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Synthesis of Conjugated Polymers Containing Biphenyl Group and Their Electro-Optical Properties

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Two types of conjugated polymer, poly(MEHPV-co-BPV)s and poly (MEHPV-alt-BPV), were synthesized by dehydrohalogenation and Honer-Emmons condensation, respectively. Single layer type light-emitting diodes were fabricated utilizing synthesized polymers and their electro-optical properties were examined. Emission spectrum of poly (MEHPV-co-BPV)s had two peaks in the blue and orange region which originated from BPV and MEHPV moiety, respectively. This may be due to the mixture of two homopolymers or the macroblock nature of the BPV and MEHPV unit in the poly(MEHPV-co-BPV)s. However, LED made from poly(MEHPV-alt-BPV) showed a relatively sharp single peak at the yellow-green region due to the alternating nature of the repeat units.

Keywords: light-emitting diode; conjugated copolymer; dehydrohalogenation; Honer-Emmons condensation

INTRODUCTION

Conjugated polymers have received considerable attention due to their importance in light-emitting diode(LED)s since Friend *et al.* reported LED made from poly(p-phenylene vinylene) (PPV) [1]. The microstructure of conjugated polymers have been recognized as an important factor affecting the emission color, quantum efficiency, and luminance/voltage profile of LED. In this work poly(alkoxyphenylene vinylene-co-biphenylene vinylene) type copolymers were synthesized

by two different methods and the electro-optical properties were examined from the view point of copolymer microstructure.

EXPERIMENTAL

Poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene vinylene) (MEH-PPV) was synthesized according to the reported method[2]. Poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene vinylene-co-1,1'-biphenyl-4,4'-ylene vinylene)s[poly(MEHPV-co-BPV)s] were obtained by the dehydrohalogenation of 1,4-bis(chloromethyl)-2-methoxy-5-(2-ethylhexyloxy)benzene(MEHB) and 4,4'-bis(chloromethyl)-1,1'-biphenyl (CMBP) with different feed ratio. Chloromethyl group of MEHB was converted to aldehydes by using 2-nitropropane/sodium ethoxide to give 2-methoxy-5-(2-ethylhexyloxy)-4-formylbenzaldehyde(MEHFB). 4,4'-Bis(diethoxyphosphinylmethyl)-1,1'-biphenyl(EPMBP) was prepared by the reaction of CMBP with triethylphosphite. Poly(MEHPV-alt-BPV) was obtained by the Honer-Emmons condensation[3] of MEHFB and EPMBP. The synthetic scheme is shown in FIGURE 1.

The synthesized compounds were characterized with ^{1}H-NMR, FT-IR and elemental analysis. The molecular weight was measured by Waters GPC. Photoluminescence(PL) spectrum of conjugated polymer excited at 325 nm was monitored by Optical Multichannel Analyzer (Laser Photonics). Electroluminescence(EL) propertiy was measured by Spectroscan PR 704(Photoresearch Inc.). The EL intensity was measured by using Minolta luminance meter LS-100 at room temperature.

RESULTS AND DISCUSSION

Synthesis and Characterization of Conjugated Polymers

Molecular weight and copolymer composition data of conjugated copolymers obtained by two different synthetic methods are shown in TABLE 1. The solubility of poly(MEHPV-co-BPV)s was decreased rapidly with increasing amount of 1,1'-biphenyl-4,4'-ylene vinylene (BPV) repeat unit in the copolymer in such common organic solvents as THF, chloroform and xylene. Of the copolymers made by dehydrohalogenation of MEHB and CMBP, only poly(MEHPV-co-BPV)1 in which the feed content of more rigid CMBP was 15 mol% exhibited solubility in THF and chloroform. Poly(MEHPV-alt-BPV) which is alternating

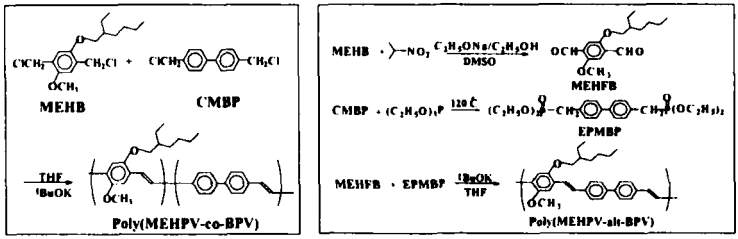


FIGURE 1. Synthesis of poly(MEHPV-co-BPV) and poly(MEHPV -alt-BPV).

TABLE 1. Copolymer composition and MW of polymers

Conjugated Polymers	Feed ratio (MEHB:CMNP)	Copolymer Composition	MW (g/mol)
MEH-PPV	100:0	100:0	36600
Poly(MEHPV-co-BPV)1	85:15	91:9	11300
Poly(MEHPV-co-BPV)2	70:30	74:26	*1
Poly(MEHPV-co-BPV)3	50:50	64:36	*1
Poly(MEHPV-co-BPV)4	30:70	35:65	*1
Poly(MEHPV-alt-BPV)	50:50*2	50:50	7200

*1; insoluble in organic solvent, *2; ratio of MEHFB/EPMBP

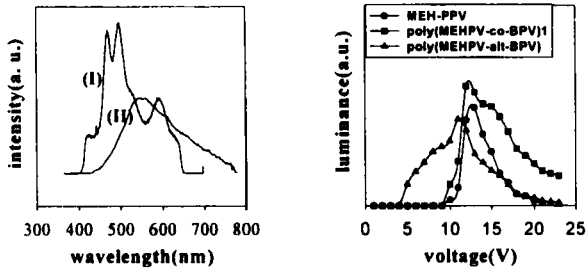
copolymer made by Honer-Emmons condensation, however, exhibited solubility in such common solvents as THF, xylene, chloroform and 1-methyl-2-pyrrolidinone at elevated temperature.

Electro-optical Properties of Conjugated Polymers

LEDs made with MEH-PPV and poly(MEHPV-co-BPV)1 exhibited very close emission maximum at 590 nm and 586 nm, respectively. The EL spectrum of ITO/poly(MEHPV-co-BPV)1/Mg device and the PL spectrum(due to lack of solubility in organic solvent) of poly(MEHPV-co-BPV)2 sample showed only small shift(about 50 nm) compared to that of MEH-PPV. FIGURE 2(a) shows PL(I) and EL(II) spectra of poly(MEHPV-co-BPV)4 and poly(MEHPV-alt-BPV), respectively. PL spectrum of poly(MEHPV-co-BPV)4 showed two emissions in the blue[λ_{max}=469, 495 nm] and orange[λ_{max}=590 nm] regions which were assigned to be originated from BPV and MEHPV moiety, respectively. This may be due to the mixture of two homopolymer or macroblock nature of BPV and MEHPV unit in the poly(MEHPV-co-BPV)s. The EL emission of ITO/poly(MEHPV-alt-BPV)/Mg device

appeared in the yellow-green region which corresponds to CIE 1931 coordinates of x=0.412 and y=0.503 using Kelly's map in chromaticity diagram[4]. Compared to poly(MEHPV-co-BPV)4 synthesized by dehydrohalogena-tion, poly(MEHPV-alt-BPV) exhibited one emission peak which is located between blue(BPV) and orange(MEHPV) region of poly (MEHPV-co-BPV)4. This may be due to the alternating microstructure of poly(MEHPV-alt-BPV) made by Honer-Emmons condensation.

FIGURE 2(b) shows the luminance-voltage profile of single layer LEDs. MEH-PPV and poly(MEHPV-co-BPV)1 showed about same threshold voltage at 9V, but alternating copolymer poly(MEHPV-alt-BPV) had lower threshold voltage at 4V. This result indicates that poly(MEHPV-alt-BPV) had lower barrier to electron injection than that of MEH-PPV or poly(MEHPV-co-BPV)1. The LEDs had a brightness of about 20-40 cd/m^2 in our measuring system.



(a) (b)

FIGURE 2. (a) PL(I) and EL(II) spectra of poly(MEHPV-co-BPV)4 and poly(MEHPV-alt-BPV), respectively and (b) luminance vs. voltage profile of conjugated polymers.

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