Novel conjugated polymer poly(benzobisoxazole-2,6-diylvinylene): synthesis and evidence of aggregate formation in methanesulfonic acid

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Abstract

A new conjugated polymer poly(benzobisoxazole-2,6-diylvinylene) (PBOV) has been synthesized as an analogue of poly(*p*-phenylene benzobisoxazole) (PBO). The comparison between PBOV and PBO has been carried out by Fourier transform infrared spectroscopy, thermogravimetric analysis, UV, and photoluminescence (PL) spectroscopy. The UV absorption peaks, PL excitation and emission wavelengths of PBOV have a significant red-shift due to the better electronic delocalization. Similar to PBO, it can be observed in the PL spectra of PBOV at various concentrations in methanesulfonic acid (MSA) that the intensity of emission was depressed and the highly structured emission spectra gradually changed to featureless, red-shifted, and broad spectra with increasing concentration. The change in emission spectra can be attributed to the existence of the interchain aggregates, although PBOV does not show highly ordered structure as PBO does.
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1. Introduction

In the studies of the light-emitting or charge-transporting materials for organic electroluminescence (EL) devices, poly(*p*-phenylene vinylene) (PPV) and its ring-substituted derivatives have been the most widely studied conjugated polymer [1]. However, there have been several challenging problems like efficiency, color tunability and stability of the EL devices in developing conjugated polymers for the light-emitting diodes (LEDs) [2]. The rigid-rod heterocylic poly(benzazole) family including poly(*p*-phenylene benzobisoxazole) (PBO) and poly(*p*-phenylene benzobisthiazole) (PBZT) has been studied since the early 1980s [3,4]. As shown in Fig. 1, the π-conjugated structure brings many outstanding photoluminescence (PL) and nonlinear optical properties as well as mechanical properties and thermal stability. These polymers are considered as superior electron-transport and hole-blocking materials [5].

Osaheni and Jenekhe [6–8] synthesized and studied in detail the PL properties of many new conjugated rigid-rod benzobisthiazole polymers based on the structure of PBZT, including poly(benzobisthiazole-2,6-diylvinylene) (PBTV) and poly(benzobisthiazole-1,4-phenylenebis-vinylene) (PBTPV). Moreover, they synthesized rod-coil copolymers consisting of such electroactive and

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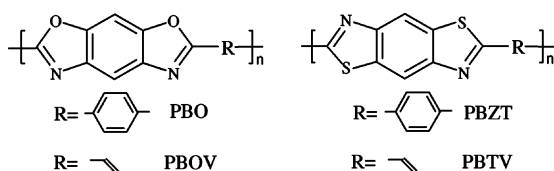
Fig. 1. Chemical structures of polymer discussed herein.

Scheme 1.

photoactive segments and observed that the luminescence quantum yield varied with the composition of copolymers, reaching over 6- and 7-fold enhancements compared to the pure conjugated polymers [9]. Previously we also reported the synthesis and characterization of new random copolymers of poly(*p*-phenylene benzobisoxazole) (PBO) and poly(2,5-benzoxazole) (ABPBO) with various compositions [10,11]. In this paper, a novel conjugated polymer poly(benzobisoxazole-2,6-diylvinylene) (PBOV) has been synthesized to make a comparison with its analogue, the rigid-rod polymer PBO. We compare the thermostability, morphology, and optical properties of PBOV with those of PBO in order to investigate the relationship between the chain structure and photophysical properties.

2. Experimental

2,4-Diamino-1,5-benzenediol dihydrochloride (DABDO) was prepared through a three-step reaction from resorcin according to the earlier report [12]. The pure DABDO was recrystallized from solution by adding concentrated hydrochloric acid under argon atmosphere before it was used as one monomer of PBO and PBOV. Terephthalic acid (TPA) was purchased from Beijing Xudong Chemical Co. and it was ground fine before it was used as the second monomer for polymerizing PBO. Fumaric acid was purchased and recrystallized twice in distilled water solution. The polymerization medium, poly(phosphoric acid) (PPA) with a P_2O_5 content of 80.8 wt.% was newly prepared using 85 wt.% phosphoric acid (purchased from Suzhou Jincheng Chemical Co.) and phosphorus pentoxide (P_2O_5) (obtained from Shanghai 1st Chemical Co.), the weight ratio of 85 wt.% phosphoric acid and phosphorus pentoxide was 1:1. Methanesulfonic acid (MSA) was purchased from Aldrich-Sigma Chemical Co.

The synthesis and characterization of the conjugated polymer PBO were reported in the literature [3,12] and the molecular weight of PBO here is 14,000 $g\,mol^{-1}$, which was estimated by the Mark–Houwink equation. In the polymerization of PBOV described in Scheme 1, 3.0 g (14.1 mmol) DABDO and 1.65 g (14.1 mmol) fumaric acid were mixed together with the newly prepared 80.8 wt.% PPA (calculated weight of 36.0 g) in a glass
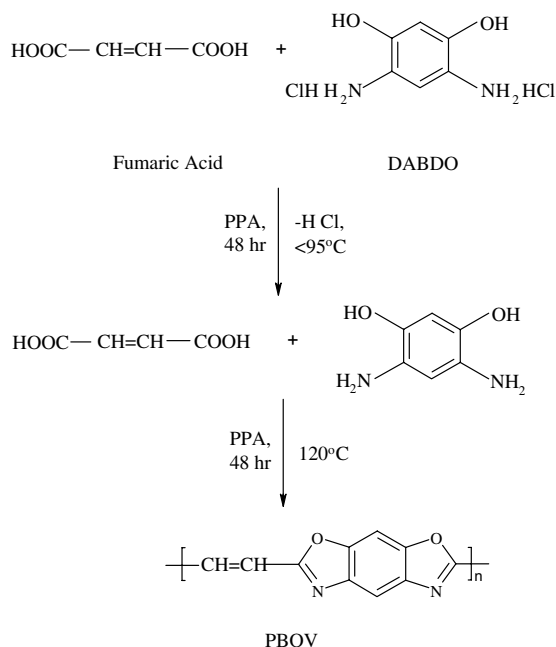
reactor vessel installed with a mechanical stainless stirrer, two gas ports and one port for feeding fresh P_2O_5 during the polycondensation. The reaction vessel was purged with argon for 1 h, and dehydrochlorination (i.e., removal of HCl from DABDO) was performed at 90 °C for at least 20 h under an argon atmosphere. During the dehydrochlorination, interval vacuum was applied to speed up the process until the gas flowing from the reaction mixture did not show acidity. After complete dehydrochlorination, 25.0 g fresh P_2O_5 was added into the reaction vessel after the vessel cooled down to 50 °C. The reaction mixture was stirred for 30 min and the temperature was progressively raised to 120 °C in 2 h and maintained at that temperature for 10 h. The final P_2O_5 content of PPA was 84 wt.% and the polymer concentration in PPA became 5 wt.%. The highly viscous dark polymerization dope was extracted on a heated glass board and then immersed in water for at least three days to remove the PPA completely. Heat treatment was performed on the polymer samples in a muffle oven at 350 °C for 5 min. Polymer solutions were prepared in MSA in the glove box. Eight PBOV solutions were used in the PL measurements with concentrations varying from 0.00044 to 0.048 $g\,dl^{-1}$. The intrinsic viscosity of PBOV in MSA is 2.4 $dl\,g^{-1}$ at 25 °C.

Fourier transform infrared (FTIR) spectra were taken on the films of the polymers at room temperature using a Nicolet Magna-IR 550 FTIR spectrometer. Thermogravimetric analysis (TGA) was done using a Du Pont Model 951 in flowing nitrogen at a heating rate

of 10 °C/min. UV–vis and PL spectra of the polymer solutions in MSA were recorded on a Varian Cary 500 UV–visible spectrophotometer and on a Varian Cary Eclipse fluorescence spectrophotometer at room temperature respectively.

3. Results and discussion

In order to make a comparison between the novel conjugated polymer PBOV with the long existing polymer PBO, both polymers have been characterized by FTIR, TGA, UV–vis and PL spectra. The polymerization of PBOV was based on the same chemistry as that of PBO polymerization, i.e., the polycondensation of a diacid and 2,4-diamino-1,5-benzenediol dihydrochloride (DABDO) to form the benzobisoxazole ring in a polymer backbone. The polymer structure was established primarily by FTIR. The FTIR spectra of the two polymers shown in Fig. 2 share many absorption peaks, such as 852, 819, 705 cm^{-1} (C=CH on the substituted phenyl rings); 1230 cm^{-1} (C=CH) and 1268 cm^{-1} (–C–O–C, asymmetric). The major differences lie at 1625 cm^{-1} and in 950–1050 cm^{-1}. The peak at 1625 cm^{-1} in PBOV is much stronger than that in PBO, which is because the absorption of C=C of vinylene in PBOV is stronger than in the phenylene ring. The difference in 950–1050 cm^{-1} is caused by the substitution of the vinylene group in the PBOV backbone. In Fig. 3, the TGA thermogram of PBOV shows that PBOV starts to decompose at ∼450 °C in nitrogen while PBO decomposes at a temperature of over 600 °C. The residue of PBOV was 66% at 720 °C. PBOV is not as stable as PBO because the aromatic ring in rigid-rod polymers is more stable than the aliphatic moieties, but PBOV still has a fairly good thermostability compared with other polymers. This result is also consistent with Jenekhe's results for PBTV and other
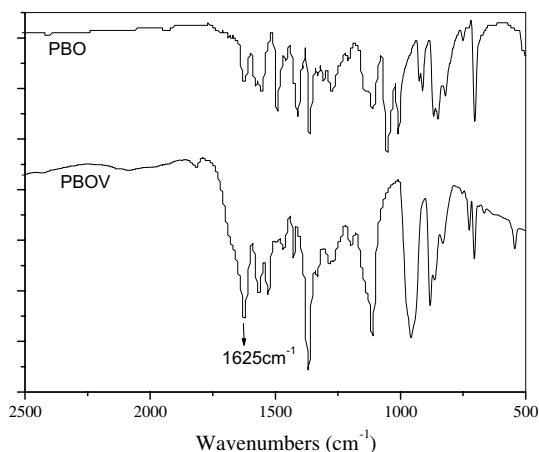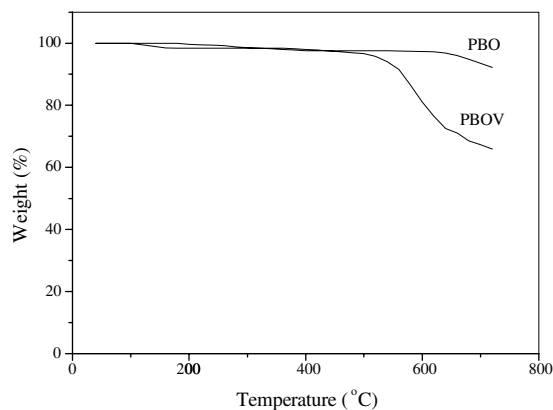

Fig. 3. TGA thermograms of PBO and PBOV heated in nitrogen.

derivatives of PBZT [5]. Wide angle X-ray diffraction (WAXD) showed a disordered and amorphous structure in the PBOV sample, while previous studies showed a highly ordered structure with intermolecular distance of 3.3–3.6 Å for PBO and other polybenzazoles. Such cofacial chain packing is proposed to be the possible origin of excimer formation in the solid state [13].

The absorption, PL excitation and emission spectra of PBOV in MSA at 0.00044 g dl^{-1} are shown in Fig. 4, together with PBO solution in MSA at the same concentration. It should be noted that the molecular weights of PBO and PBOV are not the same, and measurements for the two polymers were done using different spectrophotometers. Therefore the intensity here does not have much meaning for these two different polymers. It is evident that the optical absorption spectrum and PL spectra of PBOV in MSA have red-shifted broader peaks compared with those of PBO in MSA. The absorption spectrum of PBOV in dilute solution is well structured, as indicated by two peaks at 451 and 481 nm. Meanwhile, PBO dilute solution also shows two peaks at 404 and 428 nm, which are consistent with the literature data reported earlier [14,15]. The band gap energies of PBOV and PBO in this study, estimated from the extrapolated absorption edges, are 2.47 and 2.80 eV (2.76 eV in Ref. [15]). The results for the novel polymer PBOV are consistent with those for PBTV compared with its counterpart PBZT. The band gap energies for PBZT and PBTV are 2.48 and 2.21 eV, respectively [6]. The difference between the absorption spectra of PBOV and PBO in MSA suggests that the vinylene-linked polymer has better electronic delocalization than the phenylene-linked polymer, as reported by Jenekhe [6] for PBTV and PBZT. This conclusion can also be drawn considering that the band gap energies for poly(*p*-phenylene) and *trans*-polyacetylene are 2.8 and 1.5 eV [16]. Moreover, it was reported [17] that the introduction of vinylene into the polymer backbone could reduce the
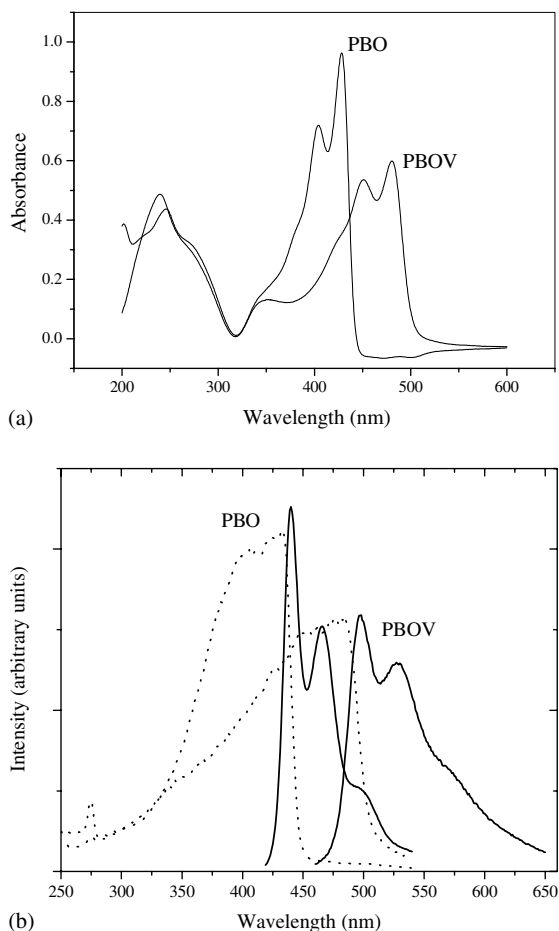

Fig. 2. FTIR spectra of polymer PBO and PBOV.

(a)

(b)

Fig. 4. PL ((a) absorption, (b) (dotted line) excitation, (solid line) emission) spectra of PBOV and PBO in MSA at the concentration of 0.00044 g dl^{-1}.

band gap energy by about 0.4 eV, which is in agreement with our results for PBOV and PBO. It can be observed that the excitation peak in Fig. 4(b) is red shifted from 433 nm for PBO solution to 484 nm for PBOV solution, also reflecting the greater electronic delocalization. The emission spectra in Fig. 4(b) also demonstrate the resolved vibronic structures for both PBO and PBOV with the same shift for both emission peaks. The emission wavelengths of 440 and 466 nm for PBO solutions are red shifted to 498 and 527 nm, respectively.

The change in PL spectra of PBOV/MSA solutions has been investigated with eight concentrations as shown in Fig. 5. The results are quite similar to the earlier reports on PBZT and PBO in solutions [13,18]. Both excitation and emission spectra show the gradual change with increasing concentration. The excitation spectrum at the lowest concentration of 0.00044 g dl^{-1} is a broad, strong peak, which splits into two peaks when the concentration is higher. The peak at the long wavelength is red shifted slightly from 482 to 516 nm with increasing concentration. The peak at the short wavelength is blue shifted from 381 nm at the concentration of 0.0022 g dl^{-1} to 333 nm at 0.0088 g dl^{-1} and this excitation peak finally vanishes at higher concentrations due to the self-quenching effect. Meanwhile, a significant change with concentration can be found in the emission spectra of PBOV in MSA. There are three types of peaks in the emission spectra which can be classified as Em1, Em2, and Em3. Em1, Em2, and Em3 are around the wavelengths of 500, 530, and 565 nm, respectively. Em3 is merely a shoulder in the spectra. When the concentration is 0.00044 g dl^{-1}, one can observe a highly structured spectrum, indicating the singlet excited state emission of the "single chain" in dilution. With increasing concentration, Em1 diminishes gradually and Em2 becomes dominant, while the relative intensity of Em3 increases. As discussed in detail for PBO/MSA [18], the formation of aggregate of PBOV molecules in MSA is suggested here to be the origin of the change in emission spectra. Aggregates, indicated by ^{1}(AA), are formed by the two or more neighboring chains with chromophore ^{1}A when they are in the ground state, and such aggregates are excited to ^{1}(AA)* after absorption in another path: ^{1}A + ^{1}A $\Longleftrightarrow$ ^{1}(AA) $\Longleftrightarrow$ ^{1}(AA)* (for simplicity, here we only show an association of two units). The ground- and excited-state wave functions are delocalized over several polymer chains, so the emission spectra at high concentrations or solid films are structureless, broad, and red-shifted. The better electronic delocalization and stronger interchain interaction of PBOV in MSA make this change more significantly dependent on concentration than that in PBZT/MSA [13] and PBO/MSA [18] solutions.

4. Conclusion

In summary, a new conjugated polymer poly-(benzobisoxazole-2,6-diylvinylene) (PBOV) has been synthesized as an analogue of poly(p-phenylene benzobisoxazole) (PBO). The comparison between PBO and PBOV shows that the novel polymer PBOV has a lower band gap energy of 2.47 eV, a fairly good thermostability with a decomposition temperature of 450 °C, and a disordered structure. The UV and PL spectra of PBOV are red shifted significantly compared with PBO because of the higher electronic delocalization. Despite the disordered and amorphous structure in the solid state, which is quite different from that for PBO with the intermolecular distance of 3.3–3.6 Å in sandwich-type chain cofacial packing expected to be the reason for excimer formation [13], the PL spectra of PBOV at various concentrations in MSA show the same evidence of aggregate formation.
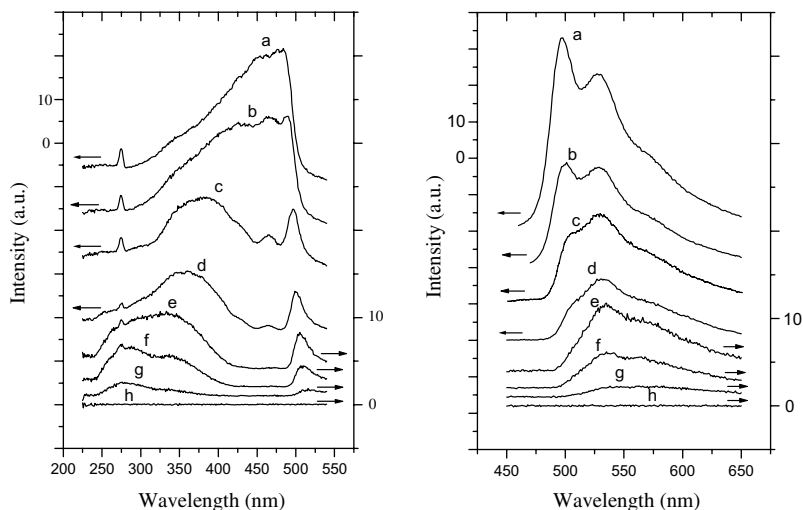
Fig. 5. PL (left: excitation, right: emission) spectra of PBOV in MSA (a–h: 0.00044, 0.00088, 0.0022, 0.0044, 0.0088, 0.011, 0.0192 and 0.048 g/dl).

Acknowledgements

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