

Synthesis and Characterization of a New PPV Derivative Containing a Sterically Hindered 2,5-Dimethylphenyl Group

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Abstract: A new poly[2-(2',5'-dimethylphenyl)-1,4-phenylenevinylene] (PDMPPV) that features a bulky 2',5'-dimethylphenyl substituent, which can induce steric hindrance between the PPV backbone and the methyl groups, was designed and synthesized. The polymer structure having no TBB defects was confirmed by ¹H-NMR and ¹³C-NMR spectroscopy. The polymer showed good thermal stability with high T_g . The polymer film showed a maximum absorption at 415 nm with an absorption onset at 480 nm. The maximum emission peak showed at ca. 515 nm, with a shoulder at 530 nm. The turn-on voltages of ITO/PEDOT/PDMPPV/Al and ITO/PDMPPV/Al devices were 8 and 10 V, respectively. The electroluminescence spectrum from the device showed a maximum peak at 510 nm with a shoulder at ca. 535 nm.

Keywords: poly(*p*-phenylenevinylene), TBB defects, Gilch polymerization, electroluminescence.

Introduction

Organic polymers have traditionally been considered as insulators, and the electronic industry have taken advantage of this property in many applications. The concept of only being insulators changed in 1977, when Shirakawa *et al.* found that polyacetylene was capable of conducting electricity in the doped state.¹ Conjugated polymers was paid renewed research interest in 1990, when electroluminescence (EL) was found in poly(*p*-phenylenevinylene) (PPV).^{2,3} Since then, extensive research has been focused on the development of polymers suitable for use as the active substances in light emitting diodes (LEDs).⁴⁻⁶ Today, PPV and its derivatives are still one of the most promising class of conjugated polymers in LEDs.⁷⁻¹¹ This is mainly due to high luminescence efficiencies and readiness to polymerize to high molecular weight. The most frequently used polymerization method for soluble PPVs is dehydrogenation of 1,4-bis(halomethyl) benzenes, known as the Gilch route. This procedure normally yields high molecular weight materials, number average molecular weight on the order of 10^5 , which gives the PPVs good film forming properties. A wide variety of PPV derivatives had been synthesized and applied in LED applications, very few show high PL efficiencies in solid states.¹²⁻¹⁵ The major reasons are that TBB defects and conjugated backbones

tend to stack with each other due to the favorable interchain interactions, which lead to a self-quenching process of excitons. Introducing appropriate substituents to the PPV backbone to prevent its close packing and formation of TBB defects should therefore increase its PL efficiency.¹⁶⁻¹⁸ It has been shown that phenyl substituted PPVs have a higher resistance to photooxidation than other PPVs.⁴ Recently, Becker *et al.* reported that longer lifetimes of LEDs, with phenyl substituted PPVs as the active substances, could be reached by decreasing the formation of TBB defects during polymerization.

Thus, we designed and synthesized new PPV derivative, poly[2-(2',5'-dimethyl)phenyl-1,4-phenylenevinylene] (DMPPV) containing 2',5'-dimethylphenyl in PPV. It is expected that steric hindrance between the methyl group in the phenyl substituent and PPV backbone enhances high efficiency due to minimized intermolecular interactions and reduced TBB defects. And the bulky and rigid substituent makes the polymer to have good solubility and thermal stability.

Experimental

2,5-Dimethylbenzeneboronic Acid (DMBBA). After 30 g (0.162 mol) of 2-bromo-*p*-xylene was reacted with 4.72 g (0.194 mol) of Mg, 33.6 g (0.324 mol) of trimethylborate was added. The reaction mixture was stirred for 24 h and worked up with 4 N H₂SO₄ and ice. The crude product was recrystallized in hexane. Yield; 11.7 g (48%), mp: 187 °C.

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FT-IR (KBr pellet, cm^{-1}): 3600, 3020, 2950, 1400, 750. $^1\text{H-NMR}$ (CDCl_3): δ 7.0 (s, 3H, aromatic), 4.5 (s, 2H, $\text{B}(\text{OH})_2$), 2.1 (s, 6H, $-\text{CH}_3$).

Synthesis of 2-(2',5'-Dimethylphenyl)-1,4-Dimethyl Benzoate. In the 2.75 g (18.3 mmol) of 2,5-dimethylbenzene boronic acid, 5 g (18.3 mmol) of 2-bromo-1,4-dimethyl terephthalate, $\text{Pd}(\text{Ph}_3)_4$, 10 mL of THF and 10 mL of 2 M K_2CO_3 were added and refluxed. After reaction, the mixture was extracted with ether and washed with water. The product was recrystallized in methanol. Yield: 3.27 g (60%). Mp: 104 °C. FT-IR (KBr pellet, cm^{-1}): 3020, 2950, 1700, 1250, 750. $^1\text{H-NMR}$ (CDCl_3): δ 8.2-6.8 (m, 6H, aromatic), 3.8 (s, 3H, $\text{O}-\text{CH}_3$), 3.5 (s, 3H, $\text{O}-\text{CH}_3$), 2.3 (s, 3H, $-\text{CH}_3$), 2.1 (s, 3H, $-\text{CH}_3$).

Synthesis of 2-(2',5'-Dimethylphenyl)-1,4-Benzene-dimethanol. The reduction reaction of 2 g (6.8 mmol) of 2-(2',5'-dimethylphenyl)-1,4-dimethyl benzoate was carried out by 1 g (27.2 mmol) of LiAlH_4 in 100 mL of THF. After reaction, the mixture was washed with water, and extracted with ether. The product was obtained after evaporating of ether. Yield: 1.67 g (95%). Mp: 146 °C. FT-IR (KBr pellet, cm^{-1}): 3250, 2900, 1500, 1000, 750. $^1\text{H-NMR}$ (CDCl_3): δ 7.7-7.0 (m, 6H, aromatic), 4.6 (s, 2H, $\text{O}-\text{CH}_2$), 4.3 (s, 2H, $\text{O}-\text{CH}_2$), 4.1 (s, 1H, $-\text{OH}$), 3.8 (s, 1H, $-\text{OH}$), 2.3 (s, 3H, $-\text{CH}_3$), 2.1 (s, 3H, $-\text{CH}_3$).

Synthesis of 2-(2',5'-Dimethylphenyl)-1,4-Bis(chloromethyl)benzene. 2-(2',5'-Dimethylphenyl)-1,4-dimethylbenzoate (DMPDMB) was obtained by the Suzuki coupling reaction of 2,5-dimethylbenzeneboronic acid and 2-bromo-1,4-dimethyl terephthalate. The obtained DMPDMB was reacted by LiAlH_4 to give 2-(2',5'-dimethylphenyl)-1,4-benzene-dimethanol (DMPBDM). The 1 g (4.1 mmol) of DMPBDM was reacted with 1 g (16.2 mmol) of thionyl chloride for 4 h in 10 mL of methylene chloride. The crude product was purified by column chromatography. Yield: 96%. FT-IR (KBr pellet, cm^{-1}): 3050, 2900, 1500, 1000, 750. $^1\text{H-NMR}$ (CDCl_3): δ 7.7-6.8 (m, 6H, aromatic), 4.3 (s, 3H, CH_2Cl), 4.1 (s, 3H, CH_2Cl), 2.2 (s, 3H, $-\text{CH}_3$), 1.8 (s, 3H, $-\text{CH}_3$).

Synthesis of Poly[2-(2',5'-dimethyl)phenyl-1,4-phenylenevinylene] (PDMPPV). 0.5 g (1.79 mmol) of 2-(2',5'-dimethylphenyl)-1,4-bis(chloromethyl)benzene was refluxed with 0.6 g (5.4 mmol) of potassium *t*-butoxide in THF for 10 h. After cooling, 0.02 g of sodium methoxide was added and refluxed for 4 h. After reaction was terminated, the solution was precipitated in methanol. The precipitate was filtered off and dried under vacuum. The yield of the polymer after complete work up was 60%. FT-IR (KBr pellet, cm^{-1}): 3050, 2900, 1600, 1500, 960, 780. $^1\text{H-NMR}$ (CDCl_3): δ 7.3-6.8 (m, 8H, aromatic and vinylic), 2.2 (s, 3H, $-\text{CH}_3$), 1.8 (s, 3H, $-\text{CH}_3$). Anal. Calcd for $\text{C}_{16}\text{H}_{11}$: C, 94.58%; H, 5.42%. Found: C, 94.39%, H, 5.37%.

Characterization. $^1\text{H-NMR}$ spectra data were expressed in ppm relative to the internal standard and were obtained on a DRX 500 MHz NMR spectrometer. FT-IR spectra

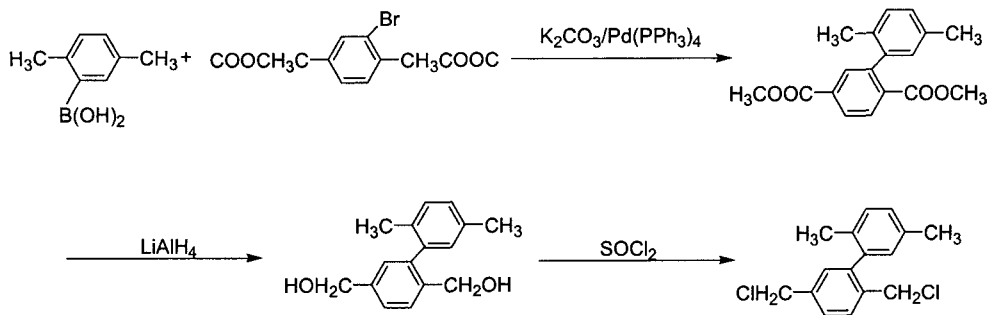
were obtained with a Bomem Michelson series FT-IR spectrometer, and the UV-Vis absorption spectra obtained in chloroform on a Shimadzu UV 3100 spectrometer. Molecular weight and polydispersity of the polymer were determined by gel permeation chromatography (GPC) analysis with polystyrene standard calibration (Waters high pressure GPC assembly model M590 pump μ -styragel columns of 105, 104, 103, 500, and 100 Å, refractive index detectors, solvent THF). Elemental analysis was performed by Leco Co. CHNS-932. TGA measurements were performed on a Perkin-Elmer series 7 analysis system under N_2 at a heating rate 10 °C/min. The photoluminescence spectra were recorded on a Perkin-Elmer LS-50 fluoremeter utilizing a lock-in amplifier system with a chopping frequency of 150 Hz. For the measurements of device characteristics current-voltage (I-V) changes were measured using a current/voltage source (Keithly 238) and optical power meter (Newport 818-SL).

Fabrication of the LED: Poly(styrenesulfonate)-doped poly(3,4-ethylenedioxythiophene) (PEDOT) for a conducting polymer hole-injection layer was coated on an indiumtin oxide coated glass substrate which had been washed with water, acetone, and isopropyl alcohol sequentially. A tin polymer film was spin coated (3,000 rpm, 50 s) from a filtered (0.2 μm filter) 1.0 wt% polymer solution in chlorobenzene on a PEDOT layer. An aluminium electrode was deposited on top of the device at a high vacuum (below 1×10^{-5} Torr). Wires were attached to the respective electrodes with a conductive epoxy adhesive. All fabrication steps were performed in clean room conditions. Measurements were done at room temperature in air.

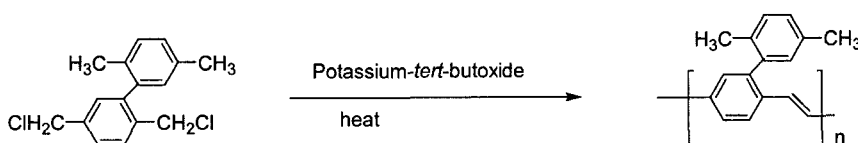
Results and Discussion

The polymer was prepared according to Scheme I. The substituted dimethyl terephthalate was synthesized by Suzuki coupling reaction. The reduction of ester with LiAlH_4 followed by chlorine substitution of resulting hydroxy groups with thionyl chloride yielded the monomer. The poly[2-(2',5'-dimethyl)phenyl-1,4-phenylenevinylene] (PDMPPV) was obtained through the typical Gilch method. FT-IR, $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra agree with the proposed structure of polymer. In the IR-spectrum, the stretching absorption bands for C-Cl in the monomer at 680 cm^{-1} disappeared after polymerization, while a new band with strong intensity occurred at 960 cm^{-1} , which is due to the vinylic out of plane deformation. This result suggests that the vinylene group formed through Gilch route is in the trans configuration (Figure 1). The $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of polymer are shown in Figure 2. The signals around 1.8~2.1 ppm arise from the methyl attached to phenyl in the side chain. Becker *et al.* assigned the CH_2CH_2 groups from HH couplings to peaks around 2.7~2.9 ppm. The peaks due to TBB defects did not show in the around 2.7~2.9 ppm. In the $^{13}\text{C-NMR}$, the aliphatic carbons appeared at 20 ppm, and aromatic and

• Monomer Synthesis



• Polymer Synthesis



Scheme I. Synthetic scheme of monomer and PDMPPV.

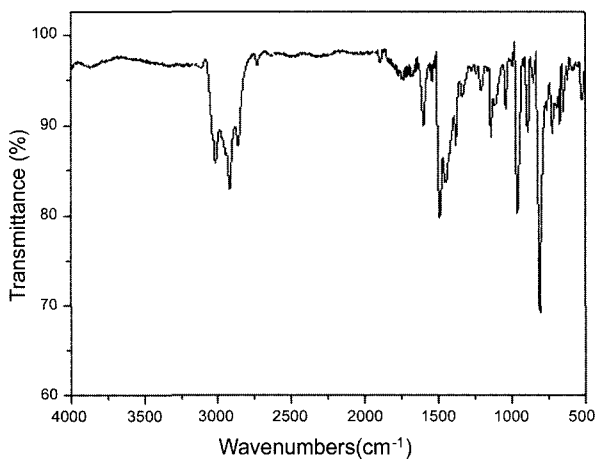


Figure 1. ^1H -NMR and FT-IR of PDMPPV.

vinylc carbons appeared at 120~150 ppm (Figure 2). The acetylenic carbon peaks due to TBB defects didn't show in the around 80 ppm. The result may be due to inhibited head-

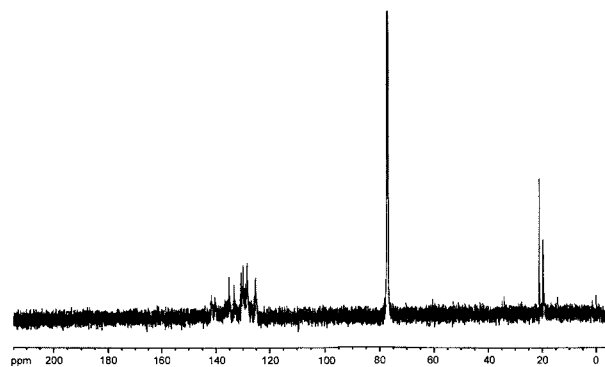


Figure 2. ^{13}C -NMR spectrum of PDMPPV.

to-head addition by steric hindrance 2,5-dimethylphenyl substituent of PPV.

The polymer was soluble in organic solvent such as chloroform and chlorobenzene. The number average molecular weight (M_n) and the weight average molecular weight (M_w) of the polymer were determined to be 31,000 and 74,000 (with the polydispersity index of 2.4), respectively, by gel permeation chromatography (GPC) using polystyrene as a standard.

It has been known that the materials with a high glass transition temperature as the active emissive can provide device longevity. Thermogravimetric analysis (TGA) was carried out for the bulk state polymer with a rate of $10\text{ }^\circ\text{C}/\text{min}$ in a nitrogen gas. The polymer was thermally stable up to $410\text{ }^\circ\text{C}$. The glass transition temperature (T_g) of polymer

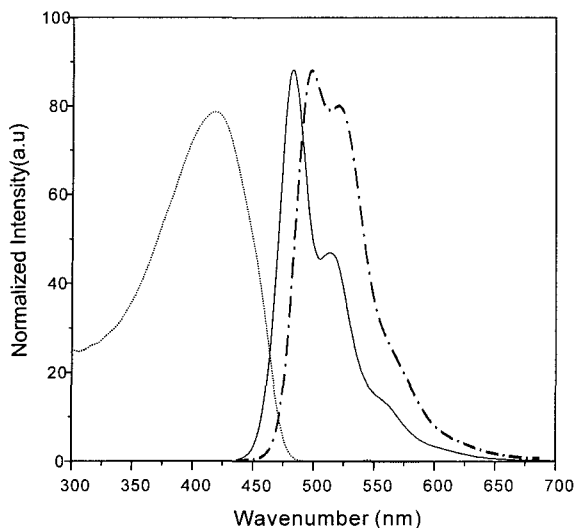


Figure 3. UV-Vis and photoluminescence of PDMPPV in solution (—) and solid (---).

by means of differential scanning calorimetry (DSC) with a rate of 10 °C/min in a nitrogen atmosphere, showed at 180 °C.

The absorption and photoluminescence (PL) spectra of the polymer in chloroform solution and solid state are shown in Figure 3. The polymer exhibit maximum peak of 415 nm attributed to $\pi \rightarrow \pi^*$ transition of the conjugated backbones. The absorption onset wavelength of the polymer was 480 nm, which correspond to band gap of 2.6 eV. The polymer film showed the maximum emission peak around 515 nm and shoulder at 530 nm, which is blue-shifted compared with the two emission peaks (520 and 551 nm) of the parent polymer, poly(*p*-phenylenevinylene) (PPV). The result may be due to steric effect of 2,5-dimethylphenyl group in PPV backbone. The PL spectrum in film is red shifted compared to that of solution. The PL spectrum shows two distinct maxima in both solution and film, which implies relatively ordered local structures. PL_{eff} was $28 \pm 5\%$, which was two times that of analogous and well established poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) (15%), when the film PL efficiency of the obtained polymer using optically dense configuration and diphenylanthracene (dispersed in PMMA film with a concentration less than 10^{-3} M, assuming PL_{eff} of 0.83) as a standard was measured.^{8,19,20}

The double-layered and single-layered polymer light emitting diodes (PLEDs) with configuration of ITO/PEDOT/PDMPPV/Al and ITO/PDMPPV/Al were fabricated to investigate the electroluminescent properties of the new polymer. As shown in Figure 4, the EL spectrum of polymer show a maximum peak around 510 nm and a shoulder around 535 nm, which is very similar to the PL spectrum of the corresponding polymer film. It can be explained that both EL and PL originate from the same radiative decay process

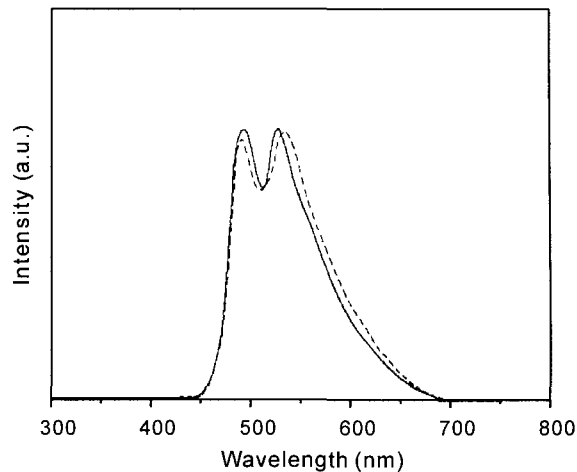


Figure 4. The electroluminescence spectra of ITO/PEDOT/PDMPPV/Al (—) and ITO/PDMPPV/Al (---) devices.

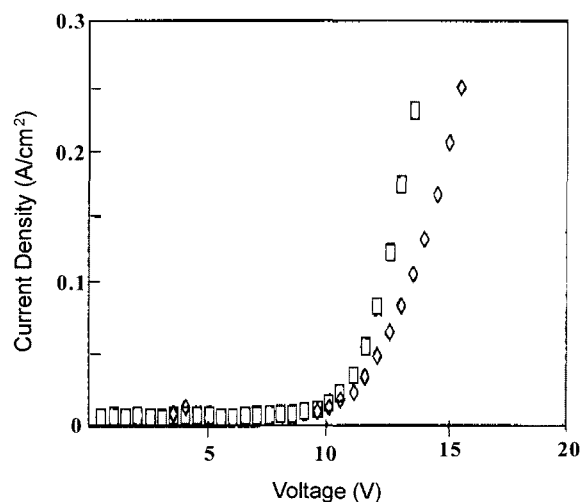


Figure 5. The current-voltage characteristics of ITO/PEDOT/PDMPPV/Al (□) and ITO/PDMPPV/Al (◇) devices.

of the singlet exciton. Figure 5 compares the I-V curves for the ITO/PEDOT/PDMPPV/Al and ITO/PDMPPV/Al device. With an increasing forward bias voltage, the current in the all of the devices increases, which is a typical rectifying characteristic. The device of structure ITO/PEDOT/PDMPPV/Al showed turn on voltage of 8 V and maximum brightness of 125 cd/m^2 at 12 V and the device structure of ITO/PDMPPV/Al showed a turn on voltage of 10 V and the maximum brightness of 80 cd/m^2 at 15 V. To achieve a higher EL performance, optimization of the device structure will be necessary.

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