

A Novel Emitting Polymer with Bipolar Carrier Transporting Abilities

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ABSTRACT: A luminescent bipolar polymer containing 1,3,4-oxadiazole and triphenylamine has been synthesized. A smooth and dense thin film of polymer is easily obtained by spin coating its chloroform solution. This film exhibits a strong blue fluorescence under the irradiation of ultraviolet

(UV) light. The synthesized polymer possesses a high glass transition temperature (T_g) of 167°C. A single-layer electroluminescence (EL) device indium-tin oxide (ITO)/polymer/Mg:Ag emitted blue light with a turn-on voltage of 13 V. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 50–53, 2003

INTRODUCTION

In the past decade, conjugated polymers have received considerable attention because of their promising applications in optic-electronic devices,^{1, 2} such as organic light-emitting devices, lasers, and transistors. In particular, significant progress has been achieved in the development of light-emitting diodes (LEDs) based on conjugated polymers.^{3, 4} It is known that balanced and efficient charge injection/transport for both holes and electrons is essential for high a device efficiency. Two approaches have been applied to facilitate the charge injection/transport. One is to apply an additional hole-transporting layer between the emitter and the anode and/or an electron injection/transport layer between the emitter and cathode.^{5, 6} However, the fabrication of multilayer polymer LEDs is usually difficult. For a polymer LED, single-layer devices are preferred. Another approach is a polymer blend, which contains a polymer matrix doped with necessary components, usually small molecules to facilitate electron/hole transporting properties, have been often used.^{7,8} However, phase separation is unavoidable, especially at the high current density and local heating that can occur during device operations. To solve the above problems, polymers containing both electron and hole transporting segments as well as emissive groups^{9, 10} have been synthesized. 1,3,4-Oxadiazole has a good electron transporting property but low solubility in common organic solvents^{4, 11, 12}; triphenylamine has good hole transporting and solubility.^{13,14} They are usually used in polymeric emitting materials.

Here we report the synthesis and properties of a new bipolar polymer containing both triphenylamine and 1,3,4-oxadiazole groups. To improve the balance of electron and hole transporting in this polymer, the oxadiazole unit is directly interlinked to the triphenylamine, which is the backbone of the main chain. This article presents the detailed synthesis and device evaluation of this new polymer.

EXPERIMENTAL

Materials

4-Aldehydetriphenylamine and Ni(PPh₃)₂Cl₂ and Bu₄NBr₃ were prepared in our laboratory; *N,N*-dimethylacetamide (DMAC) was purified by distillation under reduced pressure. PPh₃, 2,2-dipyridyl, and other chemicals were used as purchased without further purification.

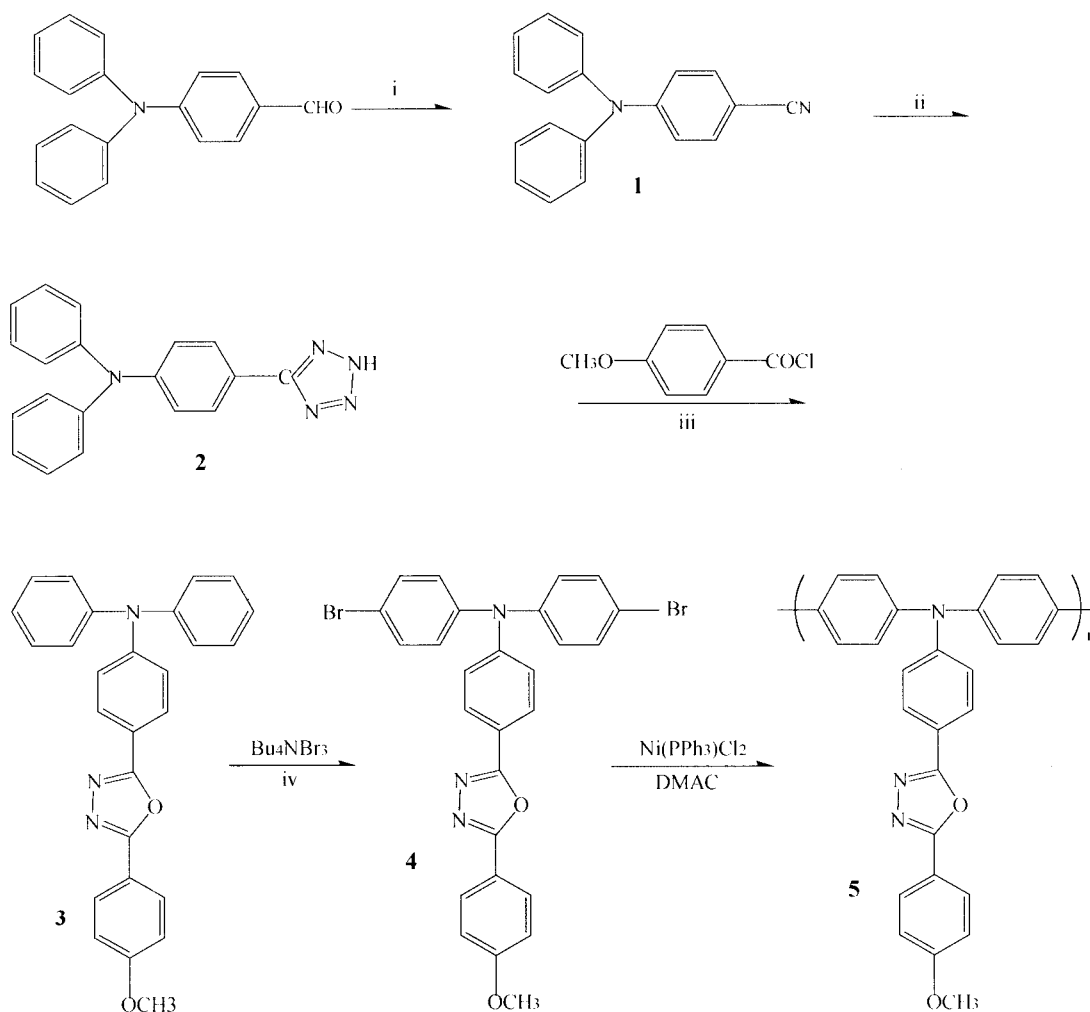
Synthesis procedure

The chemical structure and the synthetic route to new polymer 5 is shown in Scheme 1. ¹H nuclear magnetic resonance (¹H-NMR) spectra were recorded with a Varian 400 MHz spectrometer.

Monomer 1

A mixture of 11.25 g (41 mmol) 4-aldehydetriphenylamine and 6.9 g (100 mmol) hydroxyamine hydrochloride in 40 mL purified *N*-methylpyrrolidone was heated at 115°C under a nitrogen atmosphere for 6 h. After cooling to room temperature, this reaction was poured into water. The reaction mixture was extracted twice with 40 mL of CHCl₃. The organic layer was washed with brine and dried over Na₂SO₄. The sol-

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Scheme 1 Chemical structure and the synthetic route of the polymer.

vent was removed to yield a solid. Recrystallization of the residue from ethanol gave the pure nitrile, monomer **1**; 10.2 g (yield 90%). mp 125.8–126.5°C. $^1\text{H-NMR}$ (CDCl_3 δ): 6.94–6.99 (d, 2H), 7.12–7.20 (m, 6H), 7.30–7.37 (m, 4H), 7.39–7.44 (d, 2H).

Monomer 2

A mixture of 10 g (37 mmol) 4-cyanotriphenylamine, 37.5 g (590 mmol) sodium azide, and 32 g (590 mmol) ammonium chloride in dried dimethylformamide (DMF) 150 mL was stirred and heated under reflux for 75 h. After cooling, 250 mL of aqueous hydrochloric acid was added to the reaction mixture and yielded a precipitate. The precipitate was collected by filtration and washed with water. Recrystallization of the precipitate from toluene gave monomer **2**, 10.1 g (yield 90%); mp 216–217°C. $^1\text{H-NMR}$ (CDCl_3 δ): 7.88–7.94 (d, 2H), 7.24–7.34 (m, 4H), 7.04–7.16 (m, 9H).

Monomer 3

A solution of 9 g (30 mmol) 4-tetrazolyltriphenylamine and 5.6 g (33 mmol) *p*-methoxybenzoyl

chloride in 50 mL dried pyridine was heated under reflux for 96 h. After cooling, 150 mL of water was added to the reaction mixture, and then the mixture was extracted with 40 mL of CHCl_3 . The organic layer was washed with brine and dried over Na_2SO_4 . The solvent was removed by evaporation to yield a solid. This solid was purified by column chromatogram (eluent: ethyl acetate (EA)/petroleum ether (PE) 1:1 v/v) to afford the pure product, monomer **3**, 9.2 g (yield 73%); mp 134°C. $^1\text{H-NMR}$ (CDCl_3 δ): 3.87 (s, 3H), 7.01–7.03 (d, 2H), 7.09–7.17 (m, 8H), 7.30–7.34 (m, 4H), 7.91–7.93 (d, 2H), 8.03–8.06 (d, 2H).

Monomer 4

A solution of 9.6 g (20 mmol) Bu_4NBr in 10 mL CH_2Cl_2 was added to a solution of 4.2 g (10 mmol) monomer **3** in 10 mL CH_2Cl_2 at 25°C. The reaction mixture was allowed to continue 5 h. The organic layer was washed with a solution of sodium hydrogen sulfite two times and dried over Na_2SO_4 ; the solvent was removed by evaporation. The crude product was purified by recrystallization from acetic ester to give

the pure product, monomer **4**, 5.5 g (yield 95%); mp 172°C. $^1\text{H-NMR}$ (CDCl_3 δ): 3.88 (s, 3H), 7.00–7.04 (m, 5H), 7.09–7.15 (m, 4H), 7.31–7.43 (m, 3H), 7.93–7.95 (m, 2H), 8.04–8.06 (d, 2H). Anal Br: cal. 27.73; found, 27.79%.

Polymer synthesis

A mixture of 1.31 g PPh_3 , 0.68 g Zn, 0.14 g 2,2'-dipyridyl, and 0.33 g $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$ in 10 mL DMAC was stirred about 15 min at room temperature. Then 0.5 g of monomer **4** was added into the reaction mixture; this mixture was heated to 100°C and allowed to continue for 2 days. Then the solvent was removed in a reduced pressure. The residue was dissolved in tetrahydrofuran (THF) and the insoluble solid was filtered from THF solution. The polymer in THF solution was precipitated from methanol to yield the crude polymer. The crude polymer was redissolved in THF and precipitated to afford the polymer (60% yield). $^1\text{H-NMR}$ (CDCl_3 δ): 3.89 (s, 3H), 7.01–7.04 (d, 2H), 7.16–7.55 (m, 11H), 7.794–8.07 (m, 3H). The polymer readily dissolved in polar solvent, such as THF, CHCl_3 , and CH_2Cl_2 . The molecular weight of the polymer was measured by a Waters 410 instrument with polystyrene as a standard and THF as eluent at a flow rate of 1.0 mL/min. Gel permeation chromatography (GPC) analysis showed that the number-average molecular weight (M_n) and polydispersity (PD) were 9270 and 1.17, respectively.

RESULT AND DISCUSSION

The thermal property of the synthesized polymer was conducted on a Perkin-Elmer DSC 7 instrument (DSC: dynamic scanning calorimetry) at a heating rate of 20°C/min under a nitrogen atmosphere. DSC measurements revealed a high glass transition temperature of 167°C, implying that this polymer has good stability and is a promising candidate as an electroluminescence (EL) material. This polymer has good solubility in polar organic solvents, such as CHCl_3 , CH_2Cl_2 , THF, and DMF.

Cyclic voltammograms

Figure 1 shows the cyclic voltammograms of the polymer, triphenylamine, and 2,5-diphenyl-1,3,4-oxadiazole. Cyclic voltammetry (CV) was performed on a computer-controlled EG&G Parc model 283 potentiostat/galvanostat with a three-electrode electrochemical cell in a 0.1M tetrabutylammonium perchlorate solution in acetonitrile with a scan 100 mV/s at room temperature. A platinum wire was the counter electrode and a KCl-saturated Ag/AgCl was the reference electrode. A platinum square plate (1 cm²) for the polymer, and a microplatinum electrode ($\phi = 0.8$ mm) for the triphenylamine and 2,5-diphenyl-1,3,4-ox-

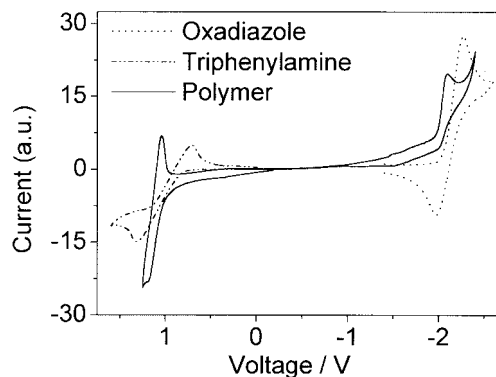


Figure 1 The cyclic voltammograms of the polymer, oxadiazole, and triphenylamine measured using the model 283 potentiostat/galvanostat with a scan rate of 100 mV/s.

adiazole, as work electrode were used. The polymer exhibits a reversible and a quasi-reversible redox process for the anodic and cathodic range, respectively. Comparing the CV curves of triphenylamine and 2,5-diphenyl-1,3,4-oxadiazole, the oxidation and reduction peaks appearing in the polymer can be attributed to the redox feature of triphenylamine and 2,5-diphenyl-1,3,4-oxadiazole, indicating that polymer possesses both the electron transporting property of 2,5-diphenyl-1,3,4-oxadiazole and the hole transporting property from triphenylamine. Therefore, it is suggested that this polymer has a bipolar property.^{15,16} The onset potential of oxide and reduction are 0.8 and -1.9 eV, respectively. E_{HOMO} is estimated to be -5.2 eV and E_{LUMO} is to be -2.5 eV. The optical band gap energy, E_g , is calculated to be 2.7 eV ($E_{\text{LUMO}} - E_{\text{HOMO}}$).

Optic properties

The absorption spectrum was recorded on a Varian Cray50 instrument. The maximum wavelength of the polymer in CHCl_3 solution was at 380 nm and onset was at 431 nm. The absorption spectrum was caused by electronic $\pi-\pi^*$ transition. The band gap, E_g , was estimated from the onset wavelength as 2.88 eV, which agrees with the results of cyclic voltammograms.

The polymer can form uniform smooth and clear film on a substrate (quartz plates or ITO-coated glasses). The polymer film on the quartz plate was obtained by spin coating its chloroform solution. The photoluminescence (PL) spectra were measured by using a Perkin-Elmer Ls50B Luminescence Spectrometer. The polymer in film or in solution can all emit intense blue fluorescence under the irradiation of UV light of wavelength 380 nm, shown in Figure 2. The fluorescence spectrum of polymer in CHCl_3 solution and in film exhibits a maximum at 479.5 and 480 nm, respectively. This indicates that polymer is a blue emissive polymeric material.

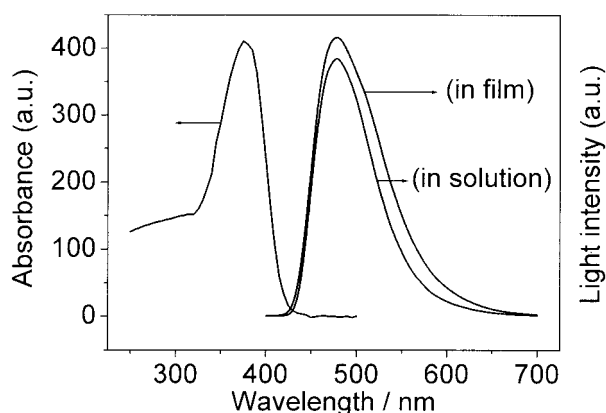


Figure 2 PL of the polymer in HCCl_3 solution and in film; UV of polymer in HCCl_3 solution.

EL properties

To investigate the EL properties of the polymer, a single-layer device, ITO/polymer/Mg:Ag, was fabricated. The polymer film was formed by spin coating its the toluene solution onto precleaned ITO-coated glass substrates and its thickness was about 80 nm. Then the Mg:Ag electrode was thermally evaporated onto the polymer film under 10^{-6} Torr, as about 140 nm. The turn-on voltage for the device was about 13 V and emitting blue light. The EL peak wavelength was 482 nm (Fig. 3), and the EL spectrum was in agreement with the photoluminescence spectrum of polymer 5, indicating that the EL emission results from the polymer layer. The single-layer device exhibited a maximum luminance of 32 cd/m^2 and efficiency of 0.12 cd/A . The typical current-voltage and luminance-voltage curves of this device are shown in Figure 4. The current-voltage-luminance (I-V-L) characteristics of the device reveal an excellent diode behavior; the intensity of the emitting light increases superlinearly with the increase of applied voltage after surpassing the turn-on voltage. The well superposition of the curves for current voltage and luminance voltage

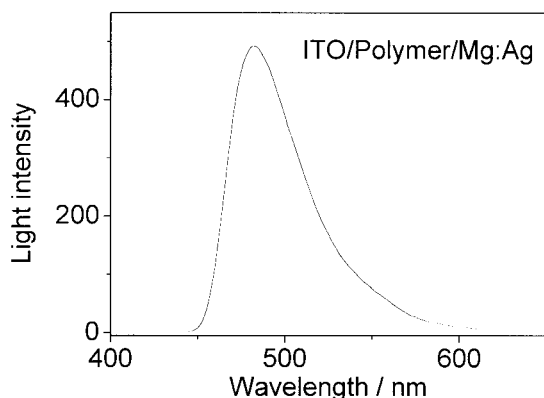


Figure 3 Electroluminescent spectra of ITO/polymer/Mg:Ag.

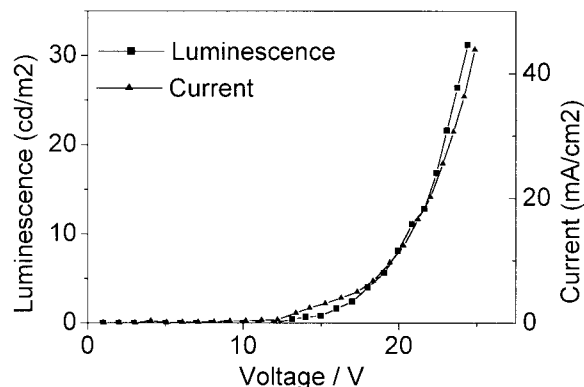


Figure 4 I-V-L characteristics for device of ITO/polymer/Mg:Ag

indicates that the transporting of hole and electron in device is well balanced.

CONCLUSION

In summary, the new bipolar blue emitting polymer has been designed and synthesized. Introduction of an oxadiazole component increases the electron-transporting ability of synthesized polymer. Blue light is obtained from a single-layer device using this polymer as emitting material with the maximum brightness of 35 cd/m^2 . This polymer is expected to be a promising candidate for practical use in organic light-emitting devices.

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