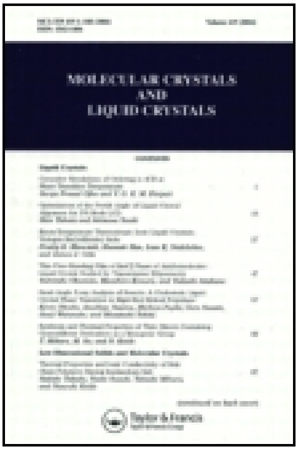

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Synthesis and Characterization of New Blue Light Emitting Poly(arylenevinylene) Derivatives Containing Fluorene Pendant

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To cite this article: Yun-Hi Kim, Sang-Yun Jung & Soon-Ki Kwon (2006): Synthesis and Characterization of New Blue Light Emitting Poly(arylenevinylene) Derivatives Containing Fluorene Pendant, Molecular Crystals and Liquid Crystals, 444:1, 169-176

To link to this article: http://dx.doi.org/10.1080/15421400500365342

Mol. Cryst. Liq. Cryst., Vol. 444, pp. 169–176, 2006
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400500365342

Synthesis and Characterization of New Blue Light Emitting Poly(arylenevinylene) Derivatives Containing Fluorene Pendant

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New poly(arylenevinylene) derivatives composed of biphenyl or terphenyl units in the main chain and fluorene pendant groups are synthesized by Yamamoto coupling reaction or Suzuki coupling reaction. The obtained polymers showed high color pure blue emission due to controlled conjugation length and inhibited intermolecular interaction as well as high solubility and good thermal stability.

Keywords: controlled conjugation length; inhibited intermolecular reaction; poly(arylenevinylene); pure blue emission

INTRODUCTION

Since light emitting devices (LED) using conjugated polymers were first realized in the early 1990s, a great number of different conjugated polymers suitable for LEDs have been investigated and developed. These conjugated polymers are especially attractive for use as the emitting layers in LEDs, because the polymers show good processability, high quantum efficiency, long lives under stress, and a wide selection of emission colors through molecular design [1].

Efficient organic stable blue light emitting materials are desirable both to complete the luminescence color spectrum and to serve for energy transfer when used in conjunction with small band gap

This work was supported by Korea Research Foundation Grant (KRF-2000–005-D00251) and Program for Cultivating Graduate Students in Regional Strategic Industry.

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fluorophores. The first report of blue emission from a conjugated polymer LED was for poly(p-phenylene) (PPP), PPP and its derivatives have good thermal and oxidative stability. PPP, however, exhibits low solubility and a high turn on voltage. Low work function metals are required for efficient carrier injection into PPP derivatives. Furthermore, PPP and its derivatives are intrinsically violet blue emitters and present some difficulties in color tunability [2]. Poly(p-phenylene-vinylene) (PPV) derivatives have several advantages as an emitting material such as high thermal stability, good film quality, suitable color tunability. However, the design of blue emitting electroluminescent polymers based on PPVs with interrupted conjugation suffers from the drawback that their emission is usually broadened and red-shifted because of the more conjugated segments. The carbon carbon double bond of PPV can be subject to degradation [3]. Polyfluorene derivatives have aroused special interest because of their high efficiencies both in photoluminescence (PL) and in electroluminescence (EL).

Recently, we report the poly(biphenylenevinylene) derivatives and poly(terphenylenevinylene) derivatives for efficient blue OLED [4–6]. In connection with the recent report, we designed and synthesized the new poly(arylenevinylene) derivatives containing fluorene pendant. We also studied the physical and optical properties and LED characteristic as the variations of aryl group with different conjugation length.

EXPERIMENTAL

4,4′-Bis[2-(4-Bromophenyl)-1-(9,9-Dihexylfluorene-2-yl) styryl]Biphenyl (BBDB)

17.6 g (34.26 mmol) of 4-bromobenzyl phosphonium salt and 3.3 g (0.137 mmol) of NaH are dissolved and refluxed in the toluene. After cooling to room temperature, 12 g (13. 71 mmol) of 4,4′ -bis(9,9-dihexylfluorene-2-carbonyl)biphenyl obtained from Friedel Crafts acylation reaction of 9,9-dihexylfluorene and isophthaloyl dichloride was added. The mixture was refluxed for 12 h, and worked up with dilute aqueous HCl. The crude product was extracted with methylene dichloride, and the solvent was evaporated. The product was obtained by column chromatography with hexane and methylene dichloride as eluent. Yield = 84%, mp = 72°C, ^{1}H-NMR ($CDCl_3$) δ 7.8 – 7.2 (m, 30H), 7.0 (m, 2H), 2.0 (t, 8H), 1.2 – 1.1 (m, 8H), 1.1 – 1.0 (m, 16H), 0.8 (t, 12H), 0.6 (m, 8H). FT-IR (KBr pellet, cm^{-1}): 3004 (aromatic C–H), 2920 (aliphatic C–H), 1064 (aromatic C–Br).

2-(2-Ethylhexyloxy)-5-Methoxybenzene-1,4-Diboronic Acid (EMD)

90 g (0.228 mol) of 2-(2-ethylhexyloxy)-5-methoxybenzene-1,4-dibromobenzene and activated 22 g (0.913 mol) of Mg were reacted in the THF solvent. After the Grignard reagent was obtained, the solution was cooled down to –60°C, and 71 g (0.685 mol) of trimethyl borate was added. The mixture was refluxed for 24 h, and worked up with 2N-HCl . The crude product was extracted with ethyl ether, and the solvent was evaporated. The product was obtained by recrystallization in ethyl acetate. Yield = 25%, mp = 200°C. ^{1}H-NMR ($CDCl_3$) δ 7.2 (m, 2H), 6.3 (b, 4H), 3.6 (d, 2H), 3.5 (s, 3H), 1.5 (m, 1H), 1.2 – 0.8 (m, 8H), 0.6 (m, 6H). FT-IR (KBr pellet, cm^{-1}): 3500 (O–H), 3010 (aromatic C–H), 2950 (aliphatic C–H).

Poly[4,4′-(2-(4,4″-Biphenyl)-1-(9,9-Dihexylfluorene-2-yl)ylene-vinylene-1-(9,9-Dihexylfluorene-2-yl)Biphenylenevinylene]

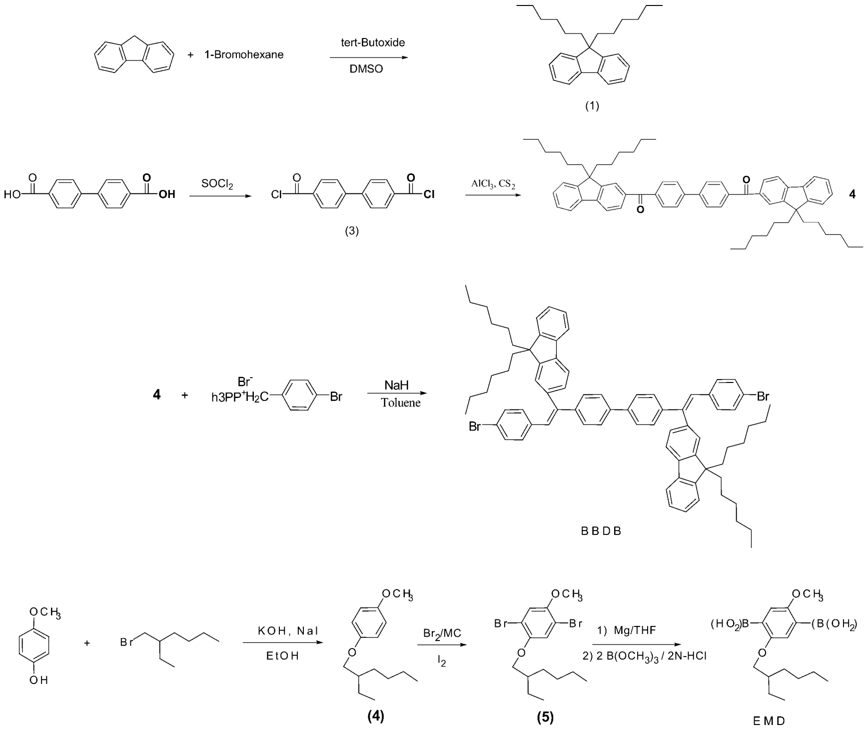
All handling of catalysts and polymerization was done in a nitrogen atmosphere. Into a 50 mL three necked flask equipped with a nitrogen inlet, 6.3 mg (0.047 mmol) of nickel chloride, 8.5 mg (0.054 mmol) of 2,2′ -bipyridine), 0.27 g (1.016 mmol) of PPh3, 0.14 g (2.13 mmol) of Zn powder, 0.8 g of BBDB and 20 mL of N,N-dimethylformamide (DMF) were added. The reaction mixture was stirred at 90°C for 12 h. After stirring, excess bromobenzene was added in the reaction mixture for end capping. After adding bromobenzene, the reaction mixture was stirred at 90°C for 6 h. The products were precipitated into large excess of 20% HCl/methanol solution. The white solids that remained were washed with methanol, water, and methanol sequentially. The polymer was collected and dried under vacuum. The yield of the polymer after complete work-up was 54%.

Poly[4,4′-(2-(2″-methoxy-5″-(2-Ethylhexyloxy)-4,4″-Terphenyl)-1-(9,9-dihexylfluorene-2-yl)ylenevinylene-1-(9,9-Dihexylfluorene-2-yl)Biphenylenevinylene)]

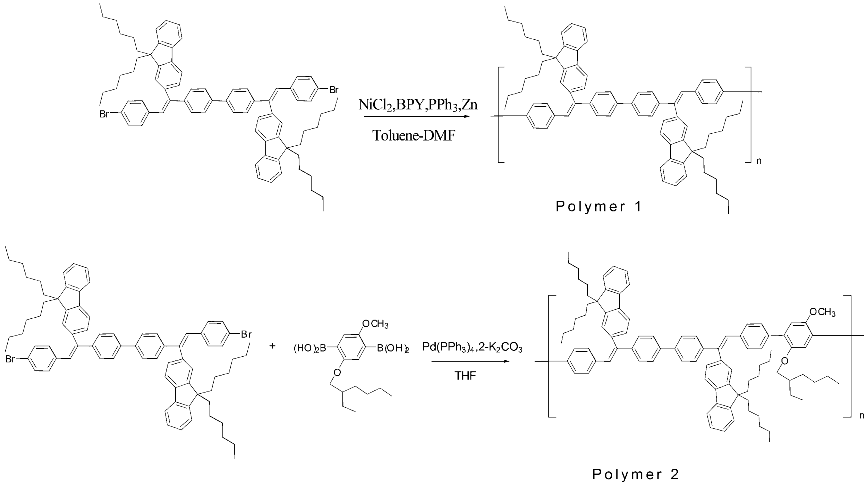
All handling of catalysts and polymerization was done in a nitrogen atmosphere. To a stirred solution of 1 g (0.8465 mmol) of BBDB, 0.27 g (0.8465 mmol) of EMD in 5 mL THF and 5 mL of 2 M K_2CO_3 solution, Pd(PPh3)4 was added. The mixture was heated to 90°C, and refluxed for 24 h. 4-Bromo-tert-butylbenzene and tert-butylbenzene boronic acid was added with small amount of catalysts for end capping. After 2 h, the reaction mixture was poured into methanol and filtered with glass filter. The residue was dissolved in $CHCl_3$ and washed with waters. After being dried over $MgSO_4$, precipitaion was twice repeated with chloroform/methanol. The yield of the polymer after complete work-up was 43%.

RESULTS AND DISCUSSION

The method for preparing monomers and these polymers are outlined in the Scheme 1 and Scheme 2. The Wittig reaction of 4-bromobenzyl phosphonium salt and 4,4' -bis(9,9-dihexylfluorene-2-carbonyl)-biphenyl obtained from Friedel Crafts acylation reaction of 9,9-dihexylfluorene and isophthaloyl dichloride gave BBDB monomer. 2-(2-Ethylhexyloxy)-5-methoxybenzene-1,4-dibronic acid (EMD) monomer was obtained by Grignard reaction. The polymer 1 which is composed of biphenylenevinylene units in the main chain was obtained by polymerization of BBDB using a nickel-catalized coupling reaction.



SCHEME 1



SCHEME 2

The polymer 2 which was composed of biphenylenevinylene-terphenylenevinylene units in the main chain was obtained by polymerization of BBDB and EMD using a Suzuki coupling reaction. The polymer structures shown were consistent with spectroscopic data from 1H-NMR and FT-IR. The obtained polymers were readily soluble in common organic solvents such as chloroform and toluene. The weight average molecular weights of polymers, as determined by gel permeation chromatography using polystyrene standard, were 18700 (2.15) for polymer 1 and 8200 (1.5) for polymer 2, respectively. The thermal property of synthesized polymers was evaluated by the means of TGA under nitrogen atmosphere. The 5% weight loss of the polymer1 and polymer 2 was observed at 443°C and 420°C, respectively. The DSC measurement showed glass transition at around 135°C for polymer 1 and 94°C for polymer 2, respectively. From the results, it was known that the obtained polymers showed good thermal stability with good Tg. And polymer 1 which is composed of biphenylenevinylene units in the main chain showed better thermal stability than polymer 2 which is composed of biphenylenevinylene-terphenylenvinyene units in the main chain. The relatively low thermal stability of polymer 2 may be due to the long alkyl chain in the main chain of polymer 2.

Figures 1 and 2 showed the optical absorption, excitation spectra and photoluminescence spectra of the polymers in dilute solution (chloroform) and solid state. The absorption spectra of the thin solid

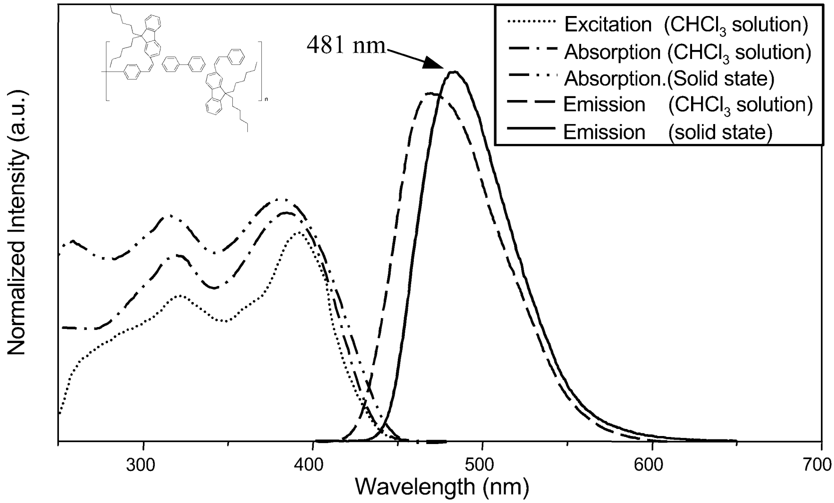


FIGURE 1 UV-visible & PL spectra of polymer 1 in $CHCl_3$ solution and in solid state.

film and dilute solution of polymer 1 had maximum peak of 382 nm and 385 nm, respectively. For polymer 2, the absorption spectra of the thin solid film and dilute solution had maximum peak of 385 nm

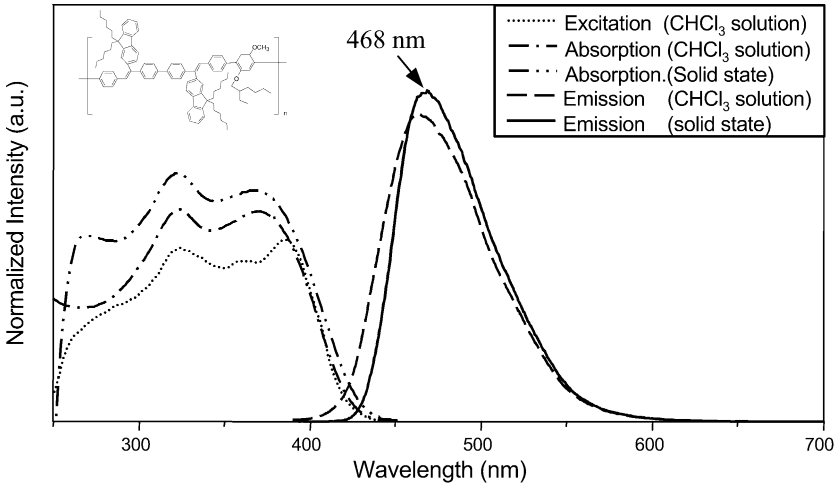


FIGURE 2 UV-visible & PL spectra of polymer 2 in $CHCl_3$ solution and in solid state.

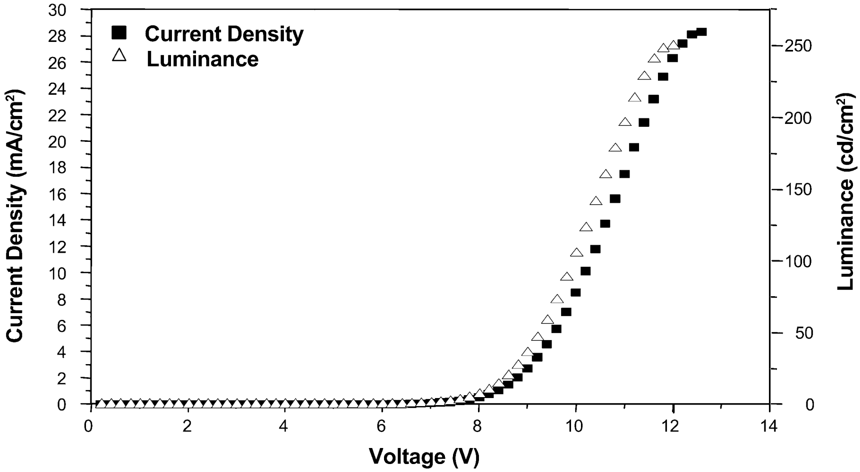


FIGURE 3 Current-voltage-luminance curves of ITO/PEDOT/polymer/LiF/Al.

and 387 nm, respectively. The PL spectra of the dilute solution of polymer 1 and polymer 2 have maximum peak at 469 nm and 463 nm, respectively. Although the PL spectra of the solid film of polymers showed slight bathochromic shift (~10 nm for polymer 1, ~5 nm for polymer 2) compared with those of dilute solution, the long wavelength emissions due to intermolecular interaction were not observed. It is supposed that the fluorene pendant groups in the vinyl bond inhibited intermolecular interaction. Polymer 2 having biphenylenevinylene-terphenylenevinylene units in the main chain showed slightly blue shifted emission, compared with polymer 1 having biphenylenevinylene units in the main chain.

Figure 3 shows the current-voltage luminescence curves of ITO/PEDOT/polymer1/LiF/Al device using PEDOT as hole injection layer and LiF as an electron injection layer. The device showed a turn-on voltage of 7.5 V and maximum brightness of 250 cd/m^2. The electroluminescence from the device shows the maximum at 480 nm.

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