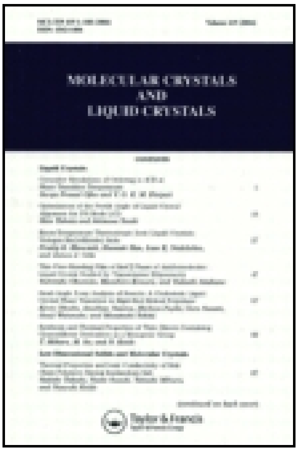

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Synthesis and Electroluminescence Properties of Heterocyclic Conjugated Copolymers and Blends

Lee Soon Park [a] , Hyeon Sool Ryu [a] , Hyeon Jin Seo [a] , Woo Sik Kim [a] , Dong Ho Lee [a] , Kyung Eun Min [a] , Kwan Ho Seo [a] & Inn Kyu Kang [a]

[a] Dept. of Polymer Science, Kyungpook Nat. Univ., 702-701, Korea

Version of record first published: 29 Oct 2010

Mol. Cryst. Liq. Cryst., Vol. 377, pp. 37-40
1058-725X/02 $12.00 + .00
DOI: 10.1080/10587250290088483

Synthesis and Electroluminescence Properties of Heterocyclic Conjugated Copolymers and Blends

LEE SOON PARK, HYEON SOOL RYU, HYEON JIN SEO, WOO SIK KIM, DONG HO LEE, KYUNG EUN MIN, KWAN HO SEO and INN KYU KANG

Dept. of Polymer Science, Kyungpook Nat. Univ., 702-701, Korea

Improved electroluminescent efficiencies in polymer light-emitting diodes(LEDs) have been reported to be obtained either by constructing multi-layer devices or by using polymer blends in a light emitting layer. In this work, conjugated copolymers, poly((PZV-PV)-co-(CZV-PV)) containing (N-2-ethylhexyl)-3,6-phenothiazinylene vinylene(PZV) unit and (N-2-ethylhexyl)-3,6-carbazolylene vinylene(CZV) unit in different ratio were synthesized by Horner-Emmons reaction utilizing potassium *t*-butoxide. Homopolymers, poly(PZV-PV) and poly(CZV-PV) were also synthesized. Polymer LED's fabricated with poly(PZV-PV) and poly(CZV-PV) homopolymers as light emitting layers exhibited EL maximum at 570nm amd 500nm, respectively. LED's made with poly((PZV-PV)-co-(CZV-PV)) copolymers, however, showed EL maxima shifted to longer wavelengths.

Keywords light-emitting diode; heterocyclic conjugated copolymer; Horner-Emmons condensation; light emitting layers

INTRODUCTION

Conjugated polymers have received considerable attention due to their application in light-emitting diode(LED)s, since R. H. Friend et al. reported LED made from poly(p-phenylene vinylene) (PPV) [1]. The microstructures of conjugated polymers are known to be one of most important factors affecting the emission color, quantum efficiency, and luminance/voltage profile of LED. In this work, we describe synthesis and electro-optical properties of conjugated copolymers containing phenothiazine and carbazole moiety in the main chain in order to increase the hole injection and transporting property. We also examined the usefulness of Horner-Emmons reaction for obtaining conjugated copolymers with different microstructure for application to the electroluminescence devices.

EXPERIMENTAL

Heterocyclic copolymers, poly((PZV-PV)-co-(CZV-PV)) containing N-(2-ethylhexyl)-3,6-phenothiazinylene vinylene(PZV) unit and N-(2-ethylhexyl)-3,6-carbazolylene vinylene(CZV) unit in different ratio were synthesized by Horner-Emmons reaction utilizing potassium *t*-butoxide [2]. The synthetic scheme of heterocyclic copolymer is shown in FIGURE 1. N-(2-ethylhexyl) phenothiazine(EHPZ) was obtained from phenothiazine and 2-ethylhexyl bromide in dimethylsulfoxide solvent with sodium hydroxide. EHPZ was reacted with $POCl_3$ and DMF in dichloroethane solvent to give aromatic dialdehyde monomer, N-(2-ethylhexyl)-3,6-diformylphenothiazine(DFPZ). N-(2-ethylhexyl)-3,6-diformylcarbazole(DFCZ) was synthesized by a synthetic method similar to that of DFPZ starting from carbazole. 1,4-Bis(diethoxyphosphinylmethyl)benzene(PHBZ) was synthesized by reacting α,α-dichloro-*p*-xylene with triethylphosphite.

The molecular weights of synthesized copolymers were measured by Waters gel permeation chromatograph(GPC). Electroluminescence(EL) spectra and color coordinates of LED's were measured with 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 synthesized by Horner-Emmons reaction are shown in TABLE 1.

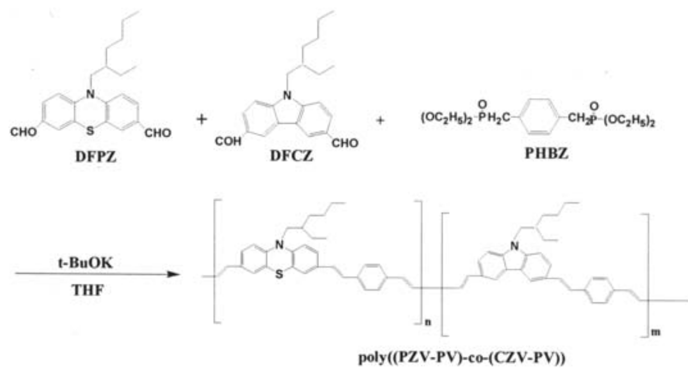

FIGURE 1. Synthetic route to heterocyclic conjugated copolymers.

TABLE 1. Composition and M_W of EL polymers

Conjugated Polymers	Feed ratio (DFPZ:DFCZ:PHBZ)	Copolymer Composition	MW (g/mol)
Poly(PZV-PV)	50:0:50	50:0:50	15,900
Poly(CZV-PV)	0:50:50	0:50:50	12,100
Poly(PZV-co-CZV)19	5:45:50	9:41:50	15,900
Poly(PZV-co-CZV)37	15:35:50	18:32:50	13,900
Poly(PZV-co-CZV)55	25:25:50	29:21:50	16,900
Poly(PZV-co-CZV)73	35:15:50	38:12:50	17,600
Poly(PZV-co-CZV)91	45:5:50	43:7:50	43,400

The molecular weights of copolymers were in the range of 12,000-43,000 g/mol as determined by GPC with THF as eluent. The low Mw copolymers may be due to the deviation from the stoichiometric balance of two comonomers which is a critical factor controlling the Mw of polymer in the condensation polymerization. The composition of copolymers determined by the elemental analysis was close to the feed ratio of monomers as normally observed in the polycondensation reaction. The good solubility in common organic solvents at room temperature was one of the important properties of the synthesized copolymers. The high solubility of the conjugated copolymers seemed to be due to the presence of heterocyclic aromatic ring in the main chain and also due to the ethylhexyl group in the phenothiazine and carbazole moiety.

Electro-optical Properties of Conjugated Polymers

Polymer LED's fabricated with poly(PZV-PV) and poly(CZV-PV) homopolymers as light emitting layers exhibited EL maximum at 570 nm and 500 nm, respectively. The LED's made with blends of homopolymers as light emitting layers exhibited EL maxima between the those of homopolymers. LED's made with poly((PZV-PV)-co-(CZV-PV)) copolymers, however, showed EL maxima shifted to longer wavelengths. The detailed data on the $\lambda_{max,EL}$ for the EL polymers are listed in TABLE 2. This may be due to the enhanced exciplex formation in the case of conjugated copolymers with different microstructures of the repeating units in the polymer chain.

TABLE 2. EL properties of conjugated copolymers

Conjugated Polymers	Feed ratio (DFPZ:DFCZ:PHBZ)	$\lambda_{max,EL}$(nm)
Poly(PZV-PV)	50:0:50	570
Poly(CZV-PV)	0:50:50	500
Poly(PZV-co-CZV)19	5:45:50	578
Poly(PZV-co-CZV)37	15:35:50	586
Poly(PZV-co-CZV)55	25:25:50	598
Poly(PZV-co-CZV)73	35:15:50	592
Poly(PZV-co-CZV)91	45:5:50	584
Polymer blend	**Poly(PZV-PV):poly(CZV-PV)**	**$\lambda_{max,EL}$**
Blend 19	1 : 9	552
Blend 55	5 : 5	564
Blend 91	9 : 1	562

ACKNOWLEDGMENTS

This work was supported by grant No.2000-30800-003-1 from the University-Industry Collaborative Research Program of the Korea Science & Engineering Foundation.

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. K. L. Brandon, P. G. Bently, D. D. C. Bradley, and D. A. Dunmur, *Synth. Met.*, **91**, 305(1997).