

SYNTHESIS OF POLY(2,5-DIPHENYL-1,3,4-THIADIAZOLYL)-4,4'-VINYLENE AND ITS ELECTROLUMINESCENT PERFORMANCE*

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Abstract The synthesis, characterization and electroluminescence performance of a new type of conjugated polymer, poly(2,5-diphenyl-1,3,4-thiadiazolyl)-4,4'-vinylene (TPPV) are presented. A light-emitting diode consisted of ITO/TPPV/Al is driven at about 4.0 V and has a peak emission wavelength of 485 nm. This blue-shift of the peak is due to the decrease of conjugate degree of TPPV compared to PPV. This result is in accord with that determined by XPS and theoretical model of MNDO/3

Keywords PPV, Electroluminescence, XPS, MNDO/3

INTRODUCTION

Conjugated polymers have attracted much interest, both fundamental and applied, in recent years due to the many possibilities identified for their potential exploitation in electronics, optoelectronics and other optical materials since a light-emitting diode (LED) with poly(*p*-phenylene vinylene) (PPV) as the active layer was firstly reported in 1990^[1, 2]. The perceived advantages of these materials lie in their ability to be used in ways that complement the use of traditional inorganic semiconductors. For instance, polymer LEDs can be made on flexible substrates, and large areas are obtainable from low cost film spin-coating. Moreover, chemical tuning of the polymer electronic structure allows the colour range including the three colours (red, green and blue) required for full colour displays^[3, 4]. Blue light emitting is very important for LEDs, and has been realized by using different organic polymers, which can be easily constructed into large area display. Controlling of conjugation length by introducing non-conjugated segments into the main chain of conjugated polymers is an effective way to obtain blue light-emission^[5]. In addition, the introduction of non-conjugated segments not only results in confinement of electrons in conjugated part, but also reduce its aggregation to improve the luminescent efficiency.

In the course of our studies on synthetic routes to poly(2,5-diphenyl-1,3,4-thiadiazolyl)-4,4'-vinylene (TPPV), we successfully introduced the electron-withdrawing thiadiazole unit to the main chain of PPV structure. Compared with the diode (ITO/PPV/Al) which emits yellow-green light, the device (ITO/TPPV/Al) emits blue light.

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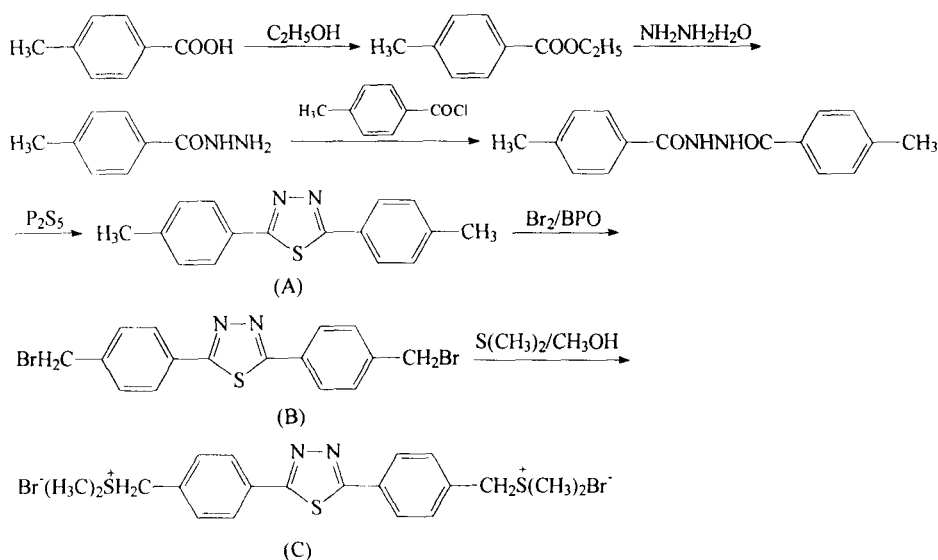
EXPERIMENTAL

$^1\text{H-NMR}$ spectra were obtained on Varian Unity Plus-400 spectrometer, IR spectra were recorded on Nicolet 5DX FT-IR spectrometer, the photoelectron spectra were recorded using a Perkin Elmer PHI1600 ESCA System, photoluminescence spectra were measured using a Hitachi-F4010. ITO-coated glass ($\sim 80 \Omega/\square$) was used as the positive electrode, a layer of polymer precursor was then deposited by spin-coating, and thermally converted to a ~ 80 nm thick TPPV film, and then Al was evaporated onto the polymer.

Monomer Synthesis

2,5-Bis(*p*-tolyl)-1,3,4-thiadiazole (A) was synthesized according to the following scheme. *N,N'*-benzoylhydrazine was synthesized using a procedure as described by Hayes *et al.*^[6]. To a solution of *N,N'*-benzoylhydrazine (0.05 mol, 13.4 g) in 150 mL of anhydrous pyridine, phosphorus pentasulfide (0.1 mol, 22.2 g) was slowly added. When the spontaneous reaction subsided, the mixture was refluxed for 12 h, and then cooled and added to a solution composed of 80 mL ethanol and 850 mL ice water. The product A was filtered and recrystallized from ethanol (9.5 g, m.p. $160\sim 162^\circ\text{C}$, yield 71.4%).

2,5-Bis(*p*-bromomethylphenyl)-1,3,4-thiadiazole (B) can be prepared by the following procedure:

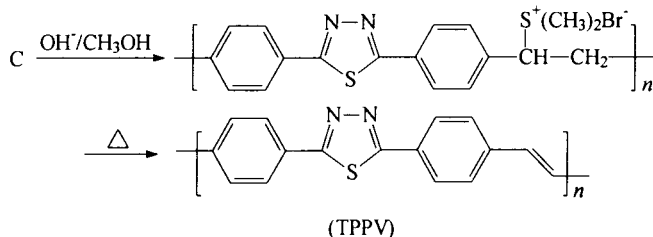


To a stirring solution of compound A (0.05 mol, 13.3 g) in 150 mL tetrachloromethane, dibenzoyl peroxide (0.25 g) and *N*-bromosuccinimide (0.1 mol, 17.8 g) was added slowly. The mixture was heated to 70°C , and gently refluxed for 6 h. The solution was then cooled and filtered, the solid product B was washed with hot water ($85\sim 90^\circ\text{C}$). Product B was crystallized from ethanol (30.9 g, m.p. $177\sim 179^\circ\text{C}$, yield 68.5%). $^1\text{H-NMR}$ (CDCl_3), δ : 7.6, 8.2 (8H, s, phenyl), 4.6 (4H, s, $-\text{CH}_2\text{Br}$).

2,5-Bis(*p*-methylenephenyl dimethylsulfonium bromide)-1,3,4-thiadiazole (C) was prepared according to the following procedure. To a stirring solution of the compound B (20 mmol, 8.48 g) in 100 mL MeOH was added 10 mL of dimethyl sulphide and the reaction mixture was refluxed for 4 h. The solvent and excess dimethyl sulphide were distilled off and the white solid of monomer salt was precipitated by adding 300 mL acetone. The solid was recrystallized twice from a mixture of methanol and acetone (1:1) to afford colourless crystals (7.16 g, m.p. $138\sim 139^\circ\text{C}$, yield 65.4%), $^1\text{H-NMR}$ (D_2O), δ : 7.6, 8.1 (8H, s, phenyl), 4.5 (4H, s, $-\text{CH}_2\text{S}$), 2.8 (12H, s, SCH_3).

Polymer Synthesis

The polymer TPPV was synthesized using a procedure described by Wessling^[7]. A thoroughly degassed and stirred solution of the monomer salt C (50 mmol in 10 mL MeOH) was maintained at $-10 \sim -5^{\circ}\text{C}$ and was treated with NaOH (50 mmol in 2 mL MeOH maintained at -5°C). The reaction mixture became viscous and a thick gel was obtained within 4 h; this was then quenched by neutralization with 0.5 mol/L HCl. The gel was dialyzed in MeOH containing 1% water for 3 days until bromide ion was not detected by silver nitrate. The purified gel was allowed to evaporate slowly at room temperature and the solution of the polymer precursor was cast into films, which were converted to the desired polymer TPPV by heating at 200°C under nitrogen for 3 h.



RESULTS AND DISCUSSION

Due to the rigid structure of styryl, the polymer TPPV is insoluble and infusible. The IR spectrum of the polymer TPPV (Fig. 1) shows a characteristic transvinylene absorption peak at 965 cm^{-1} .

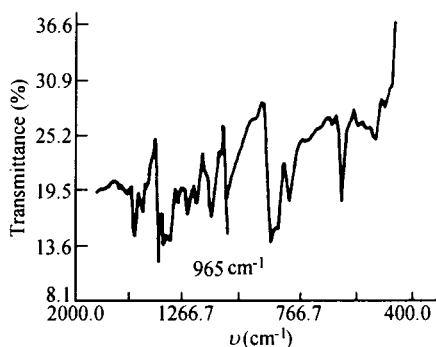


Fig. 1 IR spectrum of TPPV

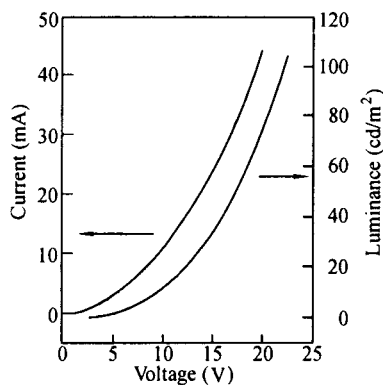


Fig. 2 Current/brightness-voltage characteristics for a device of ITO/TPPV/Al

The single-layer device ITO/TPPV (80 nm)/Al fabricated with the novel polymer of thiadiazole-substituted PPV (TPPV) can be driven in a dc mode, and the forward bias corresponds to the positive polarity of the voltage on the ITO electrode. Light emission observed only under forward bias was measured from as low as about 4.0 V. Figure 2 shows a plot of the current and brightness versus voltage characteristics, respectively. At 8.0 V, the forward bias light emission can be clearly observed under ambient conditions. From Fig. 3 we know that the device emits blue light ($\lambda_{\text{max}} = 485\text{ nm}$), while the diode constructed by PPV (ITO/PPV/Al)^[1] emits yellow light ($\lambda_{\text{max}} = 507, 540\text{ nm}$). The most likely explanation for this difference is that the decrease of conjugated degree of the heterocyclic-substituted PPV makes the values of band gaps (HOMO-LUMO) higher than that of PPV, and the emission wavelength of the device shifts to blue. Obrzut^[8] reported that the energy band gap of PPV measured by XPS technique is about 3 eV and the VEH band gap of PPV calculated by Fablman^[9] is about 2.3 eV. Figure 4 shows that the energy band gap of TPPV measured by XPS technique is about 4 eV, which is higher than that of PPV.

Also we calculate the HOMO-LUMO gaps of TPPV and PPV using quantum mechanical molecular model of MNDO/3 (modified neglect of diatomic overlap). Table 1 exhibits the energy gap parameters of TPPV and PPV respectively. So, this is fairly in agreement with the results of the luminescence spectrum observed in the experiments.

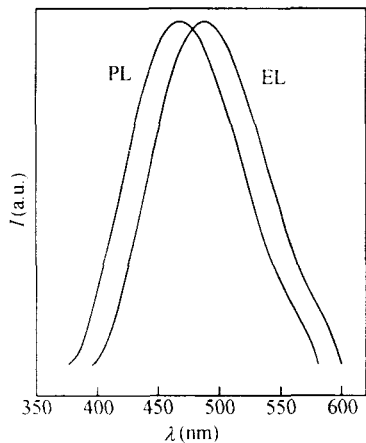


Fig. 3 EL and PL spectra of a device with an ITO/TPPV/Al structure

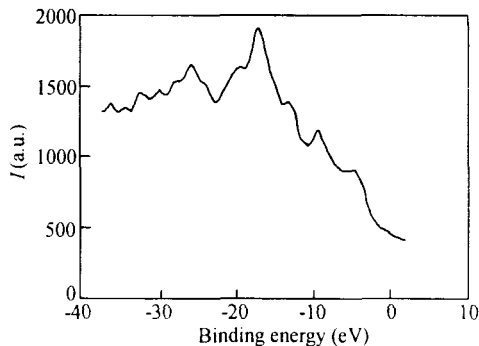


Fig. 4 XPS spectra of TPPV

Table 1 Parameter of energy gap		
Parameter	TPPV(eV)	PPV(eV)
HOMO	-8.613	-7.953
LUMO	-1.457	-1.058
Energy gap(ΔE_g)	7.156	6.895

CONCLUSIONS

A novel polymer, poly(2,5-diphenyl-1,3,4-thiadiazolyl)-4,4'-vinylene (TPPV) was synthesized. Unlike the yellow light emitting from the device of ITO/PPV/Al, the device of ITO/TPPV/Al fabricated with this novel polymer TPPV emitted blue light, and both the results measured by the XPS technique and theoretically calculated by the MNDO/3 model can explain the emission results.

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