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Synthesis and properties of poly(*p*-phenylenevinylene-*co*-sulfonylene) for a blue light-emitting diode

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Summary

Novel class of *p*-phenylenevinylene copolymer with sulfonylene group in the main chain (**PPVS**) was synthesized through the Wittig reaction of bis(bromomethyl-*p*-phenyl)-sulfone triphenylphosphonium salt with terephthaldehyde. **PPVS** was highly soluble in common organic solvents and showed strong blue-shifted fluorescence because the polar sulfonylene group provided better solubility and limited π-conjugation in polymer chain. A single layer device with **PPVS** sandwiched between indium-tin-oxide (ITO) and aluminum electrodes showed a blue electroluminescence (EL) peaked at 470 nm under the threshold voltage of 14 V. HOMO and LUMO levels of **PPVS** were found to be 0.46 and 0.28 eV, respectively, lower than those of poly(*p*-phenylenevinylene) (PPV).

Introduction

Since the first report on electroluminescence (EL) of PPV (1), polymeric EL materials have attracted much attention because of their applications as large area full-color display (2-4). One of the key challenges in this field is to achieve a high-efficiency blue emission to realize a practical polymer device. Two different molecular design rules were suggested for this purpose only with limited success. One of them is to incorporate a kink or nonconjugated chemical structure to the main chain of *p*-phenylenevinylene polymer for blue light emission, which inevitably prevented charge carrier injection and transport in EL device, leading to the much lowered EL efficiency (5-8). The other is to attach a pendant group with good electron affinity for the enhanced efficiency of electron injection and transport like in poly(cyanoterephthalidene) (2). Although the latter approach was very successful to increase the EL efficiency, particularly for the red-shifted emission (2), it still suffers from the difficulty in obtaining high-efficiency blue light emission.

Combining these two design rules, we came to consider that the sulfonylene group

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could be very promissing for the high-efficiency blue EL, because the incorporation of this group to the main chain of *p*-phenylenevinylene polymer provides not only the molecular kink but also the favorable electron affiniy.

In this contribution, we report the synthesis and properties of a new class of sulfone-containing main chain PPV polymer for blue light emitting diode (LED) application. Sulfone moiety was introduced to obtain predictable blue emission and exciton confinements on molecular scale by restricted π-conjugation length through molecular kink structure. It was also expected that the electron injection and transport properties are enhanced by lowering of lowest unoccupied molecular orbital (LUMO). In addition, the kinked structure and polarity of sulfonylene group were considered to make the polymer more soluble than PPV.

Experimental

Monomer Synthesis:

Bis(bromomethyl-*p*-phenyl)-sulfone **(1)***:*

A mixture of *p*-tolyl sulfone (10 g, 41 mmol) and N-bromosuccinimide (22 g, 123 mmol) in 500 mL of $CCl_4$was refluxed in the presence of benzoyl peroxide (0.1 g, 0.41 mmol). After stirring overnight, the reaction mixture was cooled and suction-filtered. The transparent yellow filtrate was washed with distilled water and dried over $MgSO_4$. The solvent was removed under reduced pressure to give pale yellow solid. The resulting compound **1** (11.8 g, 70% yield) was used in the next step without further purification: mp 134 - 135 °C ; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.46 (s, 4H), 7.53 (d, 4H), 7.91 (d, 4H) ; IR (KBr, cm^{-1}) 1303 (S=O), 1151 (S=O).

Bis(bromomethyl-*p*-phenyl)-sulfone triphenylphosphonium salt **(2)***:*

A mixture of compound **1** (5 g, 12.4 mmol), triphenyl phosphine (9.6 g, 37.2 mmol) and 30 mL of DMF was heated to reflux for 2 h. The reaction mixture was cooled to room temperature. The brown solid was filtered, washed with ether, dried in vacuo and recrystallized from ethanol to give 7 g (60% yield) of yellow monomer **2**, mp 239 - 240 °C; ^1H NMR ($CDCl_3$,300 MHz) δ 5.58 (d, 4H), 7.38 - 7.80 (m, 38H); IR (KBr, cm^{-1}) 1411 (P-CH_2). Elem anal. Calcd: C, 64.66; H, 4.56; S, 3.45; Br, 17.21. Found: C, 63.91; H, 4.26; S, 3.64; Br, 18.18.

Polymerization:

A solution of potassium *tert*-butoxide (0.6 g, 5.28 mmol) in 10 mL of ethanol was added to a stirred solution of terephthaldehyde (0.3 g, 2.2 mmol) and monomer salt **2** (2 g, 2.2 mmol) in 40 ml, of chloroform and 20 ml, of ethanol at room temperature. The mixture was stirred at room temperature for 12 h. The precipitated yellow solid (**PPVS**) was filtered and washed thoroughly with methyl alcohol, and then dried in vacuo.

Characterization:

IR spectra were taken by transmission on a MIDAC M FT-IR spectrometer. ^{1}H NMR spectra were recorded with a Jeol JNM-LA300 spectrometer. Elemental analysis was carried out with a Carlo Erba 116 Elemental Analyzer with a LECO CHNS 932. Differential scanning calorimetry (DSC) measurement was performed on a PERKIN-ELMER DSC 7 under heating rates of 10 °C/min. Thermogravimetric analysis (TGA) was conducted with a Du Pont 2950 at a heating rate of 10 °C/min under nitrogen atmosphere. The molecular weight was determined with a Perseptive Voyger Biospectrometry (MALDI-TOF). UV-visible spectra were measured on Shimadzu UV-2101 PC Spectrophotometer.

EL Device Fabrication and Measurement of Electroluminescence:

Single layer EL device of ITO/**PPVS**/Al was prepared. Active electrode area was 12 MM^2, and the thickness of **PPVS** was 40 nm.

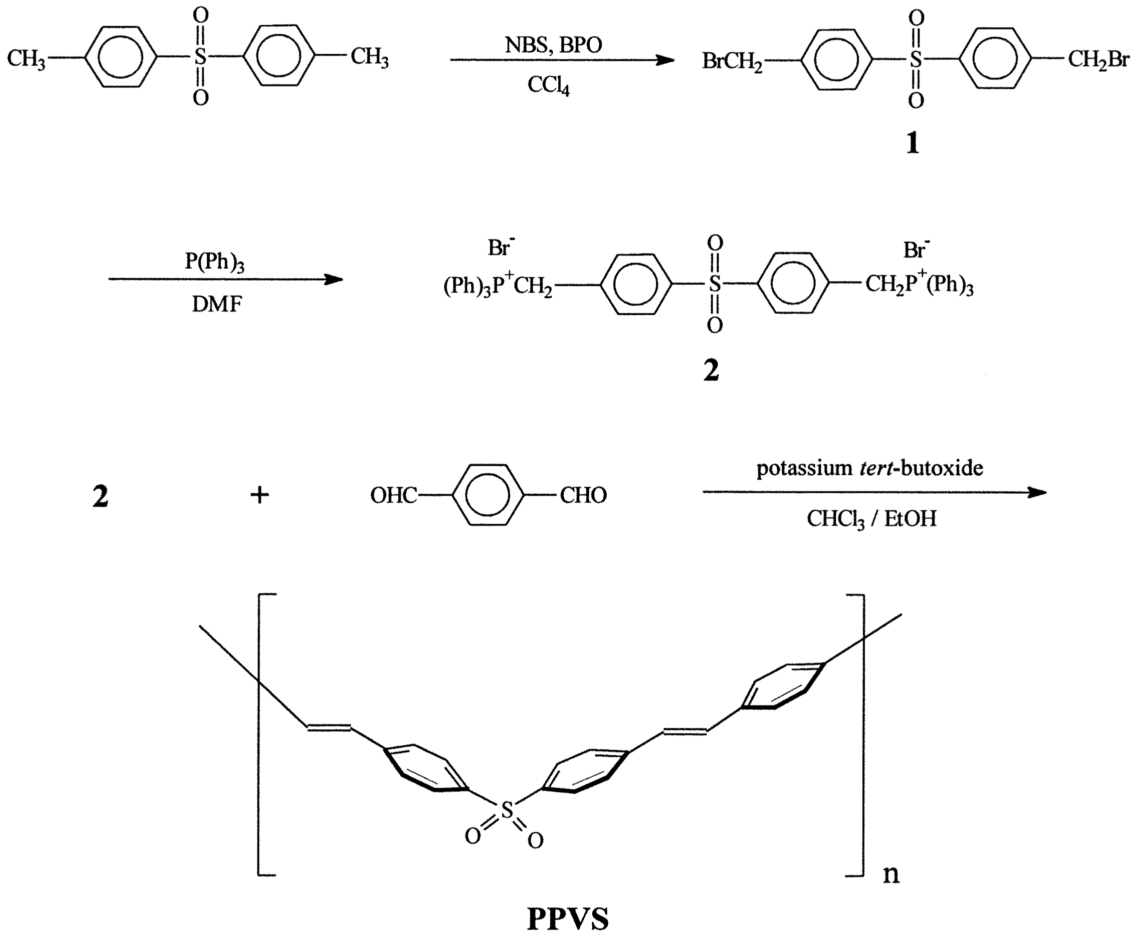
Photoluminescence (PL) and electroluminescence (EL) spectra were recorded with an ISS PCI Fluorometer. I-V-L characteristics were recorded by a Keithley 236 Source/Measure Unit for voltage-current relationship and by a Newport 818-SL photodiode for voltage-EL intensity.

Cyclic voltametry measurement:

The ionization potential of **PPVS** was measured electrochemically with an acetonitrile solution containing 0.1 M $LiClO_4$ by using a EG&G Model 362 Scanning Potentiometer. The HOMO energy level of **PPVS** film was calibrated with that of ferrocene which is –4.8 eV with respect to zero vacuum level. Band gap energy was taken from the edge of UV-visible absorption spectrum of **PPVS**. The LUMO energy level was calculated from the HOMO level and band gap.

Results and Discussion

Synthesis and Characterization:



Scheme 1. Synthesis of monomer and polymer for **PPVS**.

As shown in Scheme 1, monomer salt **2** was prepared in two steps from *p*-tolyl sulfone. Through a radical reaction using N-bromosuccinimide (NBS) and benzoyl peroxide (BPO) in CCl_4, *p*-tolyl sulfone was converted to bis(bromomethyl-phenyl)-sulfone **1** in 70 % yield. Reaction of **1** with triphenyl phosphine in DMF led to the bis(bromomethyl-*p*-phenyl)-sulfone triphenylphosphonium salt **2** in 60% yield. In the FT-IR spectrum of monomer salt **2**, characteristic absorption peaks due to sulfone group appeared at 1300 and 1150 cm^{-1}. ^{1}H-NMR signals of the benzylic protons shifted from 4.46 ppm of **1** to 5.58 ppm of **2** as a result of the successful phosphonation. The structure of monomer salt **2** was further verified by the elemental analysis.

Polymerization was achieved by the well-known Wittig reaction between the dialdehyde monomer and the diphosphonium salt **2**, as shown in Scheme 1. The molar ratio of terephthaldehyde and **2** was fixed to equimolar quantity. The obtained polymer was highly soluble in common organic solvents such as chloroform, methylene chloride, 1,1,2,2-tetrachloroethane, although it was insoluble in hexane and methanol. It was speculated that the bent and polar sulfonylene structure in the rigid *p*-phenylenevinylene backbone enhanced the solubility significantly.

Table 1. Polymerization yield and polymer properties of **PPVS**

	Yield (%)	M_n	T_g (℃)	T_{ID} (℃)	UV λ_{max} (nm)	PL λ_{max} (nm)	EL λ_{max} (nm)
PPVS	68	5400 [a]	180	397	370 (solution) 343 (film)	460 (solution) 470 (film)	470

[a] obtained by MALDI-TOF analysis.

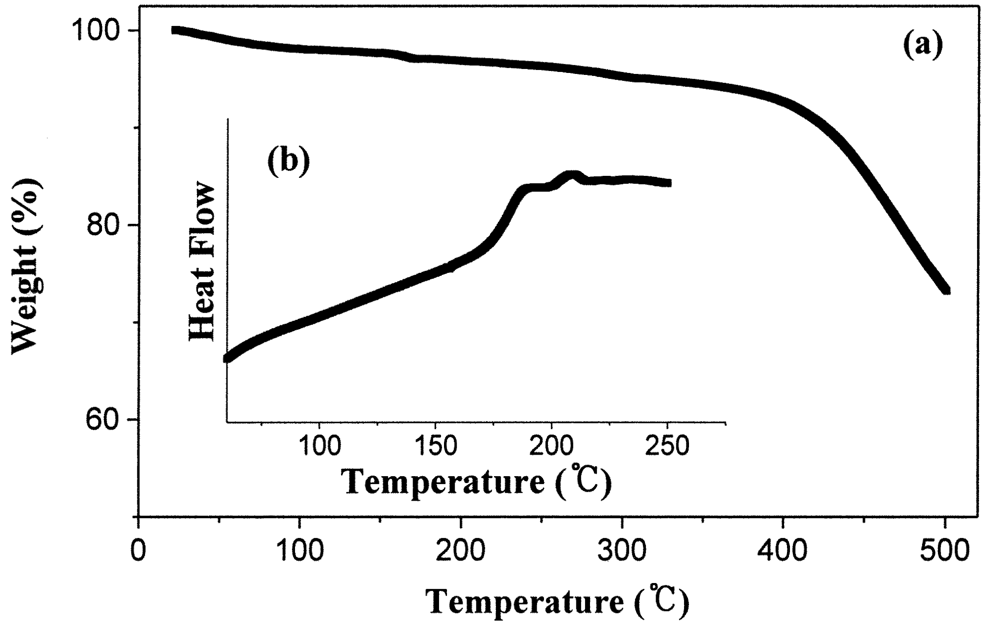


Figure 1. (a) TGA and (b) DSC thermograms of **PPVS**.

The number-average molecular weight of the polymer was about 5,400 as was determined by MALDI-TOF. Glass transition temperature of **PPVS** was measured to be 180 °C. The polymer gradually lost weight by 5% on heating to 315 °C showed a fast decrease in weight starting at about 400 °C as shown in Figure 1 (a). Table 1 summarizes the results of polymerization and the properties of **PPVS**.

Electroluminescence properties:

UV-Visible spectrum of **PPVS** in 1,1,2,2-tetrachloroethane solution and that of thin film coated on quartz are shown in Figure 2(a). **PPVS** solution showed absorption maximum and edge at about 370 nm and 450 nm, respectively. Compared to the solution, **PPVS** film showed *ca.* 30 nm blue-shifted absorption maximum as shown in Figure 2(a). It is speculated that there exists some aggregation of polymer backbones in the solid state.

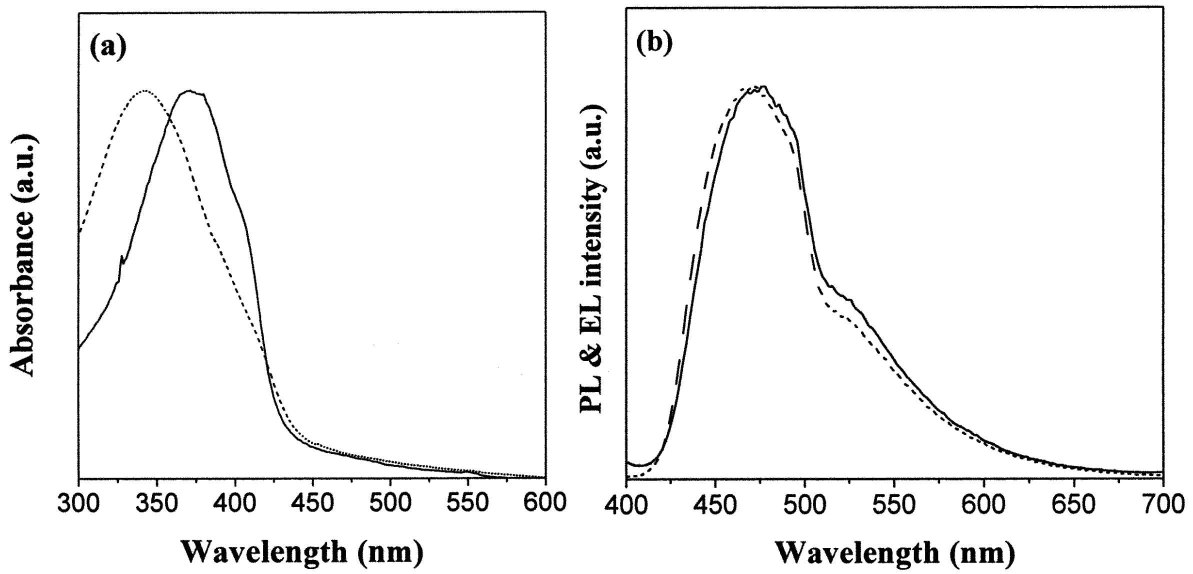


Figure 2. (a) UV-visible absorption of solution (——) and film (- - -) of **PPVS**, (b) PL film(- - -) and EL (——) spectra of **PPVS**.

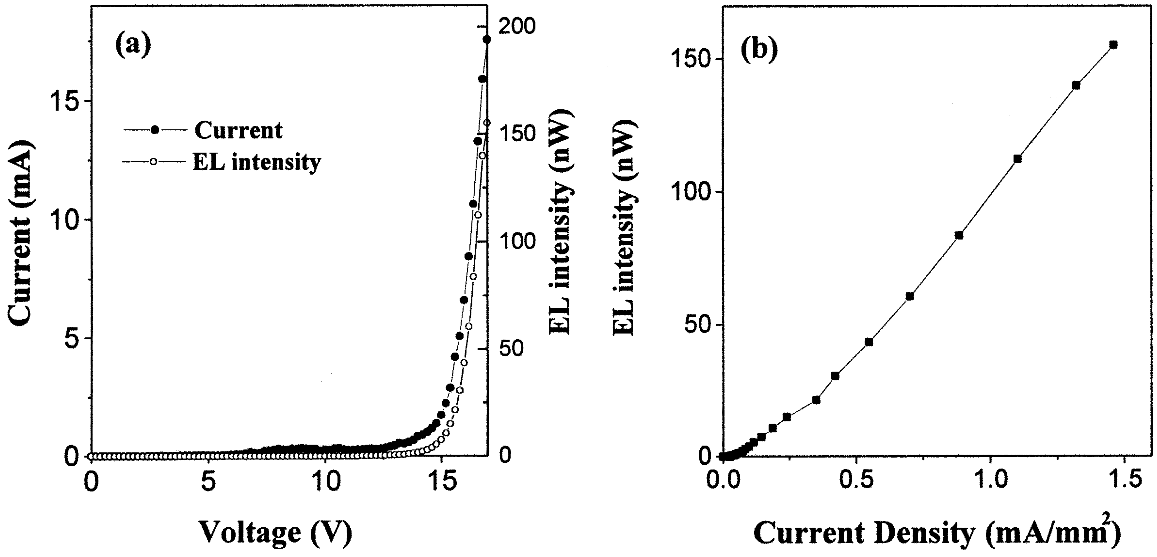


Figure 3. (a) Voltage-current-EL intensity (V-I-L) and (b) Current-EL intensity (I-L) characteristics of **PPVS**.

PL emission maxima in solution and thin film were at 460 nm. and 470 nm, respectively, with the weak shoulder at 530 nm when excited at 370 nm. Such a blue PL of **PPVS** compares well with the green emission (λ_{max} PL 560 nm) of PPV. It is evident that the blue-shifted PL of **PPVS** resulted from the reduced length of π-conjugation through the molecular bent structure of sulfonylene group. The EL emission spectrum from the ITO/**PPVS**/Al device was identical to the PL emission spectrum of **PPVS** film, as shown in Figure 2(b).

The current-voltage (I-V) and EL intensity-voltage characteristics (L-V) from the ITO/**PPVS**/Al device are shown in Figure 3(a). Typical diode characteristics were observed and a blue light emission was visible above the threshold voltage of 14 V. The external quantum efficiency of this device was 3.4 x 10^{-4} % (photons/electron) at the current density of 146 mA/cm^2 in air and at room temperature condition. Considering that the reported EL efficiency of ITO/PPV/Al is 4.0 x 10^{-5} % (9), this single layer efficiency seems to support our molecular design of **PPVS**. Figure 3(b) shows that the EL intensity increased very linearly with current density.

Table 2. The HOMO-LUMO levels of PPV and **PPVS**

	HOMO (eV)*	LUMO (eV)*	E_g (eV)
PPV	-5.10	-2.60	2.50
PPVS	-5.56	-2.88	2.68

* relative to zero vacuum level.

Table 2 summarizes the HOMO-LUMO levels of **PPV** and **PPVS** measured by cyclic voltametry and UV-visible absorption. Compared with the HOMO and LUMO levels of PPV, those of **PPVS** were lowered by 0.46 eV and 0.28 eV, respectively. Evidently these are due to the electron withdrawing effect of sulfonylene group. Higher amount of HOMO level lowering than that of LUMO level resulted in the increase of band gap and consequently the blue-shift of emission, which is undoutedly caused by the restricted π-conjugation in **PPVS**.

Conclusion

Novel main chain EL polymer containing sulfonylene moiety for the high-efficiency blue emission was successfully synthesized and characterized.

Acknowledgment

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