



## Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl20>

### Synthesis and Electro-Optical Properties of Carbazole Containing Copolymers with Different Conjugated Structures for Polymer Light-Emitting Devices

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Version of record first published: 18 Mar 2009

To cite this article: Jin Woo Kim, Eun Jung Park, Eon Joo Lyu, Yun-Su Lee, Younghwan Kwon & Lee Soon Park (2009): Synthesis and Electro-Optical Properties of Carbazole Containing Copolymers with Different Conjugated Structures for Polymer Light-Emitting Devices, *Molecular Crystals and Liquid Crystals*, 499:1, 112/[434]-127/[449]

To link to this article: <http://dx.doi.org/10.1080/15421400802620030>

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## Synthesis and Electro-Optical Properties of Carbazole Containing Copolymers with Different Conjugated Structures for Polymer Light-Emitting Devices

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*New copolymers such as Poly(9-(4-(2-ethyl-hexyloxy)-3,5-dimethylphenyl)carbazole-alt-aminonaphtalene) [P1] and Poly(4-(bis-methylbiphenyl-alt-9H-carbazol-9-yl)benzenamine) [P2] with chromophores separated by non-conjugated methylene spacers, and Poly(4-(dioctylfluorene-alt-9H-carbazole-9yl)benzenamine) [P3] based on alternating fluorene and amine units in the polymer backbone were synthesized by palladium catalyzed polycondensation reaction. Optical properties of these polymers were characterized in terms of UV/visible absorption and photoluminescence (PL) emission in solution and film state. Maximum PL emission ( $\lambda_{max, PL}$ ) of synthesized copolymers were observed in the blue region of 426 nm–460 nm in solution state, but the three polymers all showed large red shift in film state with the green emission. The electro-optical properties of these polymers in polymer light-emitting diode (PLED) devices were investigated from the viewpoint of utilizing the new polymers as emitting layer and hole injection/transport layer. The polymer P3 was found to function both as hole injection and hole transport layer with performance better than that of well known PEDOT:PSS hole injection layer material.*

**Keywords:** amine; carbazole; fluorine; non-conjugated spacer; palladium-catalyzed polycondensation reaction; polymer light-emitting diode

This work was supported by the Advanced Display Manufacturing Research Center (ADMRC) Program of the Ministry of Commerce, Industry and Energy of Korea.

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## INTRODUCTION

Organic light-emitting diodes (OLEDs) and polymeric light-emitting diodes (PLEDs) are currently the subject of an intense research effort due to their promise as devices for new full-color flat panel display and luminating applications [1,2]. Electroluminescent conjugated polymers have the possibility of uniformly coating various layers in OLED by low cost solution process in addition to the ability of fine-tuning optical and electrical properties by varying their structures [3,4]. Recently increased interest has been paid to carbazole- or fluorene-based polymers for PLED devices. Polymers containing carbazole moiety have been studied widely because they have a good charge – transporting property, wide band gap, and blue emission [5]. The introduction of charge-transporting group into the  $\pi$ -conjugated polymers has also been the subject of active research [6,7]. Several polymers containing an arylamine group were synthesized by Suzuki coupling and Witting-Horner reaction for the improvement of hole-transport property [8–11].

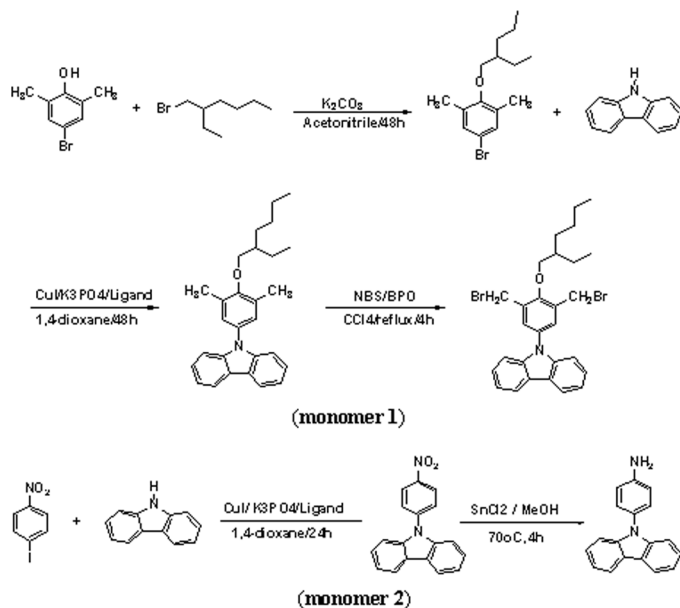
In this paper, we synthesized some new polymers with aromatic amine repeat unit and carbazole moiety in a non-conjugated structure for the blue emitting layer with good charge transporting property. We also synthesized new conjugated copolymer based on alternating fluorene and arylamine units by using Pd-catalyzed polycondensation reaction for investigating the effects of the incorporation of aromatic amines into  $\pi$ -conjugated copolymer system. These polymers were characterized in terms of their UV/visible and photoluminescence (PL) properties in solution and solid film state. The effect of the polymer structure on the electro-optical property of OLED devices was examined from the viewpoint of utilizing the new polymers as emitting layer and hole injection/transport layer.

## EXPERIMENTAL

### Synthesis of Monomers

#### ***9-(4-(2-Ethylhexyloxy)-3,5-dibromomethylphenyl)carbazole (monomer 1)***

Was synthesized according to the previously reported process [12–14]. As shown in Scheme 1(a), 4-bromo-2,6-dimethylphenol (0.02 mol) in 50 ml of acetonitrile was added to a suspension of potassium hydroxide (0.06 mol) in 200 ml of acetonitrile which was prepared by vigorous stirring for 30 min under nitrogen. 2-Ethylhexyl bromide (0.02 mol) was added to the solution, followed by reflux for 48 hr. Potassium



**SCHEME 1** Synthesis of the monomers.

hydroxide was filtered out, and the solvent was evaporated, then the crude product was washed with water and dried with magnesium sulfate. The orange color intermediate, 5-bromo-2-(2-ethylhexyloxy)-1,3-dimethylbenzene was obtained by silica column chromatography (eluent: hexane) Yield: 60%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$ : 7.15 (2H, Ar-H), 3.6 (2H, -O-CH<sub>2</sub>-), 2.26 (6H, Ar-CH<sub>3</sub>), 2.18 (9H, -CH-, -CH<sub>2</sub>), 0.91 (6H, -CH<sub>3</sub>).

In the second step, 5-bromo-2-(2-ethylhexyloxy)-1,3-dimethylbenzene (112.79 mmol), carbazole (15.25 mmol),  $\text{K}_2\text{PO}_4$  (26.72 mmol), CuI (0.64 mmol) and trans-1,2-cyclohexane diamine (2.54 mmol) were used to obtain a white solid product, 9-(4-(2-ethylhexyloxy)-3,5-dimethyl-phenyl)carbazole according to the Ullmann reaction. Yield: 30%,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$ : 7.38 (4H, Ar-H), 7.26 (4H, Ar-H), 7.16 (2H, Ar-H), 3.6 (2H, -O-CH<sub>2</sub>-), 2.30 (6H, Ar-CH<sub>3</sub>), 2.18 (9H, -CH-, -CH<sub>2</sub>), 0.91 (6H, -CH<sub>3</sub>).

In the third step a mixture of 9-(4-(2-ethylhexyloxy)-3,5-dimethyl-phenyl)carbazole (3.68 mmol), NBS (8.09 mmol) and BPO (0.1618 mmol) were added to  $\text{CCl}_4$  at room temperature. The following reaction and workup were carried out as reported previously [13,14]. The orange liquid product, N-4-(2-ethylhexyloxy)-3,5-dibromomethylphenylcarbazole was obtained in 50% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$ : 7.48

(4H, Ar-H), 7.45 (4H, Ar-H), 7.35 (2H, Ar-H), 4.6 (4H, CH<sub>2</sub>Br-), 3.96 (2H, -O-CH<sub>2</sub>-), 2.25 (9H, -CH-, -CH<sub>2</sub>), 0.91 (6H, -CH<sub>3</sub>).

### ***N*-(4-aminophenyl)-carbazole (monomer 2)**

A 250 ml, round-bottom flask was equipped with a reflux condenser and was then flushed with dry nitrogen. 4-Iodonitrobenzene (40 mmol), carbazole (30.6 mmol) and potassium phosphate (84 mmol) were added to 150 ml of 1,4-dioxane at room temperature. After stirring for 40 min, CuI (0.8 mmol) and trans-1,2-cyclohexanediamine (4.8 mmol) were added to the mixture. The reaction mixture was stirred for 24 hr at refluxed temperature. After cooling down to room temperature, the resulting mixture was filtered. 1,4-Dioxane was evaporated, and ethyl acetate was added. The mixture was washed with distilled water, and dried with MgSO<sub>4</sub>. *N*-(4-nitrophenyl)-carbazole was obtained through column chromatography (hexane:ethylacetate = 20:1) with 20% of yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ: 8.58 (1H, Ar-H), 8.55 (1H, Ar-H), 8.26 (1H, Ar-H), 8.23 (1H, Ar-H), 8.01 (1H, Ar-H), 7.98 (1H, Ar-H), 7.60 (1H, Ar-H), 7.58 (1H, Ar-H), 7.51 ~ 7.45 (2H, Ar-H), 7.39 ~ 7.33 (2H, Ar-H).

The synthesized intermediate, *N*-(4-nitrophenyl)-carbazole (NPHCZ) (6.9 mmol), SnCl<sub>2</sub> (42.1 mmol) and EtOH (25 ml) was heated at 70°C for 4 hr 30 min. After the mixture was cooled to room temperature, 1 M NaOH solution was added until the mixture became basic. After extraction with ethyl acetate, the combined organic layers was washed and treated with MgSO<sub>4</sub> and then dried in vacuum. The deep brown product, monomer 2, was obtained with 65% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ: 8.15 (1H, Ar-H), 8.12 (1H, Ar-H), 7.42 ~ 7.22 (8H, Ar-H), 6.87 (1H, Ar-H), 7.84 (1H, Ar-H), 3.81 (2H, Ar-NH<sub>2</sub>).

### **Polymerization**

Three new polymers were synthesized by palladium-catalyzed polycondensation reaction. A mixture of **monomer 1** (3.6 mmol) and 1-naphtylamine (3.6 mmol) was dissolved in toluene (40 ml). Catalysts consisting of NaO-*t*-Bu (10.8 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (0.09 mmol), P(*t*-Bu)<sub>3</sub> (0.55 mmol) was added to the monomer solution at room temperature and then stirred at 100°C for 48 hr. After cooling to room temperature, the mixture was quenched by adding aqueous ammonia (100 ml) and the product was extracted with chloroform solvent. The organic fraction was concentrated and reprecipitated from CHCl<sub>3</sub>/methanol several times. Then product [**P1**] was filtered and dried in vacuum. Poly(4-(bismethylbiphenyl-*alt*-9H-carbazol-9-yl)benzenamine) [**P2**] was obtained from **monomer 2** (CYBZ) (4.4 mmol) and 4,4'-bis

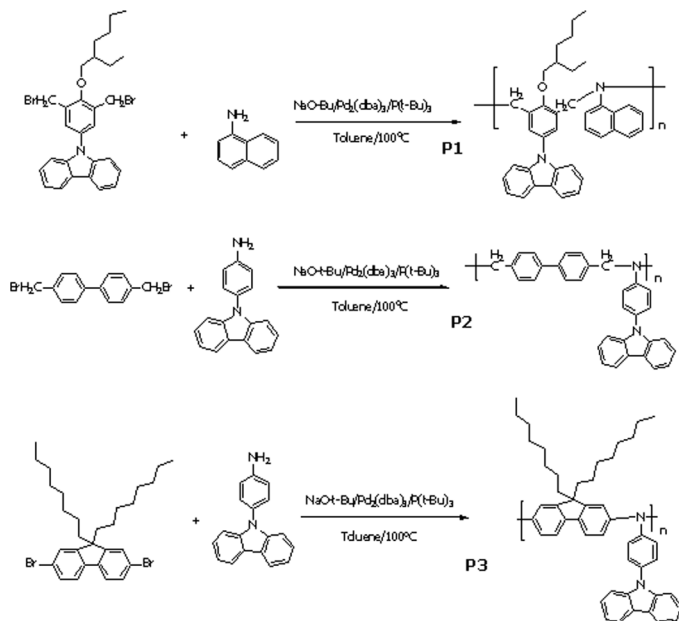
(bromomethyl)biphenyl (4.4 mmol) by same reaction as polymer **P1**. Poly(9,9-dioctyl-fluorene-*alt*-9H-carbazol-9-yl)benzenamine [**P3**] obtained from **monomer 2** (CYBZ) (3.8 mmol) and dioctylfluorene (3.8 mmol) by same reaction as shown in Scheme 2 [15].

## Fabrication of PLED

PLEDs with three different configurations (1) ITO/PEDOT:PSS/polymer **P1**, **P2**, or **P3** (EML)/BCP/Alq<sub>3</sub>/LiF/Al, (2) ITO/PEDOT:PSS/polymer **P1**, **P2**, or **P3** (HTL)/Alq<sub>3</sub>/LiF/Al and (3) ITO/polymer **P1**, **P2**, or **P3** (HIL)/Alq<sub>3</sub>/LiF/Al were fabricated by spin coating and thermal evaporation method by using OLED device fabrication system (Sunic Plus 200).

## Measurements

Infrared spectra were obtained with a JASCO FT-IR 620 spectrometer and <sup>1</sup>H-NMR spectra was recorded on a Bruker 400 NMR spectrometer. The average molecular weight (Mw) of the polymers were evaluated using gel permeation chromatography (GPC, Waters,



**SCHEME 2** Synthesis of the polymers.

alliance 2000, THF, polystyrene universal calibration) at room temperature. UV-visible absorption spectra and photoluminescence spectra of synthesized product were measured on a JASCO V-650 spectrometer and JASCO FP-6500 fluorescence spectrometer, respectively. The ionization potential (IP) of polymers was obtained using atmospheric photoelectron spectroscopy (Riken Keiki AC-2). Electroluminescence (EL) spectra and color coordinates were measured by using Spectroscan PR 650 (Photoresearch Inc.). Current and luminance vs. voltage profiles were obtained by using a dc power supply connected with model 8092 A digital multimeter (Hyun Chang Product Co. Ltd) and luminance meter (Minolta LS-100), respectively.

## RESULTS AND DISCUSSION

### Synthesis and Characterization

Two monomers, 9-(4-(2-ethylhexyloxy)-3,5-dibromomethylphenyl) carbazole [**monomer 1**] and N-(4-aminophenyl)-carbazole [**monomer 2**] were synthesized through several steps with a moderate yield as presented in Scheme 1. The polymers (**P1** and **P2**) with carbazole ring and aromatic amine containing methylene spacer unit, and polymer (**P3**) based on fluorene and aromatic amine unit in the polymer backbone were obtained in good yield by using Pd-catalyzed polycondensation as shown in Scheme 2. FT-IR spectra of polymer **P1** and **P2** exhibited strong absorption peaks at  $1230\text{ cm}^{-1}$  coming from tertiary aliphatic amine in addition to the peak at  $1315\text{ cm}^{-1}$  due to tertiary aromatic amine. Polymer **P3** showed only tertiary aromatic amine absorption peak at  $1307\text{ cm}^{-1}$ . The carbazole and methylene groups in **P1** and **P2** polymers and fluorene group in **P3** were also confirmed in the FT-IR spectra.

All polymers showed increased solubility in common organic solvents, due to the presence of long alkyl groups such as 2-ethylhexyl and octyl groups. They were found to be soluble in chloroform, tetrachloroethane, toluene and THF. The weight-average molecular weights (Mw) of synthesized polymers, **P1**, **P2** and **P3**, determined by GPC using polystyrene as the standards, were summarized in Table 1. As shown in Table 1 three polymers have relatively low molecular weights, which might be caused by steric effect of twisted conformation between bulky carbazole and aryl groups. Copolymers, however, were easily spin coated onto the ITO substrate, and were found to produce transparent and homogeneous thin film.



TABLE 1 Electro-Optical Properties of the Polymers

Polymer	Mw	Solution (10 <sup>-4</sup> M TCE)			Solid state on glass				$\phi_s$ (%) <sup>a</sup>	Band gap (eV) <sup>d</sup>	HOMO (eV) <sup>b</sup>	LUMO (eV) <sup>c</sup>
		UV abs. (nm)	PL $\lambda$ max (nm)	FWHM (nm)	UV abs. (nm)	PL $\lambda$ max (nm)	FWHM (nm)					
P1	4,300	342	460	119	343	460, 512	146	0.68	3.32	5.30	1.98	
P2	4,900	341	436	97	342	527	92	0.58	3.06	5.39	2.33	
P3	4,500	357	426	43	372	456	109	2.80	2.88	5.33	2.45	

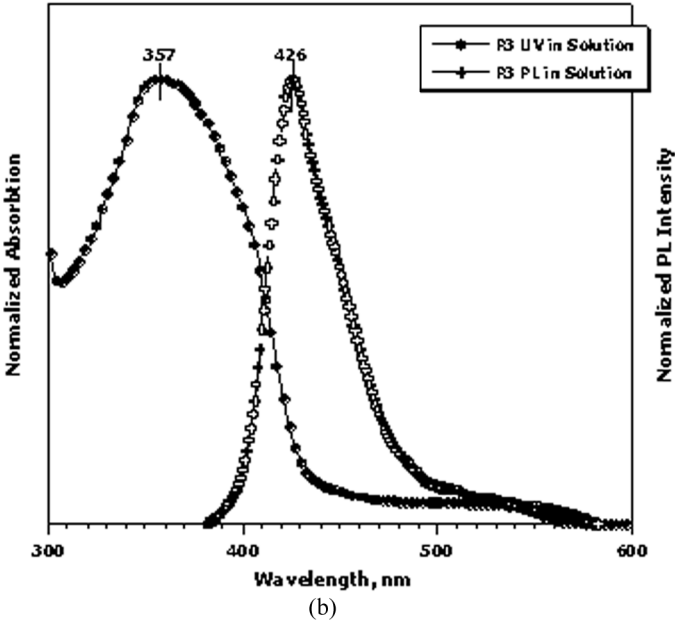
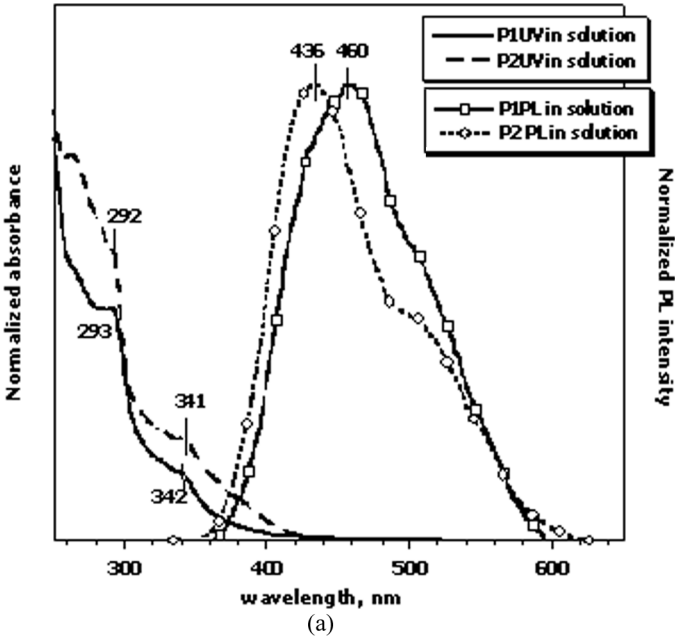
UV<sub>abs</sub>: The wavelength of the absorbance value.  
PL  $\lambda$ max: The wavelength of the maximum fluorescence.  
 $\phi_s$ : quantum yield of samples in THF solution.  
<sup>a</sup>Calculated from the cutoff wavelength of UV-vis absorption.  
<sup>b</sup>Measured by a RIKEN Keiki AC-2.  
<sup>c</sup>Estimated from the HOMO and band gap.

## Optical and Electrochemical Properties

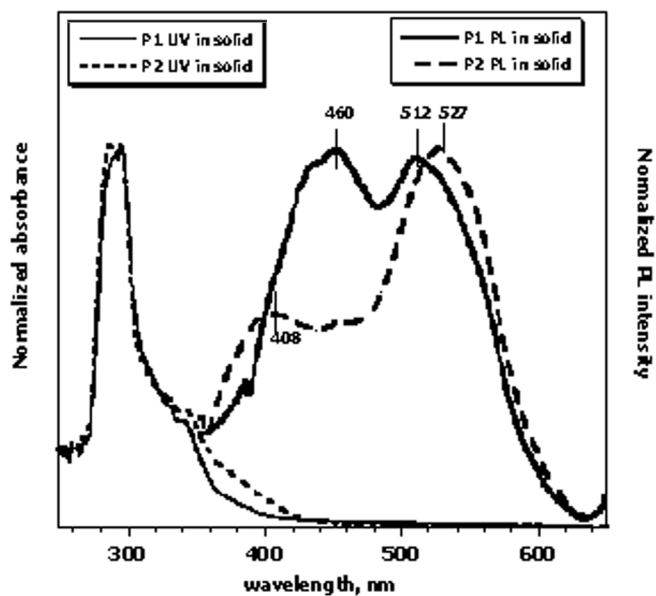
Figures 1(a) and (b) exhibit UV/visible absorption and PL emission spectra of the synthesized polymers in dilute 1,1,2,2-tetrachloroethane (TCE) solution, respectively. As shown in Figure 1(a), UV/visible absorption maxima ( $\lambda_{\text{max,UV}}$ ) of copolymers, **P1** and **P2**, with non-conjugated spacer appeared at 293, 342 nm and 292, 341 nm, respectively. On the other hands, the polymer **P3** exhibited maximum absorption peak at 357 nm due to extended conjugation. The red shifted absorption peak of **P3**, compared to polymer **P1** and **P2** also implied that the band gap of **P1** and **P2** is larger than that of **P3** polymer. When excited at their  $\lambda_{\text{max,UV}}$ , polymers **P1**, **P2**, and **P3** showed maximum PL emission peaks ( $\lambda_{\text{max,PL}}$ ) in the blue region of 460 nm, 436 nm and 426 nm, respectively. Polymer **P1** and **P2** showed large Stoke's shift compared to **P3**, which may be explained by the increased transfer in the vibrational energy levels owing to free rotations through the single bonds provided by the methylene spacers. All of polymers exhibited longer PL emission peak in the film state than in solution, as shown in Figures 2 (a) and (b). In general,  $\pi$ -conjugated polymers exhibit increased full width at high maximum(FWHM) due to the stacked  $\pi$ -aggregates in solid film compared to the dilute solution [16]. Such aggregation leads to red-shifted emissions with low quantum efficiencies. As shown in Figure 2(a), **P2** exhibited large red shift in film state due to excimer cluster or aggregate formation. This might be originated from less sterically hindered simple repeating units of **P2**, compared to **P1** and **P3** polymers. The extent of red shift in PL emission of **P3** was a little smaller than **P1** and **P2** polymers. This small red shift and single PL peak of **P3** may be due to the presence of bulky fluorene repeat unit in the polymer chain. This may also led to higher quantum efficiency than other polymers, as shown in Table 1. The electro-optical and other characterization data of polymers are summarized in Table 1. As shown in Figure 3, HOMO energy levels of **P1**, **P2**, and **P3** were estimated to be 5.30, 5.39 and 5.33 eV, and LUMO energy levels were determined to be 1.98, 2.33 and 2.45 eV, respectively. This indicates that the optical band gap of the polymer **P1** with non-conjugated segment is larger than that of **P2** or **P3** polymer. It is also noted from Figure 3 that **P2** has lower energy barrier for transporting holes from HIL or ITO than **P1** or **P3**. This property is discussed in terms of performance of OLED devices.

## Electroluminescent Properties

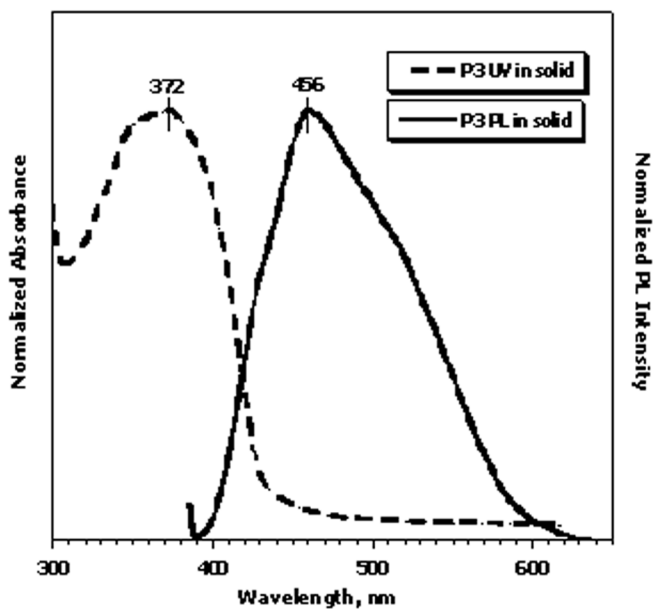
To investigate EL properties of the polymers, we first fabricated multilayered PLED devices with ITO/PEDOT:PSS/Polymer (**P1**, **P2**,



**FIGURE 1** UV-Vis and PL spectra in TCE solution; (a) P1 and P2 polymer (b) P3 polymer.

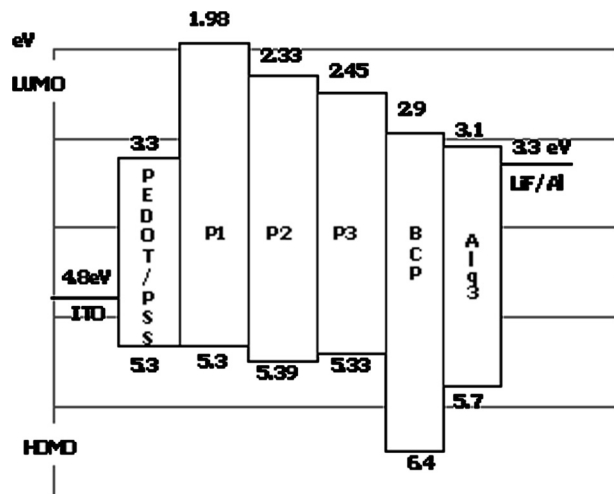


(a)



(b)

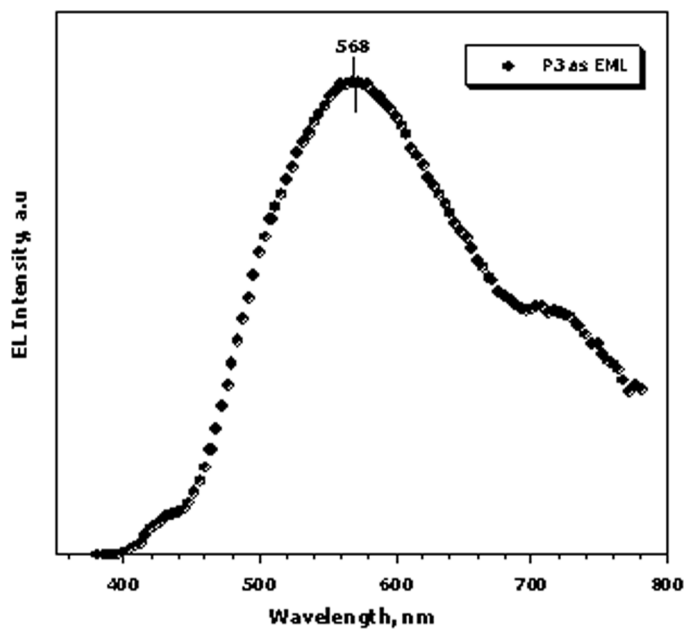
**FIGURE 2** PL spectra of the polymers with fluorene and aromatic amine in Solid film state.



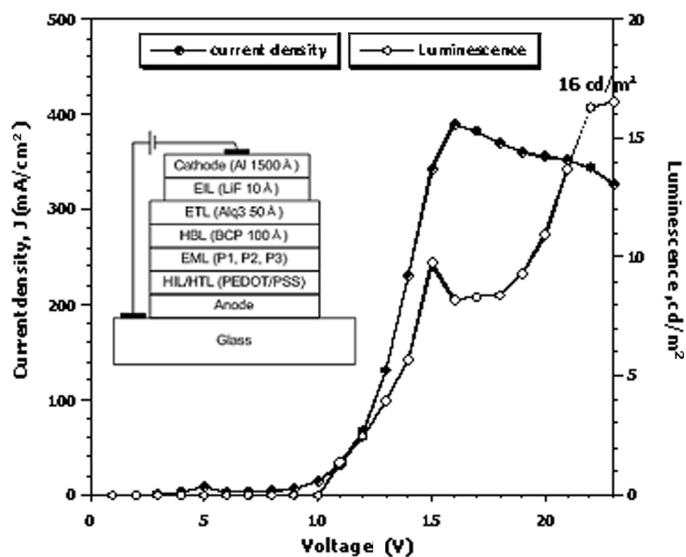
**FIGURE 3** The energy band gap of synthesized polymers.

or **P3**)/BCP/Alq<sub>3</sub>/LiF/Al configuration by using the synthesized polymers as light emitting layer (EML) as shown in Figure 4. When **P1** and **P2** were used as EML, the resulting PLED exhibited very low light emission due to the presence of methylene spacer in the polymer chain which may result in low charge (electron) transport. **P3** exhibited a little luminance of 16 cd/m<sup>2</sup> at 23 V and maximum EL peak at 568 nm. This may be owing to the lower LUMO level of **P3** compared to polymer **P1** and **P2**, inducing electron injection into the emitting layer.

Then we investigated the hole injection and transporting property of the synthesized polymers. Since the HOMO energy levels of the polymers were very close to that of PEDOT:PSS, well known hole injection material. We fabricated multilayered PLED devices with ITO/PEDOT: PSS/polymer (**P1**, **P2**, or **P3**)/Alq<sub>3</sub>/LiF/Al configuration as shown in Figure 5. In this PLED devices Alq<sub>3</sub> was used as an emitting layer, PEDOT:PSS as hole injection layer (HIL) and synthesized polymer as an hole transport layer (HTL). For comparison, a typical device without the synthesized polymer (HTL) was made as a reference. The devices showed EL emission of Alq<sub>3</sub> in the range from 528 to 532 nm, as shown in Figure 5(a). I-V-L profiles of the PLED devices were also shown in Figure 5(b). The turn on voltages of the devices containing **P1**, **P2**, and **P3** as HTL were 11 V, 9 V and 10 V, respectively. The device fabricated with **P3** as HTL resulted

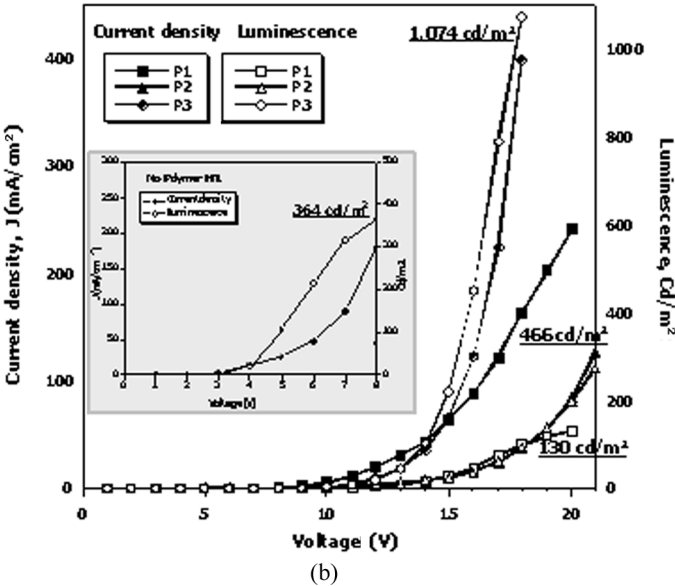
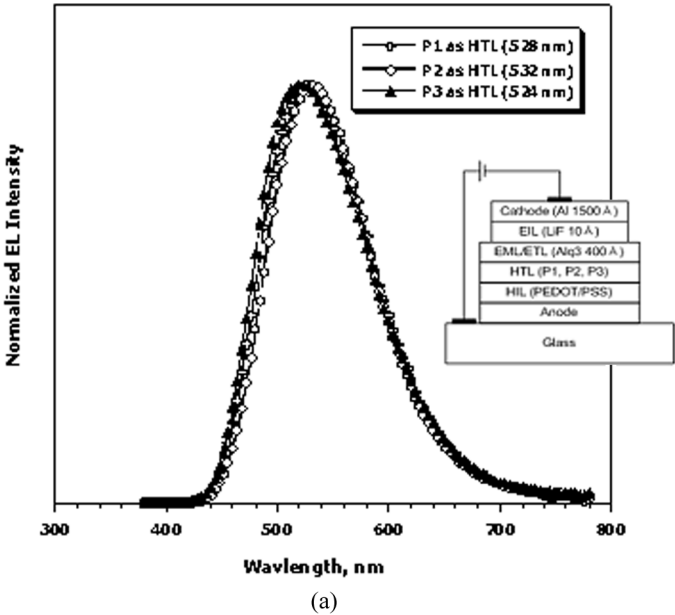


(a)

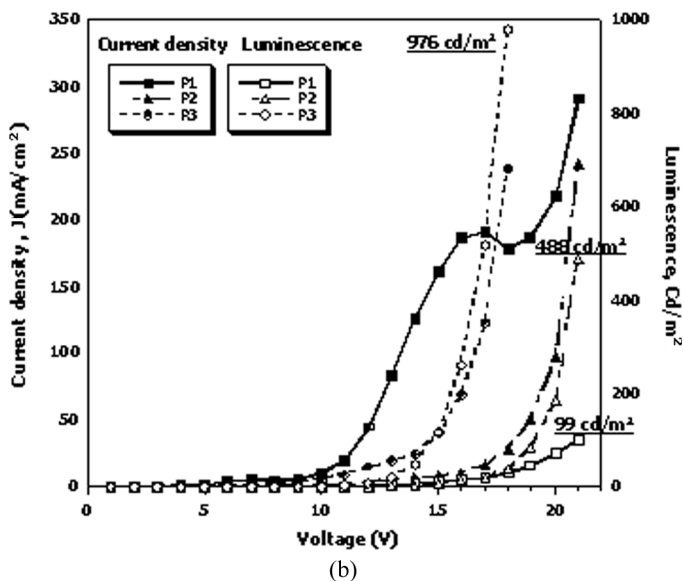
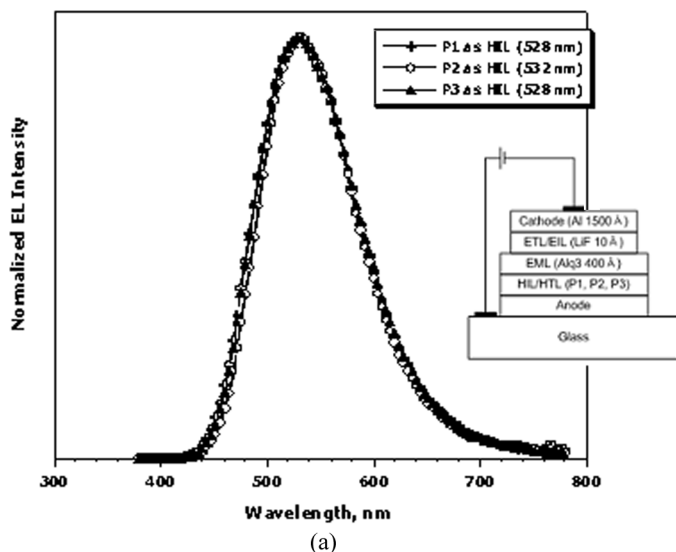


(b)

**FIGURE 4** (a) EL spectra of Polymer **P1**, **P2**, and **P3** (b) IVL characteristics of Polymer **P1**, **P2**, and **P3** as a EML material in the multilayered PLEDs.



**FIGURE 5** (a) EL spectra of Polymer P1, P2, and P3 (b) IVL characteristics of Polymer P1, P2, and P3 as a HTL interlayer as compared reference devices in the multilayered PLEDs.



**FIGURE 6** (a) EL spectra of Polymer **P1**, **P2**, and **P3** (b) IVL characteristics of Polymer **P1**, **P2**, and **P3** as a HIL interlayer without PEDOT/PSS layer in the multilayered PLEDs.



in much better EL performance with  $1,074 \text{ cd/m}^2$  at 18 V than the devices containing **P1** ( $130 \text{ cd/m}^2$ , 20 V) and **P2** ( $466 \text{ cd/m}^2$ , 21 V) with non-conjugated segments. The reference PLED with ITO/PEDOT:PSS/Alq3/LiF/Al configuration exhibited maximum luminance of  $364 \text{ cd/m}^2$  at 8 V. Thus it may be concluded that the combination of PEDOT:PSS(HIL)/polymer **P3** (HTL) increased the recombination of holes and electrons in the Alq3 light emitting layer with proper energy level and balanced charge carrier mobilities.

We also fabricated devices with ITO/polymer (**P1**, **P2**, or **P3**)/Alq3/LiF/Al configuration in order to replace typical HIL material, PEDOT:PSS, with the synthesized polymers. As shown in Figure 6(a), Alq3 emission was observed at the usual emission peak. The maximum luminescence of devices fabricated with **P1** or **P2** both as hole injection and transport layer were  $99 \text{ cd/m}^2$  at 21 V and  $488 \text{ cd/m}^2$  at 21 V, compared to  $364 \text{ cd/m}^2$  at 8 V in the PLED device containing only PEDOT:PSS as HIL/HTL layer. On the other hand, the device fabricated with **P3** as HIL/HTL exhibited  $976 \text{ cd/m}^2$  of maximum luminescence at 18 V. It was of interest to note that polymer **P3** could perform both as hole injection and hole transport layer and also the combined performance of **P3** as HIL/HTL was better than that of PEDOT/PSS which is usually used as hole injection layer in the PLED devices.

## CONCLUSIONS

New copolymers such as Poly(9-(4-(2-ethyl-hexyloxy)-3,5-dimethylphenyl)carbazole-*alt*-amino naphthalene) [**P1**], Poly(4-(bis-methylbiphenyl-*alt*-9H-carbazol-9-yl)benzenamine) [**P2**] and Poly(4-(dioctylfluorene-*alt*-9H-carbazole-9yl)benzenamine)[**P3**] were obtained by using Pd-catalyzed polycondensation reaction. The synthesized copolymers were soluble in common organic solvents and showed good film forming property. These polymers showed  $\lambda_{\text{max, PL}}$  value in the blue emission region at 460 nm, 436 nm and 426 nm, respectively, in solution state. The three polymers exhibited large red shift in the film state by the formation of  $\pi$ -stacking structures. The polymers were not useful as light emitting layer materials, especially polymer **P1** and **P2** which had non-conjugated spacers. The synthesized polymers especially **P3** were found to function as both hole injection and hole transport material and the combined performance of **P3** as HIL/HTL was higher than that of PEDOT:PSS mainly used as HIL in the PLED devices.

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