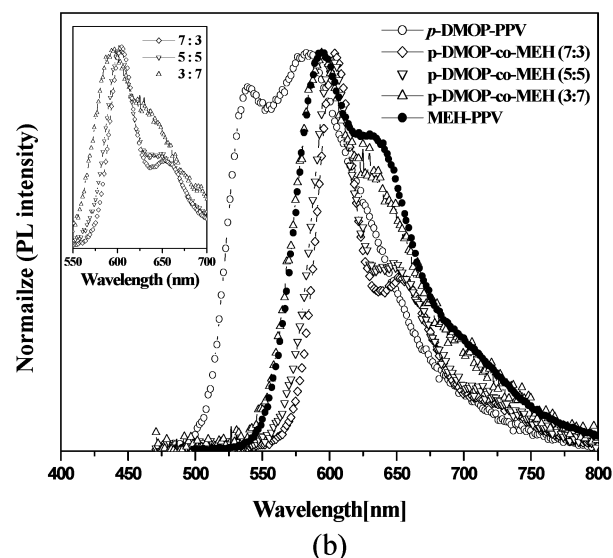
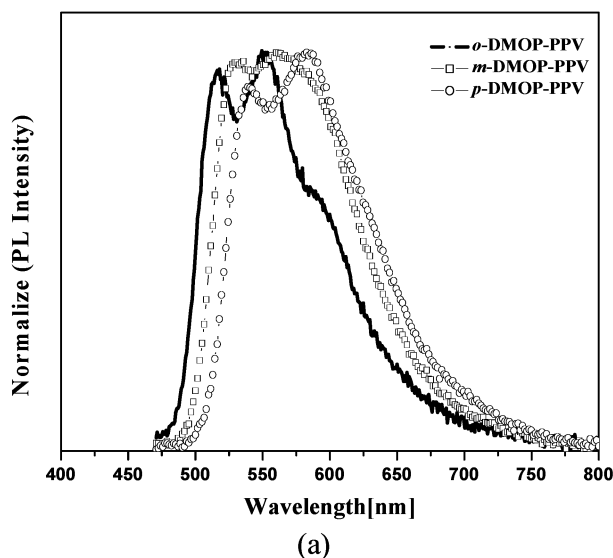
Figure 1. UV-visible absorption spectra of the homopolymers (a) and *p*-DMOP-PPV, copolymers, and MEH-PPV (b).

red shift for the copolymer system could be attributed to an intramolecular energy transfer from the high band gap of *p*-DMOP-PPV segment to the low band gap of MEH-PPV segment of the copolymers. The inset of Figure 2b shows that the PL maximum peak of copolymers is almost the same at about 596 nm. However, the maximum peaks of the copolymers are more red-shifted by about 10 nm than that of MEH-PPV in the solid state. This is originated from the increase of the electron density along the π -conjugated polymer backbone by incorporation of the MEH-PPV segment and extension of the effective conjugation length in copolymers. The external PL quantum efficiencies of the *o*-, *m*-, *p*-DMOP-PPV, *p*-DMOP-PPV-*co*-MEH-PPV (7:3), and MEH-PPV for comparison in solid state were measured by using an integrating sphere method. According to the external PL quantum efficiency measurements,²² a value of $10 \pm 2\%$ was obtained for the MEH-PPV. However, the values of *o*-, *m*-, *p*-DMOP-PPV and *p*-DMOP-PPV-*co*-MEH-PPV (7:3) were determined to be as high as $43 \pm 1\%$, $54 \pm 1\%$, $40 \pm 2\%$, and $23 \pm 2\%$, respectively. The

(26) Tokito, S.; Tanaka, H.; Noda, K.; Okada, A.; Taga, Y. *Appl. Phys. Lett.* **1997**, *70*, 1929.

Table 2. Absorption, PL, EL Maxima, and Eg, Ip, and Ea Parameters, and External PL Quantum Efficiency of the Polymers

polymer	<i>o</i> -DMOP-PPV	<i>m</i> -DMOP-PPV	<i>p</i> -DMOP-PPV	<i>p</i> -DMOP-PPV- <i>co</i> -MEH-PPV		
				(7:3)	(5:5)	(3:7)
Abs (nm)	451	455	464	451	467	503
PL (nm)	549	560	585	596	598	593
	(518) ^a	(531) ^a	(543) ^a	(622) ^a	(627) ^a	(623) ^a
EL (nm)	538	553	582	605	600	589
Eg (eV) ^b	2.41	2.37	2.31	2.03	2.09	2.13
Ip (eV) ^c	5.41	5.43	5.42	5.44	-	-
Ea (eV) ^d	3.00	3.06	3.11	3.41	-	-
QE (%) ^e	43 ± 1	54 ± 1	40 ± 2	23 ± 1	-	-

^a Shoulder. ^b Determined from edge of the absorption spectra. ^c Determined from onset of the oxidation curve of the cyclic voltamogram.^d Calculated from subtraction of the band gap from the Ip. ^e Calculated from integrating sphere method.**Figure 2.** Photoluminescent spectra of the homopolymers (a) and *p*-DMOP-PPV, copolymers, and MEH-PPV (b). Inset: PL spectra of the copolymers.

values of the *o*-, *m*-, *p*-DMOP-PPV are almost four or five times larger than that of MEH-PPV. The larger external PL quantum efficiencies of the resulting polymers than that of MEH-PPV arise from the fact that the bulky 3,7-dimethyloctyloxyphenoxy side group in the π -conjugated polymer backbone distorts the coplanarity and inhibits the intermolecular interaction between the polymer backbones.

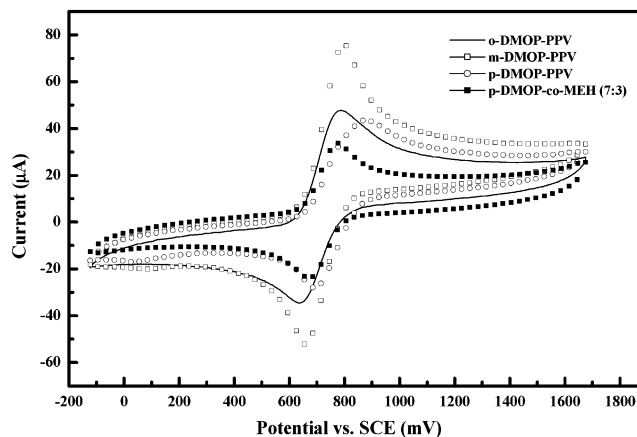
**Figure 3.** Cyclic voltammograms of the polymer on ITO glass (as measured in acetonitrile solution of (*n*-Bu)₄NPF₆ (0.1 M) at 40 mV/s, and referenced with Ag/AgCl).

Figure 3 shows the cyclic voltammograms of the *o*-, *m*-, *p*-DMOP-PPV and *p*-DMOP-PPV-*co*-MEH-PPV (7:3). The polymers exhibit a reversible doping/dedoping process. The oxidation potential of the polymers exhibits slightly different results in each position of the 3,7-dimethyloctyloxy substituent in the phenoxy side groups. The onset potentials of the oxidation in *o*-, *m*-, *p*-DMOP-PPV and *p*-DMOP-PPV-*co*-MEH-PPV (7:3) were located at 0.605, 0.625, 0.616, and 0.635 V, respectively. Cyclic voltammograms reveal that the oxidation potential peaks are slightly changed from *o*-DMOP-PPV to *p*-DMOP-PPV-*co*-MEH-PPV (7:3). Regarding the energy level of the ferrocene/ferrocenium (4.8 eV), the ionization potential (*I*_p) of the resulting polymers was 5.41, 5.43, 5.42, and 5.44 eV, respectively. The electron affinity (*E*_a) levels are obtained from the values of the band gap and *I*_p energy level. The electrooptical characteristics of the present polymers are summarized in Table 2. The barrier heights of the present polymers were found to be 1.30–0.96 eV at the interface of Al (4.3 eV)/Ea state for electron injection. The *p*-DMOP-PPV-*co*-MEH-PPV (7:3) is relatively easier in the injection of the electron from the Al electrode than *o*-, *m*-, *p*-DMOP-PPV. The work function and the surface condition of the ITO have a crucial effect on the device performance.²⁷ To improve the device performances such as low turn-on voltage, high luminescent efficiency, and removing the electrical shorts between ITO and the luminescent polymer layer, the PEDOT:PSS buffer layer was coated onto the ITO-coated glass substrate as a hole injection and transport

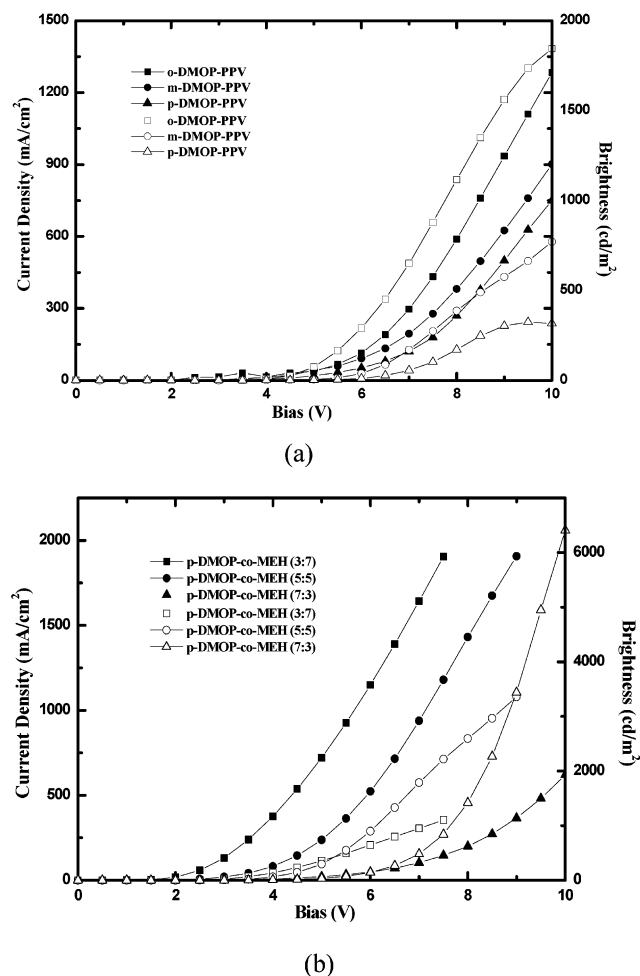


Figure 4. Voltage–current density (V–J) (closed) and voltage–luminescence (V–L) (open) characteristics of the ITO/PEDOT:PSS/homopolymers (a) and copolymers (b)/Al devices.

layer. The luminescent polymer layer was consecutively spun on top of the PEDOT:PSS layer. After all solvent had been removed by heating at 100 °C under vacuum for 1 h, an Al electrode was deposited by evaporation at a pressure of 10^{-6} Torr.

Figure 4 shows the current density–voltage–luminescence (J–V–L) characteristics of the ITO/PEDOT:PSS/homopolymer (Figure 4a) or copolymer (Figure 4b) /Al devices. The turn-on voltage for the light emission varies from approximately 1.8 V for *p*-DMOP-PPV-*co*-MEH-PPV (3:7) to 4.5 V for the homopolymers. The current densities of the present polymers increase exponentially with increasing the forward bias voltage. The brightness of *o*-, *m*-, and *p*-DMOP-PPV reaches about 1845, 770, and 316 cd/m² at 10 V, respectively. Because the poor solubility of *m*- and *p*-DMOP-PPV compared to *o*-DMOP-PPV, the brightness decrease from *o*-DMOP-PPV to *p*-DMOP-PPV. However, the brightness of *p*-DMOP-PPV-*co*-MEH-PPV (7:3) is 7000 cd/m² at 10 V, which is much higher than those of *o*-, *m*-, and *p*-DMOP-PPV. The highest brightness of the *p*-DMOP-PPV-*co*-MEH-PPV (7:3) is attributed to the lower band offset between the E_a energy level and the Al electrode than those of homopolymers, resulting in an easy injection for the electron.

Figure 5 shows the EL spectra of the ITO/PEDOT:PSS/polymer/Al device. The EL spectra were essentially

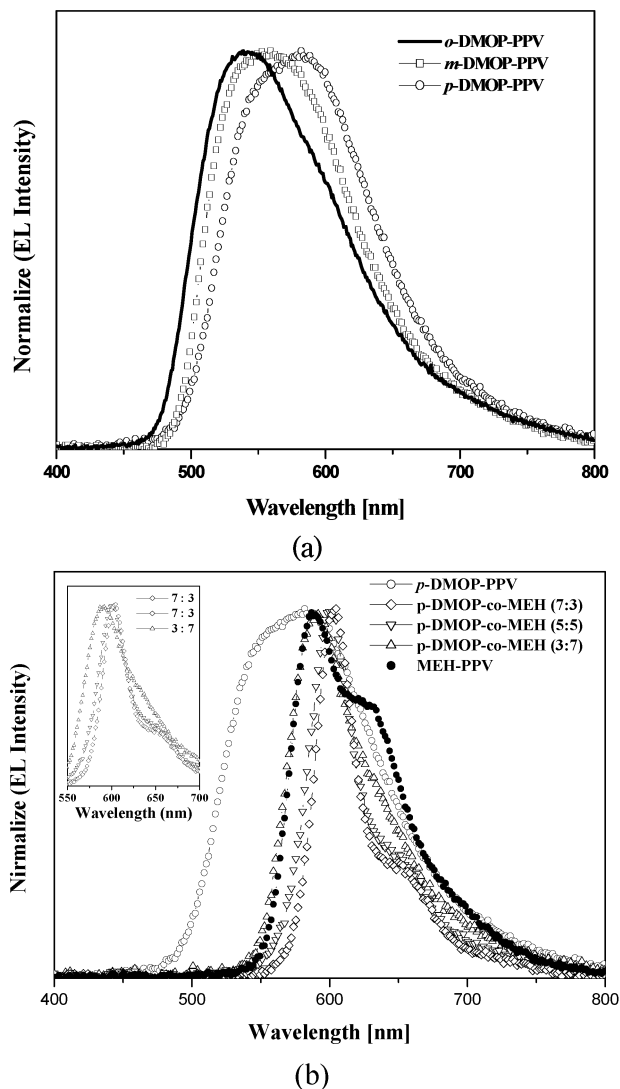


Figure 5. Electroluminescent spectra of the ITO/PEDOT:PSS/homopolymers (a) and *p*-DMOP-PPV, copolymers and MEH-PPV (b)/Al devices. Inset: EL spectra of the copolymers.

identical to the PL spectra of the resulting polymers. This result indicates that the EL of the device occurs at the same emission center with the PL in the luminescent polymer layer. The EL spectra are also red-shifted upon going from *o*-DMOP-PPV to *p*-DMOP-PPV-*co*-MEH-PPV similar to the PL and the absorption spectra. The sharper emission colors are an important parameter for realizing full color displays. In comparison to MEH-PPV, the copolymer, *p*-DMOP-PPV-*co*-MEH-PPV (Figure 5b) shows narrow emission peaks with a full width at half-maximum (fwhm) approaching 40 nm. This phenomenon is in good agreement with the explanation of higher external PL quantum efficiency as described earlier. Because of inhibition of the intermolecular interaction by the 3,7-dimethyloctyloxyphenoxy groups in solid state, the emission spectrum of the *p*-DMOP-PPV-*co*-MEH-PPV is much narrower than that of MEH-PPV.

Controlling the position of the bulky substituents in the polymer backbone by molecular architecture, therefore, the corresponding EL spectra clearly demonstrate a tunability of the emission colors in these electroluminescent polymer systems.

Conclusions

We have synthesized the novel series of color-tunable PPV-based electroluminescent polymers, which give green to orange-red emission by controlling the substituent position in the emitting polymer backbone. The resulting electroluminescent polymers were completely soluble in common organic solvents with high molecular weights and good thermal stability without decomposition up to 400 °C, which might be promising as materials for longer device operation. The external PL quantum efficiencies of the *o*-, *m*-, and *p*-DMOP-PPV are four or five times larger than that of MEH-PPV. The fluorescent emission spectra of the *p*-DMOP-PPV-*co*-

MEH-PPV exhibit a sharp peak at about 600 nm with 40 nm of fwhm in solid state. The copolymers show higher device performance as compared to the homopolymers and MEH-PPV. The EL devices of an ITO/PEDOT:PSS/polymer/Al configuration exhibit a turn-on voltage of 1.8–4.5 V and maximum emission brightness up to 7000 cd/m² with 1.0 cd/A at 10 V.

Acknowledgment. This work was supported by the Korea Research Foundation Grant (KRF-2001-042-D00039).

CM020610T