Molecular Crystals and Liquid Crystals

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

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Version of record first published: 22 Jul 2010

To cite this article: Suk-Kyung Kim, Jae-Hoon Kim & Do-Hoon Hwang (2009): Synthesis and Light-Emitting Properties of Polyfluorene Copolymers, Molecular Crystals and Liquid Crystals, 498:1, 306-313

To link to this article: http://dx.doi.org/10.1080/15421400802619701

Mol. Cryst. Liq. Cryst., Vol. 498, pp. 306–313, 2009

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400802619701

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Synthesis and Light-Emitting Properties of Polyfluorene Copolymers

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Poly[9,9-bis(4′-n-octyloxyphenyl)fluorene-2,7-diyl] (PBOPF), and their random copolymers with alkylphenothiazine [poly(BOPF-co-PTZ)], were synthesized through Ni(0) mediated polymerization. Light-emitting devices were fabricated using these polymers in an ITO (indium tin oxide)/PEDOT:PSS/polymer/Ca/Al configuration. Each EL device constructed with a poly(BOPF-co-PTZ) copolymer exhibited significantly enhanced efficiency and brightness compared to devices constructed from the PBOPF homopolymer. The EL device constructed with poly(84BOPF-co-16PTZ) exhibited the highest luminous efficiency and brightness (8,600 cd/m^2 and 2.83 cd/A respectively).

Keywords: light-emitting diode; polyfluorene copolymer; phenothiazine

1. INTRODUCTION

Polymer light-emitting devices (PLEDs) fabricated from conjugated polymers have been intensively studied during last few decades because such PLEDs have properties that are well-suited to flat panel display [1–3]. Poly(*p*-phenylenevinylene) (PPV) derivatives and polyfluorene (PFs) derivatives are well-known as promising materials suitable for practical applications [4,5]. Recently, more attention has been paid to polyfluorenes (PFs) for use as emissive layers in light-emitting diodes than to PPV derivatives because of their high

This article was supported by the Research Fund of the Kumoh National Institute of Technology.

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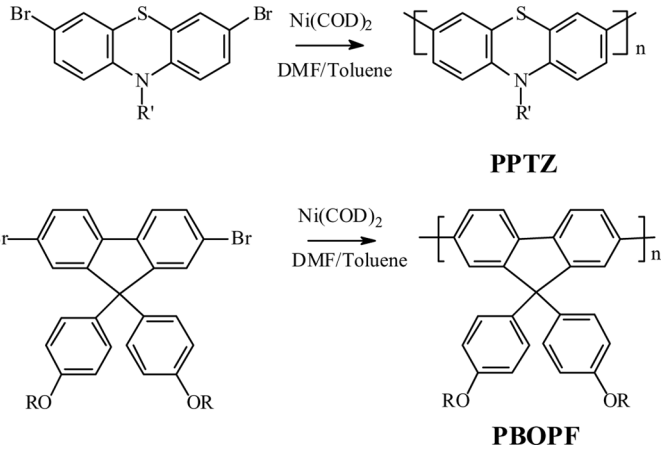
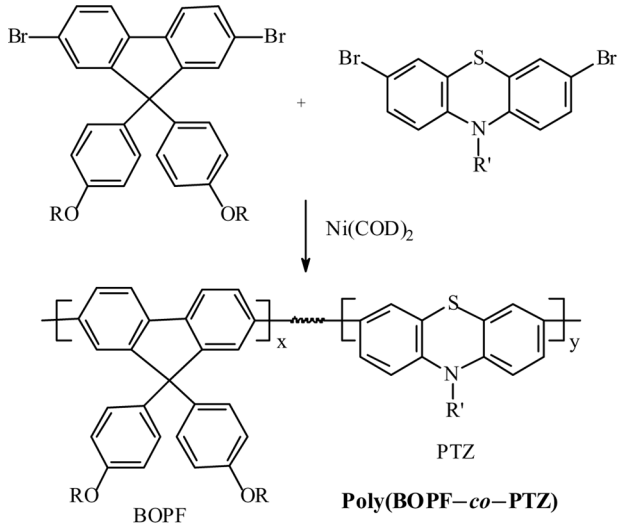


SCHEME 1 The synthetic route and chemical structure of PBOPF.

photoluminescence quantum efficiency, thermal stability, and also easy color tuning via the introduction of low band gap comonomers [6–12]. The poor efficiency of polyfluorene has been improved by blending, copolymerization, and end-capping with charge transporting



SCHEME 2 The synthetic route and chemical structure of poly(BOPF-*co*-PTZ).

materials to obtain improved chare injection [13–16]. Recently we reported that copolymers containing 9,9-bis(n-octyl)fluorene and phenothiazine showed highly improved EL device performances due to better charge carrier balance in EL devices [17]. In this article we synthesized copolymers composed of 9,9-bis(4′-n-octyloxyphenyl)fluorene (BOPF), and phenothiazine (poly(BOPF-*co*-PTZ)) because poly [9,9-bis(4′-n-octyloxyphenyl)fluorene] (BOPF) showed more stable and efficient device performances than poly(dioctylfluorene) [18]. The synthetic routes for the PBOPF, PPTZ, and fluorene-based random copolymers, poly(BOPF-*co*-PTZ), are given in Schemes 1 and 2.

2. EXPERIMENTAL

Syntheses of the Monomers and Polymers

2,7-Dibromo-9,9-bis(4′-n-octyloxyphenyl)fluorene (BOPF) and 3,7-Dibromo-10-(2′-ethylhexyl)-phenothiazine were synthesized according to procedures outlined in the literature. Copolymers were synthesized by Ni(0) mediated polymerization with the monomers, BOPF and PTZ according to procedures outlined in the literature [15,16]

Measurements and LED Fabrication

UV-vis and PL spectra were recorded on Jasco V-530 and Spex Fluorolog-3 spectrofluorometers. The molecular weights of the polymers were determined by gel permeation chromatography (GPC) on a Waters GPC-150C instrument, using tetrahydrofuran (THF) as the eluent and polystyrene as the standard. In the fabrication of the EL devices, a modified water dispersion of PEDOT [poly(3,4-ethylenedioxy-thiophene)] doped with poly(styrene sulfonate) (PSS) (Bayer AG, Germany) was used as a hole-injection/transport layer. Metal contacts (Ca) were deposited through a mask on top of the polymer films by vacuum evaporation at pressure below 4×10^{-6} Torr, yielding active areas of 4 mm^2. Additional encapsulating layers of Al ($\sim$200 nm) were thermally evaporated onto the Ca cathodes ($\sim$50 nm).

RESULTS AND DISCUSSION

The synthesized PBOPF and poly(BOPF-*co*-PTZ)s were soluble in common organic solvents such as THF, chloroform, and toluene. However, this solubility was found to decrease with increasing in the percentage of PTZ in the copolymer. The feed ratios of PTZ used in the present work were 3.0, 10.0, and 25 mol% of the total amount

of monomer and the resulting ratios of PTZ units in the poly (BOPF-*co*-PTZ)s were 10, 16, and 30 mol%, respectively. These results indicate that in polymerization reactions the PTZ comonomer is more active than the fluorene comonomer. All the polymers exhibited very good thermal stabilities, losing less than 2% of their weight on heating to about 390°C, as determined with TGA under a nitrogen atmosphere. The weight average molecular weights (M_w) of PBOPF, PPTZ and the copolymers were determined by GPC using a polystyrene standard, and were found to range from 25,000 to 50,000 with polydispersity indices ranging from 1.6 to 4.0.

Figure 1 shows the UV-vis absorption spectra of the thin films of PBOPF, PPTZ and the copolymers coated onto fused quartz plates. PBOPF showed a maximum absorption and absorption edge at 377 and 440 nm respectively. The UV-visible absorption peaks of the copolymer films become slightly blue-shifted as the fraction of PTZ in the copolymers increases. The optical band gaps of the polymers were determined from the absorption onset. The optical band gaps of PBOPF and PPTZ were found to be 2.92 and 2.77 eV, respectively. The band gaps of the copolymer films were found to decrease as the fraction PTZ in the copolymers increased. The optical band gaps of poly(90BOPF-*co*-10PTZ), poly(84BOPF-*co*-16PTZ) and poly(70BOPF-*co*-30PTZ) were found to be 2.82, 2.82, and 2.81 eV, respectively.

Figure 2 shows the PL emission spectra of the thin films of PBOPF, PPTZ and the copolymers coated onto fused quartz plates. The PBOPF

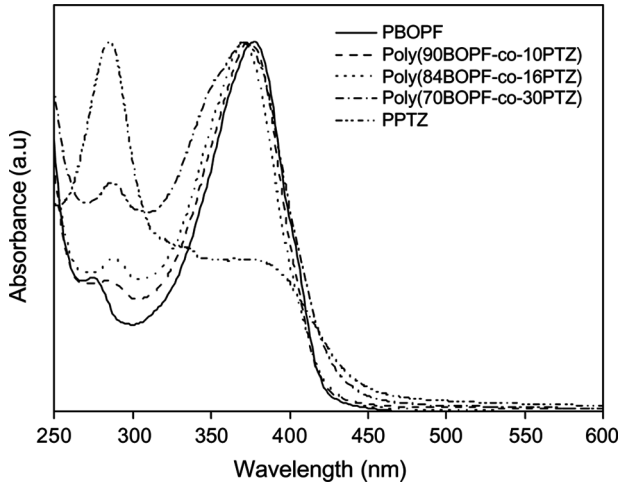


FIGURE 1 UV-visible absorption spectra of the polymer films.

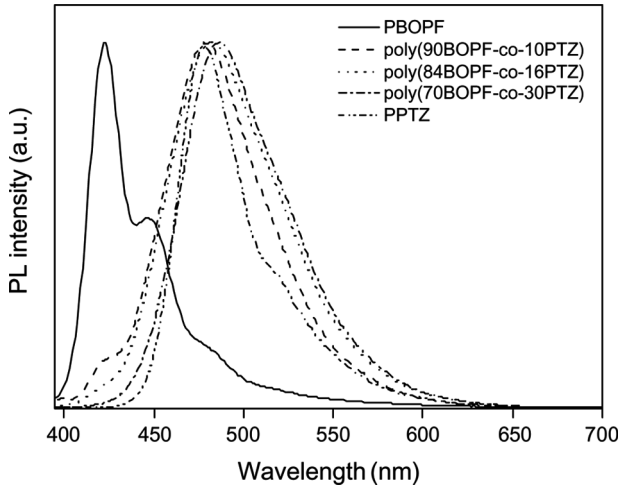


FIGURE 2 PL emission spectra of the polymer films.

homopolymer film showed a maximum PL emission in the blue region of the spectrum at 422 nm. The PL emission spectrum of the PPTZ film was slightly red-shifted from that of the PBOPF film and was exhibited peak emission at about 478 nm. The copolymer films exhibited peak PL emissions at almost the same wavelength as the PPTZ homopolymer film regardless of the copolymer composition. The results for molecular weights, actual compositions, UV-visible absorption, PL emission and optical band gap of the polymers are summarized in Table 1.

TABLE 1 Summary of the Molecular Weight and Physical Properties of PBOPF, PPTZ, and Copolymers

Copolymers	PBOPF	Poly(90BOPF-*co*-10PTZ)	Poly(84BOPF-*co*-16PTZ)	Poly(70BOPF-*co*-30PTZ)	PPTZ
M_w	50,000	37,000	31,000	29,000	25,000
PDI (M_w/M_n)	4.0	1.9	1.7	1.6	3.9
Feed y ratio (%)	–	3	10	25	–
Actual y ratio[a] (%)	–	10	16	30	–
UV_{max} (nm)[b]	377	378	371	371	285
PL_{max} (nm)[b]	422	481	482	486	478
Band gap (eV)	2.92	2.82	2.82	2.81	2.77

[a]The actual PTZ fractions in the copolymers were determined by elemental analysis of their nitrogen content.

[b]Measured for thin films on fused quartz plates.

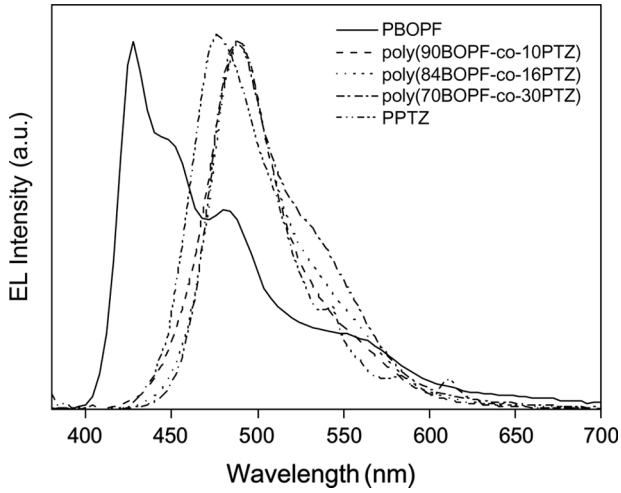


FIGURE 3 EL spectra of the devices using the polymers.

EL devices with the configuration ITO/PEDOT:PSS (50 nm)/ polymers (80 nm)/Ca (50 nm)/Al (200 nm) were fabricated and characterized as a function of applied voltage. The EL spectra of the devices are shown in Figure 3. The EL spectra of PBOPF, PPTZ, and copolymer devices are similar to the PL spectra of the corresponding polymer films.

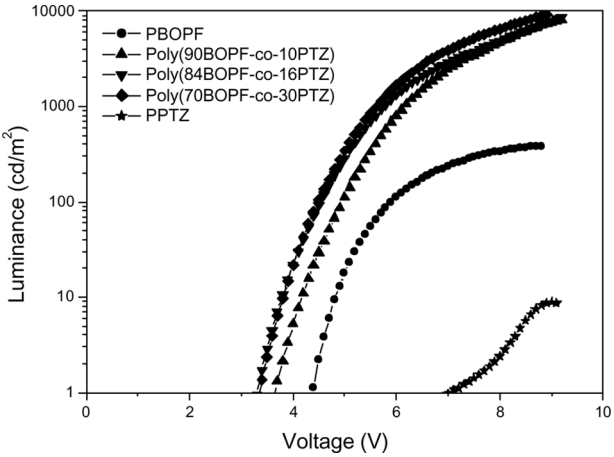


FIGURE 4 Voltage-luminance characteristics of the devices using the polymers.

TABLE 2 Summary of Characteristics of the EL Devices

Copolymers	PBOPF	Poly(90BOPF-*co*-10PTZ)	Poly(84BOPF-*co*-16PTZ)	Poly(70BOPF-*co*-30PTZ)	PPTZ
EL_{max} (nm)	428	488	488	488	476
$V_{turn\text{-}on}$ (V)	4.2	3.3	3.1	3.1	6.4
Maximum Brightness (cd/m^2)	375	8,200	8,600	9,200	9.0
Efficiency (cd/A)	0.184	2.712	2.831	2.278	0.002

Figure 4 shows the voltage-luminance characteristics of the EL devices. In the EL device constructed from the PPTZ homopolymer, the forward current increased with increasing in the forward bias voltage and the curve showed typical of diodes. Light emission from this device was observable at voltages greater than 6.4 V(@1 cd/m^2). The maximum brightness of the device was 9.0 cd/m^2 with a maximum luminous efficiency of 0.002 cd/A. Light emission from PBOPF homopolymer device was observable at voltages greater than 4.2 V (@1 cd/m^2). The maximum brightness of this device was 375 cd/m^2 with a luminous efficiency of 0.184 cd/A. Interestingly, all the EL devices constructed from the copolymers exhibited significantly better device performances than the devices constructed from the each PBOPF and PPTZ homopolymers. The EL devices constructed using the copolymers, the poly(84BOPF-*co*-16PTZ) exhibited a maximum brightness of 8,600 cd/m^2 and a maximum luminous efficiency of 2.83 cd/A. The characteristics of the EL devices are summarized in Table 2.

3. CONCLUSION

PBOPF, PPTZ, and poly(BOPF-*co*-PTZ) copolymers were successfully synthesized through the Yamamoto coupling reaction, and the light emission properties of these polymers were compared. The devices fabricated using the copolymers exhibited significantly enhanced device performances in both efficiency and brightness because of their enhanced hole injection and charge carrier balance.

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