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Synthesis and characterization of poly(1,5-naphthylene vinylene) and its copolymers with poly(2-methoxy-5-(2′-ethylhexyloxy)-*p*-phenylene vinylene)

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Abstract

Poly(1,5-naphthylene vinylene) (PNV) and its copolymers with poly(2-methoxy-5-(2′-ethylhexyloxy)-*p*-phenylenevinylene) (MEH–PPV) were synthesized via a liquid–solid two-phase reaction. The liquid phase was a tetrahydrofuran (THF) solution of the monomers, 1,4-bis(bromomethyl)-2-methoxy-5-(2-ethylhexyloxy)benzene (MOEHODCX) and 1,5-bis(bromomethyl) naphthalene (DBMN), and contained a certain amount of tetrabutylammonium bromide (TBAB) as a phase transfer catalyst. The solid phase was potassium hydroxide particles with diameters smaller than 2 mm. The structures of the polymers were studied by infrared and Raman spectroscopies. The solutions of the copolymers emitted green light. The UV–vis and photoluminescence spectral bands of the copolymers showed blue shifts with the increase in their PNV contents. A polymer light-emitting diode was fabricated with the copolymer prepared by copolymerization MOEHODCX and DBMN with feeding molar ratio of 1:1, and its luminescence efficiency was measured to be 0.069.

Keywords: Poly(1,5-naphthylene vinylene); Copolymer; Raman spectrum

1. Introduction

In the past decades, conjugated polymers have been widely studied for their applications in fabrication of polymer light-emitting diodes (PLED) [1–3]. Among these polymers, poly(*p*-phenylenevinylene) (PPV) and its derivatives attracted significant attention because of their advantages such as low turn-on voltage, short switching time, high efficiency and good stability [4–7]. Similarly, poly(naphthalenevinylene) (PNV) and its derivatives [8,9] also have been synthesized as blue light emitting materials. However, PNV is insoluble in usual organic solvents such as toluene and tetrahydrofuran (THF), which limits its applications. Furthermore, PPV and PNV or their derivatives are usually synthesized via Wittig reaction [10], Heck reaction [11] and Gilch polymerization [12], etc. These reactions involve multi-step processes and the bases used for dehydrohalogenations are usually expensive and unstable in air. Recently, we developed a novel one-step solid–liquid two phase reaction route to PPV and its derivatives [13]. In this article, we desire to report synthesis of PNV and its copolymers with poly(2-methoxy-5-(2′-ethylhexyloy)-*p*-phenylenevinylene) (MEH–PPV) using this solid–liquid two phase reaction. In these cases, the reactions were carried out at room temperature and solid KOH particles were used as the base. Furthermore, the introduction of MEH–PPV block into the PNV chains improved the solubility of PNV.

2. Experimental

2.1. Materials

1,4-Bis(bromomethyl) benzene (P-DBX; ≥98%) was purchased from Fluka and 1,5-dimethyl naphthalene (95%) was bought from Alderich. Both of them were used as received. 1,4-Bis(bromomethyl)-2-methoxy-5-(2-ethylhexyloxy)benzene (MOEHODCX) and 1,5-bis(bromomethyl) naphthalene (DBMN) were synthesized in our lab through published procedures [14,15]. Their purity was confirmed by the use of ^{1}H NMR spectroscopy and capillary melting-point measurements. Solid KOH (≥84%; Beijing Fine Chemical

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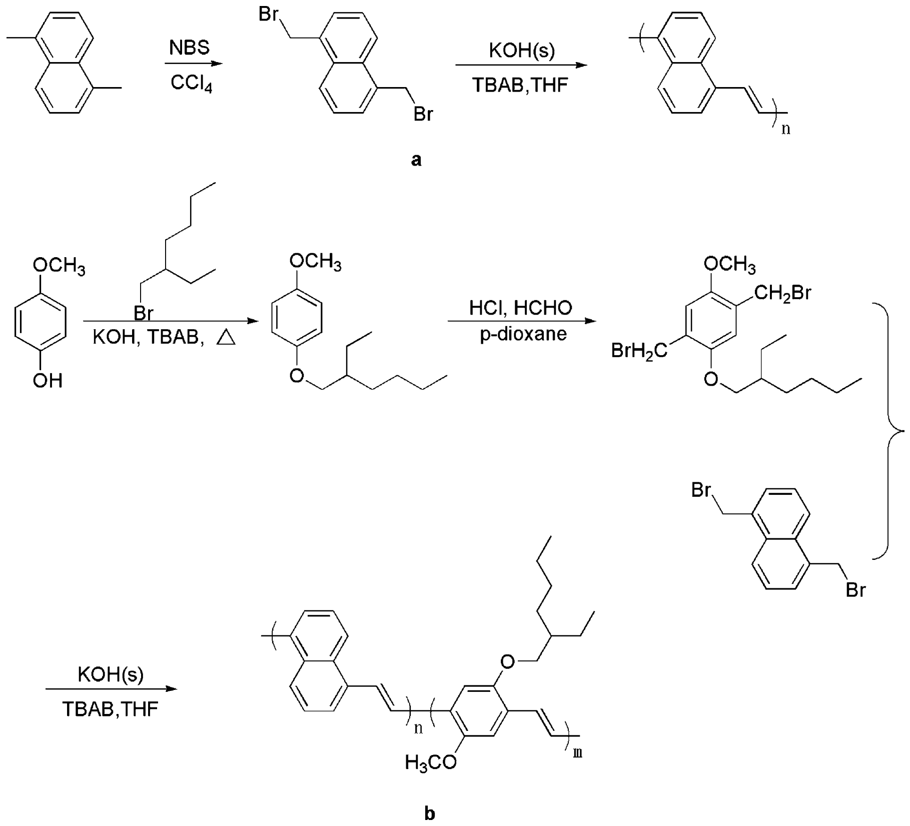
Co. Ltd.) sheets were analytical-grade pure and used after being ground into particles with diameters smaller than 2 mm. Tetrahydrofuran (THF; Beijing Fine Chemical) was also analytical-grade. It was treated by reflux with sodium for 30 min under nitrogen protection and then purified by distillation.

2.2. Polymerization

The synthesis reactions are simply represented in Scheme 1. A typical synthesis process of PNV was as follows. 1.0 g DBMN and 0.15 g tetrabutylammonium bromide were dissolved in 40 mL of THF, and then 4.0 g KOH (particles) was added. The system was stirred magnetically at room temperature for 2 days. Finally, 100 mL of distilled methanol was poured into the system to dissolve the solid KOH, and the salt formed in the reaction. PNV precipitate was filtered and washed repeatedly with distilled water and methanol. It was sheet-like and dried at 60 °C in vacuo for 24 h. The copolymerizaions were also carried out through the same procedures described above. The feeding molar ratios of the monomers, DBMN and MOEHODCX, were controlled to be 4:1, 1:1 and 1:2, respectively; and the resulting copolymers were nominated as PNV80, PNV50 and PNV33, correspondingly. Furthermore, MEH–PPV was also synthesized for comparison [13].

2.3. Characterizations

^{1}H NMR spectra were carried out on an JNM-ECA300 spectrometer (JOEL). IR spectra were recorded on a GX Fourier transform infrared (FTIR) spectrometer (Perkin–Elmer) with KBr pellets of the polymers. The molar masses and dispersities of the soluble polymers were measured by using a model 1100 gel permeation chromatograph (HP Co.) at 30 °C with polystyrene standards and THF as the solvent. Raman spectra were taken out by the use of an RM 2000 microscopic confocal Raman spectrometer (Renishaw PLC, England) employing a 785 or a 633-nm laser beam, and a charge coupled device detector with 4-cm^{-1} resolution. The spectra were obtained by a 1–2 μm laser spot focused on the sample with a 20× objective and accumulated three times for 10 s each. The power of laser beam was always kept very low ($\leq$0.05 mW) to avoid the destruction of the samples. A Raman spectrum of PNV was recorded on a GX-FT-Raman (Perkin–Elmer) using a 1064-nm laser beam to reduce the influence of fluorescence. Fluorescence spectra were recorded with a LS 55 spectrometer (Perkin–Elmer) with a front surface accessory and electroluminescent spectra were recorded by using a Hitachi F4500 fluorescence spectrometer. Ultraviolet–visible (UV–vis) spectra were performed on a U-3010 UV–vis spectrometer (Hitachi). The UV–vis spectra of the powders were recorded with an alumina pellet as the reference.



Scheme 1. Synthesis route for PNV (a) and its copolymers with MEH–PPV (b).

The current–voltage (*I–V*) and light intensity–voltage (*L–V*) curves of PLEDs were measured by using a Keithley 236 source measure unit and Keithley 195 multiplier coupled with a Si photodiode as the light sensor.

2.4. EL device fabrication

The PLEDs were fabricated with PNV50 as the active luminescent layer. The thickness of the emitting layer was 35 nm, as measured by Ambios XP-2 step profiler (USA). An indium tin oxide (ITO) glass sheet was used as the anode. A 30 nm thick hole injection layer of poly(ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonate) (PSS) (Bayer Corp.) was spin-coated on the surface of a ITO electrode, and a poly(*N*,*N*′-bis(4-butylphenyl-*N*,*N*′-bis(phenyl) benzidine) (poly-TPD) layer of 45 nm was induced between PEDOT and emitting layer. On the top of PNV50 layer a thin Ca layer with the thickness of 10 nm was deposited as cathode, and finally, a 190-nm-thick Al layer was thermally evaporated on top of Ba as a capping layer. All the steps described above were carried out in a glove box under N_2 atmosphere.

3. Results and discussion

PNV is insoluble in usual organic solvents such as toluene and THF, mainly due to the lack of a side chain attaching to its backbone. The introduction of MEH–PPV units to the PNV chains can increase the solubility of PNV. However, only 10% (by weight) PNV80 and about 70% (by weight) PNV50 is soluble in THF. GPC tests showed that the molar mass of soluble portion of PNV50 was 1.0×10^4 g mol^{-1} with polydispersity of 1.90, and those of PNV80 were 8.3×10^3 mol^{-1} g and 1.41, respectively. The copolymer PNV33 was tested to have good solubility. However, its molar mass and optical properties are similar to those of MEH–PPV. The molar mass of MEH–PPV was measured to be 2.6×10^5 g mol^{-1} with polydispersity of 2.5.

The IR spectra of PPV, PNV and two copolymers are shown in Fig. 1 [13]. In Fig. 1(a), the relative intensity of CH_2 bands in the region of 2850–2880 cm^{-1} is weaker than those in the other spectra, and the intensities of these bands increased gradually from Fig. 1(a)–(d). This indicates the increase in MEH–PPV unit contents in the polymers. This conclusion can also be derived by comparing the relative intensity of =C–O–C stretching band (1203 cm^{-1}) of the spectra. The bands of naphthalene rings with three adjacent hydrogen atoms at 783 cm^{-1} exist in the spectra of PNV and two copolymers, indicating the existence of PNV units, and its intensity is related to the naphthalene unit content in the polymer sample.

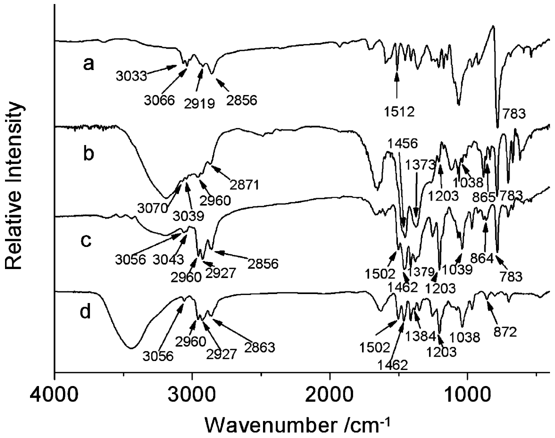


Fig. 1. FT-IR spectra of four polymers. (a) PNV; (b) PNV50%; (c) PNV80%; (d) MEH–PPV.

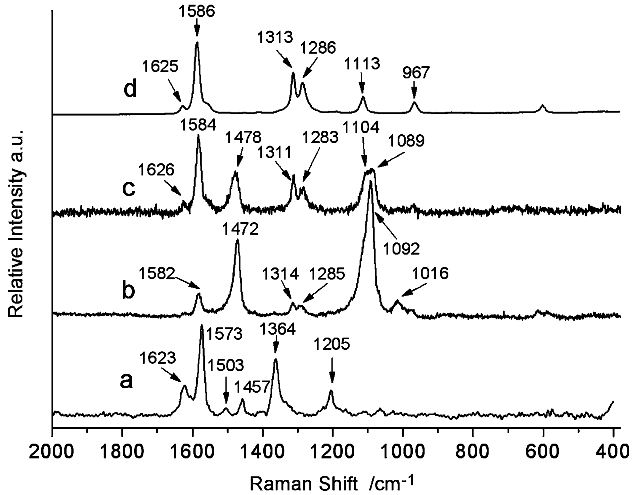


Fig. 2. Raman spectra of four polymers. (a) PNV; (b) PNV50%; (c) PNV80%; (d) MEH–PPV.

The Raman spectra of PNV, MEH–PPV and their copolymers are presented in Fig. 2. The 1623 cm^{-1} band in Fig. 2(a) is assigned to the asymmetric stretching of C=C double bond, which is similar to those shown in the spectrum of MEH–PPV and two copolymers. The C–C stretching band of the naphthalene rings appears at 1573 cm^{-1}, while that of benzene rings is at about 1584 cm^{-1} as shown in Fig. 2(b)–(d) [16,17]. Some new bands shown in the spectra of the copolymers, such as 1478 and 1092 cm^{-1} in Fig. 2(b), are not found in the spectra of PNV and MEH–PPV.

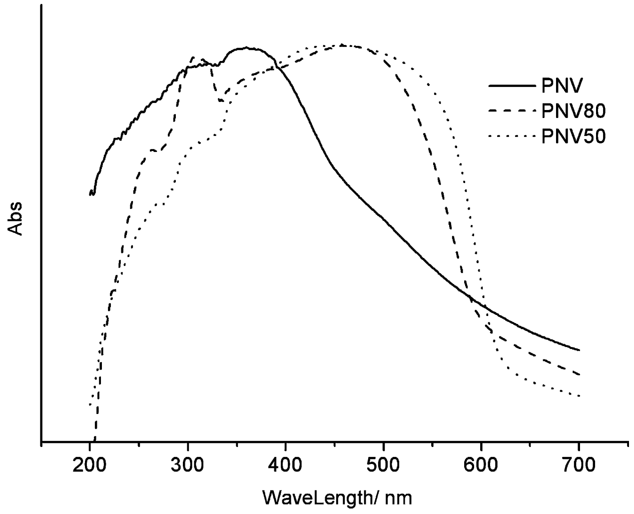


Fig. 3. UV–vis spectra of three polymers containing naphthalene rings in solid state.

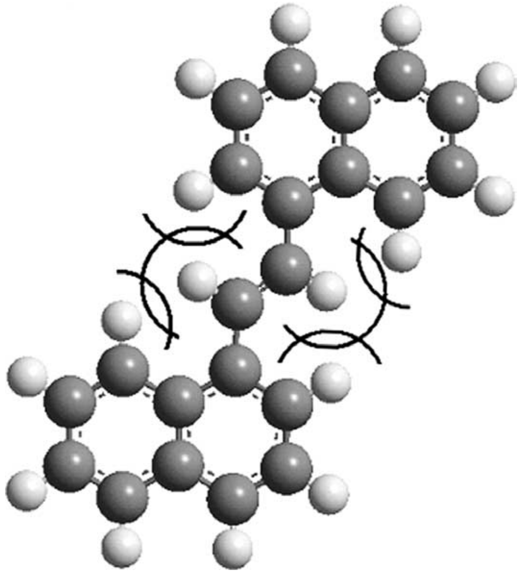


Fig. 4. Molecule model of a PNV unit. The arc indicates the repulsion between two hydrogen atoms.

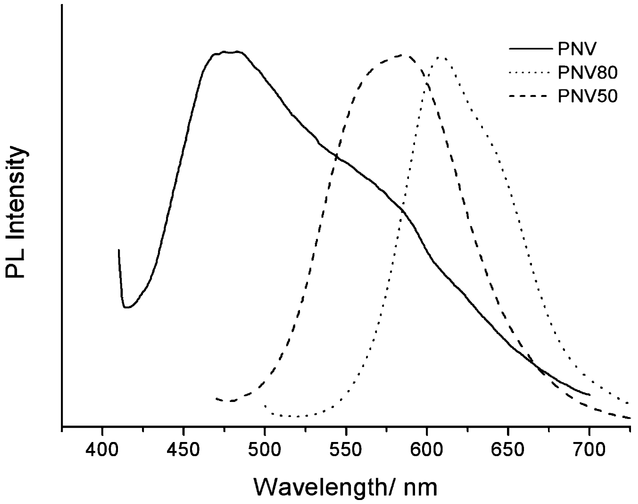


Fig. 6. Solid photoluminescence spectra of the polymers. The excitation wavelengths are 390 nm (PNV), 445 nm (PNV80) and 475 nm (PNV50), respectively.

The 1478-cm^{-1} band is related to the C–C stretching and the 1092 cm^{-1} band is associated with the C–H winding of a naphthalene ring between two benzene rings, correspondingly. Some bands of PNV spectrum do not appear in the spectra of the copolymers. The Raman spectral results indicated that the copolymers were successfully synthesized and the naphthalene rings were distributed separately between MEH–PPV blocks in the copolymers.

PNV is a khaki powder, while PNV80 and PNV50 are orange and pink in color, respectively. Fig. 3 shows the UV–vis spectra of three polymers in solid state. As can be seen from this figure, the maximum absorption of PNV is at 361 nm, which is much shorter than that of MEH–PPV (>500 nm). This blue shift is owing to the destruction of conjugated structure in main chain by PNV units. Although the double bond between two naphthalene rings reduces the repulsion of the two rings, the distance between the hydrogen atoms at the double bond and the 2 or 8 hydrogen of naphthalene ring is too short to be in one plane as demonstrated in Fig. 4. Thus, this new steric effect twists the double bond and shortens the conjugation length of the polymer. Another possible reason for the blue shift of UV–vis spectral band is the diminishing of electron-donating groups attached on the benzene ring in the main chain [18]. The introduction of MEH–PPV units into the copolymer resulted in a red shift of the UV–vis band of PNV. The maximum absorptions of PNV80 and PNV50 are appeared at 460 and 465 nm, respectively (Fig. 3).

The photoluminescence (PL) spectra of the THF solutions of the soluble parts of PNV80 and PNV50 and MEH–PPV are presented in Fig. 5. As can be seen from this figure, the maximum of the PL spectra for PNV80 and PNV50 are found at 537 and 551 nm, respectively. These wavelengths are much shorter than that of MEH–PPV (at about 600 nm). However,

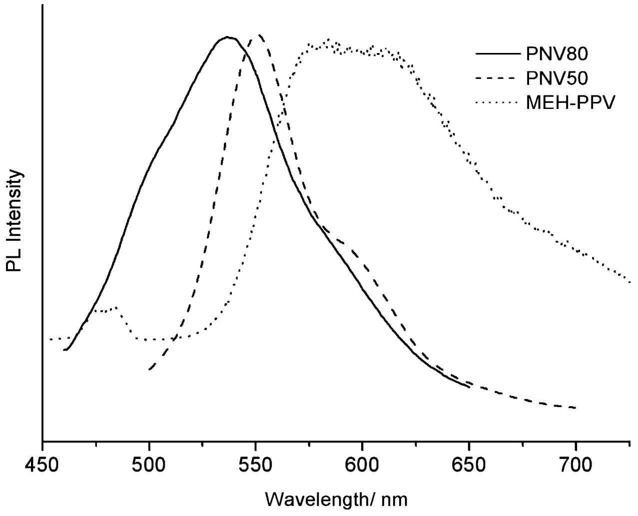


Fig. 5. Photoluminescence spectra of the polymer solutions. The spectra were excited at 445 nm (PNV80), 475 nm (PNV50) and 485 nm (MEH–PPV), respectively.

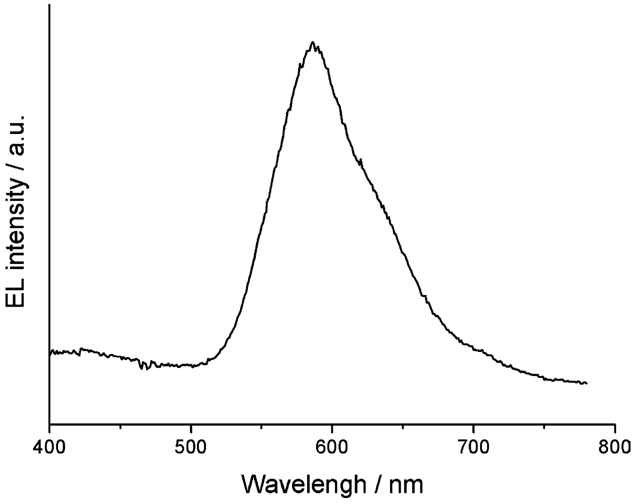


Fig. 7. Electroluminescence spectrum of PNV50.

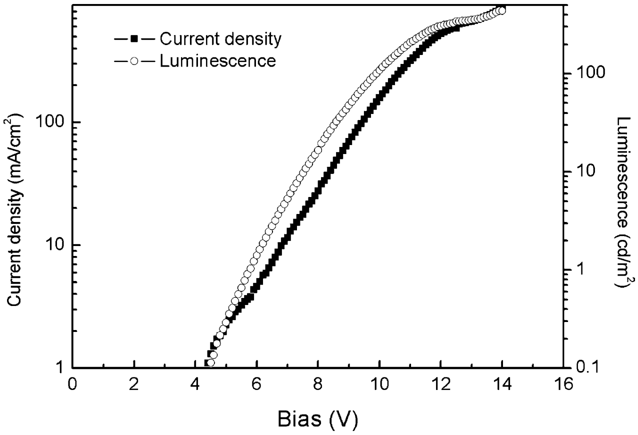


Fig. 8. Current–voltage and luminescence–voltage curves of the ITO/PEDOT/poly-TPD/PNV50/Ca/Al device.

the fluorescence bands of the copolymers are much narrower than that of MEH–PPV, mainly due to their smaller polydispersity. Accordingly, the UV–vis and PL spectral properties of the copolymers can be easily modulated by changing the feeding molar ratio of the monomers. The emission bands of PNV, PNV80 and PNV50 powders were found at 480, 584 and 608 nm, respectively, as shown in Fig. 6. In comparison to their solution spectra shown in Fig. 5, the PL maximum of the solid copolymers red shifted for about 50 nm each. This can be attributed to the chain aggregation and extended conjugated range of the polymer in solid state [19].

A PLED device based on PNV50 with an ITO/PEDOT/poly-TPD/PNV50/Ca/Al configuration was fabricated. Fig. 7 shows the electroluminescence (EL) spectrum of the device. The EL spectrum shown in Fig. 7 is similar to that of PL spectrum of PNV50, with a maximum at 586 nm. The current–voltage and luminescence–voltage curves are represented in Fig. 8. The turn-on voltage of this device was measured to be 4.3 V, a little higher than that of the device based on MEH–PPV [20]. The EL intensity was measured to be 108 cd/m^2 at 10.0 V, and its luminescence efficiency was 0.069. This value is close to that of MEH–PPV single-layer device [21,22].

4. Conclusions

PNV and its copolymers with MEH–PPV can be synthesized by dehydrohalogenation of MOEHODCX and DBMN with solid KOH particles. The introduction of MEH–PPV units into PNV makes the copolymers are partly soluble in usual organic solvents such as THF and toluene. The optical properties of the resulting copolymers can be easily modulated by changing the feeding molar ratio of the monomers. Two typical copolymers, PNV80 and PNV50 are green light emitters, and the PLED device based on PNV50 has a medium turn on voltage, luminescence intensity and efficiency.

Acknowledgements

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