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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:
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Online publication date: 30 August 2010

To cite this Article Xu, Xiaohui , Liu, Xiaoyun , Zhuang, Qixin and Han, Zhewen(2010) 'Protonation Effect of Polybenzoxazole: Experimental Evidence', Journal of Macromolecular Science, Part A, 47: 10, 977 — 982

To link to this Article: DOI: 10.1080/10601325.2010.506112

URL: http://dx.doi.org/10.1080/10601325.2010.506112

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Journal of Macromolecular Science, Part A: Pure and Applied Chemistry (2010) **47**, 977–982

ISSN: 1060-1325 print / 1520-5738 online
DOI: 10.1080/10601325.2010.506112

Protonation Effect of Polybenzoxazole: Experimental Evidence

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Received April 2010, Accepted May 2010

In order to investigate the protonation effect of polybenzoxazole, a type of soluble thiophene-based polybenzoxazole (PBOP-Th) is synthesized and characterized by the FTIR, ^{1}H-NMR, elemental analysis, thermogravimetric analysis (TGA), UV-Vis and photoluminescence (PL) spectra. Another polymer aminophenols-based polybenzoxazole (PBOP-Ph) was also synthesized as reference polymer. Unlike usual polybenzoxazoles such as poly(*p*-phenylenebenzobisoxazole) (PBO) and poly(2,5-thienylbenzobisoxazole) (PBOT), PBOP-Th and PBO-Ph have greatly enhanced solubility due to the introduction of isopropylidene and/or thiophene cycle. The effect of protonation on photophysical properties of polybenzoxazoles is studied by an experimental method for the first time. The 30 nm red shift on the UV-Vis and PL spectra of polymer is observed in methanesulfonic acid (MSA) solution compared with that of polymer in neutral *N*, *N*-dimethyl fomamide (DMF) solution, which is believed to be due to the protonation effect.

Keywords: Polybenzoxazole, thiophene, photoluminescence, protonation effect

1 Introduction

Heterocyclic polybenzoxazoles belong to the aromatic heterocyclic polymers and have been of considerable interest because of their outstanding thermal stabilities, optical properties, as well as mechanical properties (1–4). Recently, many novel polybenzoxazoles were synthesized and their mechanical and optoelectronic properties have been investigated (5–14). However, the rigidity of the benzoxazole cycle makes them insoluble in most organic solvents and the reported polybenzoxazoles usually are characterized and studied in strong protonic acids, (15) such as sulfuric acid (SA), methanesulfonic acid (MSA), trifluoroacetic acid (TFA) and chlorosulfonic acid (CSA). The acids protonate the nitrogen atoms of the benzoxazole and transform the neutral chains to polyelectrolytes. This may bring some variance with the true values. Firstly, the conformation of polymer chains will be affected by the protonation. By virtue of the positive charges on the chain, repulsive Coulombic interactions between nitrogen atoms may tend to extend and stiffen the chain because of aggregation effects. Secondly, shielding effects of the counter-ions and the strong acid medium may in turn greatly suppress the aggregation effects. Thirdly, protonation can affect the energy levels of molecular orbital, which are believed to influence photo-electronic properties of polymers (16). Consequently, the experimental electronic optical spectra in protonic acids will inevitably deviate from the actual or proper values. Although some soluble polybenzoxazoles have been prepared, there are few reports about the protonation effect on photophysical properties.

Farmer et al. once calculated the influence of protonation on the conformation and internal rotation barriers of poly(*p*-phenylenebenzobisoxazole) (PBO) by using the molecular orbital calculations and model compound (17).The calculations showed that the barrier of internal rotation about the C–C bond between the phenyl ring and the heterocycle increases from 10.55 kJ/mol for the neutral molecule to 16.83 kJ/mol for the protonated molecules. Our group also once calculated the effects of protonation on the behavior of PBO polymer model by using AM1 method (16,18). The results showed that the PBO chain was distorted and stiffened by protonation and consequently, the torsion energy barrier became substantially higher than that of neutral PBO chain.

Some experimental study about protonation effects had also been reported. For example, Wang et al.compared a model compound's spectra in both toluene and MSA solutions and observed that a significant red shift takes place in PL spectra when the solvent changes from toluene to

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MSA[10]. Similar behavior was also reported by D.Y. Shen (19) and Y.H. So (20).

However, to the best of our knowledge, no representation or experimental fact about protonation effect on photophysical properties of polybenzoxazoles has thus been made although some benzoxazole model compounds have been employed in the effect of protonation (10, 19, 20). In this paper, we synthesized a novel thiophene-based polybenzoxazole PBOP-Th. Another polymer, PBOP-Ph, was also synthesized in this study as a reference polymer, which was a homopolymer, but had a similar structure as a copolymer previously reported by Josepha that were based on bisaminophenols, terephthaloyl chloride and optionally isophthaloyl chloride (21). The polymer PBO-Th and PBO-Ph not only are soluble in protonic acids, but also dissolve in neutral organic solvents. The structure, thermal stability, and effect of protonation medium on photophysical properties of these polybenzoxazoles are studied in detail.

2 Experimental

2.1 Materials

Phosphorus pentoxide (P_2O_5), poly(phosphoric acid) (PPA), and terephthalic acid were purchased from Shanghai Lingfeng Chemical Co. Thiophene-2,5-dicarboxylic acid, bisphenol A, and methane sulfonic acid (MSA) were obtained from Aldrich Chemical. All the materials were analytically pure and used as received unless otherwise specified.

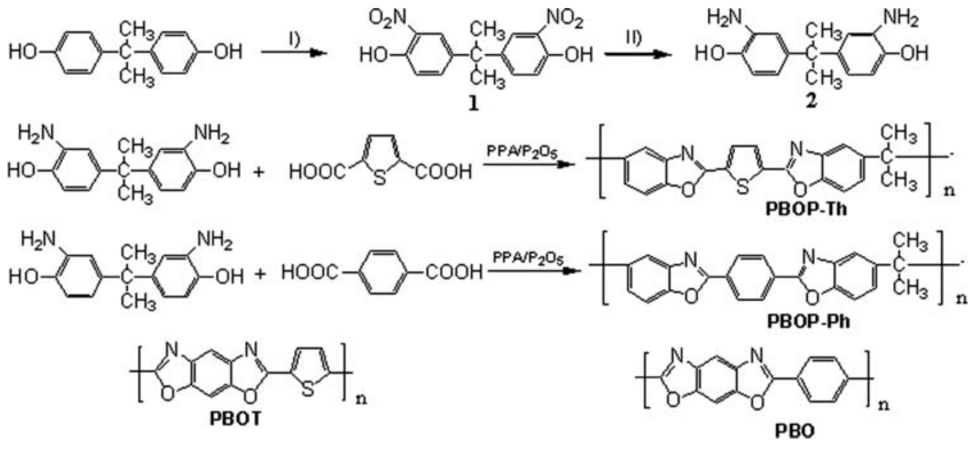
2.2 Measurements

Fourier transform infrared (FTIR) spectra were taken on the films of the polymers at room temperature using a Nicolet Magna-IR 550 FT-IR spectrometer. Thermogravimetric analysis (TGA) was done using a Du Pont Model 951 in flowing nitrogen at a heating rate of 10°C/min. ^{1}H-NMR spectra were measured using a Bruker Avance DRX-500 (500 MHz) spectrometer with tetramethylsilane as the standard. Elementary analysis was done with a Elementar Vario EL. The UV-Vis and PL emission spectra of the polymer solutions were recorded on a Varian Cary 500 UV-visible spectrophotometer and on a Varian Cary Eclipse fluorescence spectrophotometer at room temperature, respectively. Intrinsic viscosities of all the samples were measured in ketopyrrolidine (NMP) at 30°C by the Ubbelohde capillary viscometer.

2.3 Synthesis of Monomers

The synthetic route of monomers is illustrated in Scheme 1. 2,2-Bis(3-nitro-4-hydroxyphenyl)-propane (1) is synthesized and purified as the following. Bisphenol A (5.7 g, 25 mmol) powder is added to 17% (w/w) aqueous HNO_3 (75 mL) at 20°C in three equal lots of 1.9 g each. The reaction mixture is stirred at 20°C for 4 h and then poured into 200 mL of ice water. The resulting yellow acicular crystal was obtained by filtrating, rinsing, purifying by chromatography on silica using warm toluene as eluent. Yield: 84.3%. mp: 120–122°C. ^{1}H-NMR (acetone-d_6, ppm): $\delta = 7.74$ (d, $J = 4.0$ Hz, 2H), 7.36 (q, $J = 11.0$ Hz, 2H), 7.05 (d, $J = 13.0$ Hz, 2H), 1.62 (s, 6H). FTIR (KBr, cm^{-1}): 3340 (N-O), 3260 (O-H), 2983 (C-H), 1583, 1480 (C=C), 1428, 1335 (C-C). Anal. calcd for $C_{15}H_{14}N_2O_6$: C, 56.80; H, 4.46; N, 8.90. Found: C, 56.76; H, 4.51; N, 8.86.

2,2-Bis(3-amino-4-hydroxyphenyl)-propane (2) is synthesized and purified according to Reference 22. Yield: 94.9%. mp: 249–251°C. ^{1}H-NMR (acetone-d_6, ppm): $\delta =$ 8.72 (s, 2H), 6.50 (d, $J = 13.0$ Hz, 2H), 6.41 (d, $J = 3.5$ Hz, 2H), 6.28 (t, $J = 10.0$ Hz, 2H), 4.30 (s, 4H), 1.44(s, 6H). FTIR (KBr, cm^{-1}): 3420 (N-H), 3323 (O-H), 2983 (C-H), 1863, 1295 (C-N), 1595, 1508 (C=C), 1448, 1355 (C-C),



Sch. 1. Synthetic route for the monomers and polymers. The conditions are as follows: 1) HNO_3 (17% w/w), 20°C for 4 h; 2) ethanol, hydrazine hydrate, $FeCl_3{\cdot}6H_2O/C$, 70°C for 2 h.

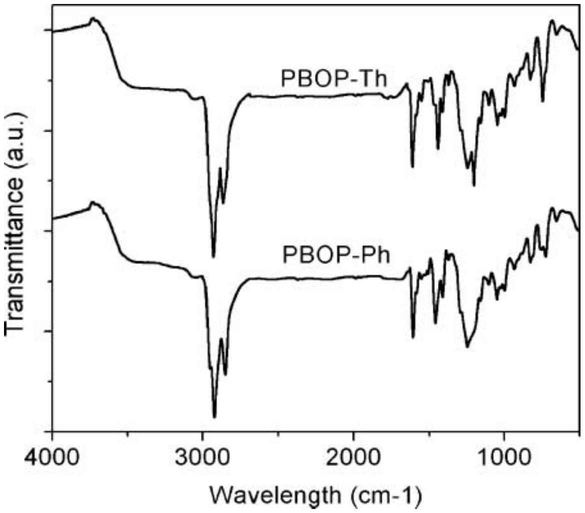


Fig. 1. FTIR spectra of PBOP-Th and PBOP-Ph.

1190 (C-O). Anal. calcd for $C_{15}H_{18}N_2O_2$: C, 72.21; H, 6.92; N, 11.12. Found: C, 72.20, H, 6.96, N, 11.08.

2.4 Synthesis of Polymers

The polymer PBOP-Th and PBOP-Ph are prepared from facile one-step condensation polymerizations. The structure and synthetic route are shown in Scheme 1. Taking PBOP-Th as an example, the synthesis procedure is as follows. 2,2-Bis(3-amino-4-hydroxyphenyl)-propane (2.583 g, 10 mmol), thiophene-2,5- dicarboxylic acid (1.721 g, 10 mmol), PPA (42.0 g) and P_2O_5 (26.0 g) are added into a reactor vessel under argon at room temperature. After a 30 min of stirring at 60°C, the mixture is heated at 100°C for 6 h, then 130°C for 6 h, finally 160°C for 8 h. After being cooled to 60°C, 300 mL of deionized water is added and the mixture is stirred for 1 h. Then, filtering and washing are done to remove the residual PPA completely. PBOP-Th is obtained as a brown powder after drying *in vacuo* to give a yield of 99.9% (3.580 g). PBOP-Ph is synthesized by a similar procedure. FTIR (KBr pellet, cm^{-1}) with PBOP-Th: 2931, 2870 (C-H), 1373 (-CH_3), 1612, 1053 (benzoxazole), 1442, 1200, 749 (thiophene ring framework). Anal. calcd: C, 69.98; H, 4.47; N, 7.77; S, 8.90. Found: C, 69.92; H, 4.40; N 7.72, S, 8.89. FTIR (KBr pellet, cm^{-1}) with PBOP-Ph: 2930, 2868 (C-H), 1510, 1411 (aromatic ring framework), 1372 (-CH_3), 1611, 1055 (benzoxazole). Anal. calcd: C, 77.95; H, 5.12; N, 7.90. Found: C, 77.83; H, 5.03; N 7.83.

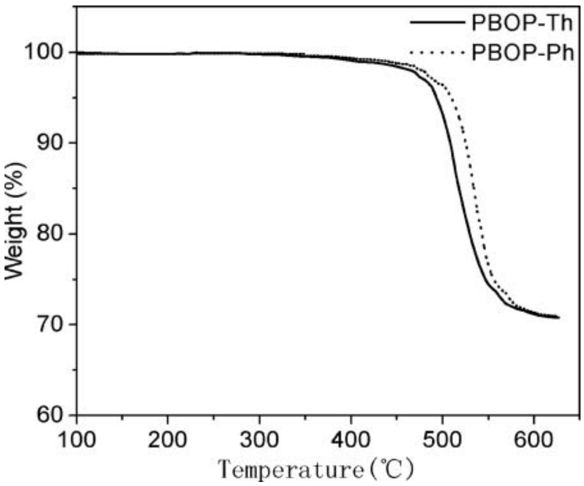


Fig. 3. TGA thermograms of PBOP-Th and PBOP-Ph.

3 Results and Discussion

3.1 Polymer Characterizations

Figure 1 shows the FTIR spectra of polymers PBOP-Th and PBOP-Ph. The complete cyclodehydration polymerization process occurs as indicated by the disappearance

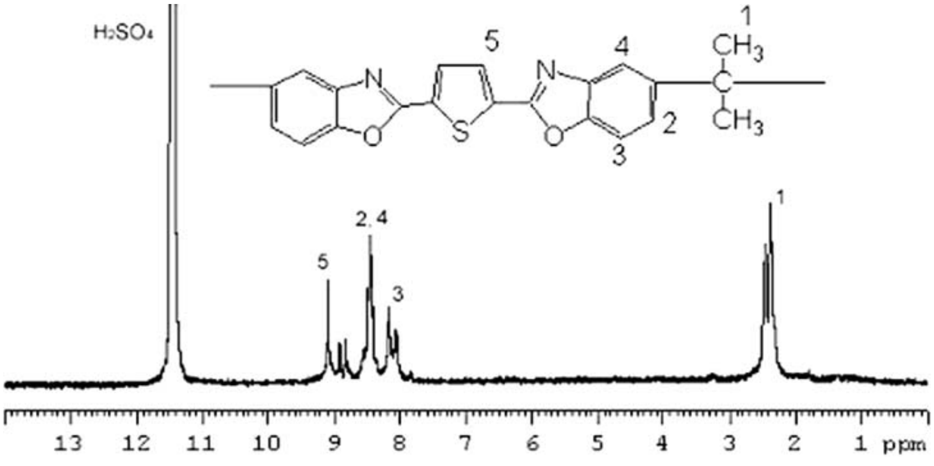


Fig. 2. ^{1}H-NMR spectrum of PBOP-Th.

Table 1. Physical properties of the polymers

Polymers	*$[\eta]^a$ g/dL*	*T_d^b (°C)*	*Residual Weight^c (%)*
PBOP-Th	1.32	492	71.35
PBOP-Ph	1.51	509	71.19

^{a}Intrinsic viscosities in NMP measured at 30.0°C; ^{b}Decomposition temperature determined by TGA in N_2 based on 5% weight loss; ^{c}at 600°C.

of absorption of carboxyl and *o*-hydroxy amino group at 1706 and 3420 cm^{-1}, together with the appearance of characteristic benzoxazole absorptions at 1612 cm^{-1} (C=N) and 1053 cm^{-1} (C=O=C) (23). For PBOP-Th, the peaks at 1442 and 745 cm^{-1} are assigned to -C_4SH_2- stretching in thiophene rings (24, 25). As for PBOP-Ph, the spectrum shows two peaks at 1510 and 1411 cm^{-1} which belongs to vibrations of *para*-substituted phenyl nucleus (26). Figure 2 shows the ^{1}H NMR spectrum of polymer PBOP-Th.

Figure 3 illustrates typical TGA curves of PBOP-Th and PBOP-Ph in nitrogen. Both of the TGA curves of PBOP-Th and PBOP-Ph show two weight loss stages. The first slight weight loss stage is in the range of 350 and 450°C. This weight loss is due to the decomposition of methyl in isopropylidene (27). The second weight loss occurs at around 500°C, which is thought to be a result of the decomposition of the benzoxazole ring. Table 1 lists the physical properties of PBOP-Th and PBOP-Ph. The 5% weight loss temperatures (T_d) in nitrogen is 492°C for PBOP-Th and 509°C for PBOP-Ph, both showing excellent thermal stabilities. Polymer PBOP-Ph displays a little higher T_d than PBOP-Th, and this is probably due to better stability of the benzene ring. The overall thermal stability of PBOP-Th and PBOP-Ph is weaker than PBO and PBOT, in which the onset of weight loss did not occur until over 600°C (27).

It is known that most aromatic polybenzoxazoles are insoluble in ordinary organic solvents. For example, the well-known PBO and PBOT only dissolve in strong protonic acids such as MSA and H_2SO_4 (28, 29). However, both PBOP-Th and PBOP-Ph are soluble in strong polar organic solvents, such as NMP, DMAC, DMSO etc. The qualitative solubility of PBOP-Th and PBOP-Ph in various solvents is shown in Table 2. The greatly improved solubility of PBOP-Th and PBOP-Ph may be attributable to the introduction of isopropylidene which interrupts the rigidity of polybenzoxazoles chains. This prevents the close chain packing and makes solvent molecules diffuse into the polymer chains easily. The good solubility makes it possible to study the effect of protonation on the spectral properties of polybenzoxazoles through experimental facts.

3.2 The Influence of Protonation Effect on the Optical Properties in Solutions

Figure 4 shows the experimental optical absorption spectra of the polymers PBOP-Th (Fig. 4a) and PBOP-Ph (Fig.4b) in neutral organic solvent DMF and protonic solvent MSA. The spectral data are summarized in Table 3. The optical band gaps (E_g) of the polymers are calculated from the onset wavelength of their UV-vis spectra according to the empirical equation (8). The absorption profile of PBOP-Th in DMF solution is featured with two main peaks at 361 and 379 nm; the strongest band (λ_{max}) is located at 379 nm and it involves HOMO to LUMO transition of benzoxazole chromophore ($\pi - \pi^*$ transition). Upon protonation with MSA, the peaks of benzoxazole chromophore (379 and 361 nm) disappear, and a new wide band forms at 409 nm. The disappearance of peaks at 379 and 361 nm is owing to the protonation of the nitrogen on benzoxazole by protonic acid. A similar bathochromic shift of 26 nm is also found in the spectra of polymer PBOP-Ph (Fig. 4b). These results are in good agreement with our previous simulation results, which shows that protonation effect can result in red shifts in the polybenzoxazole solution by the semi-empirical method AM1/ZINDO-C1 (16).

Moreover, the new band around 409 nm could be attributed to the formation of an aggregate after protonation. It is known that protonation not only can suppress the aggregation through shielding effects of the counterions and the strong acid medium, but also can stiffen the polymer chains and facilitate aggregation by virtue of repulsive coulombic interactions between nitrogen atoms (18). In concentrated MSA (>99%) solutions, repulsive coulombic interactions prevail and the aggregations form (30).

Absorption spectra of polymers as a function of the MSA concentration are not taken because the polybenzoxazoles are insoluble in hydrous acids.

It can also be found from Figure 4 that the energy gap Eg varies from 2.91 eV for PBOP-Th to 3.05 eV for PBOP-Ph. The lower band gap for thiophene-based polymer PBOP-Th can be ascribed to the weaker steric hindrance between thiophene ring and benzoxazole heterocycle than that between benzene ring and heterocycle (28). The easier rotation consequently broadens the conjugation range and brings better electronic delocalization.

Table 2. Solubility behaviors of PBOP-Th and PBOP-Ph

Polymers	*MSA*	*H_2SO_4*	*NMP*	*DMAC*	*DMSO*	*DMF*	*Dioxane*	*THF*	*Acetone*
PBOP-Th	++	++	++	++	++	+	−	−	−
PBOP-Ph	++	++	++	+	+	+	−	−	−

Symbols: ++, soluble at room temperature; +, slightly soluble; −, insoluble.

Table 3. Spectral data of the PBOP-Th and PBOP-Ph

Polymers	*Abs (nm)* λ_1	λ_2	*Em (nm)* λ_1	λ_2	*Ex (nm)* λ	λ_{onset} *(nm)*	E_g *(eV)*
PBOP-Th[a]	361	379*	445*	474	380	426	2.91
PBOP-Th[b]	409*		459*	488	400	472	2.63
PBOP-Ph[a]	346*	368	388	404*	365	407	3.05
PBOP-Ph[b]	374*	394[c]	402	419*	380	456	2.72

[a]In DMF; [b]in MSA; [c]Optical band gap calculated from the onset absorption spectra; *The strongest absorption or emission wavelength.

The photoluminescence emission spectra of PBOP-Th and PBOP-Ph in DMF and MSA solution are exhibited in Figure 5. The PL emission spectrum of PBOP-Th (solid line), obtained in neutral solvent DMF at the excitation wavelength of 380 nm, reveals two characteristic emission bands at about 445 and 474 nm. While the PL spectrum of PBOP-Th (dotted line) obtained in protonic solvent MSA displays the strongest emission peak at 459 nm and a shoulder peak at 488 nm, showing a red shift of 14 nm. This bathochromic shift is attributed to the increased interchain interaction due to the protonation of benzoxazole groups in the molecular chains. By the positive charges on the chain, repulsive coulombic interactions between adjacent heterocycles tend to extend and stiffen the chain because of aggregation effects. A similar bathochromic shift is also found in the spectra of polymer PBOP-Ph (Fig. 5b). The PL experimental results are also in agreement with the previous simulation results with the polybenzoxazole models (18).

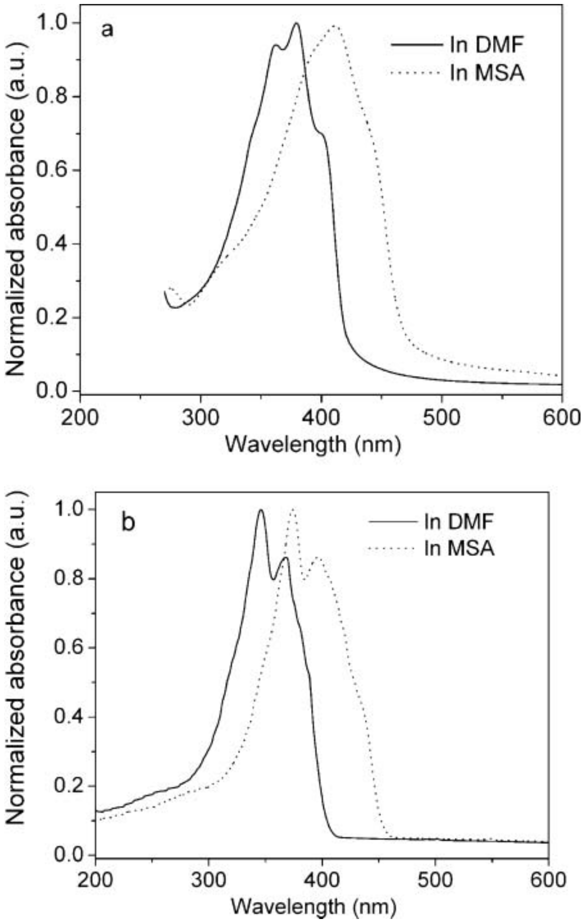


Fig. 4. Normalized absorbance spectra of PBOP-Th (a) and PBOP-Ph (b), 0.00035 g/dL.

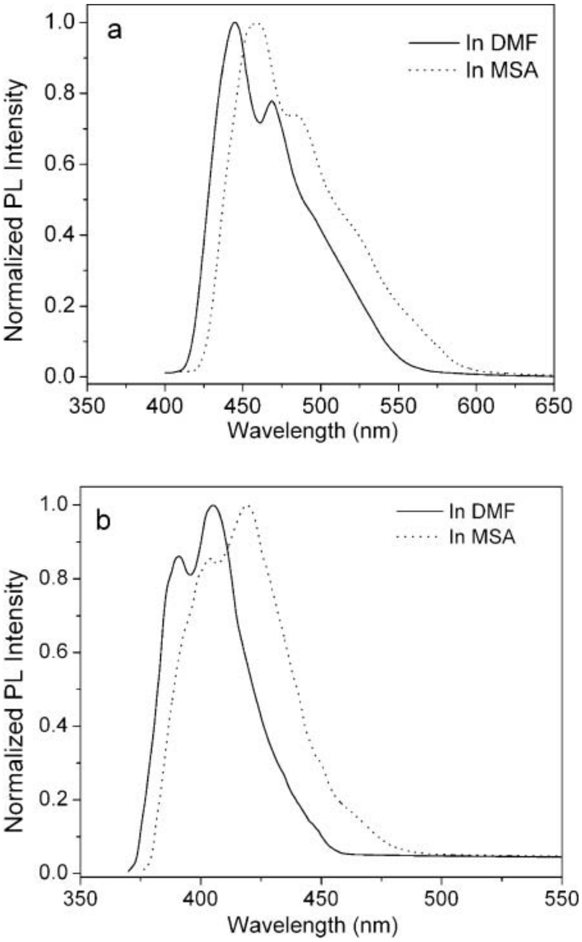


Fig. 5. Normalized PL spectra of PBOP-Th (a) and PBOP-Ph (b), 0.00035 g/dL.

3.3 The Interdiction Effect of Isopropylidene Group on Photoluminescence Property

As shown in Figure 5, the PL emission spectra of PBOP-Th and PBOP-Ph in MSA display the λ_{max}at 459 and 419 nm. In comparison with the conjugated rigid-rod polymers PBOT and PBO with similar structures which show maximum emissions at around 500 and 439 nm, respectively, (28) PBOP-Th and PBOP-Ph show obvious blue-shifting photoluminescence (PL) emissions spectra (Fig. 5). The hypsochromic shift is attributed to the reduction of effective conjugation length in the polymer backbone by the interruption of the isopropylidene group. The isopropylidene group interdicts the conjugation of main chain and reduces π electron delocalization, thus increasing the energy of $\pi - \pi^*$ transition.

4 Conclusions

A novel polybenzoxazole incorporating isopropylidene is synthesized and characterized in detail. The polymers not only are soluble in protonic acid such as MSA and H_2SO_4 but also dissolve in DMF, DMSO and NMP, showing greatly improved solubility than conventional polybenzoxazoles reported previously such as PBO and PBOT. The optical absorption and photoluminescence emission spectra have been investigated in the protonic solvent MSA and neutral solvent DMF, respectively for the first time. In protonation medium MSA, obvious red shifts are observed compared with that of polymers in neutral DMF solution. This bathochromic shift is attributed to the increased interchain interaction and smaller energy gap due to the protonation of benzoxazole groups in the molecular chains.

Acknowledgments

The authors express their gratitude to the National Natural Science Foundation of China (NSFC) for their financial support, contract grant numbers 50703010 and 50973028. This project is also supported by “the Fundamental Research Funds for the Central Universities.”

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