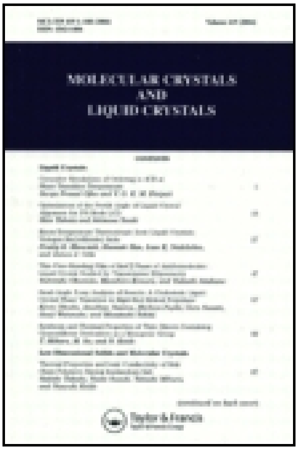

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Synthesis and Characterization of a Light-Emitting Poly(p-phenylenevinylene)-Based Copolymer Containing 1,3,4-Oxadiazole Functionality

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A new class of high brightness and luminance efficiency of poly[2-{4-[5-(3-(3,7-dimethyloctyloxy)phenyl)-1,3,4-oxadiazole-2-yl]phenyl}-1,4-phenylenevinylene] (C_{10}PhOxa-PPV) was synthesized by Gilch polymerization. The weight average molecular weight (Mw) and the polydispersity of C_{10}PhOxa-PPV were found to be 2.7×10^4 and 2.6, respectively. Double-layer light-emitting device with an ITO/PEDOT/C_{10}PhOxa-PPV/Al was fabricated and characterized. The maximum brightness, and luminance efficiency of C_{10}PhOxa-PPV showed values of up to 8.3 cd/A and 4,426 cd/m^2, respectively.

Keywords: brightness; efficiency; electroluminescence; photoluminescence; PLED; PPV

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INTRODUCTION

Since the first reports of light-emitting diodes (LEDs) based on either small molecule fluorescent dye [1] or π-conjugated polymer [2] emitting layers, progressive efforts have been devoted to synthesizing highly efficient emitting materials for LED applications. Of these two types of emitting materials, π-conjugated polymer-based LEDs (PLEDS) appear to be the most promising for the development of low-cost, full-color, large area flexible displays. However, these materials have low electron injection and/or transport rates compared to the number of injected holes within the emitting layer, resulting in an imbalance in the injected charge rates and a concomitant reduction in device performance [3]. Oxadiazole-containing polymers have been investigated since the 1960s and only a few reports on using oxadiazole-containing polymer, poly(1,4-phenylene-1,3,4-oxadiazole), as a charge transporting materials into the electronic devices [4]. The most important low molecular weight oxadiazole compound, 2-biphenyl-4-yl-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD), was first utilized by Tsutsui *et al.* in vapor deposited organic LEDs [5]. Since then, many research groups have developed various oxadiazole-containing materials, which have been widely used as electron transporting materials [6–10]. Previously, we described the synthesis of various poly(*p*-phenylenevinylene)s (PPVs) [11–13] and poly(9,9-dialkylfluorenyl-2,7-vinylenes) (PFVs) [14–16], which were found to exhibit high performance as PLEDs. In this paper, we report the synthesis and characterization of PPV derivative with oxadiazole pendant group by Gilch polymerization method, and highlight its ability to achieve strong brightness and high luminous efficiency.

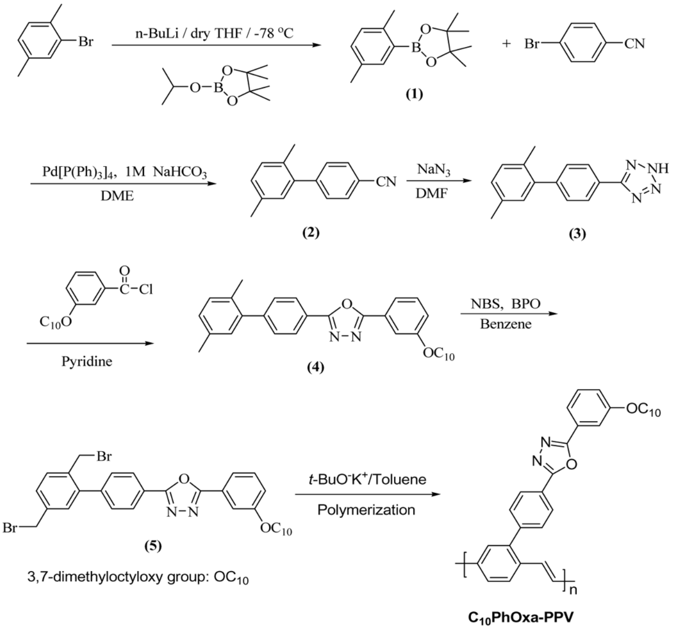
EXPERIMENTAL

Emission spectra of a dilute ($\sim 10^{-6}$ M) solution of the polymer were recorded on a Perkin-Elmer LS-50 fluorometer utilizing a lock-in amplifier system with a chopping frequency of 150 Hz. Solid-state emission measurements were achieved using films supported on a glass substrate and mounted with front-face excitation at an angle of <45°. The polymer film was excited with several portions of visible light from a xenon lamp. To measure EL, a polymer LED was constructed as follows: The glass substrate, coated with a transparent ITO electrode, was thoroughly cleaned by successive ultrasonic treatments in acetone, isopropyl alcohol, and distilled water, and heated under nitrogen gas for drying. The polymer film was prepared by spin casting a chlorobenzene or 1,2-dichlorobenzene solution (0.5–1.5 wt%).

Uniform and pinhole free films with a thickness around 100 nm were easily obtained from the resulting polymer solution. Aluminum metal was deposited on the top of polymer film through a mask by vacuum evaporation at pressure below 1×10^{-6} torr, yielding active areas of $4\,mm^2$. For the measurements of device characteristics, current density-voltage-luminescence (*J-V-L*) changes were measured using a current/voltage source (Keithley 238), an optical power meter (CS-1000, LS-100). All processes and measurements mentioned above were carried out in the open air at room temperature. To examine electrochemical properties, polymer solution was prepared and the electrochemical measurements were performed under 0.1 M tetrabutylammonium tetrafluoroborate solution containing acetonitrile. ITO, $Ag/AgNO_3$ and platinum wire were used as a working, reference and counter electrode, respectively.

RESULTS AND DISCUSSION

Scheme 1 outlines the synthetic route of the monomer and polymer. To introduce the 4-{5-[3-(3,7-dimethyloctyloxy)phenyl]-1,3,4-oxadiazoyl-2-yl}phenyl substitutent into the *p*-xylene backbone by coupling



SCHEME 1 Synthesis scheme.

reaction, 1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,5-dimethyl benzene **(1)** was first synthesized via the reaction of 2-bromo-*p*-xylene with 2-isopropoxy-4,4,5,5,-tetramethyl-1,3,2-dioxaborolane in dry THF at –78°C (Scheme 1). 4-Bromobenzonitrile was then introduced into the *p*-xylene derivative via Suzuki coupling to produce 4-(4-cyanophenyl)-2,5-dimethylbenzene **(2)**. The third step involves the formation of 5-[4-(2,5-dimethylphenyl)phenyl]tetrazole **(3)** by the reaction between 4-(4-cyanophenyl)-2,5-dimethylbenzene and sodium azide, in the presence of an equivalent amount of NH_4Cl in dry DMF. The key reaction between **3** and 3-(3,7-dimethyloctyloxy)benzoyl chloride proceeds via an intramolecular ring transformation to give 2-[3-(3,7-dimethyloctyloxy)phenyl]-5-[4-(2,5-dimethylphenyl)phenyl]-1,3,4-oxadiazole **(4)** in high yield (*ca*. 70%) and excellent purity.

The oxadiazole pendant group is typically linked through a rigid biphenyl moiety, which often causes poor solubility. Consequently, the bulky 3,7-dimethyloctyloxy groups were introduced into the meta-position of the phenyl side group in order to increase the overall solubility of the final monomer and corresponding polymer. The target 2-{3-[2,5-bis(bromomethyl)phenyl]phenyl-5-[4-(3,7-dimethyloctyloxy)-phenyl]-1,3,4-oxadiazole **(5)** monomer was obtained via bromination of compound **(4)** in the presence of benzoyl peroxide (BPO), and purified by column chromatography using hexane as an eluent. The synthesis of the oxadiazole unit through the use of the tetrazole intermediate exhibits several advantages compared to the ring closure procedure using dehydrating agents [17,18]. Ring closure via the tetrazole pathway typically proceeds to completion within 2 h, whereas heating with phosphorus oxychloride can take up to 1–3 days. Moreover, purification of the tetrazole intermediate **(3)** requires only extraction from methanol. The formation of the target polymer, poly[2-{4-[5-(3-(3,7-dimethyloctyloxy)phenyl)-1,3,4-oxadiazole-2-yl]phenyl}-1,4-phenylenevinylene] (C_{10}PhOxa-PPV), was synthesized by Gilch polymerization, affording a high molecular weight polymer with narrow polydispersity, and good thermal stability. Under a N_2 atmosphere, monomer **(5)** was polymerized in dry toluene with an excess of potassium *tert*-butoxide for 3 h. During polymerization, the viscosity of the reaction mixture was increased through irradiation with intense fluorescent light. The resulting polymer was obtained as fragile orange fibers after several purification steps [15]. Interestingly, the bent 3-(3,7-dimethyloctyloxy)phenyl substitutent in the oxadiazole moiety enhances the solubility of C_{10}PhOxa-PPV in common organic solvents. The structure and purity of the intermediates, monomer, and final C_{10}PhOxa-PPV polymer were confirmed by NMR spectroscopy and elemental analysis, respectively. The number average molecular weight (M_n) and polydispersity of C_{10}PhOxa-PPV were determined as 2.7 × 10^4 and 2.6, respectively. The thermal stability at 5% weight loss (385°C) and high glass transition temperature ($T_g = 147°C$) of C_{10}PhOxa-PPV are sufficient to prevent deformation of, or morphological changes in the emitting layer during the operation of PLEDs.

Figure 1 shows the optical absorption and photoluminescence (PL) spectra of C_{10}PhOxa-PPV in the thin film state, together with the EL spectrum of a ITO/PEDOT/Polymer/Al device, fabricated in order to investigate the current density-voltage-luminescence (*J-V-L*) characteristics of C_{10}PhOxa-PPV. UV-visible absorption of the C_{10}PhOxa-PPV in both solution and film almost identically show two peaks at about 300 and 429 nm. The longer wavelength (380–500 nm) is attributed to the π-π^* absorption of the conjugated polymer chain, whereas the shorter wavelength (297–303 nm) originates from the aromatic oxadiazole side chain. The C_{10}PhOxa-PPV band gap was estimated from the absorption edge to be 2.47 eV. The maximum emission peak of C_{10}PhOxa-PPV was 561 nm. The external PL quantum efficiencies (Φ_{PL}) of C_{10}PhOxa-PPV and MEH-PPV for comparison, in the solid state, were measured and compared using the integrating sphere method [19]. The Φ_{PL} values were determined to be approximately 37±2% and 10±2%, respectively, with the C_{10}PhOxa-PPV Φ_{PL} being almost 4 times higher than that of MEH-PPV. The higher external PL quantum efficiency is attributed to the

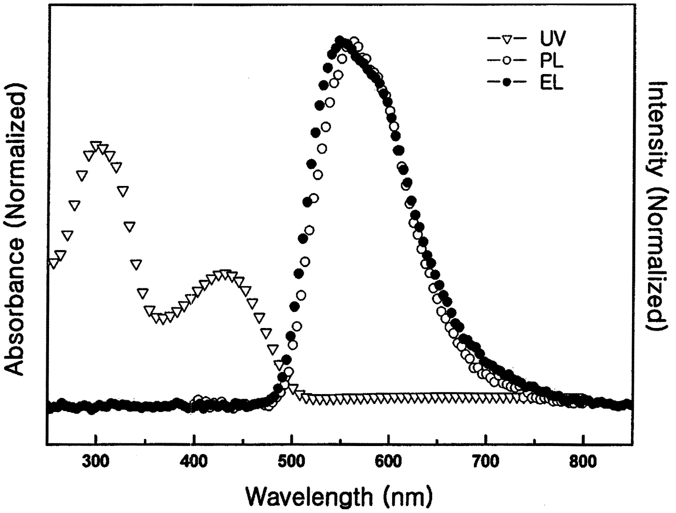


FIGURE 1 UV-Visible, PL, and EL spectra of the C_{10}PhOxa-PPV thin film.

bent configuration of the 4-{5-[3-(3,7-dimethyloctyloxy)phenyl]-1,3,4-oxadiazoyl-2-yl}phenyl substitutents in the π-conjugated polymer backbone, which are believed to increase the free volume effect and inhibit the intermolecular interaction between the polymer backbones. From cyclic voltammetry (CV) and optical absorption edge studies, the HOMO and LUMO energy levels of C_{10}PhOxa-PPV were observed at 5.47 and 3.00 eV, respectively. As shown in Figure 1, the EL and PL spectra of C_{10}PhOxa-PPV were identical, revealing maximum peaks at 547 nm with green color. The current density-voltage-luminescence (*J-V-L*) characteristic of C_{10}PhOxa-PPV is shown in Figure 2. The turn-on voltage of C_{10}PhOxa-PPV was observed at about 4.0 V. The linear dependence of the luminescence intensity on the voltage is indicated that charge carriers are easily injected from the both electrode by increasing the voltage or efficiency of the current density. The maximum brightness of C_{10}PhOxa-PPV was determined to be 4,426 cd/m^2 at 28 V. The luminance efficiency of C_{10}PhOxa-PPV, shown as a function of current in the inset in Figure 2, was determined to be 8.3 cd/A at 28.2 mA/cm^2 and 2,234 cd/m^2, based on double-layer PLEDs using an Al cathode.

The higher luminance efficiency of C_{10}PhOxa-PPV is attributed to the oxadiazole pendant group, which is believed to form electron transport channels through orbital interactions between the oxadiazole units.

In summary, we have synthesized a highly luminescent PPV derivative containing an electron transporting oxadiazole functionality. The maximum brightness and luminance efficiency of C_{10}PhOxa-PPV

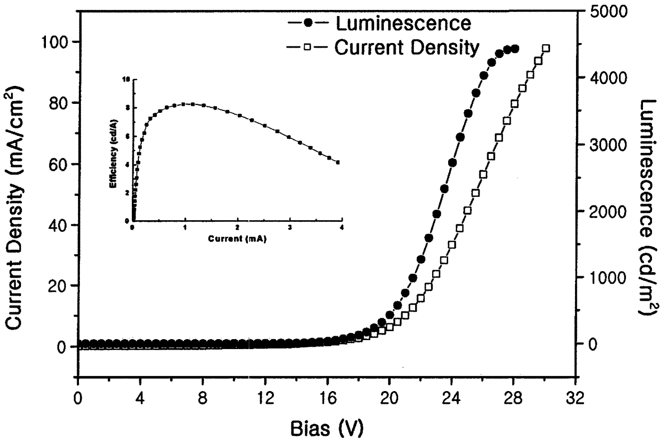


FIGURE 2 Current density-voltage, luminescence-voltage, and luminance efficiency-current characteristics of C_{10}PhOxa-PPV.

showed values of up to 8.3 cd/A and 4,426 cd/m^2, respectively. Further optimization of the molecular structure by copolymerization with various monomers, together with a more detailed study of the EL properties of C_{10}PhOxa-PPV is currently in progress.

CONCLUSIONS

This study focused on the design and synthesis of multifunctional light-emitting polymer through Gilch polymerization. The introduction of electron-deficient 1,3,4-oxadiazole units as side chains on the PPV backbones enhances the polymers' electron affinity and increases their LUMO energy levels, both of which produce improvements in device performance. The turn-on voltage, maximum brightness and luminance efficiency of the resulting polymer was 4.0 V, 4,426 cd/m^2 at 28 V, and 8.3 cd/A at 2,234 cd/m^2.

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