Novel Blue Light Emitting Copolymer with Both Conjugated and Nonconjugated Segments

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Through a base-induced copolymerization of 4,4′-bis(bromomethyl) biphenyl and styrene, a series of poly(*p*-biphenylenevinylene-*co*-styrene) (PBPV-*co*-PS) copolymers (P_1, P_2, and P_3) have been synthesized. The obtained PBPV-*co*-PS copolymers were characterized with FTIR spectra, ^{1}H NMR spectra, and GPC. The photoluminescence (PL) spectra showed a clear blue shift as an increase in the amount of styrene added in the copolymerization, which indicates that the average conjugating length of PBPV segment in the copolymer is adjustable. Blue light emission with a maximum at 457 nm and a turn-on voltage of 9.0 V were observed from a single-layer device (ITO/ P_3/Al) in which P_3 was used as an emitting material.

Introduction

Since the first report of poly(*p*-phenylenevinylene) (PPV) as a polymeric electroluminescent (EL) material in 1990,[1] remarkable progress has been made in the discovery of new polymers that can be useful for the fabrication of light-emitting diodes (LEDs).[2,3] EL materials are expected to exhibit high chemical stability, high luminescent efficiency, and high carrier mobility. In addition to these properties, the color of emitting light is also important for display applications. Recently, some research works have focused on the synthesis of blue light emitting polymers.[4−9] In organic conjugated systems, the conjugation length influences the band gap from HOMO to LUMO. Generally, a shorter conjugated length leads to a larger band gap. If a nonconjugated segment is incorporated into a fully conjugated backbone, the interruption of conjugation leads to the broadening of the energy band as well as blue-shifting the luminescence.[10,11] Recently, we reported a new approach to incorporate nonconjugated polystyrene (PS) segments into the PPV backbone.[12,13] The resulting conjugated/nonconjugated copolymers exhibit not only blue-shifted photoluminescent (PL) spectra but also good solubility if the content of PS segment is high enough. This method might provide a new strategy for the synthesis of EL materials. In this work, we report for the first time the copolymerization of 4,4′-bis(bromomethyl) biphenyl with styrene under similar conditions. It is well-known that the biphenyl is an electron-rich group. If the biphenyl group is incorporated into the PPV main chain, it can modify the band structure and molecular conformation, which might induce torsion of the main chain and consequently reduce the planarity of the copolymer.[14,15] All these can lead to shortening of the effective conjugation length and result in a blue shift in PL emission.[16] The obtained poly(*p*-biphenylenevinylene-*co*-styrene) copolymers were characterized and both PL and EL properties were investigated.

Experimental Section

Synthesis of 4,4′-Bis(bromomethyl) Biphenyl. 4,4′-Bis(bromomethyl) biphenyl was synthesized according to the

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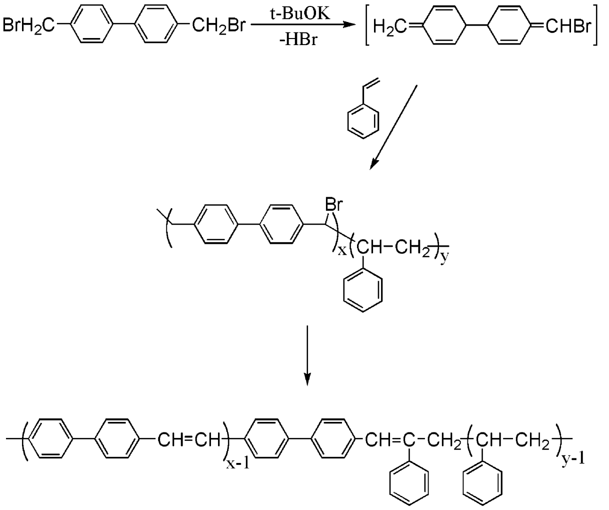
Table 1. Results of Copolymerizations by Using Different Feed Ratios of Styrene and 4,4′-Bis(bromomethyl) Biphenyl

sample	styrene (mL)	4,4′-bis(bromomethyl) biphenyl (g)	color of product	solubility (in CH_3Cl)	elemental analysis		styrene units content (%)
					found (%)	calcd (%)	
PBPV	0 (0 mmol)	0.68 (2 mmol)	yellow	insoluble	C, 94.02; H, 5.21	C, 94.38; H, 5.62	0
P_1	3.44 (30 mmol)	0.68 (2 mmol)	yellow-green	slightly soluble	C, 93.83; H, 5.59	C, 94.11; H, 5.89	20.61
P_2	5.74 (50 mmol)	0.68 (2 mmol)	pale-green	slightly soluble	C, 93.13; H, 6.05	C, 93.88; H, 6.12	35.45
P_3	9.20 (80 mmol)	0.68 (2 mmol)	white	soluble	C, 93.04; H, 6.26	C, 93.53; H, 6.47	54.21

Scheme 1. Synthetic Route of PBPV-*co*-PS Copolymers



procedure given in the literature.[17] ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.54 (s, 4H), 7.50 (s, 8H). mp 166−167 °C.

Synthesis of the Poly(*p*-biphenylenevinylene) (PBPV). 4,4′-Bis(bromomethyl) biphenyl (0.68 g, 2 mmol) was dissolved in 1,4-dioxane (10 mL) under N_2. The solution was stirred and heated to 60 °C and a solution of *t*-BuOK (2.24 g, 20 mmol) in 1,4-dioxane (10 mL) was added slowly. The reaction mixture was refluxed for 4 h. A bright yellow precipitate was isolated and washed with methanol several times. The solid was dried in vacuum at room temperature for 12 h.

Synthesis of the Poly(*p*-biphenylenevinylene-*co*-styrene) (PBPV-*co*-PS). The reaction route for the synthesis of the copolymers is described in Scheme 1. The experimental procedures are as follows: Under N_2 and with vigorous stirring, a solution of 4,4′-bis(bromomethyl) biphenyl (0.68 g, 2 mmol) in 1,4-dioxane (10 mL) was added to a solution of *t*-BuOK (2.24 g, 20 mmol) and the required volume of styrene in dry 1,4-dioxane (10 mL). The reaction temperature was maintained at 60 ° C for 4 h and then cooled to room temperature. The properties of the resulting copolymers strongly depend on the feed ratios of the styrene and 4,4′-bis-(bromomethyl) biphenyl monomer. By using 3.44, 5.74, and 9.20 mL of styrene, we obtained three kinds of copolymers (P_1, P_2, and P_3). Due to poor solubility, P_1 and P_2 precipitated from the reaction system. They were washed with large amounts of methanol and dried in vacuum at room temperature. P_3 was soluble in the reaction mixture. It precipitated as the reaction mixture was poured into 100 mL of methanol. The crude product was dissolved in chloroform and reprecipitated from methanol. The purification procedure was repeated three times and the final product was dried in vacuum at room temperature for 12 h. P_3 is soluble in common organic solvents such as chloroform, THF, and DMF. GPC: $M_w = 27000$, $M_w/M_n = 2.37$. The results of copolymerizations are summarized in Table 1.

General Measurements. The ^{1}H NMR spectra were recorded on a Bruker 500 MHz NMR spectrometer with tetramethylsilane as the internal reference. Gel permeation chromatography (GPC) was performed on a Waters 410 evaporative mass detector instrument using THF as the solvent and polystyrene as the calibration standard. The FTIR spectra were obtained on a Bruker IFS66VFT-IR spectrometer. UV−vis spectra were obtained on a Shimadzu UV-3100 spectrometer.

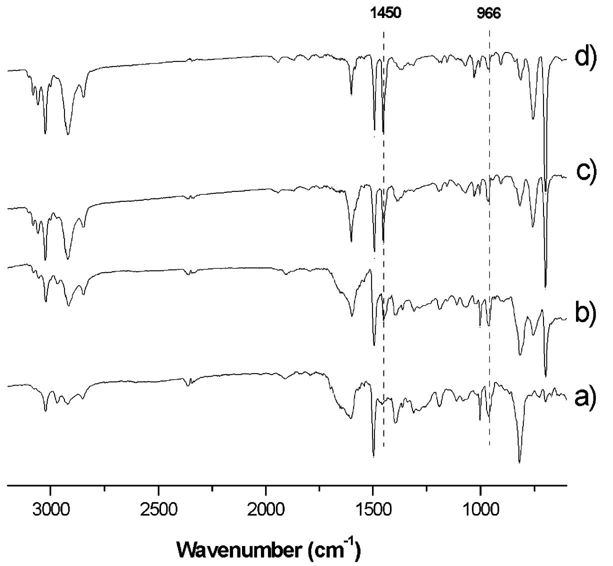


Figure 1. FTIR transmission spectra of PBPV (a), P_1 (b), P_2 (c), and P_3 (d).

EL Device Fabrication and Measurements. The copolymer P_3 was spin-coated on an ITO-covered glass plate from a solution in chloroform (10 mg/mL). The thickness of the polymer film was about 30−50 nm, and the active area was 2 × 2 mm^2. The Al electrode was deposited on the polymer surface at a pressure of about 10^{-5}−10^{-6} Torr. The photoluminescence (PL) and electroluminescence (EL) spectra were obtained on a Shimadze RF-5301 PC spectrofluorophotometer. The luminance was measured using a U.S.1980 luminescent meter. All measurements were carried out at room temperature in an ambient atmosphere.

Results and Discussion

All the samples were first characterized by elemental analysis as shown in Table 1. The results show that the remaining amount of Br in every polymer is very low, which indicates that during the base-induced polymerization the HBr has been eliminated effectively. Therefore, the structure of all polymers can be described as shown in Scheme 1. The FTIR transmission spectra of all the polymers, PBPV, P_1, P_2, and P_3, are shown in Figure 1. The spectrum of homopolymer PBPV shows a characteristic peak at 966 cm^{-1}, which is assigned to the C−H bending on trans C=C double bonds. The spectra of copolymers (P_1, P_2, and P_3) show additional peaks near 1450, 756, and 696 cm^{-1} (C−H bending on a monosubstituted phenyl ring). These absorbances result from styrene units only. Their relative intensities reflect the content of styrene units in the copolymers.

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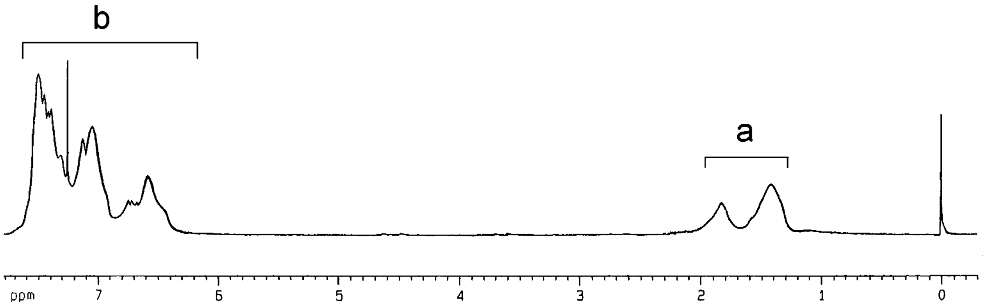

Figure 2. ^{1}H NMR spectrum of P_3.

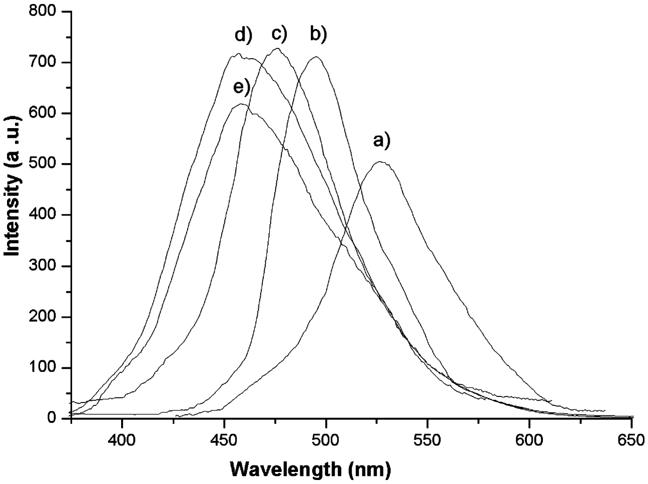

Figure 3. Solid-state PL spectra of PBPV (a), P_1 (b), P_2 (c), P_3 (d), and EL spectrum of P_3 (e) recorded from a single-layer LED.

Using the integrated values of the two peaks at 1450 and 966 cm^{-1} as references, we can calculate the mole percentage of styrene units in the copolymers. The relative content of styrene units in P_1, P_2, and P_3 was determined to be $\mathrm{St\%(P_1):St\%(P_2):St\%(P_3)} = 1:1.72:2.63$. Figure 2 shows ^{1}H NMR spectrum of P_3. The peaks at $\delta = 1.43-2.06$ ppm (region a) belong to the $CH-CH_2$ present in the styrene units, and the peaks at $\delta = 6.2-7.7$ ppm (region b) can be assigned to aromatic units and double bonds. The mole percentage of styrene unit in P_3 was determined to be 54.21%, which was calculated according to the following equation:

$$\mathrm{St\%(P_3)} = 10I_a/(5I_a + 3I_b)$$

where I_a and I_b represent the integrals of peaks in regions a and b, respectively. Using the results from IR spectra, we calculate the mole percentage of styrene units in P_1 and P_2 to be 20.61% and 35.45%, respectively. Thus, the mole percentage of styrene unit in the copolymer can be controlled using the feed ratio of styrene to 4,4′-bis(bromomethyl) biphenyl monomers.

Figure 3 shows the PL spectra of PBPV, P_1, P_2, and P_3 in the solid state ($\lambda_{excite} = 350$ nm). The homopolymer PBPV exhibits green emission with λ_{max} at 526 nm. The λ_{max} for the emission of homopolymer PPV is also green at 551 nm. PBPV can be considered a hybrid of PPV and poly(*p*-phenylene) (PP). The latter has blue emission with λ_{max} near 450 nm. It is reasonable that PBPV shows an intermediate PL spectrum between that of PPV and PP with the λ_{max} of emission for PBPV closer to that of PPV. With the introduction of styrene units in the copolymers, the λ_{max} of emission shifts toward shorter wavelengths. As seen in curves a–d, the λ_{max} blue-shifts by 31 nm (P_1), 51 nm (P_2), and 69 nm (P_3). The PL intensity also varies with the composition of the copolymer. If the integral of the PL spectrum for PBPV is defined as one unit, P_1, P_2, and P_3 have corresponding values of 1.28, 1.57, and 1.83, respectively. Thus, the PL efficiency increases as styrene units are introduced into the copolymers. The PL efficiency of P_3 in THF was measured as 0.63 using dilute quinoline solution in 0.1 N H_2SO_4 as a standard ($\Phi_{pl} = 0.58$, $\lambda_{excite} = 350$ nm). Since the styrene units are randomly incorporated, it can be inferred that the average length of PBPV blocks will become shorter as more styrene units are incorporated into the copolymer backbone. The observed blue shift in the PL spectra is the result of the shortening of the conjugation length of PBPV block. In addition, the incorporation of styrene units into the copolymers also leads to an improvement in PL efficiency of the conjugated block. This agrees with previous reports where PL efficiency improvement has been interpreted as the reduction in nonradiated processes such as the diffusion of the excited states to quenching sites.[18]

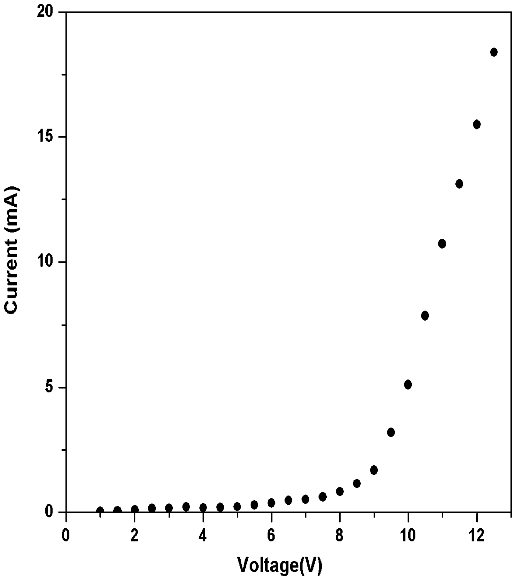

Figure 4. Current vs applied voltage characteristics for a single-layer LED device fabricated from P_3.

The EL spectrum of the copolymer P_3 is also shown in Figure 3e. It is very similar to the PL spectrum with λ_{max} at 457 nm, indicating the PL and EL processes

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experience the same excited state. The steady-state $I-V$ characteristic curve of a P_3 single-layer LED is shown in Figure 4. It shows a turn-on voltage at 9.0 V and current density of 42.0 mA/cm^2. The maximum luminance of the blue-emissive color was 47 cd/m^2 at the applied voltage of 12.5 V (495.5 mA/cm^2) with an EL efficiency of 0.0026 lm/W. The relatively low brightness and EL efficiency might be attributed to the poor electron injection from the Al electrode. An electron transportation layer is needed to improve the EL efficiency.

Conclusion

Poly(*p*-biphenylenevinylene-*co*-styrene) (PBPV-*co*-PS) copolymers can be synthesized through the base-induced copolymerization of 4,4′-bis(bromomethyl) biphenyl and styrene. The content of styrene units in the copolymer can be controlled by the feed ratio of the two monomers. The PL spectra blue shifts indicate that the average length of PBPV block becomes shorter with the increase in the content of styrene units in the copolymer. The incorporation of styrene units also leads to the improvement in PL efficiency. The single-layer LED fabricated from P_3 exhibits blue emission with low EL efficiency due to poor electron injection.

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