A Comparative Study on the Properties of Poly(2,5dimethoxy-1,4-phenylene vinylene) by the CPR and Wessling Methods

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ABSTRACT: Poly(2,5-dimethoxy-1,4-phenylene vinylene) (PDMoPV) prepared via the chlorine precursor route (CPR) exhibits absorption at a shorter wavelength than that obtained by the Wessling method. The polymer fluoresces at a maximum of 505 nm as compared to 540 nm by Wessling method. Both the fabricated ITO-PDMoPV (via CPR)-Al and ITO/PDMoPV (via Wessling method)-Al devices emit green-blue light and the turn-on voltages are relatively low at 7 and 4 V, respectively. Significantly, the device fabricated using PDMoPV via CPR has a higher output than that via the Wessling method. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2177-2181, 1999

Key words: poly(2,5-dimethoxy-1,4-phenylene vinylene); chlorine precursor route; Wessling method; light-emitting diode; blue shift

INTRODUCTION

Poly(1,4-phenylenevinylene) (PPV) and its derivatives (PPVs) are promising new materials for polymeric light-emitting diodes (LEDs).^{1–7} PPV and its derivatives have been successfully synthesized through the Wessling method by using tetrahydrothiophene or dimethyl sulfide^{8–12} and by the chlorine precursor route (CPR).^{13–17} We now report the preparation of PDMoPV via both the CPR and Wessling methods. A comparative study on the LED properties on the devices fabricated using PDMoPV prepared by the two methods is now reported.

EXPERIMENTAL

Materials

All chemicals were used as received without further purification.

Characterization

The nuclear magnetic resonance (NMR) spectra of all samples were recorded by a Jeol JNM-EX90A (90 MHz) or a Bruker ACF-300 (300 MHz) Fourier transform spectrometer. Infrared (IR) spectra were recorded by a Perkin–Elmer 1725-X Fourier transform infrared (FTIR) spectrometer. The melting points were determined by differential scanning calorimetry DSC-7 apparatus (Perkin– Elmer) at a heating rate of 20°C/min. Elemental analysis of all samples was recorded by a CHN-LECO 600 instrument. Intrinsic viscosity (η) was measured in chloroform at 30°C with a Cannon

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ubbelohde dilution viscometer. Ultraviolet-visible (UV-VIS) absorption was recorded on HP8452 spectrometer (Hewlett Packard), and photoluminescence spectrum was measured on Flwinlab LS50B luminescence spectrometer (Perkin-Elmer).

Synthesis

Synthesis of 1,4-Dichloromethyl-2,5dimethoxybenzene (1)

Compound (1) was prepared by chloromethylation of 2,5-dimethoxybenzene according to the procedure described in the literature.⁸⁻¹² The yield of (1) was 94.5 g (80.4%).

Elemental analysis: C, 50.9%; H, 5.10%. Calcd: C, 51.1%; H, 5.11%. Melting point: 164°C; δ 4.64 (s, 4H, CH₂Cl); δ 3.86 (s, 6H, OCH₃); δ 6.92 (s, 2H, C₆H₂).

Precursors of PDMoPV via CPR (2)

Compound (1) (4.70 g, 0.02 mol) was dissolved in 50 mL of tetrahydrofuran (THF). A freshly prepared THF solution of potassium tert-butoxide (t-BuOK) (66 mL, 0.3M) was added slowly using a syringe over a period of 30 min. The reaction mixture was stirred for another 2 h at room temperature. The resulting viscous solution was yellowish-orange in color, which was then added to methanol for precipitation. The precipitate was removed by filtration. After drying, the precipitate was redissolved in 50 mL of THF and was purified by dialysis in distilled water at room temperature using a 12,000 MW cut-off cellulose membrane. The precipitate was filtered off and dried in a vacuum oven at room temperature for 24 h.

Elemental analysis: C, 59.5%; H, 5.38%. Calcd: C, 60.5%; H, 5.54%. Intrinsic viscosity (η) = 2.38 dL/g (30°C, chloroform).

Final Conjugated PDMoPV via CPR (3)

The purified (2) was dissolved in chloroform, and the solution was cast onto a cleansed quartz or glass plate, followed by heating in a vacuum oven at 210°C for 4 h to produce PDMoPV polymer.

Elemental analysis: C, 67.1%; H, 5.63%. Calcd: C, 67.4%; H, 5.62%.

Synthesis of 1,4-Dimethoxy Phenylene Dimethylene-bis-(tetramethylene sulfonium chloride) Monomer (4)

Compound (1) 11.8 g (0.05 mol) was dissolved in 100 mL of methanol in a 250-mL, three-necked

flask. The solution was purged with N_2 gas. Tetrahydrothiophene (30 mL) was then added into the flask, and the reaction was maintained at 50–60°C for 48 h. After removal of the solvent by water pump, a white solid was obtained. The crude product was then recrystallized from 30 mL acetone. The yield of monomer (4) was 9.25 g (45%).

Elemental analysis: C, 52.2%; H, 6.78%; S, 15.7%. Calcd: C, 52.6%, H, 6.81%, S, 15.6%. Melting point: 190–192°C.

Precursor of PDMoPV via Wessling Method (5)

Monomer (4) (2.5 g, 6.08 mmol) was dissolved in 50 mL of methanol. NaOH solution (0.4N, 15 mL) was added dropwise over a period of 30 min at 0°C under N₂ atmosphere. The solution was stirred vigorously for 3 h, and the excess base was neutralized using 0.4N HCl. The amount of acid used in the titration (2.0 mL) served also to compute the monomer conversation in the polymerization, which, in this case, was 87%. The reaction was continued for 24 h at room temperature. The solution was then put into a dialysis tubing with MW equal to 12,000 cut-off placed in a beaker filled with distilled water for 3–4 days. The yield of the dried solid was 0.785 g (45.1%).

Elemental analysis: C, 58.5%; H, 6.47%, S, 10.7%. Calcd: C, 58.6%; H, 6.63%; S, 11.2%. Intrinsic viscosity $(\eta) = 2.80 \text{ dL/g} (30^{\circ}\text{C}, \text{ chloroform}).$

Formation of Conjugated PDMoPV via the Wessling Method (6)

The chloroform solution of purified precursor (5) was cast onto a quartz or a cleansed glass plate and heated at 210°C for 4 h to form PDMoPV polymer.

Elemental analysis: C, 67.1%; H, 5.81%. Calcd: C, 67.4%; H, 5.62%.

RESULTS AND DISCUSSION

Properties of PDMoPV via the CPR (3) and Wessling Method (6)

In the FTIR spectra, both the PDMoPV polymers (3) and and (6) exhibit the peaks of 973 cm⁻¹ (trans-vinylene C—H) and 624 cm⁻¹ (cis-vinylene C—H) indicating that both the trans-vinylene C—H and cis-vinylene C—H structures are



Figure 1 Absorption spectra of (a) PDMoPV (CPR method) (3) and (b) PDMoPV (Wessling method) (6).

present. The absorption spectra of the conjugated polymers are shown in Figure 1. The absorption maxima of (3) and (6) are at 360 and 440 nm, respectively. This is consistent with the finding that conjugated polymers prepared via the CPR route has a lower molecular weight compared to that obtained via the Wessling method.¹⁶ The viscosity data of the present study also indicate that the molecular weight of precursor (5) is higher than (2). In the absorption spectrum of (6), the existence of a shoulder centered around 370 nm suggests that the elimination process in the present study was only partially complete.¹⁸ However, a partially converted polymer has been found to show good photoluminescence properties.^{16,19}

The fluorescence spectra of (3) and (6) are shown in Figure 2, from which it is clear that the emission maximum of (3) is at a shorter wave-



Figure 2 Fluorescence spectra of (a) (3) and (b) (6).



Figure 3 I-V and C-V curves of PDMoPV via CPR.

length. Compared to (6), (3) exhibits a maximum to maximum blue shift of around 35 nm. The shift is again attributed to the polymer's lower molecular weight by the CPR method.¹⁶

Electroluminescent Properties of LEDs



An indium-tin-oxide-(ITO)-coated glass with an electrical resistance of 60 Ω was cleaned by sonication and acetone and then dried in a vacuum at room temperature for 4 h. The LED consists of a polymer layer sandwiched directly between ITO (positive contact) and an aluminium layer (negative contact). A thin film of the polymers was formed on ITO glass substrates by spin coating from 20 mg/mL solution in chloroform solution at 1500 rpm. After evacuation for 8 h at room temperature to eliminate the residual solvent the film was subjected to heating at 210°C for 4 h under a N₂ atmosphere. The treated film was then placed

in a desiccator and dried for 8 h under vacuum. This was followed by evaporation deposition of aluminium through a mask (3 mm in diameter) at a chamber pressure of at least 5×10^{-6} Torr. The top electrode Al was evaporated onto the polymer in a JEOL JEE-400 vacuum evaporator at a rate of 2–5 Å/s. The thickness of the Al is about 1000 Å. A typical LED has an active area of 7.07×10^{-2} cm².

The basic electrical characterization involved the measurement of the device current and light output as a function of the applied voltage. A HP 6282A or a HP 6212B DC power supply supplied the voltage across the device. The current was measured by a HIOKI 3256 digital hi-tester. For the simultaneous measurement of the total integrated light output, a silicon photodiode (RS 303-674, 1.00 cm² active area) was placed right below active light emitting in forward direction. The photodiode was significantly larger than the operating device $(7.07 \times 10^{-2} \text{ cm}^2)$ and, thus, could collect all the light emitted in the forward direction. The distance between the device and photodiode was kept as small as possible. The photodiode was used under zero bias and generated current and light output was measured simultaneously. The diodes were driven with direct current. The device characteristics were measured in air at ambient temperature.

The emitted green light can be easily observed by naked eyes for all the single layer devices. For the ITO–(3)–Al single layer device, the turn-on voltage is 7 V, as shown in Figure 3; whereas the turn-on voltage of ITO–(6)–Al single layer device is 4 V, as shown in Figure 4. The ITO–(3)–Al single layer device is found to have a much higher EL output than that of ITO–(6)–Al single layer device.



Figure 4 I–V and C–V curves of PDMoPV via the Wessling method.

CONCLUSION

PDMoPV prepared via CPR has a shown blue shift in both the absorption and emission spectra when compared to that by the Wessling method. This is due to the higher-molecularweight PDMoPV obtained by the Wessling method. However, PDMoPV prepared by the CPR and Wessling methods are both suitable for the fabrication of LEDs. The devices have relatively low turn-on voltages of 7 and 4 V, respectively. Significantly, though the PDMoPV via CPR has lower molecular weight, the fabricated Al-PDMoPV-ITO simple device has much higher output. These results demonstrate that the CPR is a suitable method to yield PPV with the desired conjugated length for the fabrication of LED.

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