

# Synthesis and Properties of Polyether with Short Alternating Conjugated and Nonconjugated Blocks Containing Oxadiazole Units

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**ABSTRACT:** A polyether, poly[(2,5-dimethylene-1,3,4-oxadiazole)dioxy-1,4-phenylene-1,2-ethenylene-1,4-phenylene-1,2-ethenylene-1,4-phenylene], based on short alternating conjugated oxadiazole units, has been synthesized, which is a kind of PPV derivative that emits blue light. The resulting polymer is fairly soluble in chloroform. The synthesized polymer shows a UV-visible absorbency maximum wavelength around 310 nm in solution. The photoluminescence maximum wavelength for the resulting polymer appears

around 470 nm. The polymer also exhibits good thermal stability up to 300°C under N<sub>2</sub> atmosphere. It is also observed that the onset temperature of thermal decomposition is as high as 355°C. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2682–2686, 2002

**Key words:** luminescence; PPV derivatives; light-emitting diodes (LED); conjugated polymers; synthesis

## INTRODUCTION

Polymer light-emitting diodes (PLEDs) have drawn much attention in the past decade.<sup>1</sup> There is a strong possibility that these materials will find commercial use in a variety of display applications since a light-emitting diode with poly(*p*-phenylene vinylene) (PPV) as the active layer was first reported.<sup>2</sup> These materials have many advantages over their inorganic counterparts. One of the most important advantages lies in the easy fabrication of devices. Others include the ability to provide colors that sweep the whole range of the visible spectrum, by altering the  $\pi$ - $\pi^*$  energy gap through the molecular structure. Developing highly efficient electroluminescent materials is essential for commercialization of PLEDs.

Most initial polymers possess an extended conjugated skeleton, which is believed to be a major cause of the characteristic intractability and poor mechanical properties of these macromolecules.<sup>3</sup> The efficiency (photons emitted per injected electron) and the photoluminescence quantum yield of PPV reported by Burroughes were 0.05 and 8%, respectively.<sup>2</sup> Several years later, investigators found that a major improve-

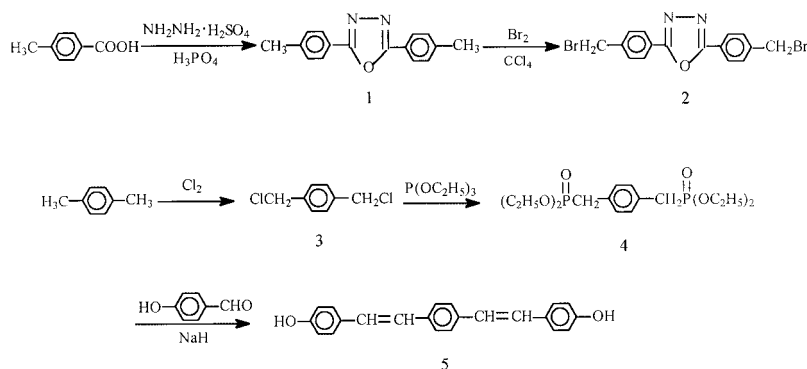
ment in electroluminescence intensity was obtained when partially conjugated PPV was used as the light-emitting layer. The efficiency of partially conjugated PPV LEDs is as high as 0.8% photons/electron. Both electroluminescence and photoluminescence decrease with increasing conjugation length.<sup>4</sup> The introduction of nonconjugated segments not only results in the confinement of electrons in conjugated parts, but also reduces polymer aggregation, thereby improving luminescent efficiency.<sup>5</sup> Furthermore, controlling the conjugation length by introducing nonconjugated segments in the main chain of conjugated polymers is an effective way of obtaining blue light emission.<sup>6</sup>

The electroluminescence results from the injection of electrons and holes on the conjugated chain. To achieve high quantum efficiency from electrons to photons, one should ensure that recombination of electrons and holes happens in the layer of the active polymer. Developing LEDs with a balanced tendency for transporting electrons and holes is a most efficient way to manufacture highly efficient PLEDs.<sup>7</sup> Unfortunately, almost all the polymers have a  $\pi$ -excessive nature and are typical *p*-doped-type polymers with much greater tendency for transporting holes than electrons. Therefore, improving the injection and transport of electrons is a key to promote quantum efficiency. Some multilayer PLEDs containing an electron-transport layer were made.<sup>8</sup> Although many polymers were made as promising emitting materials, few can be fabricated as efficient single-layer light-emitting diode devices.<sup>9</sup> Because the imperfection of the multilayer devices is unavoidable, single-layer emissive polymers are thus very important.

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Scheme 1

Electron-deficient oxadiazole units have been found to be efficient in promoting electron injection and transport when incorporated into the PPV main chain or as main-chain substituents.<sup>10,11</sup>

Completely conjugated polymers without substituents are neither soluble nor meltable, so that it is complicated to fabricate devices. To solve the problem, one can introduce aliphatic chains or soft linkages into the side chain or backbone of polymers.<sup>12</sup> The oxadiazole units introduced to the main chain can augment their solubility.

In this study, a new type of soluble electroluminescent polymeric materials was synthesized. The alternating copolymer contains PV(*p*-phenylene vinylene) and electron-withdrawing oxadiazole units.

## EXPERIMENTAL

### Materials

*p*-Toluic acid, sodium hydride, hydrazine hydrate, and quinine sulfate were purchased from Beijing Chemical Plant. *p*-Xylene, thionyl chloride, and phosphorus chloride (supplied by Shanghai Chemical Reagent Factory) were distilled under reduced pressure.

### Instruments

Melting points of monomers and intermediate compounds were determined on a Fisher-Johns melting point apparatus. <sup>1</sup>H-NMR was performed on a WH-90 NMR spectrometer referenced to TMS at 0.00 ppm. Infrared spectroscopy (KBr) was done using a Nicolet 510P FTIR spectrometer (Nicolet Instruments, Madison, WI). Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC-7 (Perkin Elmer Cetus Instruments, Norwalk, CT) at 20°C/min under nitrogen. Thermogravimetric analysis (TGA) was performed under nitrogen atmosphere at a heating rate of 20°C/min using a Perkin-Elmer TGA-7 thermal analyzer. The UV-visible spectrum of the polyether was measured using an HP-Shanghai 6010 UV-Vis spectrophotometer (Shanghai Instruments, China). The

photoluminescence (PL) spectrum of the polyether was obtained using a Shanghai Instruments (No. 3, model-960) spectrofluorophotometer. Intrinsic viscosity was determined in *N*-methyl-2-pyrrolidone (NMP) solution at 30°C. Samples were filtered through a 5-mm Millipore filter (Millipore, Bedford, MA) and equilibrated 1 h before measurement.

### Synthesis of monomers (Scheme 1)

#### 2,5-Bis(*p*-bromomethyl)-1,3,4-oxadiazole monomer

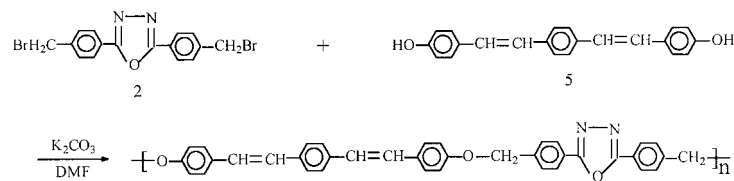
Compounds **1** and **2** shown in Scheme 1 were prepared according to a previously reported synthetic method.<sup>15,16</sup> The yield of **1** was 90%, m.p. 170–171°C; the yield of **2** was 55%, m.p. 184–185°C.

#### 4,4'-(*p*-Phenylene-di-1,2-ethenediyl)bisphenol monomer

*α,α'*-Dichloro-*p*-xylene (compound **3**). *p*-Xylene (43.0 g, 0.4 mol) was placed in a 100-mL three-neck round-bottom flask equipped with a stirrer, a reflux condenser, a thermometer, and a gas inlet. Chlorine gas was loaded into the flask with stirring and irradiating by a 200-W electric lamp until the temperature rose to 85°C. The produced hydrochloride gas was absorbed by water. Then the mixture was cooled. The precipitate was washed with methanol to give 58.1 g white crystals of compound **3**. The yield was 82%, m.p. 100–101°C.

IR (KBr, cm<sup>-1</sup>): 2960w (C—H), 1460m, 1430s, 880m, 750m, 680m (C—Cl).

Tetraethyl-*p*-xylyenediphosphonate (compound **4**). Compound **3** (8.8 g, 0.05 mol) was added in portions at 140–150°C to P(OEt)<sub>3</sub> (16.6 g, 0.1 mol) and the mixture was refluxed until the temperature rose to 200°C. Ethyl chloride was distilled off at atmospheric pressure. The residue was then cooled and recrystallized from 90 : 10 petroleum ether (60–90°C) : acetone to give 9.6 g of compound **4**. The yield was 90%, m.p. 72–73°C.



Scheme 2

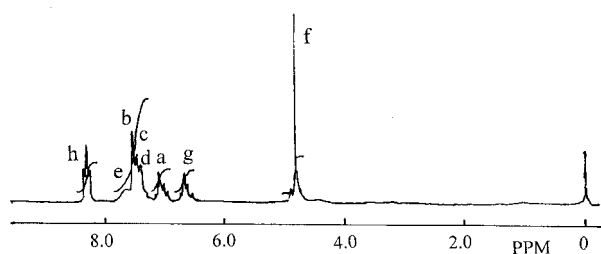
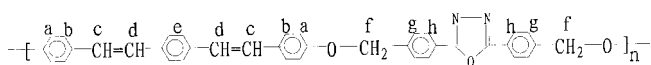
IR (KBr,  $\text{cm}^{-1}$ ): 2960w, 2860w, 1460s, 1450m, 1425m (P—C), 1240m (P=O), 1040s (C—O—C), 700m.

*Bisphenol monomer (compound 5)*. Compound 4 (2.2 g, 0.01 mol) was dissolved in 15 mL dry DMF and cooled to 0–5°C. Sodium hydride (1.5 g, 0.06 mol) was added with stirring under nitrogen below 5°C, until evolution of hydrogen ceased (approximately 1 h). The dark-red mixture was cooled to 0°C and 2.5 g (0.02 mol) 4-hydroxybenzaldehyde in 15 mL of dry DMF was added. After 3 h, the mixture was poured into 50 mL ice water and then acidified with 1N HCl. The precipitate was washed with methanol and recrystallized from DMF to give 2.3 g bright green crystals. The yield was 73%, m.p. > 300°C (decomposed).

IR (KBr,  $\text{cm}^{-1}$ ): 3410s (O—H), 2921m, 1605m, 1516m, 960w (*trans* C=C).  $^1\text{H-NMR}$  (pyridine):  $\delta$  (in ppm) 5.00 (br, s, OH), 7.23, 7.40 (doublets, 2H, =CH—), 7.24, 7.65 (doublets, 4H, arom), 7.62 (s, 4H, arom).

### Synthesis of polymers (Scheme 2)

Compound 5 (3.2 g, 0.01 mol) and compound 2 (1.2 g, 0.02 mol) were placed into 100 mL DMF and dissolved. Then  $\text{K}_2\text{CO}_3$  (2.1 g) was added with stirring. The mixture was heated at 80°C for 72 h, then poured into 100 mL water. The precipitation was filtrated and washed by ethanol and DMF, to give 2.1 g bright yellow crystals of polyether.

Figure 1  $^1\text{H-NMR}$  spectrum of the polyether.

IR (KBr,  $\text{cm}^{-1}$ ): 3030w (C=C), 2968s, 1650w (C=N), 1625s, 1250s, 1040s (C—O—C), 960w (*trans* C=C).  $^1\text{H-NMR}$  (chloroform):  $\delta$  (in ppm) 4.8 (m, 4H,  $-\text{OCH}_2$  of aromatic), 6.6–8.3 (m, 24H, aromatic and vinyl).

## RESULTS AND DISCUSSION

### Structural characterization of polymer

Structural characterization of the polymer was accomplished by FTIR and  $^1\text{H-NMR}$ , as shown in Figures 1 and 2, respectively. The formation of the designed structure was evidenced by comparing the IR spectra of the polymers with those of their corresponding monomers. The IR peaks of hydroxy groups at 3410  $\text{cm}^{-1}$  disappear completely. The appearance of the peaks at 1250  $\text{cm}^{-1}$  for the asymmetric C—O—C stretch and 1040  $\text{cm}^{-1}$  for the symmetric C—O—C stretch indicate the formation of aryl alkyl ether linkages. The peak at 960  $\text{cm}^{-1}$  is attributed to transvinylene.

From the  $^1\text{H-NMR}$  spectrum of the polymer, it is easy to determine the signals of hydrogen on the conjugated chain. The chemical shift at  $\delta$  4.80 ppm depicts the structure of  $\text{Ph}-\text{CH}_2-\text{O}-\text{Ph}$ .

### Solubility and viscosity of the polyether

The synthesized polyether was easily dissolved in chloroform without heating. It is also soluble in polar

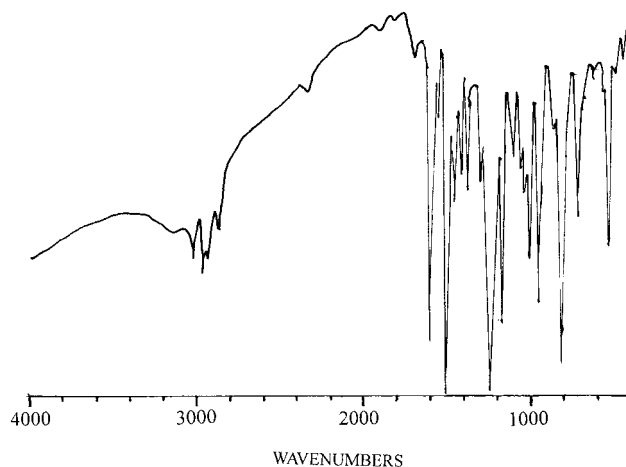


Figure 2 IR spectrum of the polyether.

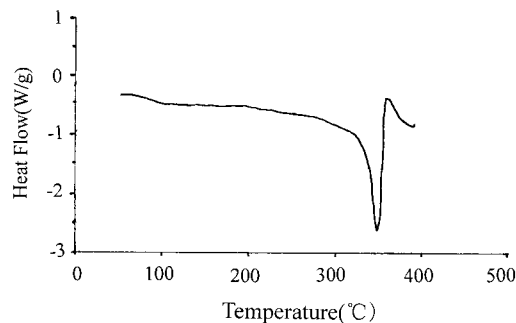


Figure 3 DSC spectrum of the polymer.

aprotic solvents such as dimethylacetamide, NMP, and dimethylsulfoxide at a suitable temperature. The enhanced solubility can be attributed to the ether and methylene linkages in the main chain. Therefore, the polyether shows good solubility in some common organic solvents, which is a necessary requirement for the spin-coating process.

The inherent viscosity of the polyether obtained in NMP at 30°C was 0.20 dL/g. This strongly suggests that the polymer is of low molecular weight.

### Thermal properties of the polymer

DSC measurement (Fig. 3) shows that the polymer has a glass transition at 141°C. It melts in the vicinity of decomposition, the onset of which is approximately 340°C (peak at 355°C). The melting and decomposition phenomena happen at the same time because of its robust structure. The result suggests that polyether is a good heat-resistant material.

The thermal stability of the polyether was evaluated by means of TGA. The thermogravimetric curve of the polymer is illustrated in Figure 4, indicating that thermal weight losses follow a two-stage process. The first stage begins at about 300°C, at which the weight losses are lower than 2%. It can be ascribed to thermal cleavage of low molecular weight ingredients. The second-stage weight loss occurs at about 350°C, which is attributed to thermal decomposition of the polymer main chain. However, the char yield at 600°C is greater than 40%, which means that carbonization seems to readily occur at a high temperature.

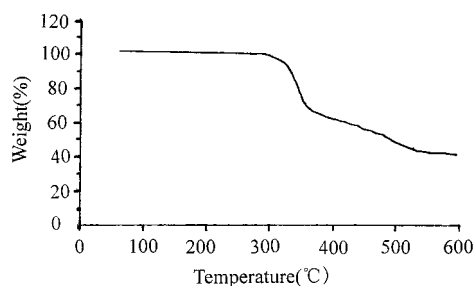


Figure 4 TGA spectrum of the polymer.

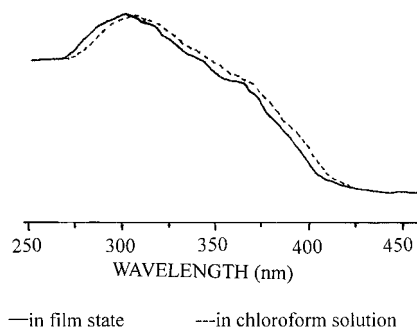


Figure 5 UV-Vis spectrum of the polymer.

### Optical properties

Because the polymer contained chromophores in the main chain, its optical properties were investigated both in solution and in the solid state. The thin film was prepared by spin coating on clean glass from a solution of the polymer.

The absorption spectra in the film state and in chloroform are shown in Figure 5. The wavelengths and corresponding data are summarized in Table I. The broad absorption bands result from the influence between the conjugated chain and oxadiazole chromophores. The optical energy gaps ( $E_g$ ) of the polymer listed in Table I were calculated from the onset wavelength of its UV-Vis spectra by  $E_g^{(opt)} = 1240/\lambda_{onset}$ .

Figure 6 depicts the PL spectra in chloroform and thin film that were obtained by excitation at 310 nm. The PL maxima of the polymer in solution and in film are 465 and 472 nm, respectively. The red shift of 7 nm is attributed to the highly ordered structure in the solid-state films. This ordered structure in the solid state arises from both intra- or intermolecular  $\pi$ - $\pi$  interactions of chromophores.

It is well known that a high PL quantum efficiency is a necessary condition for high electroluminescence efficiency. The quantum yields ( $\Phi_f$ ) of the polymer listed in Table I were determined<sup>17</sup> using quinine sulfate as a standard ( $\Phi_0 = 0.546$ ) by the formula

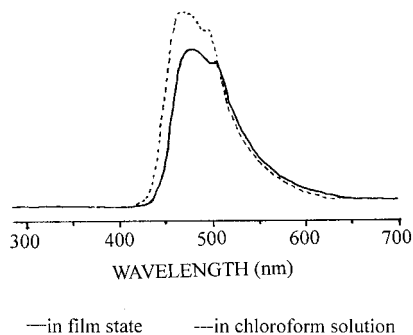
$$\Phi_f = \Phi_0 \frac{F(1 - 10^{-A})n^2}{F_0(1 - 10^{-A})n_0^2}$$

where  $F$  is fluorescence quantity,  $A$  is light density, and  $n$  is refrangibility of solution.

The  $\Phi_f$  in solution (60%) is much greater than that in the film state (41%), indicating the increased nonra-

TABLE I  
Optical Properties of the Polyether

Polymer states	UV (nm)	$E_g^{(opt)}$ (ev)	PL (nm)	$\Phi_f$ (%)
In chloroform	310,370	2.97	465	60
Thin-film	304,365	2.95	472	41



**Figure 6** PL spectrum of the polymer.

diative processes of excitons as a result of aggregation in the film state.

### CONCLUSIONS

A kind of soluble alternating copolymer containing isolated emissive *p*-aryl vinylene derivatives and oxadiazole units was synthesized and characterized. The polymer can be dissolved in general organic solvents such as chloroform. It shows a decomposition temperature in nitrogen at 355°C. In the film state, the photoluminescence and absorption maxima of the polymer are 472 and 304 nm, respectively. The optical energy gap ( $E_g$ ) of the polymer is 2.95 eV. The PL quantum yield of the polymer is 41% in the film state.

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