Rigid-Rod Polybenzoxazoles Containing Perylene Bisimide: Synthesis, Structures and Photophysical Properties

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ABSTRACT: A novel perylene bisimide dye bearing carboxylphenylene substituents on the imide N atoms was synthesized and four conjugated copolymers containing different contents of perylene bisimide dye were synthesized via PPA/P_2O_5 copolymerization method. The structures of the four copolymers were characterized by FTIR, elementary analysis, ^{1}H-NMR and XRD. The copolymers showed good thermal stabilities but poor solubilities due to the high rigidity of the backbone. The photophysical characteristics of the copolymers were investigated by UV-Vis and PL spectra in solutions and films. Because of the conformational change of perylene bisimide chromophore, the absorptions of perylene bisimide core in copolymers showed a large blue-shift (56 nm) compared to that of the perylene monomer. In PL experiments, when exciting the benzoxazole, an obvious fluorescent quenching was observed in all copolymers, which can be attributed to the energy transfer from benzoxazole units to perylene bisimide fragments and fluorescence quenching. With increasing perylene content, the copolymers turned to layered and friable. The XRD test showed that the interchain distances increased slightly with increasing perylene content. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 116: 455–460, 2010

Key words: perylene bisimide; benzoxazole; synthesis and characterization; fluorescence spectra

INTRODUCTION

Perylene and its derivatives are widely used as dyes, pigments, lasers, fluorescent solar collectors, luminescent materials, and molecular switch owing to its low band gap, high chemical stability, high photoluminescence quantum yield, excellent electron transportation property, as well as good photostability.[1–4] In the case of perylene bisimide pigments, color tuning is achieved via varying the structure such as chemical variation of the substituents of the imide functions, copolymerization, blending with another emissive polymer, doping with molecular dyes and so on. In particularly, attaching the dyes to the polymer backbone is adopted constantly because initial doping and blending methods have a tendency to show phase separation over time, which leads to instability in the device's performance.[5] Copolymerization has two significant advantages. Firstly, migration of the dye chromophore inside the polymer matrix which may lead to aggregation and poor device performance is prevented. Secondly, efficient intrachain energy transfer to the dye chromophore and the confinement of the singlet excitons in the chromophore are facilitated. However, new developments in the field of perylene bisimide based functional polymers have been limited so far by their poor solubility of perylene bisimide in common organic solvents. Müllen and coworkers designed a series of soluble perylene bisimide-based dendrimers and investigated energy and electron transfer at single-molecule level.[6] Würthner and coworkers designed many functional coordination supramolecules with soluble perylene bisimides as building blocks.[7] Li and coworkers[8] and Janssen and coworkers[9] designed foldable oligomers and polymers in which perylene bisimide units were covalently connected by oligo-(ethylene glycol) or poly(tetrahydrofuran) chains.

In this context, perylene bisimide is referred to as functional chromophore and covalently attached to the poly(*p*-phenylene benzobisoxazole) (PBO) via copolymerization. The structures of monomers and copolymers were characterized and the photophysical properties were studied via UV-vis spectrometry and PL spectrometry measurements.

PBO was chosen as the polymer backbone because of its large band gap, outstanding electron transportation property, excellent chemical and thermal
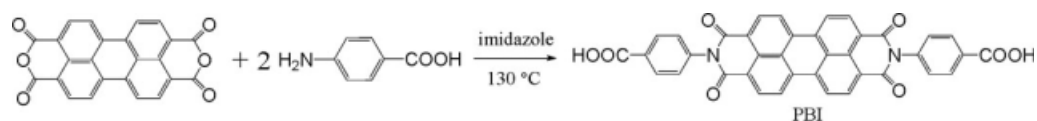
Scheme 1 Synthesis of N,N'-Bis(p-carboxyl-phenylene) perylene-3,4 : 9,10-perylene bisimide.

stability.[10–18] Some new properties could be obtained by introducing special groups into the backbone of heterocyclic rigid-rod polybenzoxazoles. Jenekhe and coworkers made systematic pioneering work on polybenzazoles.[19–23] In our previous work, we synthesized a series of copolymers containing higher band gap poly(2,5-benzoxazole) and lower band gap poly(2,5-thienyl benzobisthiazole) and found that the spectral modulation and inter- and/or intramolecular energy transfer existed in the system.[24–27]

This article focuses on the aggregation and optical properties of perylene bisimide dye in the rigid-rod copolymers. To our best knowledge, few reports on photophysical properties of perylene bisimide dye in rigid-rod backbones are reported.

EXPERIMENTAL

Materials

Poly(phosphoric acid) (PPA), phosphorus pentoxide (P_2O_5) and terephthalic acid (TA) were purchased from Shanghai Lingfeng Chemical. Imidazole and m-dihydroxybenzene were purchased from Sinopharm Chemical Reagent, 3,4 : 9,10-perylenetetracarboxylic dianhydride, p-aminobenzoic acid, methane sulfonic acid (MSA) were purchased from Sigma-Aldrich Corporation. All the materials were used as received.

Measurements

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. 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. ¹H-NMR spectra were measured using a Bruker Avance DRX-500 (500 MHz) spectrometer with tetramethylsilane as the standard. Elemental analysis was done with elementar Vario ELβ and the mass spectrum was pursued on Micromass GC/TOF MS. X-ray diffraction (XRD) patterns were collected in a 2θ scan range of 6–50° on a Rigaku D/max-rB rotating anode X-ray generator with Ni-filtered CuKα (k = 0.15401 nm) radiation operated at 100 mA and 40 kV. Intrinsic viscosities of all the samples were measured in

MSA at 30°C by using a modified device based on the Ubbelohde capillary viscometer. Thin polymer films of good optical quality were prepared using Jenekhe's method,[28] i.e., spin-coating of the polymer solution in nitromethane/$AlCl_3$ with a polymer concentration of 3 wt % onto synthetic silica substrates. The thin films were dried at 80°C in a vacuum oven for 12 h after complete decomplexation in deionized water for over 3 days.

Synthesis of N,N'-bis(p-carboxylphenylene) perylene-3,4 : 9,10-perylene bisimide

A mixture of 302 mg (0.77 mmol) 3,4 : 9, 10-perylene tetracarboxylic dianhydride, 30 g imidazole and 2 mL chloroform were stirred at 90°C. Then 257 mg (1.87 mmol) p-aminobenzoic acid was added. The mixture was refluxed at 130°C with stirring for 24 h, followed by acidizing and filtrating using G4 funnel filter. The precipitation was washed by enough water, then subjected to extraction in anhydrous ethanol and desiccation *in vacuo* to yield pure N,N'-bis(p-carboxyl-phenylene) perylene-3,4 : 9,10-perylene bisimide (PBI). The synthetic route was illustrated in Scheme 1. The ¹H-NMR spectrum was shown in Figure 1.

¹H-NMR (D_2SO_4, 500 MHz, 25°C): 9.75–9.79 (d, 8H, perylene ring), 9.19 (d, 4H, 2 × ArH_2), 8.49 (d, 4H, 2 × ArH_2). FTIR (KBr, cm^{-1}): 3403(OH, s), 1701, 1665(C=O, s), 1348, 1251(C—N, s), 1593, 1508 (aromatic ring framework, s), 856, 808(br). Elemental analysis: Calc. for $C_{38}H_{18}N_2O_8$ (%): C, 72.38, H, 2.88, N, 4.44. Found (%): C, 72.31, H, 2.95, N, 4.35. Yield, 98.8%.

Synthesis of 4,6-diamino-1,3-benzenediol dihydrochloride

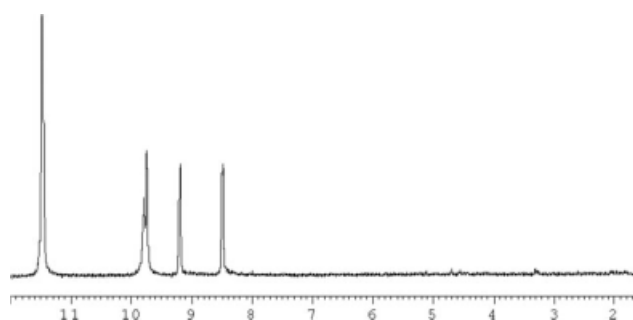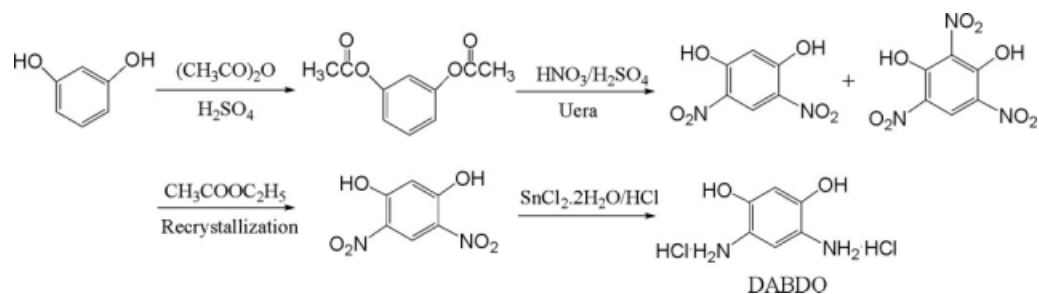4,6-Diamino-1,3-benzenediol dihydrochloride (DABDO) was prepared according to the earlier report (Scheme 2).[29]

Figure 1 ¹H-NMR spectrum of PBI.

Scheme 2 Synthesis of 4,6-Diamino-1,3-benzenediol dihydrochloride.

Mass spectrum (70 eV), m/e 140 (M-2HC1). Anal. Calcd. for $C_6H_{10}Cl_2N_2O_2$ (%): C, 33.82, H, 4.73, N, 13.15, C1, 33.28. Found (%): C, 33.74, H, 4.80, N, 13.10, C1, 32.21. Yield, 51.2%.

Synthesis of copolymers

The copolymers (PBO-P1, PBO-P2, PBO-P3, and PBO-P4) were prepared using 0.5–2.0% of dye according to an easy condenzation reaction. The synthesis route was described in Scheme 3 and the dosage was listed in Table I. Take PBO-P2 as an example. 5.3265 g (25.0 mmol) DABDO, 4.1120 g TA (24.75 mmoL) and 0.1577 g perylene bisimide (0.25 mmol) were mixed together with 33.0 g PPA and 20.0 g P_2O_5 in a glass reactor vessel. The dehydro-chlorination was performed at 90–110°C for 12 h *in vacuo*. Then the reaction temperature was raised to 130°C for 8 h, then to 150°C for 8 h, and finally to 180°C and maintained for 8 h. The highly viscous light red polymerization dope was planished to film and was then immersed in water for at least 2 days to remove the PPA completely. At last, the polymer was dried at 80°C in a vacuum oven.

RESULTS AND DISCUSSION

Polymer characterizations

All the polymers were characterized by elemental analysis, ^{1}H-NMR and FTIR. For PBO-P4, Elemental analysis: Calc. (%): C, 71.23, H, 3.40, N, 11.78. Found (%): C, 71.31, H, 3.35, N, 11.85.

Figure 2 shows ^{1}H-NMR spectra of copolymer PBO-P4. ^{1}H-NMR (D_2SO_4, 500 MHz, 25°C): 9.72 (d, weak, perylene ring), 9.17 (s, weak, perylene ring) 8.50 (d, weak, perylene ring), 8.62 (s, 2H, 2 × ArH), 8.36 (s, 2H, 2 × ArH), 8.08 (d, 2H, 2 × ArH).

Figure 3 shows FTIR spectra of PBO and copolymer PBO-P4. FTIR (KBr, cm^{-1}): 1700, 1670, 1629, 1348, 1268, 1560, 1497, 856, 814. The peak at 1629 cm^{-1} is C=C stretching in substituted aromatic rings and cyclic C=N stretching. The peak at 1268 cm^{-1} is C—C stretching in carbons linking oxazole and aromatic ring.[30] The peaks at 1497 and 1560 cm^{-1} are vibrations of aromatic ring framework. The difference between the two spectra is there are two weak peaks at near 1700 and 1670 cm^{-1} in the spectrum of PBO-P4 which can be attributed to perylene bisimide.[1]

Table I summarizes some physical properties of copolymers. With increasing the content of perylene bisimide, the intrinsic viscosities of copolymers decreased from 18.4 (68,000 in molecular weight) to 8.8 dL/g (31,000). The molecular weight values were estimated from viscometry together with the equation proposed by Roitman et al.[31] It was also found in our experiment that the copolymer films became layered and friable when the content of perylene bisimide was above 2.0%, so that the content of dye in this paper was only among 0.5–2.0%. This low content can be explained by the steric effect of bulky perylene bisimide cycle, which disturbed the regular structure of copolymers and increased interchain distances.

XRD patterns of all the copolymers in Figure 4 show two major diffraction peaks around $2\theta = 15°$ (~ 0.590 nm, labeled as peak A) and 25° (~ 0.350 nm, peak B). The periodicity for peaks A and B stands for "side-by-side" distance on (200) plane and
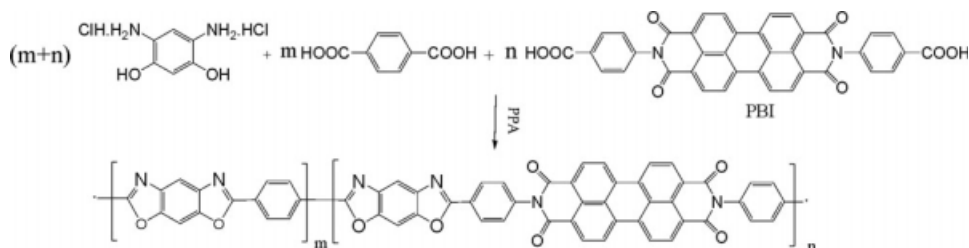
Scheme 3 Synthesis of copolymer.

TABLE I
Physical Data for the Copolymers

Polymers	PBI (%)	$[\eta]$ g/dL[a]	$M_w \times 10^3$	T_d (°C)[b]	Weight loss zat 700°C (%)
PBO	0	20.1	76	685.5	10.23
PBO-P1	0.5	18.4	68	679.0	12.06
PBO-P2	1.0	12.6	44	672.3	15.31
PBO-P3	1.5	10.5	38	663.5	19.73
PBO-P4	2.0	8.8	31	661.0	22.67

[a] Intrinsic viscosities.
[b] The 5% weight loss temperature from TGA data.

"face-to-face" distance on (010) plane between two neighboring polymer chains, respectively. The data in Table II suggest that the benzoxazole cycles and perylene bisimide cycles are nearly on the same plane with a small dihedral angle, and the monoclinic crystalline system of PBO most likely remains. However, with increasing perylene bisimide content, the "side-by-side" and "face-to-face" distances increased obviously from 0.550 to 0.604 nm and 0.346 to 0.371 nm, respectively. This indicates that high content perylene bisimide would probably change the crystalline system of copolymers. In fact, it was found in our experiment that the copolymer films became layered when the content of perylene bisimide was above 3.0%.

Figure 5 showed the TGA thermograms of copolymers. The 5% weight loss temperatures of copolymers in N_2 were all above 660°C, demonstrating excellent thermal stabilities.

The absorption spectra of perylene bisimide in rigid-rod copolymers

Figure 6 compares the absorbance spectra of the copolymers in films and perylene bisimide dye in N-methyl-pyrolidone solution ($c = 1.0 \times 10^{-6}$ mol L^{-1}). The spectrum of perylene bisimide in solution shows two obvious absorption peaks at 559 and 602 nm. The absorption bands of the pure PBO appeared in a higher energy range with the maxima 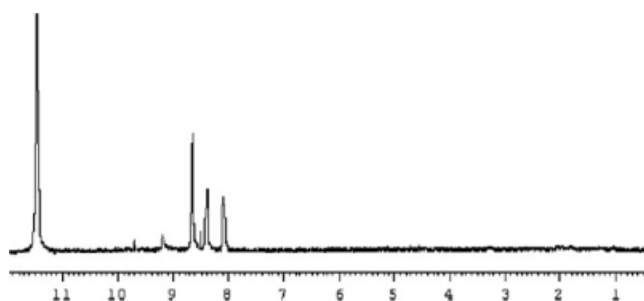at 402 and 426 nm, which can be assigned to benzoxazole chromophore.[32] For the absorption spectra of copolymer films, beside two major peaks of benzoxazole chromophore, two shoulders appear at longer wavelength of 503 and 546 nm. According to the reports published earlier,[7,33] these two shoulders should belong to perylene bisimide fragments. Compared with absorbance in solution, the absorbance of perylene bisimide fragments in copolymers has a blue shift of 56 nm. It is known that PBO chains displayed rigid-rod and coplanar conformation[34] and the PBI core without bay substituents also show a fully planar conformation. When PBI is covalently bonded with PBO chains, the planar conformation of PBI will be ruined and the dihedral angle of the preferential geometries between the perylene cycle and benzoxazole cycle will increase, so the absorption peaks will shift to shorter wavelengths. Meanwhile, stacking interaction and crystal plane slip may occur between the polymer chains, formation of aggregates similar to H-aggregates is possible, and this will also result in hypochromatic shift.

PL spectra of copolymers

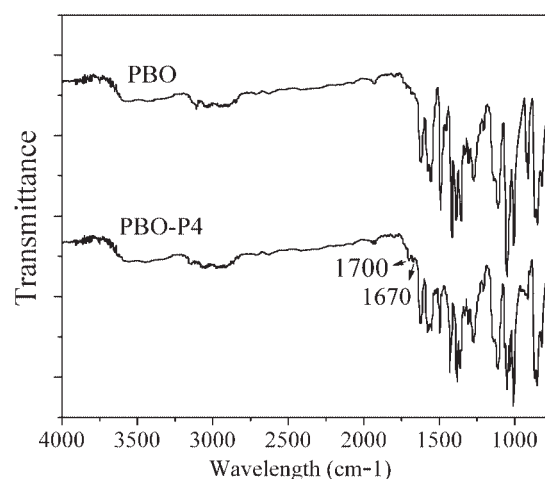The PL emission spectra of copolymer solutions (a) and films (b) are shown in Figure 7. The excitation

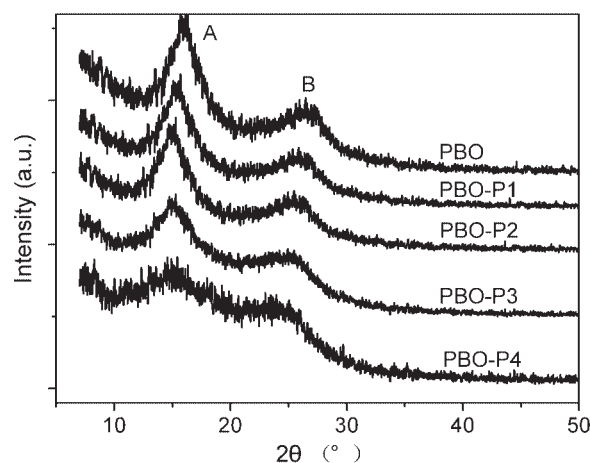

Figure 2 ^{1}H-NMR spectrum of PBO-P4.

Figure 3 FTIR spectra of PBO and PBO-P4.

Figure 4 XRD spectra of copolymer films.

Figure 5 TGA thermograms of PBO and its copolymers with PBI.

wavelength was all 402 nm and the excitation energy was the same intensity.

The spectra of copolymer solutions and films were similar, both displaying predominant emission peaks at 442 and 467 nm from the benzoxazole chromophore units[35] and a weak featureless emission peak at ∼ 622 nm belonging to perylene bisimide fragments.[36] It is noted that, for perylene bisimide monomer (PBI) in solution, no fluorescence can be observed when it was excited at 402 to 500 nm, so the PL emission spectrum of perylene bisimide was not shown in Figure 7(a). As the perylene bisimide monomer had no emission when excited at 402 nm, the appearance of peaks at 622 nm in copolymers revealed that energy transfer from the benzoxazole chromophore to the perylene bisimide chromophore occurred.

Ego et al. investigated the energy transfer of fluorene-based copolymers containing perylene bisimide dye and found that some copolymers in solution showed no energy transfer while in the solid state efficient energy transfer to the perylene bisimide chromophore occurred.[5] But in this article, no matter in solutions or in films, energy transfers were not so effective. This can be explained by the following facts. Firstly, these copolymers contain only low amounts PBI dye so the energy transfers from the

benzoxazole to the dye are inadequate, especially in dilute solutions. Secondly, we can see from Figures 6 and 7 that PBI absorptions (503 and 546 nm) overlap not so well with the PBO emission wavelengths (442 and 467 nm). Thirdly, PBI core without bay substituents is rather rigid and planar so that aggregate and self-quenching maybe happen in both solutions and films. In view of these facts, we think that the observed energy transfer to the dye on a single polymer chain and in aggregate species both existed. To avoid aggregation and self-quenching, introducing varied branched chains to PBI molecule to break its planar conformation and increase the intermolecular distances maybe are hopeful. We will take further studying in this aspect.

It can also be found from Figure 7(b) that the PL spectra of copolymers were more resolved than that of PBO. This is probably due to the larger interchain distances (Table II) after the introduction of bulky perylene bisimide, because compact stacking of
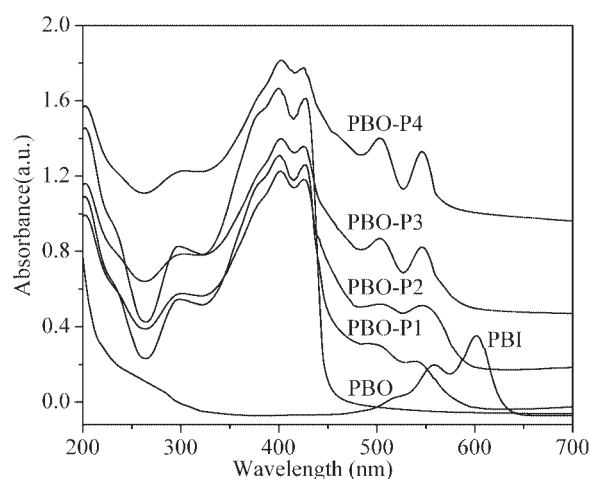
TABLE II
Summary of XRD Patterns of Copolymers

Samples	2θ (°)		d (nm)	
	A	B	A	B
PBO	16.28	26.46	0.550	0.346
PBO-P1	15.18	25.86	0.595	0.349
PBO-P2	14.88	25.54	0.596	0.355
PBO-P3	14.86	25.06	0.596	0.351
PBO-P4	14.66	24.00	0.604	0.371

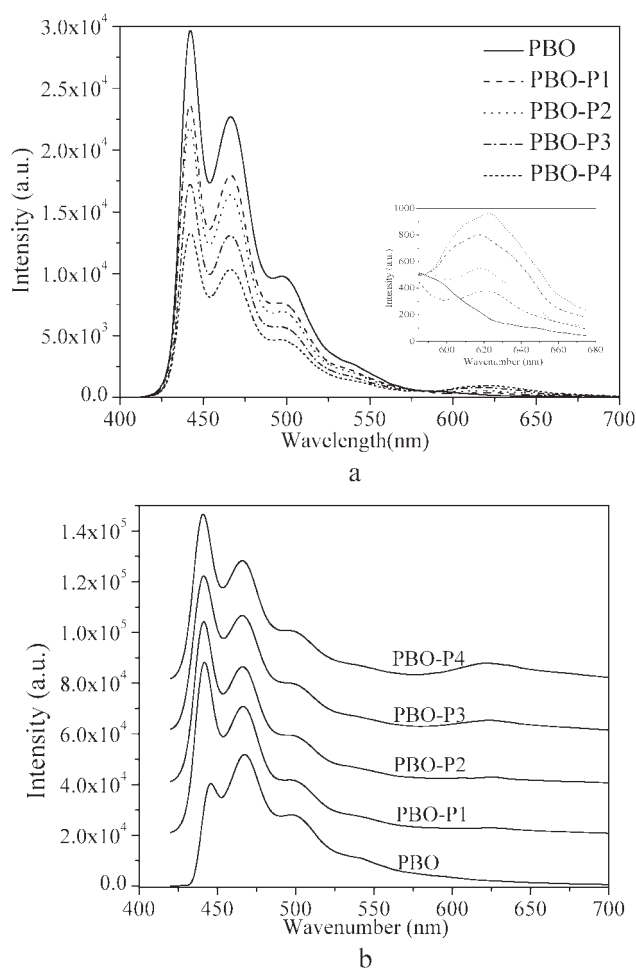**Figure 6** Absorbance spectra of PBI and the films of PBO and its copolymers.

Figure 7 PL emission spectra of copolymer solutions (a) and films (b), 0.00044 g/dL, λ_{ex} = 402 nm. Inset in (a) is the enlarged area in the range of 575–680 nm.

chains can induce excimer or aggregate and this bring featureless peaks.[13]

CONCLUSIONS

In this study, a series of novel rigid-rod polybenzoxazoles containing perylene bisimide dye is reported and characterized. These copolymers dissolve well in strong protonic acid and $AlCl_3$/nitromethane and can be made into films with good quality. They demonstrated excellent thermal stabilities and onset of weight loss do not occur until over 660°C. The conformational change of perylene bisimide chromophore in rigid copolymer chains is demonstrated by UV-Vis absorption and PL emission spectra. Energy transfer from benzoxazole units to perylene bisimide fragments and fluorescent quenching were observed in all copolymers. The XRD patterns showed that with increasing bulky perylene content the inter-

chain distances increased obviously and the polymers became friable.

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