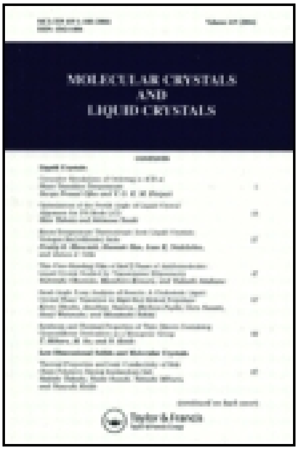

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Synthesis and Characterization of Conjugated Copolymers, and Their Color Tuning with Molecular Microstructure

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Synthesis and Characterization of Conjugated Copolymers, and Their Color Tuning with Molecular Microstructure

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Poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene vinylene-co-1,4-phenylene vinylene) (MEH-R) and poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene vinylene-alt-1,4-phenylene vinylene) (MEH-A50) containing phenylene vinylene (PV) unit and alkoxyphenylene vinylene (MEHPV) unit in the main chain were synthesized by the dehydrohalogenation and Honer-Emmons reaction using potassium t-butoxide, respectively. Single layer polymer light-emitting diodes (PLEDs) were fabricated with synthesized conjugated copolymers as emitting layers, and their emission properties were compared with PPV and MEH-PPV homopolymers. UV-Visible absorption and EL spectra of MEH-Rs were blue-shifted as increasing the amount of PV unit in the main chain. Color coordinates of single layer PLEDs made with the conjugated copolymers were compared with those of standard red, green, blue, and white established by NTSC. Color coordinates of single layer PLEDs made with MEH-Rs and MEH-A50 were shifted from red (MEH-PPV) to green region (PPV) as increasing PV unit in the main chain.

Keywords: alkoxyphenylene vinylene; color coordinates; phenylene vinylene; polymer light emitting diode (PLED)

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INTRODUCTION

Since the first report on the polymer light emitting diodes (PLED) using poly(*p*-phenylene vinylene) (PPV) by Cambridge group, numbers of different polymers have been synthesized for use as emitting materials [1–3]. The microstructure of conjugated polymers has been recognized as an important factor affecting on color, quantum efficiency, and luminance/voltage profile of PLEDs. It has been known that the PPV derivative, poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene vinylene) (MEH-PPV), has good solubility in common organic solvents and enhances the film forming properties over the parent PPV due to the introduction of alkoxy groups.

Shim *et al*. reported the synthesis of silyl-substituted PPV derivatives, poly(2-dimethyloctylsilyl-1,4-phenylene) (DMOS-PPV) and copolymers which have repeating units of DMSO-PPV and MEH-PPV, and examined the light-emitting properties of these polymers [4]. Kaeriyama *et al*. synthesized copolymers of diheptylbenzene-1,4-bis (trimethyleneborate)/1,4-dibromonaphthalene and diheptylbenzene-1,4-bis(trimethyleneborate)/1,5-dibromonaphthalene,respectively,and showed the difference of electric-optical properties according to their microstructure [5].

In this work, we synthesized random copolymers with different ratio of PPV and MEH-PPV units in the main chain, poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene vinylene-co-1,4-phenylene vinylene) (MEH-R) and alternating copolymer, poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene vinylene-*alt*-1,4-phenylene vinylene) (MEH-A50) by α-elimination and Honer-Emmons reaction, respectively. Electro optical properties of these polymers as emitting materials were examined from the viewpoint of copolymer structures.

EXPERIMENTAL

Synthesis of Monomers

1,4-Bis(chloromethyl)-2-Methoxy-5-(2-ethylhexyloxy)Benzene (MEHB)

MEHB was synthesized through two step reactions [6]. 4-Methoxy phenol was reacted with 2-ethylhexylbromide in the presence of potassium hydroxide to give 1-methoxy-4-(2-ethylhexyl)benzene. 1-Methoxy-4-(2-ethylhexyl)benzene was refluxed with formaline and hydrochloric acid in dioxane solvent to give MEHB as a white powder in 54% yield. ^{1}H-NMR ($CDCl_3$), δ: 6.80 (s, 2H, Ar), 4.51 (s, 4H, $-CH_2Cl$), 3.84 (t, 5H, $-OCH_3/-OCH_2-$), 0.86 $\sim$ 1.76 (m, 15H, $-C_7H_{15}$). FT-IR (KBr), cm^{-1}:

3020 (Ar CH), 2918 (aliphatic CH), 1440 ($-CH_2Cl$), 1223 (Ar–O–C), 701 (C–Cl).

2-Methoxy-5-(2-ethylhexyloxy)-1,4-bis(diethoxyphosphinylmethyl) Benzene (MPHBZ)

The synthesized MEHB (4.8 g, 0.014 mol) was reacted with triethylphosphite (30 g, 0.18 mol) at 120°C for 12 hr. The unreacted triethylphosphite was removed under reduced pressure. The liquid phase of MPHBZ was obtained in 90% yield. ^{1}H-NMR ($CDCl_3$), δ: 6.90, 6.93 (d, 2H, Ar H), 4.03 (m, 8H, $-CH_2O-P$), 3.81 (q, 2H, $Ar-OCH_2-$), 3.40 (s, 3H, $Ar-OCH_3$), 3.24 (q, 4H, $Ar-CH_2-P$), 0.91 ~ 1.48 (m, 29H, $-CH_2-$; $CH-$; $-CH_3$), IR (KBr), cm^{-1}: 3022 (Ar CH), 2960 (aliphatic CH), 1510 (Ar C=C), 1252 (P=O).

Synthesis of Conjugated Polymers

Poly(p-phenylene vinylene) (PPV)

The procedures used for the preparation of PPV were the same as reported [7].

Poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene vinylene) (MEH-PPV)

MEH-PPV was synthesized according to the previously reported method [8]. To a solution of MEHB (2 g, 0.006 mol) in anhydrous tetrahydrofurane (THF) (40 ml) was added dropwise a solution of potassium *tert*-butoxide (^{t}BuOK) (1.77 g of 95% purity, 0.015 mol) in THF (30 ml) at room temperature under nitrogen atmosphere. After the addition of ^{t}BuOK, the solution was stirred for 6 hr. The resulting mixture was poured into methanol, and the precipitate was washed with water. After filtration and vacuum drying, the MEH-PPV was obtained in 65% yield. FT-IR (film), cm^{-1}: 3057 (Ar CH), 2956 (aliphatic CH), 1593, 1510 (Ar C=C), 1204 (Ar–O–C), 968 (trans vinylene).

Poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene vinylene-*co*-1,4-phenylene vinylene) (MEH-R); MEH-R80, MEH-R60, and MEH-R30 (MEH-Rs) were obtained by the dehydrohalogenation of MEHB and α,α'-dichloro-*p*-xylene (DCX) in anhydrous THF using ^{t}BuOK with different ratio of comonomers, i.e., MEHB/DCX = 75/25, 50/50, 25/75, respectively.

Poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene vinylene-alt-1,4-phenylene vinylene) (MEH-A50)

MEH-A50 was synthesized by Honer-Emmons reaction of MPHBZ (2.4 g, 0.0044 mol) and terephthalaldehyde (TA) (0.59 g, 0.0044 mol)

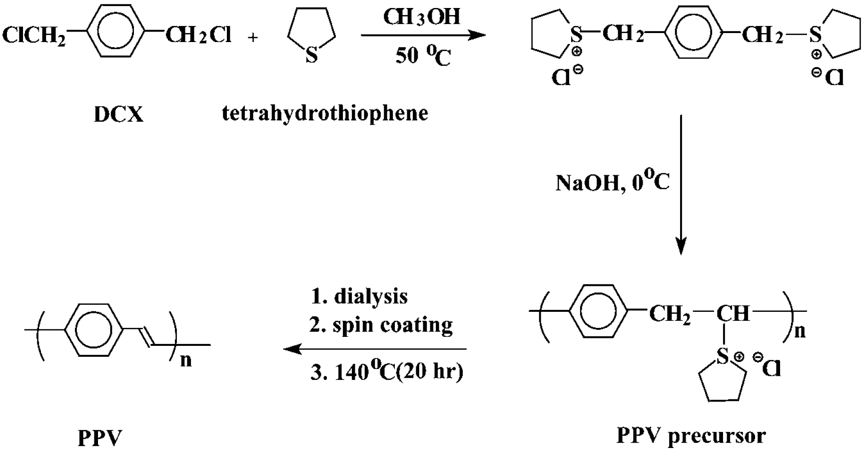

FIGURE 1 Synthesis of PPV precursor and its thermal conversion to PPV.

in anhydrous THF using ^{t}BuOK (1.35 g, 0.0114 mol) at room temperature for 6 hr [9]. The resulting mixture was purified by the same method as used in MEH-PPV, and the MEH-A50 was obtained in 60% yield. FT-IR (KBr), cm^{-1}: 3049 (Ar CH), 2925 (aliphatic CH), 1596, 1512 (Ar C=C), 1206 (Ar–O–C), 961 (trans vinylene).

The synthetic route to the polymers studied in this work are shown in Figures 1–3.

Fabrication of PLEDs

Single layer PLEDs were fabricated using PPV, MEH-PPV, MEH-Rs and MEH-A50 as emitting materials. Indium-tin oxide (ITO) coated glass with a sheet resistance of 30 Ω/□ was cut into $2.0 \times 2.0\,cm^2$, and electrode area was prepared by photoetching technique. It was cleaned successively with acetone, methanol, and mixture of isopropyl alcohol and water (1:1 by vol.) in an ultrasonic bath.

Polymer films on ITO glass were prepared by spin coating from a filtered solution, followed by removing the solvent to give an emissive layer. The procedure for the formation of emissive layers with a thickness about 500–850 Å measured by Scanning Probe Microscope (Model: Digital instruments, Nanoscope Multimode SPM & BioScope) was as follows. The PPV precursor solution was spin-coated at a rate of 2500 rpm for 30 s, and thermally converted to PPV at 140°C for 12 hr. The MEH-PPV, MEH-R80 and MEH-R60 (0.5 wt%) solution of *m*-xylene were also spin-coated at a rate of 1500 rpm (30 s), 1500 rpm

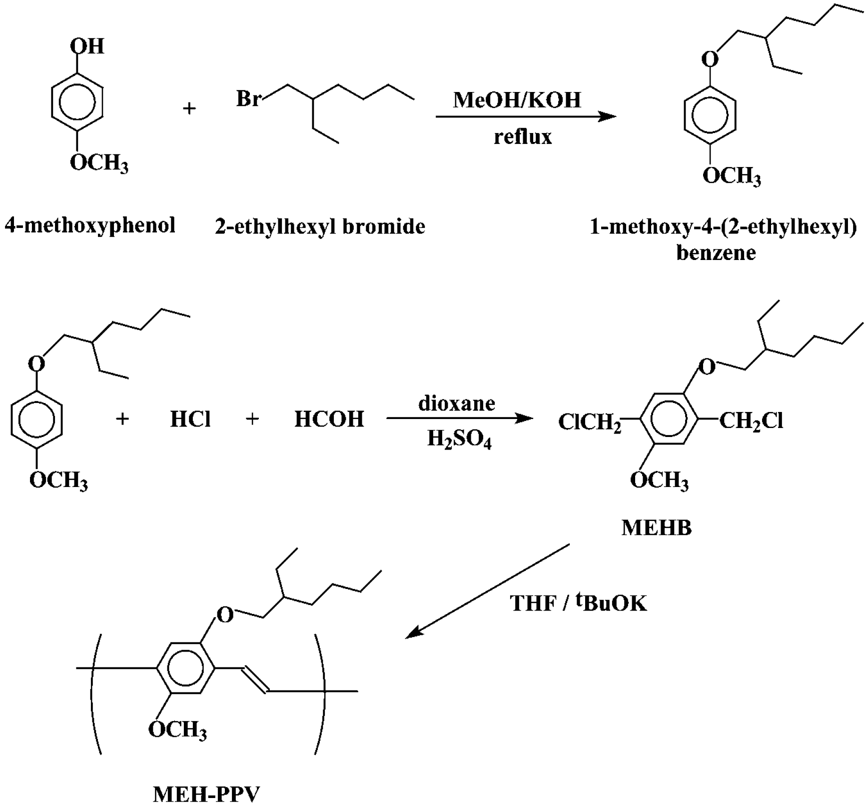

FIGURE 2 Synthetic route to MEH-PPV.

(30 s), and 4000 rpm (30 s), respectively, and dried at 100°C for 1 hr. The MEH-A50 solution (1 wt%) of 1-methyl-2-pyrrolidinone was spin-coated at a rate of 5000 rpm for 60 s, and dried at 140°C for 2 hr.

The Mg metal as cathode was deposited by E-beam method (2×10^{-5} torr) with 4000 Å thickness at 20 Å/sec rate to give [ITO/conjugated copolymer/Mg] PLED. The area of deposited Mg was approximately $0.4\,\text{cm}^2$.

Measurements

The ^{1}H-NMR and FT-IR spectra of synthesized monomers and polymers were taken on a Varian Unity Plus 300 and Jasco FT/IR-620 spectrometer, respectively. Molecular weights and molecular weight distributions of polymers was obtained by gel permeation chromatograph

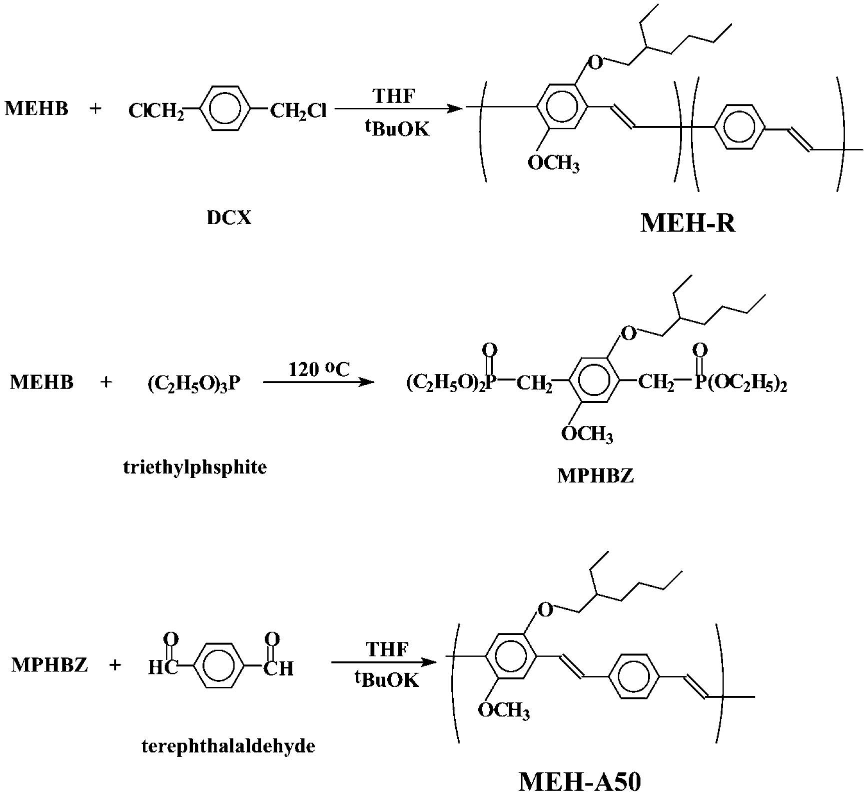

FIGURE 3 Synthetic route to MEH-R and MEH-A50.

(Waters) equipped with a 410 differential refractometer, 510 HPLC pump, and Styragel HR 5E column using tetrahydrofurane as an eluent at room temperature. The copolymer compositions were calculated from elemental analyzer (Elementar, Vario EL). Thermal analysis was performed with a TA4000/Auto DSC 2910 system (TA Instruments) at a heating and cooling rate of 20°C/min under nitrogen atmosphere. UV-visible absorption spectra of polymers were obtained by Shimadzu UV-2100. Electroluminescence (EL) spectra were recorded by Spectroscan PR 704 (Photoresearch Inc.) at 2 nm resolution and color coordinates were determined by the same instrument. Current and luminance of PLEDs fabricated with conjugated polymers were measured with a Minolta luminance meter LS-100 equipped with close-up lens (No. 110, Φ 40.5 mm) and digital multimeter (Model 8092 A, Hyun Chang Product Co.) at room temperature.

RESULTS AND DISCUSSION

Synthesis and Characterization

Conjugated polymers were synthesized to compare their electro-optical properties from the viewpoint of microstructure. Homopolymers, PPV and MEH-PPV, were obtained by previously reported method [6,7]. Random copolymers (MEH-Rs) containing PV (phenylene vinylene) and MEHPV (2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene vinylene) unit were synthesized by α-elimination (dehydrohalogenation) reaction with potassium butoxide [8]. MEH-A50 obtained by Honer-Emmons reaction should have alternating repeating unit due to the condensation reaction mechanism [9,10].

Elemental analysis of PPV showed 99.3% of conversion ratio (C:H:S = 83.78:5.57:0.26). This result revealed that a precursor polymer was almost fully converted to PPV at 140°C. This was also confirmed from ESCA (electron spectroscopy for chemical analysis) survey scan spectrum (Fig. 4 (a)) of PPV film. The spectrum showed only C peak (C_{1S}: 287.7 eV), but peak for S (S_{2P}: 165 eV) was not

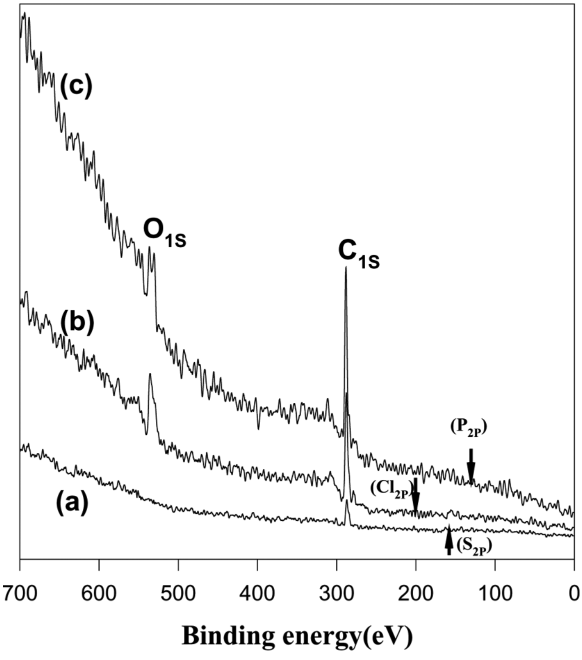

FIGURE 4 ESCA survey scan spectra of (a) PPV, (b) MEH-PPV and (c) MEH-A50.

detected. The ESCA survey scan spectra of MEH-PPV and MEH-A50 are shown in Figure 4(b) and (c), respectively. The survey scan spectrum of MEH-PPV synthesized by α-elimination had C (C_{1S}: 287.7 eV) and O (O_{1S}: 535 eV) peak, but peak for Cl (Cl_{2P}: 199 eV) contained in MEHB monomer was not shown. Also, the survey scan spectrum of MEH-A50 synthesized by Honer-Emmons condensation showed the same peaks with MEH-PPV, and there was no peak for P (P_{2P}: 133 eV) contained in MPHBZ monomer. It was confirmed from these results, therefore, that conjugated homopolymer and copolymers with high structural integrity was obtained without any unreacted monomer residue in the resulting polymers.

All synthesized monomers and polymers were characterized with ^{1}H-NMR and FT-IR, and their resulting spectral data were listed in experimental section. Figure 5 shows ^{1}H-NMR spectrum of MPHBZ monomer, the proton peaks of $Ar{-}CH_2{-}P$ and $-CH_2O{-}P$ group in MPHBZ were found at 3.24 and 4.03 ppm, respectively.

Figure 6 shows FT-IR spectra of MPHBZ and MEH-A50. The P=O stretching mode in FT-IR spectrum of MPHBZ was shown at 1252 cm^{-1} as indicated in Figure 6(a). This absorption peak was dramatically decreased after polymerization, and new peaks originated from out-of-plane bending mode [11] of trans vinylene unit (961 cm^{-1}) and C=C stretching mode (1596 cm^{-1}) were appeared in FT-IR spectrum of MEH-A50 [Fig. 6(b)].

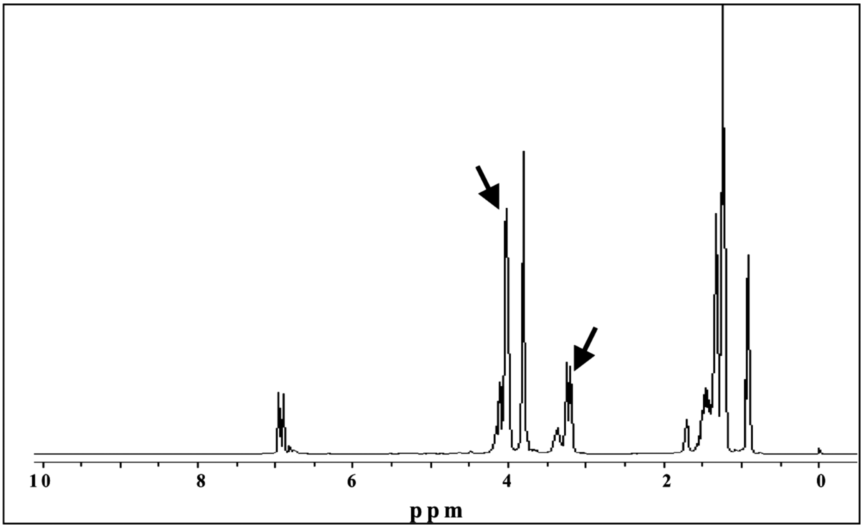

FIGURE 5 ^{1}H-NMR spectrum of MPHBZ.

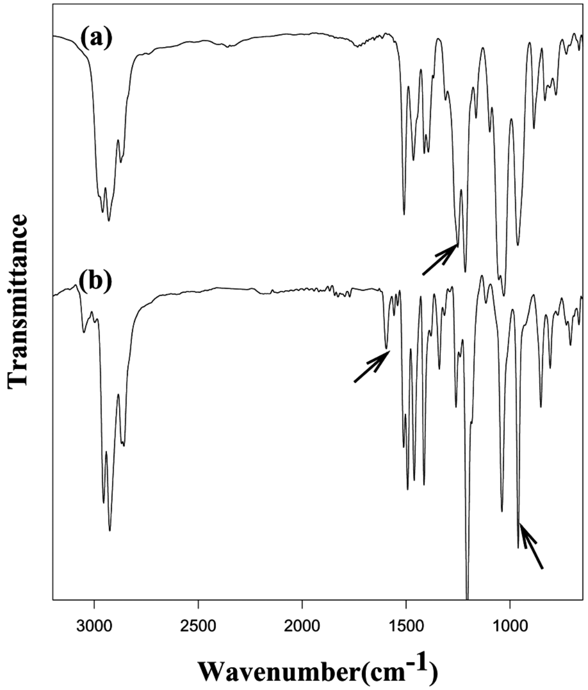

FIGURE 6 FT-IR spectra of (a) MPHBZ and (b) MEH-A50; peaks for P, Cl and S were not shown in the spectra.

The solubility of the synthesized copolymers was investigated. The solubility of MEH-Rs in common organic solvents was decreased rapidly with the increasing amount of phenylene vinylene (PV) repeat unit in the copolymer. The MEH-PPV (0 mol% of PV unit), MEH-R80 (20 mol% of PV unit) and MEH-R60 (40 mol% of PV unit) were soluble in THF, chloroform, and *m*-xylene at room temperature. But MEH-R30, which contains 70 mol% of rigid PV units in the main chain, was not soluble in any organic solvents. MEH-A50, alternating copolymer made by Honer-Emmons condensation, however, exhibited solubility in THF, 1,1,2,2-tetrachloroethane and 1-methyl-2-pyrrolidinone (NMP).

The molecular weight and thermal decomposition temperature of conjugated copolymers obtained by two different synthetic methods are shown in Table 1. The molecular weight of MEH-R30 copolymer containing 70% of rigid PV unit could not be measured because of low solubility in THF solvent. The molecular weight of alternating copolymer, MEH-A50, was about 12,000 g/mol as determined by

TABLE 1 Molecular Weights and Thermal Properties of Conjugated Copolymers

Conjugated polymers	Content of MEHPV (%)	$M_w \times 10^{-3}$ (g/mol)	M_n/M_w	T_{id}[1] (°C)
MEH-PPV	100	37	1.54	366
MEH-R80[2]	78	41	1.82	402
MEH-R60[2]	61	130	1.89	391
MEH-R30[2]	31	—	—	405
MEH-A50[3]	50	12	2.15	406
PPV	0	—	—	375

[1] Initial decomposition temperature.
[2] Random coplymers containing MEHPV and PV repeating unit.
[3] Alternating coplymer containing MEHPV and PV repeating unit.

GPC with THF as eluent. The low molecular weight of this copolymer may be due to the deviation from the stoichiometric balance of two monomers MPHBZ/TA which is a critical factor in the polycondensation reaction. TGA analysis indicated that synthesized polymers were stable up to about 360°C under nitrogen. DSC thermograms of the synthesized polymers showed no thermal transition from room temperature up to 300°C. The initial decomposition temperatures (T_{id}) determined from TGA analysis are also listed in Table 1.

PLED Device and Electro-Optic Properties

The optical absorption spectra of synthesized polymer films were shown in Figure 7. The UV absorption maximum ($\lambda_{max,UV}$) and edge ($\lambda_{edg,UV}$) corresponding to maximum π-π^* transition and HOMO (the highest occupied molecular orbital)-LUMO (the lowest unoccupied molecular orbital) band gap energy [12], respectively, were blue-shifted as increasing the amount of PV unit in the main chain of MEH-Rs (Fig. 7). From this result, we also recognized that band gab energy was increased with increasing PV unit in the main chain of conjugated random copolymers MEH-Rs.

The emission maxima ($\lambda_{max,EL}$) of MEH-PPV, MEH-R80, MEH-R60, MEH-A50 and PPV showed 588 nm (2.11 eV), 578 nm (2.14 eV), 532 nm (2.33 eV), 554 nm (2.24 eV) and 508 nm (2.44 eV), respectively. Random copolymer (MEH-R60) and alternating copolymer (MEH-A50) which have similar content of MEHPV in the main chain are compared in Table 2. PLED made from MEH-R60 showed larger FWHM (full width at half maximum) compared to that from MEH-A50. MEH-R60 also showed larger Stoke's shift [13]. This large Stoke's shift may be due

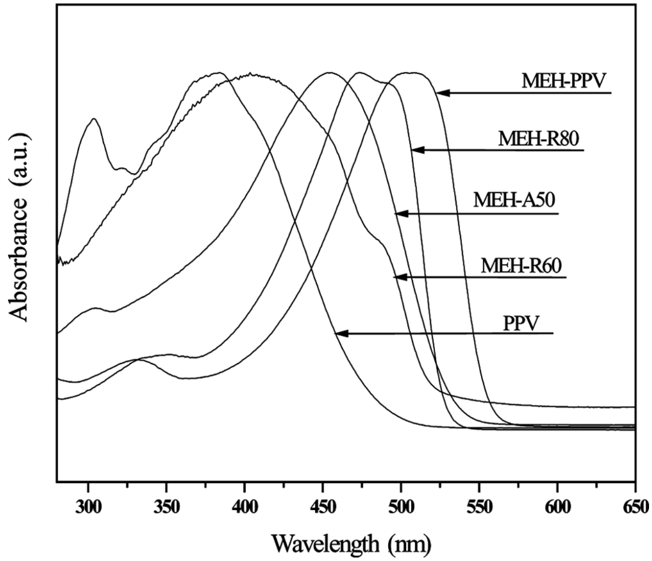

FIGURE 7 UV-visible absorption spectra of conjugated polymers.

to the various formation of excited singlet because of variety of arrangements of repeating unit [14]. These results mean that MEH-R60 has various chain segments causing various energy levels during operation of the PLED.

Color coordinates of single layer PLEDs (ITO/conjugated polymer/Mg) were compared with those of standard red, green, blue, and white color established by NTSC (national television system committee) [15] in Figure 8. The emission color could be determined from these color coordinates as measured by Spectroscan PR-704 (Photoresearch Inc.) and Kelly's map [16] in CIE (Commission Internationale de l'Eclairage) 1931 chromaticity diagram [17]. The EL light of MEH-PPV, MEH-R80, MEH-R60, and PPV showed orange (CIE coordinates of x = 0.58 and y = 0.41), yellowish orange (CIE coordinates of x = 0.54

TABLE 2 Comparison of Random and Alternating Copolymers

Conjugated polymer	Copolymer type	Content of MEHPV (%)	FWHM (nm)	Stoke's shift[1] (nm)
MEH-R60	Random	61	102	148
MEH-A50	Alternating	50	78	80

[1] $\lambda_{\max,EL} - \lambda_{\max,UV}$.

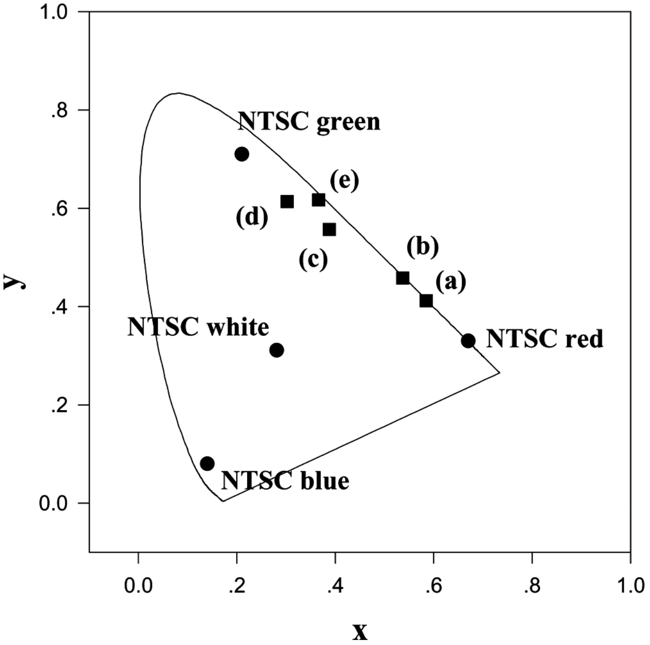

FIGURE 8 CIE 1931 chromaticity diagram showing color coordinates of (a) MEH-PPV, (b) MEH-R80, (c) MEH-R60, (d) PPV, (e) MEH-A50 and NTSC standard red, green and blue.

and y = 0.46), yellow-green (CIE coordinates of x = 0.39 and y = 0.56), and yellowish green (CIE coordinates of x = 0.30 and y = 0.61) color, respectively. The alternating copolymer, MEH-A50, emitted at the boundary region (CIE coordinates of x = 0.37 and y = 0.62) between yellow-green (MEH-R60) and yellowish green (PPV). CIE coordinates of MEH-Rs and MEH-A50 were moved from red region (MEH-PPV) to green region (PPV) as increasing PV unit in the main chain.

CONCLUSIONS

Two types of conjugated copolymers containing phenylene vinylene (PV) moiety and alkoxyphenylene vinylene (MEHPV) moiety have been synthesized by dehydrohalogenation and Honer-Emmons reaction, respectively. Both random conjugated copolymers and alternating copolymer have been designed in order to obtain similar polymeric structure, and their thermal and electro-optical properties have been compared. UV absorption and EL spectra of MEH-Rs were blue-shifted as increasing the amount of PV unit in the main chain. The microstructures of conjugated polymers were found to be an important factor affecting on the color of PLEDs.

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