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EL properties of an alternating copolymer composed of phenothiazine and thiophene heterocycles

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Abstract

An alternating copolymer composed of phenothiazine and thiophene heterocycles, poly(PTZV-*alt*-TV), was synthesized through the Witting polycondensation reaction. The synthesized polymers were characterized using UV-visible, photoluminescence (PL) and electroluminescence (EL) spectroscopy. The poly(PTZV-*alt*-TV) showed a maximum UV-visible absorption and peak PL emission at 442 nm and 584 nm, respectively. The optical band gap of the polymer was obtained to be 2.74 eV from the absorption onset. The ionization potential of poly(PTZV-*alt*-TV) was determined to be 5.04 eV. Electroluminescent device was fabricated in an ITO/PEDOT/ poly(PTZV-*alt*-TV)/Ca/Al configuration. Light emission from this device was observable at voltages greater than 4.0 V. The EL device showed a maximum brightness of 140 cd/m^2 and a luminous efficiency of 1.3 x 10^{-2} cd/A.

Keywords: light-emitting diode, phenothiazine, thiophene, copolymer

1. Introduction

Semiconducting conjugated polymers have attracted much scientific and technological research interest during the past few decades because of their potential applications in transistors [1], photovoltaic devices [2], capacitors [3], and polymer light-emitting diodes (PLEDs) [4,5]. In particular, interest in LEDs fabricated from conjugated polymers [6-9] has increased since the initial report by the Cambridge group [4] of the fabrication of polymer light-emitting diodes (PLEDs) based on poly(*p*-phenylenevinylene) (PPV). Polymer LEDs have properties well suited to use in flat panel displays such as good processability, low operating voltages, fast response times and facile color tunability over the full visible range. The development of new materials displaying proper colors with high efficiency and stability is essential for the development of full color displays. Phenothiazine is a well-known heterocyclic compound with electron-rich sulfur and nitrogen heteroatoms. Molecules and polymers containing phenothiazine moieties have recently attracted much research interest because of their unique electro-optical properties and their resulting potential in diverse applications such as light-emitting diodes [10,11], chemiluminescence [12] and transistors [11].

In this paper, we report synthesis and light-emitting properties of a new poly(arylenevinylene) composed of phenothiazine and thiophene, poly(PTZV-*alt*-TV), through the Witting polycondensation reaction. The synthetic route and polymer structure are shown in Scheme 1.

2. Experimental

Synthesis of 10-(2-Ethylhexyl)-phenothiazine (1). Phenothiazine (10.0 g, 50 mmol) and sodium hydroxide (12.0 g, 300 mmol) was dissolved in 250 mL of DMSO and reaction mixture was stirred for 30 min. Ethylhexyl bromide (7.7 mL, 55 mmol) was slowly added to the reaction mixture for 20 min and it was then stirred for 24 h at room temperature. The reaction mixture was extracted with dichloromethane and distilled water. Organic layer was separated and dried with magnesium sulfate. The oily residue was purified by column chromatography after evaporating the solvent. A color less liquid was obtained (7.5 g, 48% yield). ^{1}H-NMR (300MHZ, $CDCl_3$) : δ0.99(m, 6H), δ1.48(m, 8H), δ2.07(t, 1H) , δ3.84(d, 2H) δ6.99(m, 4H), δ7.24(m, 4H). ^{13}C-NMR ($CDCl_3$, ppm) δ10.43, 13.95, 22.98, 23.96, 28.49, 30.64, 35.68, 50.89, 115.76, 122.21, 125.73, 126.96, 127.40, 145.67. Anal. Calcd for $C_{20}H_{25}Br_2NS$: C, 77.12; H, 8.09; N, 4.50; S, 10.29. Found: C, 77.34; H, 8.13; N, 4.45; S, 10.26.

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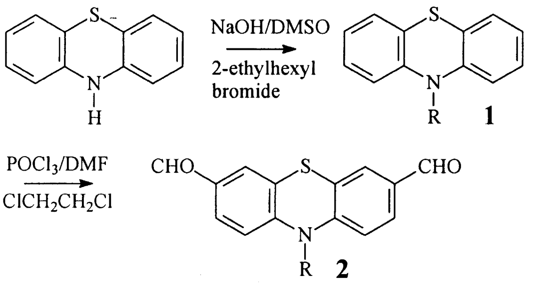
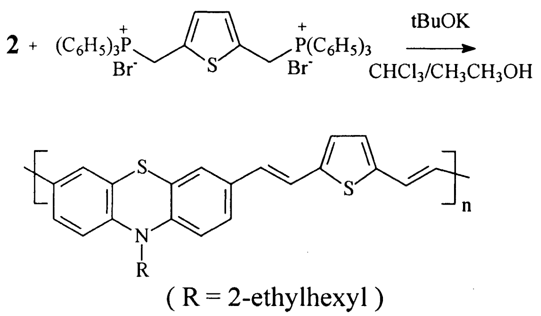
Scheme 1



Scheme 2



Synthesis of 10-(2-Ethylhexyl)-phenothiazine-3,7-dicarbaldehyde (2). The compound **1** (7.5g, 24 mmol) and DMF was dissolved in dichloroethane and the reaction mixture was cooled to 0°C. Phosphorus oxychloride (48 mL, 528 mmol) was injected by syringe for 20 min. The reaction mixture was stirred for 72h at room temperature. The reaction mixture was poured into cold sodium acetate solution and then it was extracted with dichloromethane and distilled water. Organic layer was separated and dried with magnesium sulfate. The oily residue was purified by column chromatography after evaporating the solvent. A white solid was obtained (3.0 g, 32% yield). ^{1}H-NMR (300MHZ, $CDCl_3$) : δ0.83(m, 6H), δ1.34(m, 8H), δ1.39(t, 1H) , δ3.82(d, 2H) δ6.97(d, 2H), δ7.64(m, 4H) δ9.81(s, 2H). ^{13}C-NMR ($CDCl_3$, ppm) δ13.78, 22.43, 22.66, 31.24, 48.50, 58.54, 115.54, 124.53, 128.37, 129.98, 132.10, 148.89,189.56. Anal. Calcd for $C_{22}H_{25}NO_2S$: N:3.81, C:71.90, H:6.86, S:8.73. Found : N:4.15, C:71.79, H:6.91, S:9.08

Synthesis of poly(PTZV-*alt*-TV). The compound **2** (1.0 g, 2.72 mmol) and thiophene bis(phosphonium) salt (2.07 g, 2.72 mmol) was dissolved in chloroform and ethanol co-solvent. The reaction mixture was heated up to 40 °C and potassium t-butoxide (1.22 g, 10.9 mmol) dissolved in 10 mL of ethanol was slowly added to the monomer solution. The reaction mixture was stirred for 24 h at room temperature. The reaction mixture was precipitated in methanol. A yellow-orange solid was obtained. The polymer was purified by column chromatography and Soxhlet extractor. Polymer yield was 35%.

Measurements and fabrication of EL devices. The absorption spectra were measured by a Hitachi spectrophotometer model U-3501 and steady-state photoluminescence spectra were recorded on a Spex FL3-11. The ionization potential of the polymer film was measured with a low-energy photo-electron spectroscope (Riken-Keiki AC-2) and also with a cyclic voltametry. The polymer film was prepared by spin casting the blend solutions containing 1 % of the polymers by weight in chlorobenzene. Uniform and pinhole free films with a thickness around 80 nm were easily obtained from the polymer solution. For the double layer device, a modified water dispersion of PEDOT [poly(3,4-ethylenedioxythiophene)] doped with poly(styrene sulfonate) (PSS) (Bayer AG, Germany) was used as a hole-injection/transport layer. To improve the electron injection, we deposited a thin LiF layer (~0.5 nm) onto the polymer film, and then deposited aluminum electrode (~100 nm) using the thermal evaporator at a pressure of 10^{-6} torr. The device performance was studied by measuring the current-voltage-EL (I-V-L) characteristics, electroluminescence (EL) spectra and the CIE coordinates. The I-V-L characteristics were measured with a Keithley 236 source-measure unit and a Keithley 2000 multimeter equipped with a PMT through an ARC 275 monochromator. The external quantum efficiency (QE) of the EL, defined as the ratio of the emitted photons to the injected charges, was calculated from the EL intensity measured by the calibrated Si photodiode. All processes and measurements mentioned above were carried out in air at room temperature.

3. Results and Discussion

The synthesized poly(PTZV-*alt*-TV) dissolves in common organic solvents such as THF, chloroform, and toluene without evidence of gel formation. Fig. 1 shows the UV-visible absorption and PL emission spectra of thin films of poly(PTZV-*alt*-TV) coated onto fused quartz plates. The PPTZ thin film exhibits peak UV-visible absorption and absorption onset at 442 nm and 565 nm, respectively. The optical band gap of the polymer was determined from the absorption onset. The optical band gap of poly(PTZV-*alt*-TV) was found to be 2.19 eV.

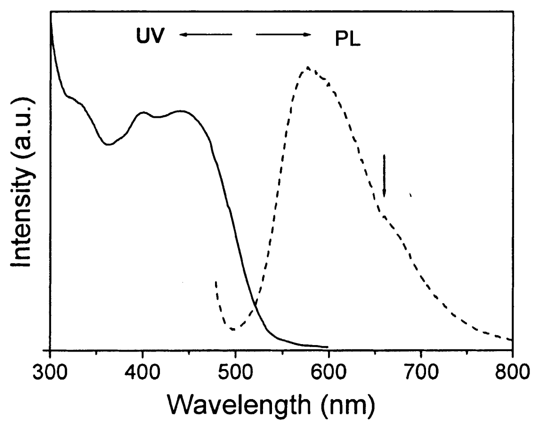


Fig. 1. UV-visible absorption and PL emission spectra of the poly(PTZV-*alt*-TV) thin film.