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Synthesis and Characteristics of Novel Poly (Terphenylenevinylene) Derivative Containing Benzoxazolyl Group

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Poly(1,4-phenylene-2'-methoxy-5'-ethylhexyl-1',4'-phenylene-1'',4''-phenylene-α-benzoxazolylvinylene) (PTPBOV) was synthesized through the Suzuki reaction of diboronic acid and dibromide and following end-capping reaction. The electron affinity level of the PTPBOV containing benzoxazolyl group was 2.76 eV.

Keywords: Electron affinity; Ionization Potential; benzoxazole; Suzuki reaction, photoluminescence; solubility

INTRODUCTION

Since the first report of polymer light-emitting diodes based on poly(*p*-phenylenevinylene) (PPV) by the Cambridge group[1], a great number of efforts have been devoted to the synthesis of light emitting polymers because of several advantages over small organic molecules, excellent mechanical properties and simple fabrication method of spin casting etc [2]. Many conjugated polymers include PPV derivatives, poly(p-phenylene) derivatives (PPPs), and polyfluorene derivatives (PFs), have been synthesized for as emissive and/or charge-transporting materials in polymer light-emitting diodes(PLED) [2]. However some important issues such as balancing of charge injection, device stability,

and color tunability remain to be addressed. To improve the device efficiency of PLEDs, it is necessary to balance the rate of injection of electrons and holes from opposite electrodes into the device. For the most of conjugated polymers including PPV derivatives, the barrier of electron injection is much higher than that of hole injection. Therefore, many substituents including CN, oxadiazole, triazole, pyridine, qunoxaline, thiadiazole etc. which have a high electron affinity have been introduced [3].

The present article deals with the synthesis and luminescent properties of novel poly(terphenylenevinylene) derivative containing benzoxazoyl substituent.

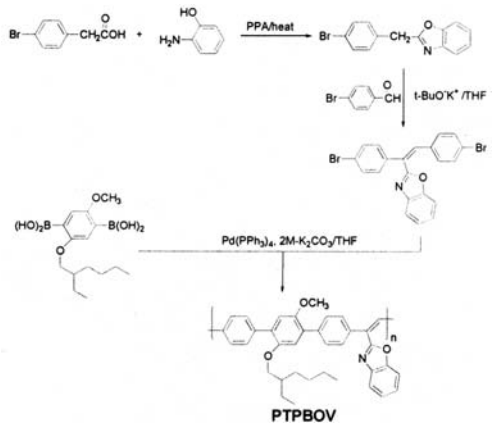

FIGURE 1. Reaction Scheme of PTPBOV

EXPERIMENTAL

1,2-bis(4'-bromophenyl)-1-benzoxazolylethene (BPBOE). 4'-Bromo phenylbenzoxazolyl methane (2 g, 7 mmol), 4-bromobenzaldehyde (1.2 g, 7 mmol) and t-butylalcohol (0.5mL, 0.7mol) were dissolved in 150 mL of dry THF under an nitrogen atmosphere in 250 mL 2-neck round flask. 1M-potassium-t-butoxide(7 mL, 7mmol) was added slowly, and then stirred for 1 hour at room temperature. The solvent was evaporated with rotary evaporator, and then 100 mL of ethylalcohol was added. The precipitate was filted and washed with water. The powdery white product was obtained. Yield = 47%, mp =199 ^{o}C, ^{1}H-NMR ($CDCl_3$) δ 7.9 (s, 1H), 7.7 (d, 1H), 7.6 (d, 2H), 7.5 (d, 1H), 7.4 (m, 4H), 7.3 (d, 2H), 7.0 (d, 2H). FT-IR (KBr pellet, cm^{-1}): 1612 ($\nu_{C=N}$).

Poly(1,4-phenylene-2'-methoxy-5'-ethylhexyl-1',4'-phenylene-1", 4"- phenylene-α-benzoxazolylvinylene) (PTPBOV). All handling of catalysts and polymerization was done in a nitrogen atmosphere. To a stirred solution of 1-methoxy[4-(2'-ethylhexyl)oxy] benzene diboronic acid (0.578 g, 1.786 mmol) [4], 1,2-bis(4'-bromophenyl)-1-benzoxazolylethene (0.813 g, 1.786 mmol) in 10 ml THF and 4 ml 2M K_2CO_3 solution in water was added catalysts, $Pd(PPh_3)_4$ (8.4 mg, 0.6 mol %). The reaction mixture was heated at 80 ℃ under nitrogen atmosphere for 8 hours. Bromobenzene (0.05 g, 0.318 mmol) was added, and then phenyl boronic acid (0.05 g, 0.41 mmol) was added with small amounts of catalysts for end-capping. After 2 hours, the reaction mixture was poured into methanol (50 ml) and filtered with glass-filter. The residue was dissolved in $CHCl_3$ and washed with waters. After being dried over $MgSO_4$, precipitation was twice repeated with chloroform/methanol. Yield : 43 %

RESULTS AND DISCUSSION

Poly(terphenylene-*a*-benzoxazolylvinylene) derivative (PTPBOV) was synthesized through the Suzuki reaction of diboronic acid, and dibromide, and following end-capping reaction (figure 1). The obtained PTPBOV was characterized by ^{1}H-NMR spectroscopy. Aromatic protons of PTPBOV appeared at the range of 6.8 – 8.1 ppm. Methoxy and oxymethylene protons of PTPBOV showed at around 3.8 ppm. The strong O-H stretching band at 3311 cm^{-1} which was assigned to the O-H stretching band of diboronic acid monomer was disappeared from the FT-IR spectrum of PTPBOV. The weight average molecular weight (Mn) of PTPBOV was about 7,100 with a polydispersity index of about 1.7. Solubility is important property for conjugated polymers used in LED's, because solubility is needed for easy preparation of the diodes. This polymer was soluble in various organic solvents such as THF, toluene, chloroform, etc. This implies that the introduction of alkoxy groups and bulky benzoxazolyl group at the side chain can enhance the solubility of polymer containing rigid backbone. Thermogravimetric analysis (TGA) of the PTPBOV showed 5 % weight loss at 360 ℃ and 10 % weight loss at 390 ℃ under nitrogen atmosphere. This result suggests that the polymer having the benzoxazole-containing aromatic ring in side chain has very good thermal stability.

Figure 2 shows the UV absorption and photoluminescence spectra of the PTPBOV in chloroform solution and solid film. As shown in the

absorption spectrum, the wavelengths of the absorption maxima (λ_{max}) of the polymer solution and polymer film were observed at around 370 nm, which is attributed to the π - π^* transition of the conjugated segment.

Upon UV excitation at 370 nm, the photoluminescence of the polymer solution and polymer film showed maxima emissions at 479 and 487 nm respectively.

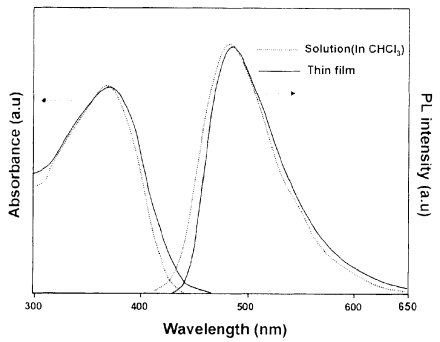

FIGURE 2. UV visible and PL spectra of PTPBOV

The Ionization Potential (Ip) and the electron affinity (Ea) level of PTPBOV were investigated by cyclic voltammetry. The HOMO, LUMO and ban gap of PTPBOV was 5.70 eV, 2.76 eV and 2.94 eV, respectively. The barrier heights for electron injiection at the interface of Ca/PTPBOV is 0.13 eV. Therfore, the PTPBOV containing benzoxazole, which is electron affinity group is a promising candidate for electron transporting material in polymer light emitting devices.

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