Synthesis and Properties of Blue Emitting Polymers Containing Carbazole Groups

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Abstract : Blue-emitting polymers containing carbazole units in main chains were synthesized by palladium catalyzed polycondensation of aniline with dibromo-substituted monomers such as 3,6-dibromocarbazole, *N*-(2-ethylhexyl)-3,6-dibromocarbazole, and bis[6-bromo-*N*-(2-ethylhexyl)-carbazole-3-yl], respectively. All synthesized polymers exhibited relatively good solubility in common organic solvents, considerable molecular weights and high resistance to thermal degradation. From UV-Vis absorption and photoluminescence (PL) spectra of these solution-processable polymers, $\lambda_{max,UV}$ were in the range of 290 ~ 340 nm and $\lambda_{max,PL}$ were in the blue emission range of 440 ~ 478 nm. The polymers had HOMO energy (-5.19 ~ -5.64 eV) and wide band gap energy (2,91 - 3.42 eV).

Key Words : Carbazole, Blue emission, palladium catalyzed polycondensation

1. Introduction

Light emitting diodes have found important applications in the information vision, communication and other display-related fields. Recently, worldwide attention to polymer light emitting diodes (PLEDs) has been paid as a candidate for a new generation of emissive flat panel displays, which offer a low-cost, simple-layer and thin film approach with reduced complexity of manufacturing process [1]. Several families of polymers have been widely studied such as poly(*p*-phenylene vinylene), fluorine-based poly(iminoarylenes), polyfluorene, carbazole-based polymers, and so on. It was reported that carbazole-based polymers exhibited good optical properties and hole-transporting ability in PLEDs. Moreover, conjugated polycarbazole showed blue emission with a wide band gap energy (3.2 eV) [2,3]. Therefore, it can be used as a host matrix polymers in doped PLEDs.

In this paper, we have designed a new series of carbazole-based polymers consisting of at least one carbazole unit and one arylamine group in the polymer backbone. Three different types of polymers were synthesized by palladium catalyzed polycondensation of dibromo-substituted carbazole and aniline. In addition, optical and electrochemical properties of the synthesized polymers were also studied.

2. Experimental

Materials: 3,6-Dibromocarbazole (monomer 1) (97%), 2-ethylhexyl bromide (95%), potassium carbonate, aniline (99.5%), sodium *tert*-butoxide (NaO-*t*-Bu, 97%), tris-*tert*-butyl-phosphine ($P(t\text{-}Bu)_3$, 90%) and tris(dibenzylidene-acetone) dipalladium(0) ($Pd_2(dba)_3$) were purchased from Aldrich Co. *N*-(2-ethylhexyl)-3,6-dibromo-carbazole (monomer 2) and bis[6-bromo-*N*-(2-ethylhexyl)-carbazole-3-yl] (monomer 3) were synthesized by the methods described previously [4,5].

Polymerization: The synthetic route to the polymers using palladium catalyzed polycondensation are depicted in Figure 1. 3,6-Dibromocarbazole and aniline were dissolved in toluene. NaO-*t*-Bu, $P(t\text{-}Bu)_3$, and $Pd_2(dba)_3$ were sequentially added to the solution at room temperature. The reaction mixture was stirred at 100 ℃ for 48 h under N_2. After cooling to room temperature, the mixture was quenched by adding aqueous ammonia and the product was extracted with $CHCl_3$. The organic fraction was concentrated and reprecipitated from $CHCl_3$/methanol several times. Then, the products were filtered and dried in vacuum.

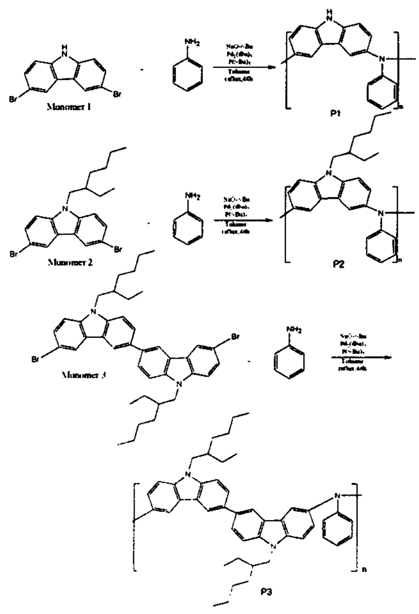

Figure 1. Synthetic route to the polymers.

Characterization: Number and weight average molecular weights of synthesized polymers were measured by using Waters gel permeation chromatography (GPC) equipped with Styragel HR 5E column using THF as an eluent against polystyrene standards at room temperature. Thermogravimetric ananlysis (TGA) was performed on a Seiko EXSTAR 6000 TG/DTA 6300 at a heating rate of 20 ℃/min. under N_2 atmosphere. UV-Visible absorption spectra were taken by using Shimadzu UV-2100. The photoluminescence (PL) spectra excited by He-Cd laser at 325 nm were monitored with Optical Multichannel Analyzer (Laser Photonics, OMA system). The ionization potential (IP) was measured by using a photoelectron spectroscopy (Riken Keiki AC-2).

3. Results and Discussion

From GPC measurement, molecular weights and molecular weight distributions of synthesized polymers were obtained. Weight average molecular weights of the polymers were in the range of 2,240 g/mol ~ 7,130 g/mol. Due to better solubility of P2 than P1 and P3 in toluene, P2 exhibited high molecular weight. It was confirmed from TGA results that all polymers had high resistance to thermal degradation. At 400 ℃, the weight losses of P1, P2, and P3 were 3.6%, 0.23%, and 0.7%, respectively.

UV-Vis absorption spectra and PL spectra of polymers are presented in Figure 2 and Figure 3, respectively. In dilute solution, $\lambda_{max,UV}$ were in the range of 290 ~ 340 nm and $\lambda_{max,PL}$ were in the blue emission range of 440 ~ 478 nm. P2 and P3 showed narrow and sharp peaks, compared to P1. UV-Vis absorption and PL spectra of P2 and P3 were similar, due to structural similarity in polymer main chain.

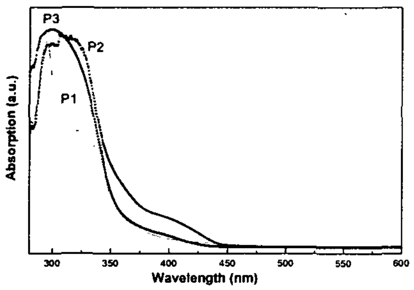

Figure 2. UV-Vis absorption spectra of the polymers.

Electrochemical properties of polymers are shown in Table 1. Band gap energy of three polymers was calculated from the cross point of UV-Vis spectrum and PL spectrum. HOMO energy was obtained from ionization potential.

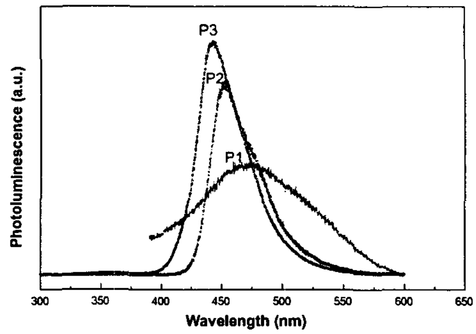

Figure 3. PL spectra of the polymers.

Table 1. Electrochemical properties of the polymers

Polymers	Band gap energy (eV)	HOME (eV)	LUMO (eV)
P1	3.42	-5.64	-2.22
P2	2.91	-5.19	-2.28
P3	3.02	-5.25	-2.19

4. Conclusions

The synthesis of a series of blue emitting polymers was achieved by palladium catalyzed polycondensation of aniline and three different types of dibromo-substituted carbazole-based monomers, respectively. All the properties measured in this study showed that the polymers are promising materials for fabrication of PLEDs and should be carefully investigated in the future.

Acknowledgments

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