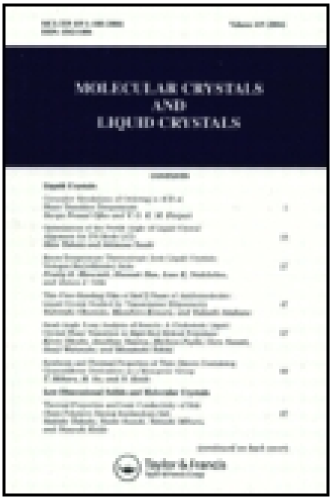

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SYNTHESIS AND ELECTROOPTICAL PROPERTIES OF NOVEL PPV DERIVATIVES CONTAINING 1,3,4-OXADIAZOLE

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SYNTHESIS AND ELECTROOPTICAL PROPERTIES OF NOVEL PPV DERIVATIVES CONTAINING 1,3,4-OXADIAZOLE

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Poly[2-{5′-(4″-t-butylphenyl)-1′,3′,4′-oxadiazole}-1,4-phenylenevinylene (BPOD-PPV)] containing 4-t-butylphenyl-1,3,4-oxadiazole pendant was synthesized by Gilch reaction. The obtained polymer shows a strong absorption centered around 300 nm and broader peak at about 350–520 nm. The efficiency of ITO/PPV/polymer/Al device is greater than by more than 2 orders of magnitude when compared with the ITO/PPV/Al device.

Keywords: 4-t-butylphenyl-1,3,4-oxadiazole; efficiency; electron transfer; PPV

INTRODUCTION

Luminescence properties of poly(p-phenylenevinylene), PPV, and other conjugated polymers have been attracting a great deal of interests since the first light emitting diodes (LEDs) based on PPV were reported a decade ago by the Cambridge group [1–2]. Electroluminescence (EL) efficiency of the devices, however, was far from satisfactory. And it soon was found that chemical modifications of PPV and use of different electrodes together with utilization of electron- and/or hole- transporting layers can improve the device efficiency to impressive extents.

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It is understood that in LED devices electrons and holes are separately injected from an anode and a cathode, respectively, under a bias voltage into the light emitting polymer layer where the injected negative and positive carriers from excitons. The excitons can disappear via various mechanisms; one of them is luminescence decay or radiative decay. To improve devices efficiency of LEDs there have been many attempts to balance the injection of carriers from electrodes and also their mobility in the emitting polymer layer. Unfortunately, the hole mobility in PPV and its simple derivatives is typically higher than that of electron mobility. This is one of the reasons why the LED devices fabricated using these polymers exhibit rather unsatisfactory efficiencies. Utilization of low work function metals as cathodes makes the electron injection easier. Calcium and lithium are representative examples. Another approach for improving electron transporting is to use of additives of electron deficient compounds such as 2-(4-biphenylyl)-5-(4-tertbutylphenyl)-1,3,4-oxadiazole (PBD). But their efficiency can be limited due to their crystallization and aggregation. This problem is mitigated by incorporating the electron transporting units into the main chain or as pendants attached to the backbone of a polymer. Or they can be included both in the main chain and in the side group [3–6].

In this article, we report synthesis, structural analysis, and spectral and luminescence properties of poly[2-{5′-(4″-t-butylphenyl)-1′,3′,4′-oxadiazole}-1,4-phenylenevinylene (BPOD-PPV)] that bears 4-t-butylphenyl-1,3,4-oxadiazole (BPOD) pendants directly attached to the PPV backbone. LED devices were fabricated using the polymer as emitting material or electron transfer material, and devices characteristics also are discussed.

EXPERIMENTAL

Synthesis of 2-(4′-t-butylphenyl)-5-(2″,5″-dibromomethylphenyl)-1,3,4-oxadiazole

In the solution of 150 mL of toluene and 30 mL of methanol, 16.3 g (302.5 mmol) of hydrazine monohydrate was added and stirred. In the mixture, 19.9 g (103.5 mmol) of methyl-t-butylbenzoate was dropped. After reflux for 6, the solvent was removed. The 4-t-butylbenzoic hydrizide was recrystallized in 10% aqueous methanol. In the solution of obtained 30 g (156 mmol) of t-butylbenzoyl hydrazine in 60 mL of pyridine and 100 mL of toluene, 26.3 g (156 mmol) of 2,5-dimethylbenzoyl chloride was dropped. After stirring for 6 h in 60°C, the reaction was terminated. After the mixture was extracted by ethylacetate, the 1-(4′-t-butylbenzoyl)-2-(2″,5″-dimethylbenzoyl)hydrazine was recrystallized in toluene. In the solution of synthesized 30 g (92.6 mmol) of 1-(4′-t-butylbenzoyl)-2-(2″,5″-dimethylbenzoyl) hydrazine, 50 g (420 mmol) of thionyl chloride was slowly dropped. After the reaction mixture was refluxed during 24 h, the solvent was removed by simple distillation. The crude 2-(4′-t-butylphenyl)-5-(2″,5″-dimethylphenyl)-1,3,4-oxadiazole was recrystallized in methanol. After the obtained 10 g (32.7 mmol) of 2-(4′-t-butylphenyl)-5-(2″,5″-dimethylphenyl)-1,3,4-oxadiazole was dissolved in CCl_4, 12.8 g (72 mmol) of N-bromosuccinimide and BPO was added. After cooling of the mixture, succinimide was filtered and the 2-(4′-t-butylphenyl)-5-(2″,5″-dibromomethylphenyl)-1,3,4-oxadiazole was recrystallized in n-hexane: ethylacetate (1:1). mp: 128°C. Yield: 43%. ^1H NMR (500 MHz, $CDCl_3$) (ppm): aromatic(C-H), δ 8.4 (m, 4H), 7.8(m, 3H), aliphatic(C-H) δ 5.3(s, 2H), 4.8(s, 2H), 1.3(s, 9H) FT-IR (KBr) (cm^{-1}) :3047(aromatic C-H), 2946(aliphatic CH_3), 1025(C=N).

Synthesis of 2-(5′-(4″-t-butylphenyl)-1′,3′,4′-oxadiazole-1,4-phenylenevinylene (BPOD-PPV)

In the ice-bath, 0.5 g of 2-(4′-t-butylphenyl)-5-(2″,5″-dibromomethylphenyl)-1,3,4-oxadiazole and catalytic amount of 18-crown ether were dissolved in 30 mL of THF, and 0.24 g of potassium t-butoxide was slowly dropped. After the polymerization was terminated by methanol, the

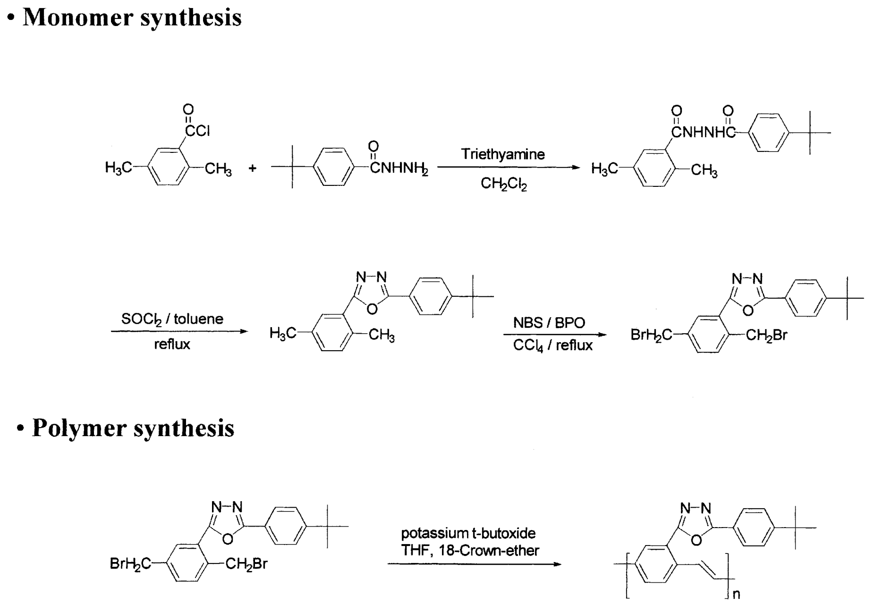

FIGURE 1 Synthetic scheme of ETS-PPV.

product was dissolved in chloroform and the solution was precipitated in methanol. Yield: 65%.

RESULT AND DISCUSSION

The synthetic scheme of the monomer and polymer is outlined in Figure 1. The monomer, 2-(4′-t-butylphenyl)-5-(2″,5″-dibromomethylphenyl)-1,3,4-oxadiazole, was prepared via cyclization and NBS reaction. The polymer, poly[2-(5′-(4″-t-butylphenyl)-1′,3′,4′-oxadiazole-1,4-phenylenevinylene)(BPOD-PPV), was obtained through the typical GILCH method. ^{1}H-NMR and FT-IR spectra agree with the proposed structures of various compounds and polymer. In the ^{1}H-NMR spectrum, the vinyl protons appeared at the range of 7.8–6.6 ppm with aromatic protons, instead of disappearing of methylene protons at around 4.5 ppm and 5.3 ppm. The molecular weight of polymer determined by gel permeation chromatography against polystyrene standards is Mn = 5600 with a polydispersity index of 1.4.

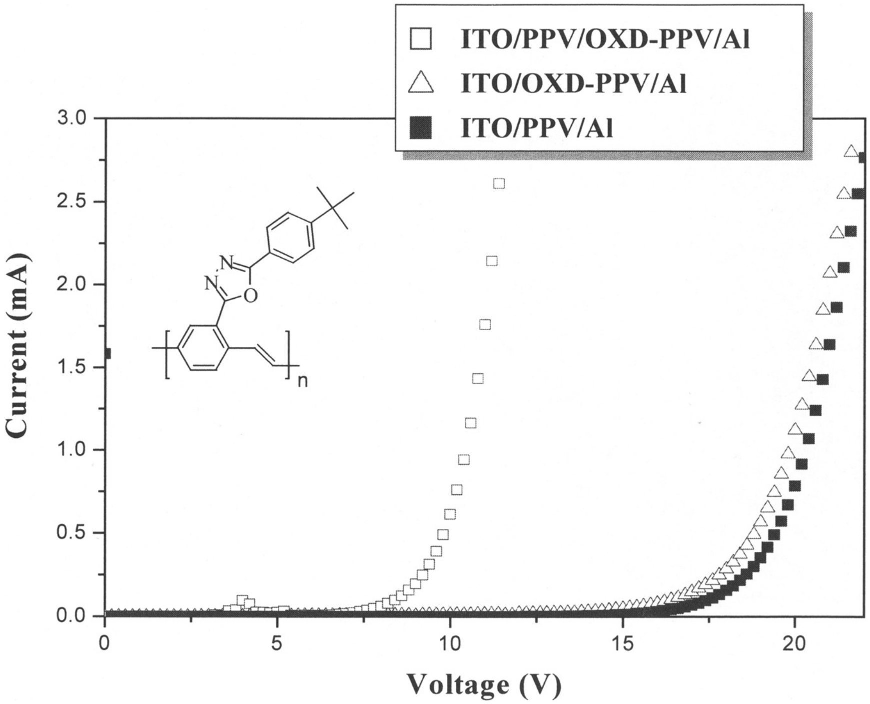

FIGURE 2 I-V characteristics of devices.

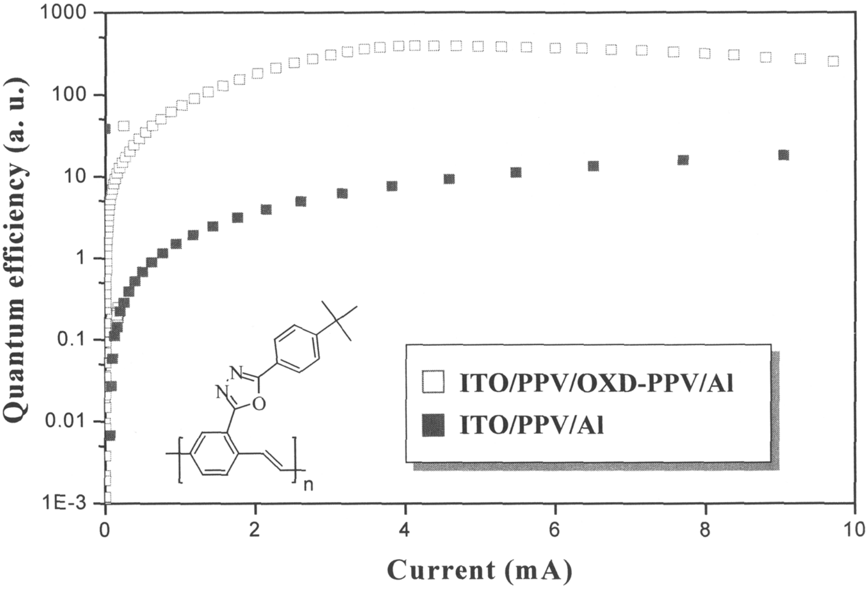

FIGURE 3 Comparison of current density-external quantum efficiency curves for devices.

When the UV-vis spectra of obtained polymer and PPV, which was prepared via the Wessling-Zimmerman water soluble precursor route and thermally treated at 270°C in vacuo for 12 h, were compared, the obtained polymer shows a strong absorption centered around 300 nm and broader peak at about 350–520 nm. In contrast, PPV absorbs broadly over the wavelength of 290–570 nm. It is suggested that the absorption in the 300 nm is attributed to the oxadiazole pendant and that in the longer wavelength region is attributed to the π–π^* transition of the main chain. In the photoluminescence spectrum of polymer, the emission maximum was observed at 505 nm.

LED devices were fabricated using the polymer as emitting material or electron transfer material. Figure 2 shows the I-V characteristics of the devices. The PPV/polymer devices showed lower turn on voltage compared with that of PPV. The result suggested that electron injection is generally more difficult than hole injection in the PPV derivatives, but the electron transfer can be ease by the introducing of oxadiazole pendant in PPV.

The current density-quantum efficiency of the devices constructed are compared in Figure 3. The efficiency of ITO/PPV/polymer/Al device is greater than by more than 2 orders of magnitude when compared with the ITO/PPV/Al device.

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