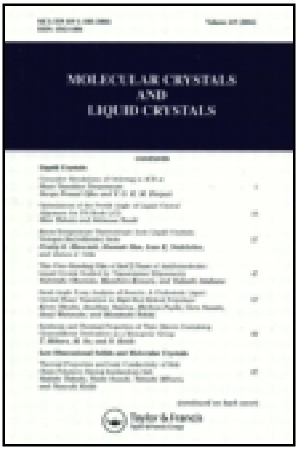

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Synthesis and Characterization of Novel Amine-Contained Electroluminescent Polymer

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SYNTHESIS AND CHARACTERIZATION OF NOVEL AMINE-CONTAINED ELECTROLUMINESCENT POLYMER.

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Abstract

A new type of processable electroluminescent polymer containing tertiary amine linkage was prepared by typical Wittig reaction between bis(4-formylphenyl) *n*-butylamine and diphosphonium salt. The resulting polymer was highly soluble in common organic solvents so that it could be spun-cast onto glass plate coated with ITO electrode to give highly transparent homogeneous thin film. The molecular weight of the polymer determined by gel permeation chromatography using polystyrene standards is $\overline{M}_n = 4{,}500$, $\overline{M}_w = 11{,}600$. The structure of the polymer was confirmed by IR, UV-visible, and ^{1}H- and ^{13}C-NMR spectroscopy. We observed successfully the electroluminescence peaked at around 530 nm from the device made of the synthesized polymer. The current -voltage (I - V) curves showed typical rectifying diode characteristic.

INTRODUCTION

Electroluminescent (EL) devices based on organic thin layers have attracted much attention because of their academic interests and potential utility of this technology in a wide variety of applications such as flat-panel displays and light-emitting diodes.[1-4] Since the first report of the polymer light-emitting diodes based on poly(*p*-phenylene vinylene) (PPV) by Cambridge group,[2] a variety of conjugated polymers[3-6] have been reported to exhibit electroluminescence.

Recently, some groups have reported new processable polymers with predictable emission wavelength which could be achieved by introducing a well-defined lumophores to the polymer main chain or to the side chain.[7] However, these polymers inevitably contain saturated and nonconjugated spacer group between the lumophores which , although they prevent extended conjugation and contribute to the solubility and film-forming properties of the polymer, act as a barrier to the injection and mobility of the charged carriers to lead to the materials requiring high threshold voltages which usually demage the organic materials. Therefore it seemed desirable to develop new series of polymers requiring low-drive voltages with predictable emission wavelengths.

In this paper, we report a series of phenylene vinylene-based polymers with tertiary amine linkage in the polymer main chain. SCHEME 1 shows the synthetic route for producing the comonomer and the polymer.

EXPERIMENTAL

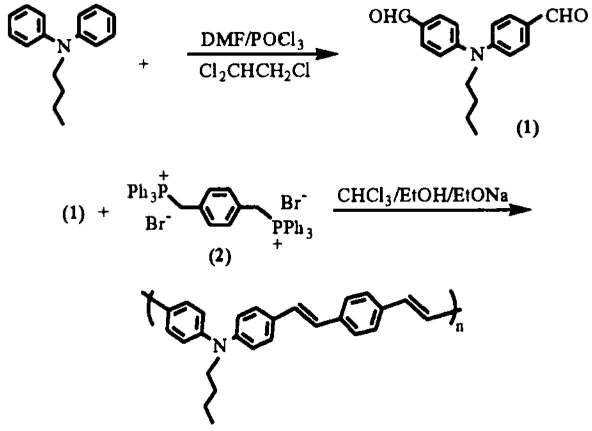
Polymerization

To a stirred solution of equimolar quantities of the dialdehyde (0.419 g, 1.5 mmol) **(1)**[8] and the 1,4-xylenebis(triphenylphosphonium bromide) (1.18 g, 1.5 mmol) **(2)** in 20 mL of absolute ethanol and chloroform (1:1) was added dropwise a solution of 85 mg (3.7 mmol) of sodium in 8 mL of absolute ethanol at room temperature. The reaction system was stirred for 5 h after the addition. The pastelike polymeric product was repeatedly washed with ethanol and water, and then dried in a vacuum oven at 40 °C for 2 days. The polymer yield was 93 %.

Characterization

^{1}H- and ^{13}C-NMR spectra were recorded with the use of Bruker AM-200, 300 spectrometers and chemical shifts were reported in ppm units. Infrared spectra were measured on a Bomem MB-100 Fourier Transform spectrophotometer using KBr pellets, UV-visible absorption spectra were obtained in chloroform on a Shimadzu UV-3100 spectrophotometer. The photoluminescence spectra were recorded on a Perkin Elmer LS-50 fluorometer utilizing a lock-in amplifier system with chopping frequency of 150 Hz and the polymer films were excited with several portions of

SCHEME 1



visible light from the xenon lamp. For the measurement of EL, the polymer light emitting diodes were constructed as follows: the glass substrate coated with transparent ITO electrode is cleaned by succesive ultrasonic treatments in acetone and isopropyl alcohol, and then dried with nitrogen gas and heated for further drying and larger conductivity of the transparent electrode. The polymer film is prepared by spin casting from 1,1,2-trichloroethane solution containing 3 % polymer by weight. The resulting polymer film has uniform surface with thickness around 70 nm. Metal contacts (aluminum) are deposited on the top of the polymer films by vacuum evaporation at pressure below 4 x 10^{-6} torr yielding active areas of 0.2 cm^2. For the measurements of device characteristics, current-voltage (I-V) characteristics were measured using the current/voltage source (Keithley 238) and optical powermeter (Newport 818SL). All processing steps and measurements mentioned above were carried out in air and at room temperature.

RESULTS AND DISCUSSION

The polymer was synthesized by using well-known Wittig reaction between the dialdehyde comonomer containing tertiary amine linkage and the appropriate diphosphonium salt as shown in SCHEME 1. The resulting polymer was highly soluble in common organic solvents such as THF, chloroform, and so on. The molecular weights of the polymer is $\overline{M}_n = 4{,}500$ and $\overline{M}_w = 11{,}600$, respectively.

IR spectrum of the polymer synthesized showed drastic decrease of the intensity of strong aldehyde carbonyl stretching band of the dialdehyde comonomer. On the other

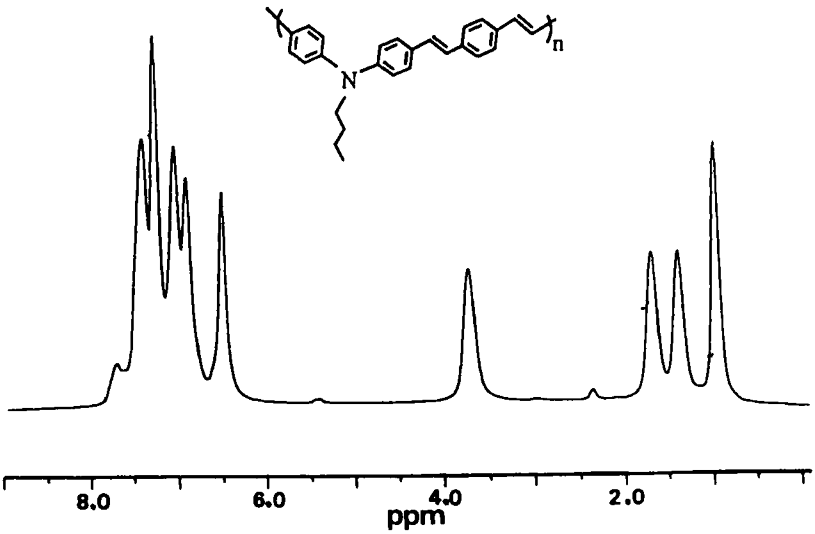


FIGURE 1. ^{1}H-NMR spectrum of the polymer in CDCl$_3$.

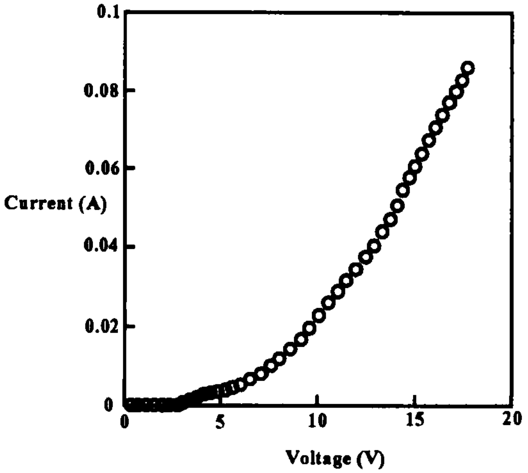


FIGURE 2. Current applied voltage (I-V) characteristic for the polymer light-emtting device.

hand, a weak sharp absorption peak at 960 cm^{-1} due to the out-of-plane bending mode of the trans-vinylene groups appeared, which suggest that the vinylene double bonds newly formed are mainly trans configuration. FIGURE 1 shows the ^{1}H-NMR spectrum of the polymer. As the polymerization proceeded, the aldehyde proton peak of the monomer present at 9.84 ppm disappeared and new vinylic proton peaks appeared at 7.48 ppm along with aromatic protons. The resulting polymer has the strong absorption band at around 410, which is due to the π–π^* transition of the conjugated segments. The photoluminescence (PL) spectra of the polymers were independent of the wavelength of the excitation.

FIGURE 2 shows the current-voltage (I-V) characteristic of the polymer diode. The forward bias current is obtained when the ITO electrode is positively biased and the aluminum electrode negatively. The current increases with increasing forward bias voltages and the reverse bias current remains small, which is a typical rectifying characteristics. As can be seen from the I-V curve, the threshold voltages of the polymer is about 3.5 V, which is considerably low compared with the PPV-based block copolymer and side-chain polymer,[9] although the conjugation length of this polymer was limited by tertiary amine group.

The room temperature electroluminescence (EL) spectrum of the polymer thin film is shown in FIGURE 3 (a). The broad EL spectrum of the polymer device is similar but not identical with the PL spectrum of the corresponing polymer thin film. Small bathochromic shifts in electroluminescent emission compared to that of photoluminescence are not unique to this polymer and may be attributable to thermal effects.[10]

The dependence of the EL intensities of the polymer diode on the injection current is shown in FIGURE 3(b). The emission intensity of the device was linearly increased with increasing injected current, tending to slight saturation at high injected current. This linear dependence of the EL intensity on the current clearly indicates that the emission is due to the recombination of the charge carriers injected from the electrodes

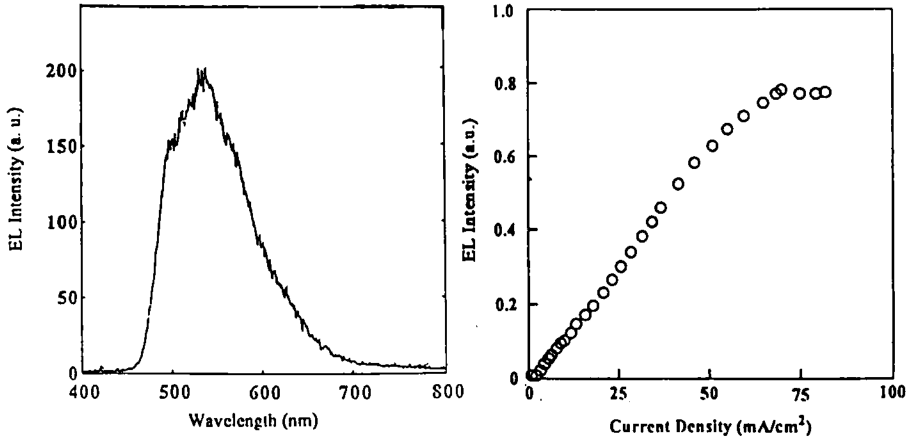


FIGURE 3.(a) Electroluminescence spectrum of the polymer light-emitting device. (b) Dependence of EL intensity on injection current of the polymer.

into the bulk of the polymer film. Current density used in this study was up to 100 mA/cm^2.

In concluson, a new class of EL polymer with uniform conjugated unit controlled by tertiary amine linkage has been synthesized by well-known Wittig condensation reaction. The present polymer with no aliphatic segments within the polymer main chain showed relatively low threshold voltage range compared with the block copolymer having similar conjugated units. The synthetic strategy for the present polymer with amine atom linkage instead of a non-conjugated segment provides a relatively simple route for the synthesis of a series of polymer with low drive voltages.

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