Optical Properties of Poly(N-arylcarbazole-alt-aniline) Copolymers For Polymer Light Emitting Devices

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Abstract

Thermally stable and solution-processable poly(N-arylcarbazole-alt-aniline) copolymers with high structural integrity were synthesized in good yields via palladium-catalyzed polycondensation of aniline with corresponding N-arylcarbazole monomers such as N-(2-ethylhexyloxyphenyl)-3,6-dibromocarbazole,bis[6-bromo-N-(2-ethyl hexyloxyphenyl)carbazole-3-yl] and N-(4-(2-ethylhexyl)-3,5-dibromomethylene-phenyl) carbazole, respectively. The optical and electrochemical properties of these copolymers were measured and compared with those of poly(N-alkylcarbazole-alt-aniline) copolymer. All synthesized poly(N-arylcarbazole-alt-aniline) copolymers showed maximum UV-Vis absorption peaks at around 300 nm in THF solution, and exhibited maximum photoluminescence peaks in the blue emission range from 430 to 460 nm. It was also found that poly(N-arylcarbazole-alt-aniline) copolymers had wider band gap energy than poly(N-alkylcarbazole-alt-aniline) copolymer.

Keywords: N-arylcarbazole, triarylamine, blue emission, host matrix

1. Introduction

Since the first report on conjugated polymers as a new class of electroluminescent materials for diodes, the research in this field has been advancing rapidly over the past 15 years [1-3]. So far, a lot of polymers such as poly(phenylene vinylene)s [4], polyphenylenes [5] and poly (fluorene-2,7-diyl) [6] have been paid much attention and have been studied as promising materials for commercial displays. Due to low cost and simplified manufacturing process, polymer light-emitting diodes (PLEDs) have been commercially applied in the fields of display manufacture, digital cameras, portable electronics, consumer goods, automotive systems and communication systems [7].

Carbazole-containing polymers have been widely investigated, since the discovery of good photoconductive properties of poly (N – vinylcarbazole) (PVK) [8,9]. It has been generally known that carbazole systems have chemical stability, hole-transporting property and wide band gap energy close to blue light emission. Among them,

N-arylcarbazoles, resembling the structure of substituted triphenylene derivatives, could be obtained by introducing a phenyl substituent on N atom of carbazole units [10,11]. Martínez et al. reported the synthesis of a series of different polysubstituted N-arylcarbazole derivatives by a highly efficient carbazole arylation method [12]. Wong et al. prepared new 9,9-dihehexylfluorene/9-arylcarbazole hybrid copolymers [13]. They pointed out that incorporating the electron-rich N-arylcarbazole groups into polyfluorene main chain can increase the HOMO levels as well as retain their blue emission. They also noted that advantage of the robust N-arylcarbazole groups increased the thermal stability and glass transition temperature of the resulting polymers compared to the N-alkyl-substituted polymers.

In this paper, we synthesized and characterized different types of poly (N – arylcarbazole – alt – aniline) copolymers as blue-emitting host matrix polymers for PLEDs. The optical and electrochemical properties of these copolymers were discussed with those of N-alkyl substituted polymer.

2. Experimental

Synthesis of Monomers

N-(2-ethylhexyl)-3,6-dibromocarbazole (Monomer 1):
As shown in Scheme 1, a mixture of 3, 6-dibromocarbazole (18.46 mmol) and K2CO3 (37 mmol) in DMF (20 ml) was refluxed in N_2 atmosphere and heated to 80 ℃. 2-Ethylhexylbromide (28 mmol) was added dropwise. After complete addition, heating was continued for 16 h. The product was isolated by diethyl ether/water extraction. The organic layer was dried with MgSO₄, then filtered and concentrated. The pure white viscous liquid, monomer 1, was obtained by silica column chromatography (eluent: hexane). (Yield: 56%,).
1H NMR (300 MHz in CDCl3): d 8.11 (2H, Ar-H), 7.48 (2H, Ar-H), 7.22 (2H, Ar-H), 4.18 (2H,-N-CH₂-), 1.23~1.44 (9H, -CH-, -CH₂-), 0.91 (6H, -CH₃).
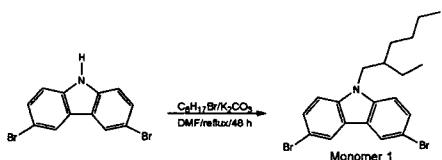
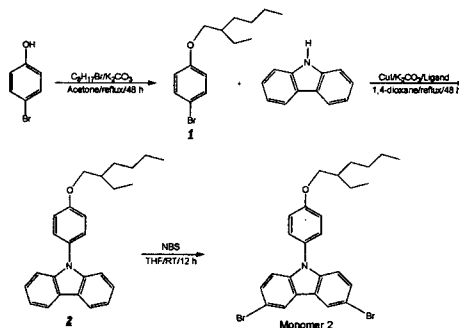Scheme 1. Synthetic route to monomer 1.

N-(2-Ethylhexyloxylphenyl)-3,6-dibromocarbazole (Monomer 2): Synthetic procedure for monomer 2 was presented in Scheme 2. In the first step, 4-bromophenol (1.5 mmol) was dissolved in 100 ml of acetonitrile, then K₂CO₃ (4.5 mmol) was added. The mixture was stirred in N2 atmosphere at 60 ℃. After 30 min., 2-ethylhexylbromide (4.5 mmol) was dissolved in 25 ml of acetonitrile and added to the flask dropwise. After 48 h of reaction, K₂CO₃ was filtered out, and the solvent was evaporated, then the crude product was washed with water and dried with MgSO₄. The pure white liquid product, 4 – bromo – (2 – ethylhexyloxy) – benzene (1), was obtained by silica column chromatography (eluent: hexane). (Yield: 66%). 1H NMR (300 MHz in CDCl3): δ 7.33 (2H, Ar-H), 6.79 (2H, Ar-H), 3.79 (2H,-O-CH₂-), 1.71(1H, -CH-), 1.29~1.46 (8H, -CH₂-), 0.91 (6H, -CH₃) 13C NMR (300 MHz in CDCl₃): 158.4, 132.0, 116.2, 112.4, 70.6, 39.2, 30.4, 29.0, 23.8, 23.0, 14.1, 11.1.

4-Bromo-(2-ethylhexyloxyl)-benzene (1) (56.4mmole), carbazole (7.6 mmol), K₃PO₄ (13.4 mmol), CuI (0.32 mmol) and trans-1, 2-cyclohexanediamine (1.27 mmol) were used in the second step. The reaction and workup procedure were carried out as described [14,15]. White solid product, N – (2 – Ethylhexyloxylphenyl) – carbazole (2), was obtained (Yield: 29%). ¹H NMR (300

MHz in CDCl3): δ 8.15 (2H, Ar-H), 7.44~7.24 (8H, Ar-H), 7.08 (2H, Ar-H), 3.94 (2H,-O-CH₂-), 1.77(1H, -CH-), 1.26~1.57 (8H, -CH₂-), 0.91 (6H, -CH₃) ¹³C NMR (300 MHz in CDCl₃): 158.6, 141.3, 129.9, 128.5, 125.8, 123.0, 120.2, 119.5, 115.5, 109.7, 70.8, 39.2, 30.4, 29.0, 23.8, 23.0, 14.1, 11.1.

In a flask, covered with aluminum oil, a stirred solution of 2 (2.43 mmol) in 60 ml of THF was cooled to 0 ℃. N-bromosuccinimide (NBS, 4.86 mmol) was added in small portion. The mixture was allowed to warm to room temperature overnight. THF was evaporated and the product was purified by extraction with diethyl ether and water. The organic layer was dried MgSO₄. The product, monomer 2, was obtained by column chromatography (eluent: hexane / methylene chloride). (Yield: 59%). 1H NMR (300 MHz in CDCl3): δ 8.18 (2H, Ar-H), 7.47 (2H, Ar-H), 7.36 (2H, Ar-H) 7.16 (2H, Ar-H), 7.08 (2H, Ar-H), 3.94 (2H,-O-CH₂-), 1.77(1H, -CH-), 1.26~1.57 (8H, -CH₂-), 0.91 (6H, -CH₃); 13C NMR (300 MHz in CDCl₃): 159.1, 140.3, 129.2, 128.9, 128.3, 123.6, 123.1, 115.7, 112.7, 111.5, 70.8, 39.3, 30.5, 29.1, 23.8, 23.1, 14.1, 11.1.
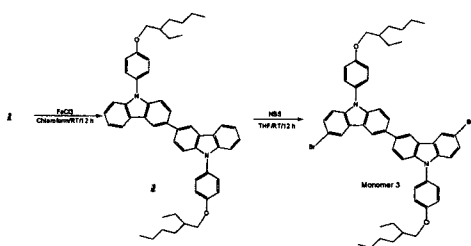

Scheme 2. Synthetic route to monomer 2.

Bis[6-bromo-N-(2-ethylhexyloxyphenyl)carbazole-3 -yl] (Monomer 3): Synthetic procedure for monomer 3 was presented in Scheme 3. To a stirred solution of 2 (2.9 mmol) in 13 ml of chloroform, FeCl₃ (8.3 mmol) was added. After stirring at room temperature for 24 h, 13 ml of water was added. The organic layer was separated, dried over MgSO₄, filtered and concentrated. Bis[N – (2 – ethylhexyloxylphenyl) – carbazole – 3 – yl] (3) was obtained by column chromatography (eluent: hexane / dichloromethane) (Yield: 67%) ¹H NMR (300 MHz in CDCl3): δ 8.44 (2H, Ar-H), 8.22 (2H, Ar-H), 7.75 (2H, Ar-H), 7.49-7.25 (10H, Ar-H), 7.14 (6H, Ar-H), 4.21 (4H, -N-CH₂-), 2.05 (2H,-CH-), 1.50-1.25 (16H, - CH₂-), 0.91 (12H, -CH₃); 13C NMR (300 MHz in CDCl₃): 158.7, 141.8, 140.5, 134.1, 130.1, 128.4, 125.9,

123.6, 123.3, 120.3, 119.6, 118.8, 115.6, 109.9, 70.8, 39.4, 30.5, 29.1, 23.9, 23.1, 14.1, 11.2.

In a flask, covered with aluminum foil, a stirred solution of **3** (2.87 mmol) in 70 ml of THF was cooled to 0 ℃. NBS (5.74 mmol) was added in small portions. The mixture was allowed to warm to room temperature overnight. The THF was evaporated and the product was purified by extraction with diethylether and water. The organic layer was dried with MgSO₄ and then monomer 3 was obtained by column chromatography (eluent: hexane/dichloromethane). (Yield: 86%) ¹H NMR (300 MHz in CDCl₃): δ 8.25 (2H, Ar–H), 7.65 (2H, Ar–H), 7.40-7.27 (10H, Ar–H), 7.12 (2H, Ar–H), 7.02 (4H, Ar–H), 4.21 (4H, –N-CH₂–), 2.05 (2H,-CH–), 1.50-1.25 (16H, –CH₂–), 0.91 (12H, –CH₃); 13C NMR (300 MHz in CDCl₃): δ 158.8, 140.8, 140.4, 134.1, 129.4, 128.6, 128.3, 126.3, 124.9, 123.0, 122.6, 118.8, 115.6, 112.4, 111.3, 110.2, 70.7, 39.4, 30.5, 29.7, 23.8, 23.1, 14.1, 11.2.

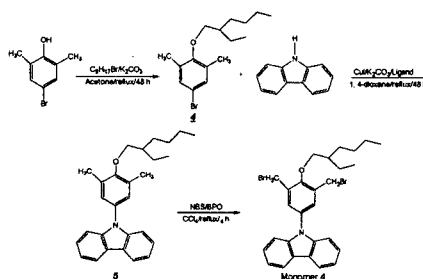Scheme 3. Synthetic route to monomer 3.

N-[4-(2-ethylhexyloxyl)-3,5-dibromomethylenephen yl]carbazole (Monomer 4): Synthetic procedure for monomer 4 was presented in Scheme 4. 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 N₂. 2-Ethylhexyl bromide (0.02 mol) was added to the solution, followed by refluxed for 48 h. Potassium hydroxide was filtered out, and the solvent was evaporated, then the crude product was washed with water and dried with MgSO₄. The pure white liquid product, 5 - bromo - 2 - (2 - ethylhexyloxyl) - 1,3 - dimethylbenzene (4), was obtained by silica column chromatography (eluent: hexane). (Yield: 63%). ¹H NMR (300 MHz in CDCl₃): δ 7.15 (2H, Ar–H), 3.6 (2H,-O-CH₂–), 2.26 (6H, Ar-CH₃), 2.18 (9H, –CH–, –CH₂), 0.91 (6H, –CH₃).

In the second step, 5 - bromo - 2 - (2 - ethylhexyloxyl) -1, 3-dimethylbenzene (**4**) (112.79 mmol), carbazole (15.24 mmol), K3PO4 (26.72 mmol), CuI (0.64 mmol) and trans - 1,2 - cyclohexanediamine (2.54

mmol) were used. The reaction and workup procedure were carried out as described [14,15]. White solid product, N-[4-(2-ethylhexyloxyl)-3, 5 – dimethyl – phenyl]carbazole (5), was obtained. (Yield: 25%). ¹H NMR (300 MHz in CDCl₃): δ 7.38 (4H, Ar–H), 7.26 (4H, Ar–H), 7.16 (2H, Ar–H), 3.6 (2H, –O-CH₂–), 2.30 (6H, Ar-CH₃), 2.18 (9H, –CH–, –CH₂–), 0.91 (6H, –CH₃).

A mixture of N-[4-(2-ethylhexyloxyl) – 3, 5 – dimethyl – phenyl]carbazole (**5**) (3.68 mmol), NBS (8.09 mmol) and BPO (0.1618 mmol) were added to CCl₄ at room temperature. The following reaction and workup procedure were carried out as described [14,15]. White solid product, monomer 4, was obtained. (Yield: 45%). ¹H NMR (300 MHz in CDCl₃): δ 7.48 (4H, Ar–H), 7.45 (4H, Ar–H), 7.35 (2H, Ar–H), 4.6 (4H, CH₂Br–), 3.96 (2H, –O-CH₂–), 2.25 (9H, –CH–,-CH₂–),0.95 (6H,-CH₃).

Scheme 4. Synthetic route to monomer 4.

Polymerization

A mixture of monomer 1 (2.60 mmol)(monomer 2, monomer 3 or monomer 4) and aniline (2.60 mmol) was dissolved in toluene (30 ml). NaO-t-Bu (7.8 mmol), Pd₂(dba)₃ (0.066 mmol) and P(t–Bu)₃ (0.4 mmol) were added to the solution at room temperature. The reaction mixture was stirred at 100 ℃ for 48 h. After cooling to room temperature, the mixture was quenched by adding aqueous ammonia (50 ml) and the product was extracted with CHCl₃. The organic fraction was concentrated and repreciphated from CHCl₃/methonal several times. Then, the products were filtered and dried in vacuum.

Characterization

NMR spectra were recorded on a Varian Unity Plus 300 using CDCl₃. Molecular weights and molecular weight distributions were measured by Water gel permeation chromatograph (GPC) equipped with Styragel HR 5E column using THF as an eluent against polystyrene standards at room temperature. Thermal

analysis was performed on a Seiko EXSTAR 6000 TG/DTA 6300 thermal analyzer at a heating of 20℃ /min for thermogravimetric analyzer (TGA) and at a heating of 10℃/min for differential scanning calorimetry (DSC). UV-Visible absorption spectra were taken by Shimadzu UV-2100. The photoluminescence (PL) spectra excited by He-Cd laser at 325 nm were monitored by Optical Multichannel Analyzer (Laser Photonics, OMA system). The ionization potential (IP) was measured by a photoelectron spectroscopy (Riken Keiki AC-2).

3. Results and discussions

Alternating copolymers such as poly[N-(2 -ethylhexyl-3,6-carbazole-alt-aniline] (P1), poly [(N – (2 – ethylhexyloxy) – phenyl) – 3,6 – carbazole – alt – aniline] (P2), poly [bis (6 – N – (4 – (2 – ethylhexyloxy) – phenyl) – carbazole – 3 – yl) – alt-aniline] (P3) and poly [N – (4 – (2 – ethylhexyloxy) – 3,5 – dimethylene – phenyl) – carbazole – alt – aniline] (P4) were prepared by using Pd – catalyzed polycondensation as presented in Scheme 5. The common structural characteristics of P1, P2 and P3 were designed to have a carbazole and a triarylamine unit in the polymer main chain. Compared to N-alkyl-substituted P1, however, N-arylation was employed for P2 and P3. It was reported [16] that the properties of carbazole oligomers were affected by replacing alkyl groups on N atom of carbazole with aryl groups. The alkyl groups on N atom activated the carbazole ring system through increasing the electron density, compared to the corresponding aryl-substituted compounds. On the other hand, the aryl group on N atom was twisted to the carbazole ring and thus could not delocalize p-electrons from carbazole. Therefore, 4, 4′ – bis (9 – carbazolyl) – biphenyl (CBP) was used as a blue-emitting host matrix for phosphorescent – doped OLED. In addition, P2 and P3 were prepared to investigate the effect of N – aryl – substituted carbazole content in the polymer backbone. The carbazole group in P4 was placed in the side chain and the conjugation of the polymer was reduced by incorporating methylene groups in polymer backbone. In all series of polymers, alkyl groups such as 2-ethylhexyl group in P1 and 2-ethylhexyloxy groups in P2, P3 and P4were incorporated to increase the solubility of alternating copolymers in common organic solvents.
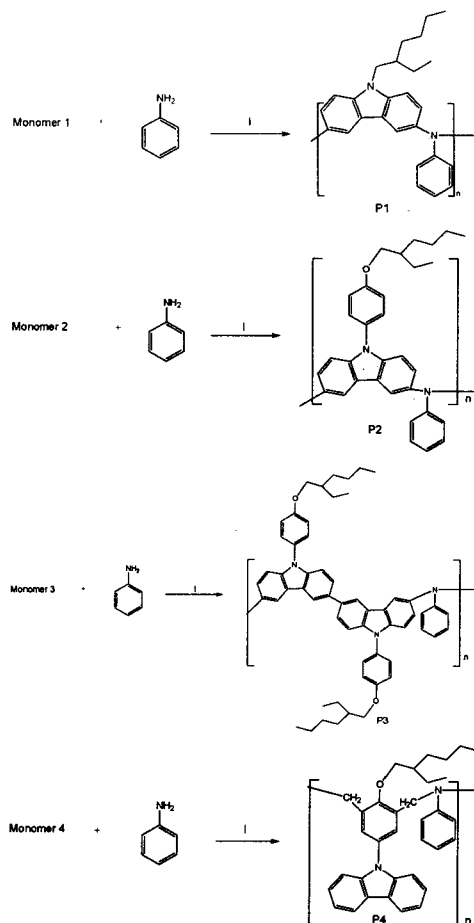
Scheme 5. Polymerizations via palladium catalyzed polycondensation Reaction condition (I) : Toluene, NaO-t-Bu, Pd2(dba)3, P(t-Bu)3, 100℃.

All synthesized copolymers were found to be soluble in common organic solvents such as benzene, toluene, chloroform and THF, and showed good quality of film forming. The molecular weights of the copolymers were measured by using GPC, and summarized in Table 1. Relatively low molecular weights of P2 and P3 might be explained by increased rigidity of polymer backbone with substituting 2 - ethylhexyloxyphenyl group on N atom, resulting in premature precipitation of the copolymers during the polymerization. The thermal stability of the copolymers was compared with decomposition temperature (T$_d$) measured at 5 wt% loss in TGA, as shown in Figure 1 and Table 1. These data revealed that the copolymers had excellent thermal stability under nitrogen atmosphere. P3 and P4 showed relatively high T$_g$ of 121℃ and 132℃, respectively, in Table 1. The T$_g$'s of P1 and P2 could not be measured

in this DSC experiment.

Table 1. Physical properties of polymers
[a] temperature resulting in 5% weight loss based on initial weight.

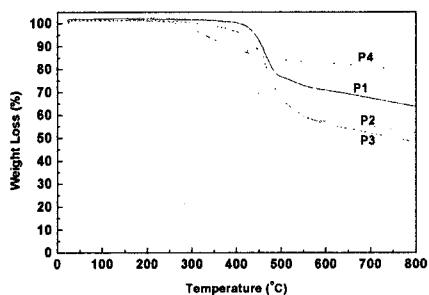| Polymers	M_w (g/mol)	M_w/M_n	T_g (°C)	T_d (°C)[a]
P1	7,100	1.3	---	442
P2	4,100	1.3	---	415
P3	4,900	1.1	121	409
P4	11,500	1.6	132	327

Figure 1. TGA curves of alternating copolymers.

UV-Visible absorption and PL emission spectra of the copolymers are presented in Figure 2 and Figure 3, respectively. In Figure 2, the maximum UV-Visible absorption peaks of all copolymers were observed at around 300 nm. When excited at their UV-Visible absorption maxima, the copolymers exhibited PL emission in the blue range from 450 nm to 460 nm. Substitution effect of alkyl and aryl groups on N atom was observed. Compared with $\lambda_{max,PL}$ of P1, $\lambda_{max,PL}$ of P2 was blue shifted to shorter wavelength, possibly attributed to localized electron density by twisted conformation between carbazole and aryl groups.
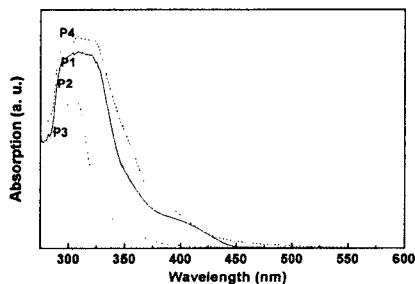

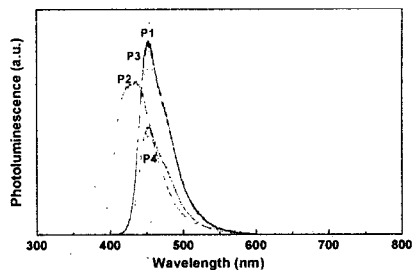Figure 2. UV-Vis absorption spectra of alterna -ting copolymers.

Figure 3. Photoluminescence spectra of alterna -ting copolymers.

Electrochemical properties of the copolymers are summarized in Table 2. Energy levels of the copolymers are also compared as shown in Figure 4. The copolymers showed HOMO energy levels of -5.19 eV for P1, -5.35 eV for P2, -5.29 eV for P3 and -5.64 eV for P4. Band gap energy levels of the copolymers were also measured from the crosspoint of UV-Visible absorption and PL emission spectra to be 2.91 eV for P1, 3.16 eV for P2, 3.32 ev for P3 and 3.05 eV for P4. It appeared that changing the substituent group on N atom of carbazole unit from 2-ethylhexyl group in P1 to 2-ethylhexyloxyloxy-phenyl group in P2 - P4 increased band gap energy as well as decreased HOMO energy levels. This might be originated from the twisted conformation between carbazole and aryl groups in P2 - P4 as mentioned previously.

Table 2. Electronic properties of the polymers
[a] calculated from the crosspoint of UV-Vis. and PL spectrum.
[b] measured by a RIKEN Keiki AC-2.
[c] estimated from the HOMO and band gap.

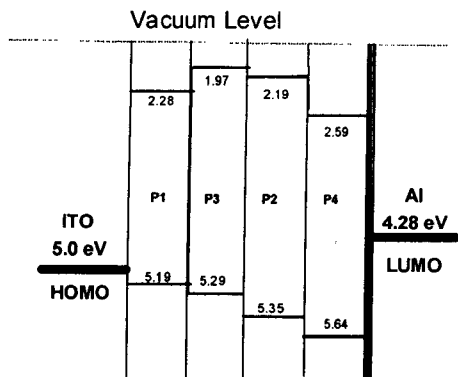| Polymers	$\lambda_{max,UV}$ (nm)	$\lambda_{max,PL}$ (nm)	Band gap (eV)[a]	HOMO (eV)[b]	LUMO (eV)[c]
P1	309	452	2.91	-5.19	-2.28
P2	296	441	3.16	-5.35	-2.19
P3	305	433	3.32	-5.29	-1.97
P4	304	451	3.05	-5.64	-2.59

Vacuum Level

Figure 4. Schematic view of energy levels of alternating copolymers.

4. Summary

Synthesis of poly(N-arylcarbazole-alt-aniline) copolymers such as poly [(N – (2 – ethylhexyloxy) – phenyl) – 3,6 – carbazole-alt-aniline] (P2), poly [bis(6 – N – (4 – (2 – ethylhexyloxy) – phenyl) – carbazole – 3 – yl) – alt – aniline] (P3) and poly [N – (4 – (2 – ethylhexyloxy) – 3,5 – dimethylene – phenyl) – carbazole – alt – aniline] (P4) was successfully accomplished by using palladium-catalyzed polycondensation. The optical and electrochemical properties of these copolymers were characterized and compared with those of N-alkyl substituted counterpart, poly [N – (2 – ethylhexyl) – 3,6 – carbazole – alt – aniline] (P1). It was observed from the optical and electrochemical properties that poly (N – arylcarbazole – alt – aniline) copolymers could be used as blue emitting host materials for PLEDs, because they showed blue emission in PL spectra and wider band gap energy compared to the poly (N – alkylcarbazole – alt – aniline) copolymer.

References

[1] Burrounghes, J. H., Bradley, D. D. C., Brown, A. R., Marks, R. N., MacKay, K., Friend, R. H., Burns, P. L., & Holmes, A. B. (1990). Nature (London), 347, 539.

[2] Mitschke, U., & Bauerle, P. (2000). J. Mater. Chem., 10, 1471.

[3] Neher, D. (2001)Macromol. Rapid Commun., 22, 1365.

[4] Berntsen, A., Croonen, Y., Liedenbaum, C., Schoo, H., Visser, R.-J., Vleggaar, J., & Vandeweijer, P. (1998). Opt. Mater., 9, 125.

[5] Tanigaki, N., Masuda., H., & Kaeriyama, K. (1997). Polymer, 38, 1221.

[6] Bernius, M., Inbasekaran, M., Woo, E., Wu, W., Wujkowski, L. (2000). J. Mater. Scien.: Mater. Electro., 11, 111.

[7] Bernius, M.T., Inabasekaran, M., O'Brien, J., & Wu, W. (2000). Adv. Mater., 12, 1737.

[8] Scott, J.C., Pautmeier, L.Th., &Moerner, W.E. (1992). J. Opt. Soc. Am. B., 9, 2059.

[9] Esen, R., Nakhimowsky, L.A., & Shanks, H.R. (1996).Mol. Cryst. Liq. Cryst., 287, 255.

[10] Simmer, J., Güsen, B., Paulus, W., Kettner, A., Schumacher, P., Adam, D., Etzbach, K.H., Siemeseyer, K., Wendorf, J.H., Ringsdorf, H., Haarer, D. (1996). Adv. Mater., 8, 815.

[11] Ochse, A., Kettner, A., Kopitke, J., Wendorf, J. H., & Bässler, H. (1999). Phys. Chem. Chem. Phys., 1, 1757.

[12] Martínez-Palau, M., Perea, E., López-Calahorra, & Velasco, D. (2004). Lett., Org. Chem., 1, 231.

[13] Wong, W.-Y., Liu, L., Cui, D., Leung, L. M., Kwong, C.-F., Lee, T.-H., &Ng, H.-F. (2005). Macromolecules., 38, 4970.

[14] Klapars, A., Antilla, J. C., Huang, X. H., &Buchwald, S. L. (2001). J. Am. Chem. Soc., 123, 7727.

[15] Hayat, S., Rahman, A., Choudhary, M. I.,Khan, K. M., Schumann, W., & Bayer, E.(2001). Tetrahedron, 57, 9951.

[16] Brunner, K., Dijken, A. V., Börner, H., Bastiaansen, J. J .A. M., Kiggen, N. M. M., & Langeveld, B. M. W. (2004). J. Am. Chem. Soc., 126, 6035.