Synthesis of Red, Green, Blue Light Emitting Polymers and Their Electroluminescence Properties

Lee Soon Park, Yoon Soo Han, Sang Dae Kim, and Dong Uk Kim*

Department of Polymer Science, Kyungpook National University, Taegu, 702-701, Korea

*Department of Science Education, Taegu National University of Education, Taegu, 705-715, Korea

Abstract

Three types of conjugated polymer, poly(DFPZ-AV), poly(MEHPV-PV) and poly(BFMP12-BPV), were obtained by Honer-Emmons condensation using potassium *tert*-butoxide from the synthesized monomers in anhydrous tetrahydrofurane. The Honer-Emmons reaction was found to be a useful synthetic method for the preparing a wide range of EL polymers. The EL devices using poly(DFPZ-AV), poly(MEHPV-PV) and poly(BFMP12-BPV) as light emitting layer gave red, green and blue emission, respectively, which were in close chromaticity with the CIE 1931 NTSC standard.

Introduction

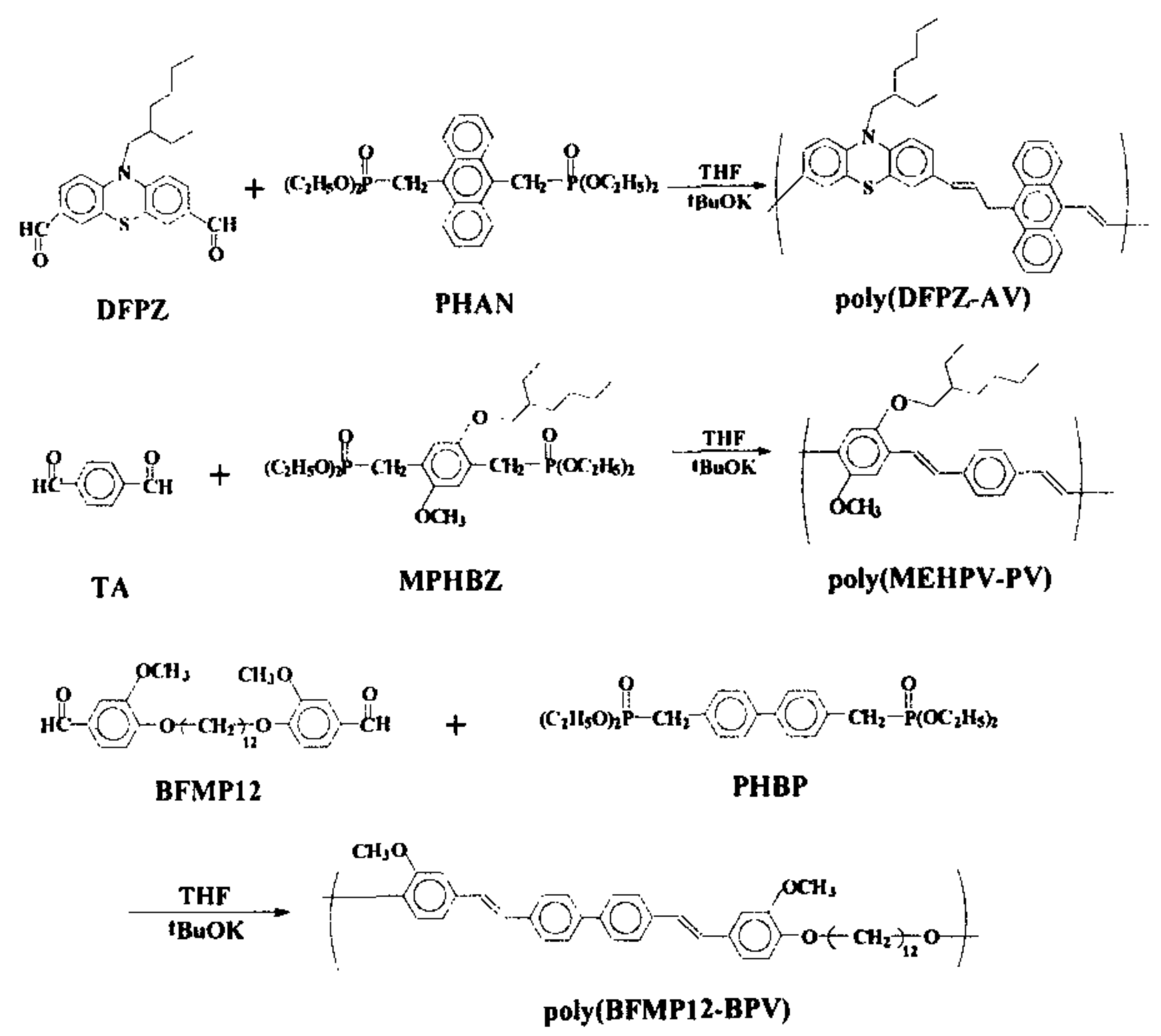
Recently conjugated polymers have received considerable attention due to their application in LED, since R. H. Friend et al. [1] reported green color emission utilizing poly(p-phenylene vinylene)(PPV). A number of polymers with basic structure similar to PPV have been synthesized for use as emitting materials in LED. The microstructures of these polymers are known to be one of most important factors affecting the emission color, quantum efficiency, and luminance/voltage profile of LED. For example, C. Zhang et al. [2] reported that the maximum wavelength of emission spectrum obtained from partially converted PPV was slighted blue region compared to the one from the fully converted PPV. F. E. Karasz et al. [3] reported the synthetic method of EL polymers with unconjugated blocks distributed evenly in the conjugated main chain. They showed that the emission colar was affected by the length of conjugated block and that the quantum efficiency was two orders of magnitude greater than that of fully converted PPV. In this work, we examined the usefulness of Honer-Emmons reaction for obtaining EL polymers with wide range of color emission and the effect of microstructure of polymers on the electroluminescence properties.

Experimentals

The synthetic schemes of poly(*N*-(2-ethylhexyl)-3,6-phenothiazinylene vinylene-alt-9,10-anthrylene vinylene) [poly(DFPZ-AV)], poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene vinylene-alt-phenylene vinylene) [poly(MEHPV-PV)] and poly(1,12-dodecanedioxy-2-methoxy-1,4-phenylene-1,2-ethenylene-1,1'-biphenyl-4,4'-ylene-1,2-ethenylene-3-methoxy-1,4-phenylene) [poly(BFMP12-BPV)] are shown in Figure 1.

Single layer LEDs were fabricated utilizing the three polymers as followings. The light emitting polymer layer was obtained on the ITO(30Ω/□) glass by spin coating of corresponding polymer solutions. Cathod was Mg metal deposited by E-beam method these polymer films to give ITO/conjugated polymers/Mg device.

The ^{1}H-NMR and FT-IR spectra of synthesized polymers were obtained by a Varian Unity Plus 300 and Jasco FT/IR-620 spectrometer, respectively. Thermal analysis was performed by using TA4000/Auto DSC 2910 system from TA Instruments with heating and cooling rate of 20 °C/min under nitrogen atmosphere UV-visible absorption spectra of polymer films were obtained by Shimadzu UV-2000, and electroluminescence (EL) spectra and CIE coordinates were measured by Spectroscan PR 704 (Photoresearch Inc.). EL intensity was measured by Minolta luminance meter(LS-100) at room temperature.



Scheme 1. Synthetic route to conjugated polymers.

Results and Discussion

Honer-Emmons polycondensation was used for the synyhesis of EL polymers as shown in Fig. 1. The polymerization was easily carried out in anhydrous THF in the presence of potassium tert-butoxide at room temperature. All synthesized monomers were characterized with ^{1}H-NMR and FT-IR. The vinyl unit produced by Honer-Emmons condensation is known to be all-trans configuration, and it was confirmed by the FT-IR spectroscopy. The out-of-plane bending mode of the trans vinylene unit was observed in FT-IR spectra of all synthesized polymers near 965 cm.$^{-1}$ However, no peak corresponding to the one of cis-vinylene bonds could be seen in the 890-900 cm^{-1}.

The solubility of the synthesized polymers varied depending on the microstructure. The poly(DFPZ-AV) was soluble in such organic solvent such as chloroform, tetrahydrofurane, xylene, 1,1,2,2-tetrachloroethane. But poly(MEHPV-PV) and poly(BFMP12-BPV) was soluble in only 1,1,2,2-tetrachloroethane and in 1-methyl-2-pyrrolidinone at an elevated temperature (about 45 °C).

TGA analysis indicated that synthesized polymers were stable up to 400 °C under nitrogen. DSC thermogram of poly(DFPZ-AV) and poly(NEHPV-PV) showed no thermal transition from room temperature up to 300 °C. But two enthothermic transitions were observed in DSC thermogram of poly(BFMP12-BPV) due to melting of conjugated and nonconjugated blocks.

The electrooptical properties were characterized by UV-visible absorption and EL spectrum of conjugated polymers. The resulting data such as maximum π-π* transition($\lambda_{max,UV}$), HOMO-LUMO band gap energy($\lambda_{edg,UV}$) and emission maximum($\lambda_{max,EL}$) are summerized in Table 1.

Table 1. Eelectrooptical properties of conjugated polymers.

Cojugated Polymers	$\lambda_{max,uv}$ (nm/eV)	$\lambda_{edg,UV}$[1] (nm/eV)	$\lambda_{max,EL}$ (nm/eV)
Poly(DFPZ-AV)	437/2.84	546/2.27	658/1.88
poly(MEHPV-PV)	474/2.62	534/2.32	554/2.24
poly(BFMP12-BPV)	360/3.44	437/2.84	466/2.66

[1] : onset point of UV-visible absorption spectrum

The band gap energy of conjugated polymers were found to be increased in the order of poly(DFPZ-AV) 〈 poly(MEHPV-PV) 〈 poly(BFMP12-BPV). This could be explained in relation to the microstructures of the repeating units of EL polymers. In poly(MEHPV-BPV) sample, the conjugated chain length is shortest in the three EL polymers synthesized with the highest band gap. Comparison of poly(DFPZ-AV) and poly(MEHPV-PV) samples exhibits that repeat unit of the former has wider conjugation length due to anthracene unit than that of the latter.

Figure 2 shows EL spectra of single layer LEDs made with the synthesized polymers. The maximum of EL spectrum appeared in red($\lambda_{max,EL}$=658 nm), green($\lambda_{max,EL}$ =554 nm) and blue($\lambda_{max,EL}$=466 nm) region as expected for the LED's made with poly(DFPZ-AV), poly(MEHPV-PV) and poly(BFMP12-BPV) as emitting materials, respectively. The LEDs had a brightness of about 20-30 cd/m^2 in our measuring system.

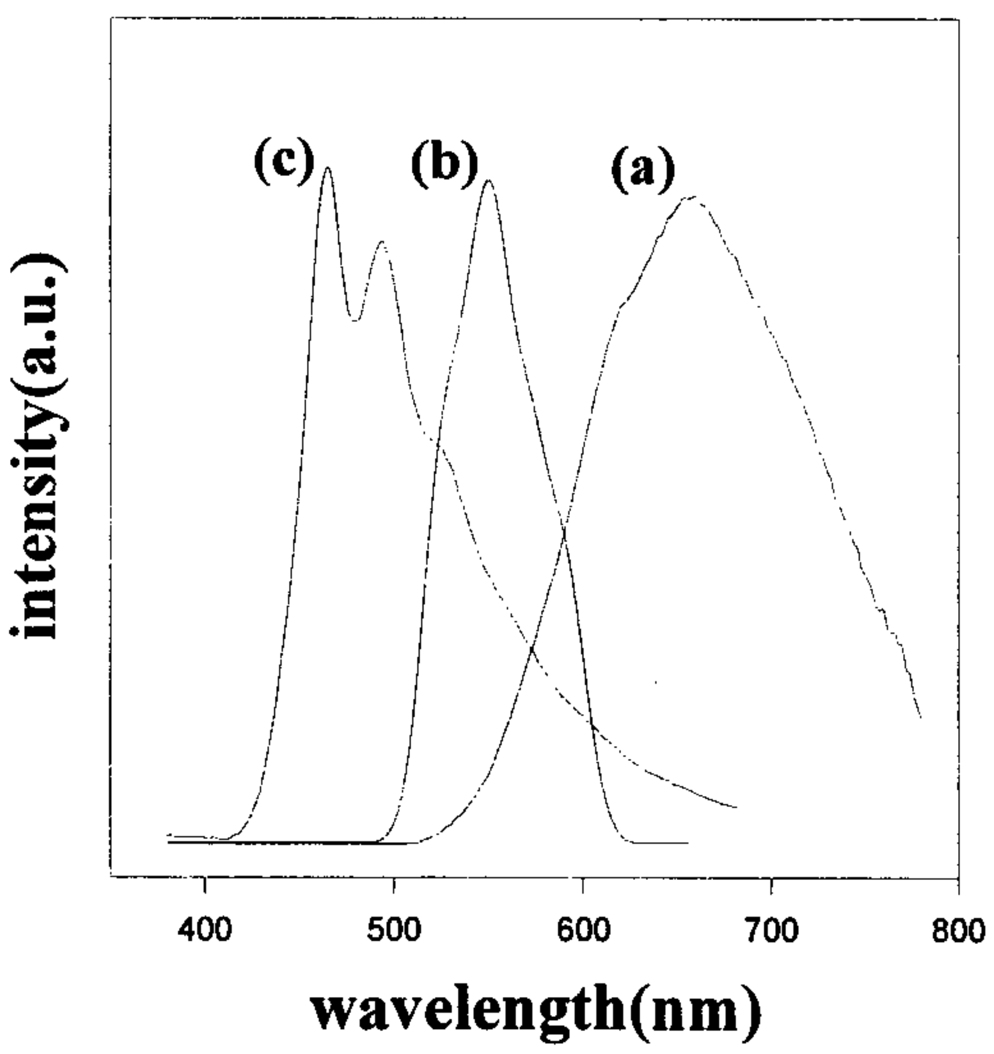


Fig. 2. EL spectra measured from (a) ITO/poly(DFPZ-AV)/Mg, (b) ITO/poly(MEHV-PV)/Mg and (c) ITO/poly (BFMP12-BPV)/Mg devices.

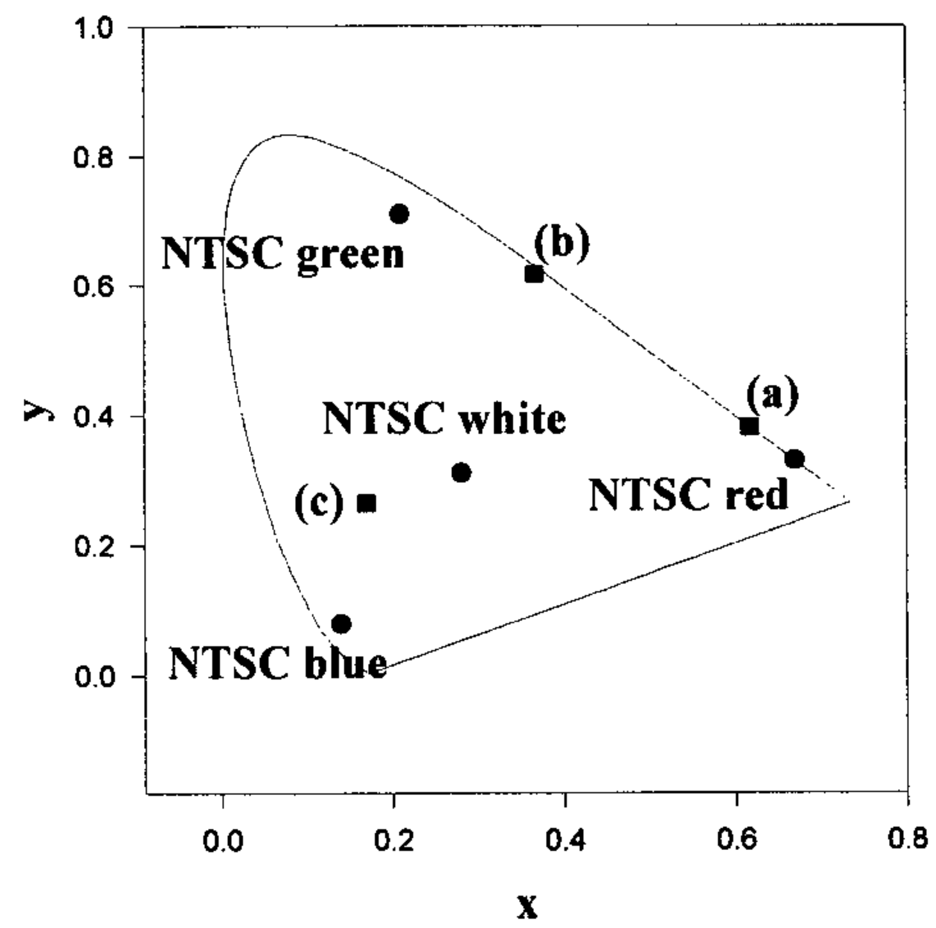


Fig. 3. CIE coordinates for standard NTSC and EL of the LEDs prepared from (a) poly(DFPZ-AV), (b) poly(MEHPV-PV) and (c) poly(BFMP12-BPV).

CIE coordinates of LED's made with the conjugated polymers were compared with those of standard red, green and blue color established by NTSC(National Television System Committee) in Figure 3. The coordinates of LED's using these polymers could be determined from the CIE coordinates and Kelly's map in CIE 1931 chromaticity diagram[4]. The EL emission of poly(BFMP12-BPV) and poly(MEHPV-PV) showed blue green(CIE coordinates x=0.1712 and y=0.2651) and yellowish green(CIE coordinates x=0.3660 and y=0.6169) color, respectively. These colors showed insufficient color purity to those of NTSC standards. The poly(DFPZ-AV) sample, however, emitted reddish orange color(CIE coordinates x=0.6173 and y=0.381) which was very similar to that of NTSC red(CIE coordinates x=0.67 and y=0.33).

Conclusion

Honer-Emmons reaction was found to be a useful synthetic method for the preparation of EL polymers with designed microstructure. The electroluminescence colors were investigated from the view point of application to full-color display. Red light-emitting polymer, poly(DFPZ-AV), showed high color purity which had CIE coordinates of x=0.6173 and y=0.3814.

References

[1] J. H. Burroushes, D. D. C. Bradley, A. R. Brown, R. N. Narks, K. Mackay, R. H. Friend, P. L. Burns, and A. B. Holmes, *Nature,* **347**, 539 (1990).

[2] C. Zhang, D. Broun, and A. J. Heeger, *J. Appl. Phys.*, **73**, 5177 (1993).

[3] Z. Yang, I. Sokolik, and F. E. Karasz, *Macromolecules,* **26**, 1188 (1993).

[4] G. A. Agoston, *Color Theory and Its Application In Art and Design*, ed. by D. L. MacAdam, Springer Series in Optical Sciences; Vol. 19, pp. 49-59, Springer-Verlag, Berlin (1979).