Polybenzimidazoles (PBIs) derived from novel noncoplanar imidazole dibenzoic acid (IDBA): synthesis, characterization and properties

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Abstract

A novel noncoplanar imidazole dibenzoic acid (IDBA) was successfully prepared, and its structure was carefully characterized by FT-IR, NMR, MS and element analysis. Polybenzimidazoles (PBIs) derived from IDBA were synthesized in conventional one-step method in polyphosphoric acid (PPA). The obtained PBIs exhibited good organic solubility, excellent thermo-stability and interesting optical properties. The initiation decomposition temperature for these PBIs ranged from 560-600 $^{\circ}$C, and the temperature of 5% weight loss (T_5) for all these PBIs was above 600 $^{\circ}$C in N_2. No obvious glass transition for these PBIs was observed below 350 $^{\circ}$C. These PBIs shows UV-vis absorption maximum around 360-380 nm and strong photoluminescence emission (blue light) around 430-440nm in solution, which is red-shifted to 490-510 nm in solid film.

Keywords: Polybenzimidazoles, Thermal properties, Solubility, Photoluminescence

1. Introduction

Polybenzimidazoles (PBIs) is a type of material that known for their excellent thermal stability, high mechanical properties, nonflammability, and good chemical resistance. PBIs have received considerable attention in the past decade because of their potential application in polymer electrolyte membrane fuel cells [1-18, 23-25]. However, the poor solubility of PBIs resulting from the highly rigid polymer backbones and the strong interchain hydrogen bonding interaction makes them hard to process, which is one of the major barriers to the extensive application of PBIs. For example, the para-structure PBI derived from 3, 3'-diaminobenzidine (DAB) and terephthalic acid (TPA) (as shown in Scheme 2, PBI-5), has a rigid polymer backbone and limited solubility in polar protic solvents and strong acids.

Many efforts have been made on the improvement of PBIs' solubility by introducing flexible groups of bulky units in main chain or side chain (including introduction of aliphatic groups [10, 11], ether group [12], sulfone linkages [13], alicyclic structures [14] to polymer structure, substitution of phenyl ring with heterocyclic rings [1, 8], etc.). But bearings of large alkyl, alkoxy, or aryloxy groups in polymers easy result in lower glass-transition temperatures and loss of thermal stability [15]. Functional group containing PBIs have also been reported such as sulfonated PBI, which have been synthesized by condensing sulfonated diacids with 3, 3'-diaminobenzidine [16, 17]. However, the sulfonic group was considered as the less thermally stable moiety in polymers and also results in decrease of thermal stability [16, 18]. Therefore, it is very important to synthesize soluble PBIs with less loss of thermal properties. The solubility of whole aromatic polymer is strongly dependent on the polymer chain rigidity, symmetry and intermolecular attraction. The incorporation of rigid but noncoplanar moieties is an effective approach to destroy the symmetry and intermolecular attraction, and then enhance the solubility [1, 15].

Here, as continuous study on soluble aromatic polymers such as polyimide (PI) [19-21],

polybenzoxazole (PBO) [22], PBI [23-25], we presented the synthesis of a novel noncoplanar imidazole dibenzoic acid (IDBA) and PBIs derived from IDBA. A detailed study on solubility, thermal stability and optical properties of the obtained PBIs are described herein.

2. Experimental

2.1 Materials

Benzyl, 4-carboxybenzaldehyde, 4-amino-benzoic acid, ammonium acetate and 3, 3'-diaminobenzidine (DAB) were purchased from Aldrich. Terephthalic acid (TPA) was purchased from Yizheng Chemical Fibre Company Limited. Ammonium acetate, glacial acetic acid, polyphosphoric acid (PPA) and phosphorus pentoxide (P_2O_5) were obtained from SCRC. Other chemicals and solvents were obtained from Shanghai Chemical Reagents Co. and all reagents were used as received.

2.2 Synthesis of monomer 4-(4, 5-diphenyl-imidazole-1,2-yl)-dibenzoic acid (IDBA)

To a 500mL thoroughly dried three-neck flask was added 6.4355g (0.03mol) of benzyl, 4.5958g (0.03mol) of 4-carboxybenzaldehyde, 8.2284g (0.06mol) of 4-amino-benzoic acid and 11.5624g (0.15mol) of ammonium acetate under nitrogen flow. The 170mL glacial acetic acid as the solvent was added into the flask, the mixture was heated at 120°C for 20h. After termination of the reaction, the solid in the reaction mixture was filtered off and then dried in vacuo at 100°C for 24h. The product is a white, flocculent solid, which was virtually pure. The yield was 60%.

2.3 Preparation of homo-polymeric PBI-1

In a 100mL dry three-neck flask, 1.3800g (3mmol) of IDBA and 0.6493g (3mmol) of DAB were added to 42g of PPA containing 84 wt% P_2O_5 and the mixture was mechanically stirred under nitrogen flow at 150°C for 2 h and 190°C for 20 h. After cooling to 120°C, the reaction mixture was poured into 500mL de-ionized water; the mixture was neutralized with sodium carbonate and then filtered. The pale yellowish solid was further neutralized with 50% ammonium hydroxide solution in a three-neck flask for 24h followed by thoroughly washing with de-ionized water. The solid was filtered off and then dried in vacuo at 100°C for 24h.

2.4 Preparation of copolymer PBIs

The copolymer PBIs were synthesized according to Scheme 2. For example, the process for synthesis of PBI-3 was shown as following. In a 100mL dry three-neck flask, 0.6900g (1.5mmol) of IDBA, 0.2490g (1.5mmol) of TPA and 0.6493g (3mmol) of DAB were added to 40g of PPA containing 84 wt% P_2O_5 and the mixture was mechanically stirred under nitrogen flow at 150°C for 2 h and 190°C for 20 h. After cooling to 120°C, the reaction mixture was poured into 500mL de-ionized water; the mixture was neutralized with sodium carbonate and then filtered. The deep yellowish solid was further neutralized with 50% ammonium hydroxide solution in a three-neck flask for 24h followed by thoroughly washing with de-ionized water. The solid was filtered off and then dried in vacuo at 100°C for 24h.

2.5 Measurements

FT-IR spectra, ultraviolet–visible (UV–vis) spectra, fluorescence spectra, differential scanning calorimetry (DSC) curves (heating rate $= 10$ °C/min in nitrogen), and thermogravimetric analysis (TGA) curves (heating rate $= 20$ °C/min in nitrogen) were recorded on Paragon FTIR 1000, Shimadzu Uv-2500, Cary Eclipse, DSC Pyris 1, and TGA-7 (PerkinElmer) instruments, respectively. The ^{1}H NMR and ^{13}C NMR analyses were performed on a Mercury 400-MHz spectrometer with dimethyl sulfoxide-d_6 (DMSO-d_6) as the solvent. The elemental analysis was conducted on an Elementar Varioel apparatus. The molecular weights were determined by gel permeation chromatography (GPC) with polystyrene as a standard on a PerkinElmer series 200 apparatus equipped with a Polymer-Lab mixed

10-μ column. The eluent was N, N-dimethylformamide (DMF) at a flow rate of 1.0 mL/min at 25 °C. The polymer solutions were filtered through a Whatman 0.45-μm poly(tetrafluoroethylene) filter before being injected into the column. The inherent viscosities (η_{inh}) were measured in DMAc with an Ubbelohde viscometer at 30°C. The wide angle X-ray diffraction patterns were measured on a Shimadzu XRD-6000 diffractometer using $Cu_{K\alpha}$ radiation (40.0kV, 30.0mA, λ =0.154nm) at the scan rate of 6° /min over the range of 2 θ=5 — 50°.

3. Results and discussion

3.1 Synthesis of monomer 4-(4, 5-diphenyl-imidazole-1,2-yl)-dibenzoic acid (IDBA)

As to its molecular structure, IDBA was designed on the frame of imidazole ring with four phenyl groups attached. In the view of molecular model of IDBA (Fig. 1, optimized by Chem3D Ultra 8.0), two benzoic acid groups on position 1 and 2 of imidazole ring are noncoplanar, and the dihedral angle of two plane is in 80~90° [26]. The other two phenyl rings on position 4 and 5 of imidazole ring are steric crowding, and expected to decrease the intermolecular stacking efficiently. Therefore, PBIs derived from IDBA will be expected to exhibit good solubility without loss of their excellent thermal properties.
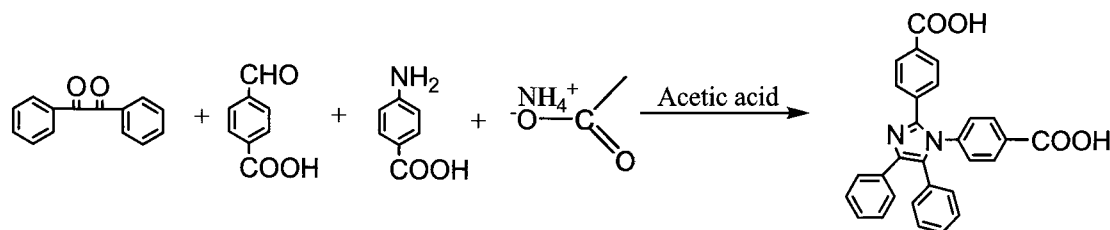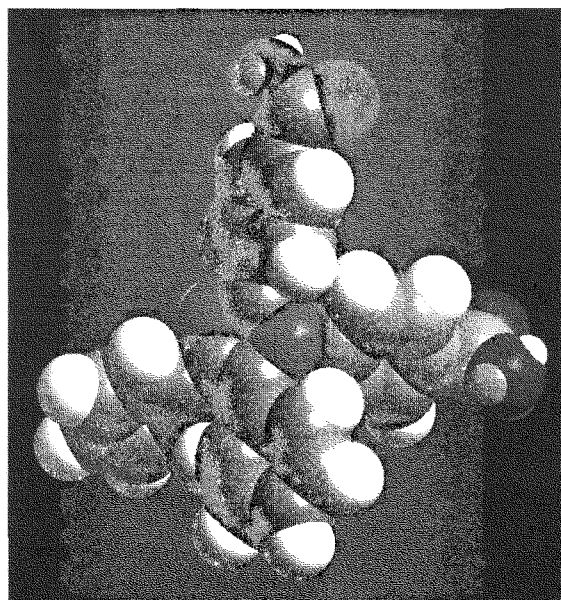

Scheme 1 Process for synthesis of IDBA

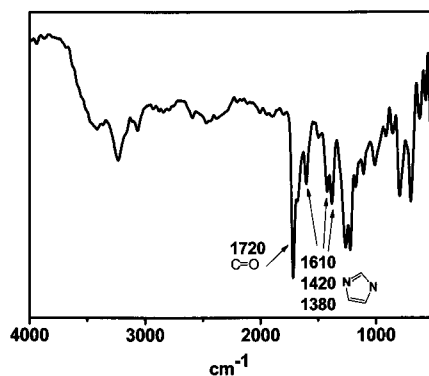**Figure 1** Molecular model of IDBA optimized by Chem3D Ultra 8.0
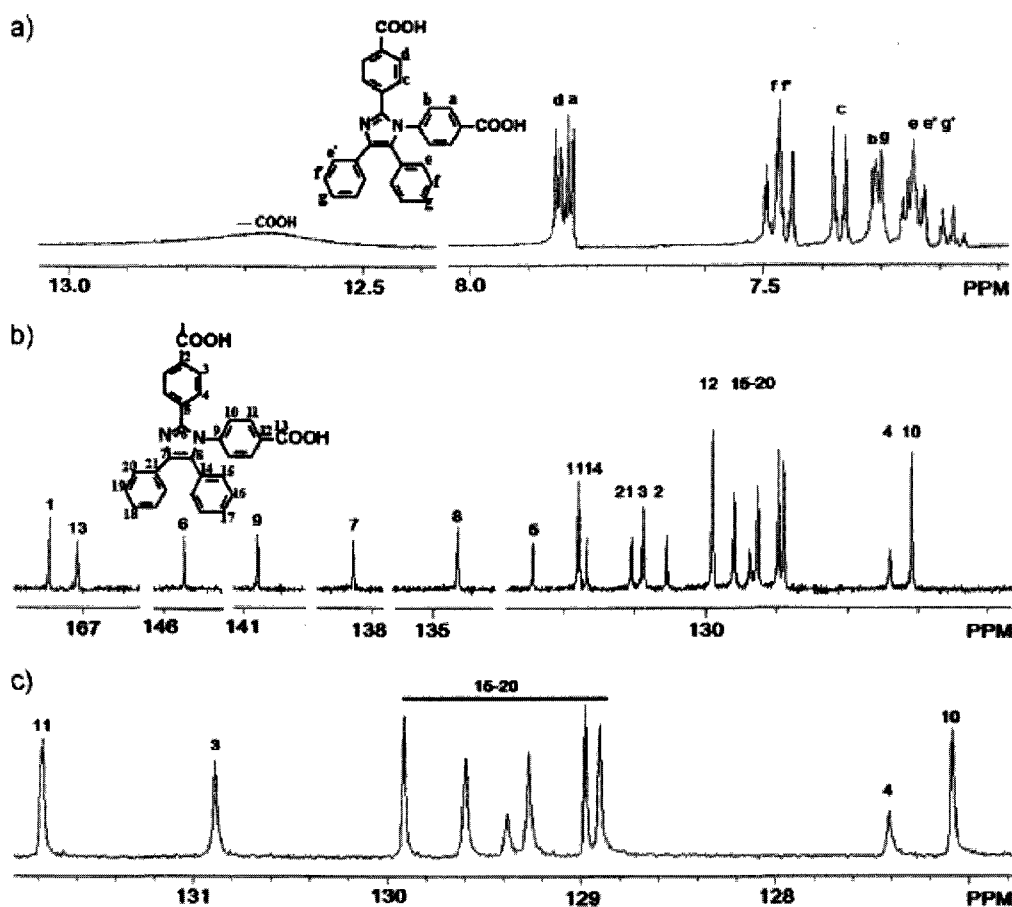
Figure 2. FT-IR spectrum of IDBA

Figure 3 ^{1}H NMR and ^{13}C NMR spectra of IDBA in DMSO (-d₆)

Through one-pot reaction of commercial available benzyl, 4-aminobenzoic acid and 4-caboxylbenzaldehyde, IDBA can be prepared according to the classical method of lophine synthesis [26] (Scheme 1). The obtained IDBA was carefully characterized by MS elemental analysis, FT-IR and NMR. Elemental analysis (%) for IDBA ($C_{20}H_{29}N_2O_4$), calc.: C, 75.65; H, 4.35; N, 6.08; found: C, 75.64; H, 4.72; N, 5.99. The FT-IR spectrum of IDBA (Figure 2) shows the characteristic absorption band of imidazole ring at 1610 cm[-1](C=N stretching), 1420cm^{-1} (in–plane deformation of imidazole rings) and

1380cm^{-1}(C-N, asymmetric), indicating the formation of imidazole rings. The broad absorption band of hydrogen bonding of 3400-3000 cm^{-1} and the band at 1720 cm^{-1} confirm the presence of carboxyl groups. ^{1}H NMR spectrum (Fig. 3(a)) shows several signals at 7.15-7.90 ppm and a wide signal at 12.65 ppm, which can be assigned to protons of phenyl rings and carboxyl groups, respectively. ^{13}C NMR (Fig. 3(b)) further confirmed the structure of IDBA which shows the aromatic carbons at 127.1-146.2 ppm and carboxyl carbons at 168.1-168.5 ppm, respectively.
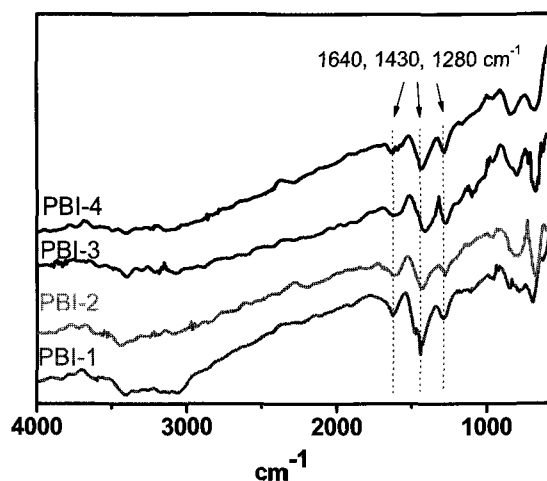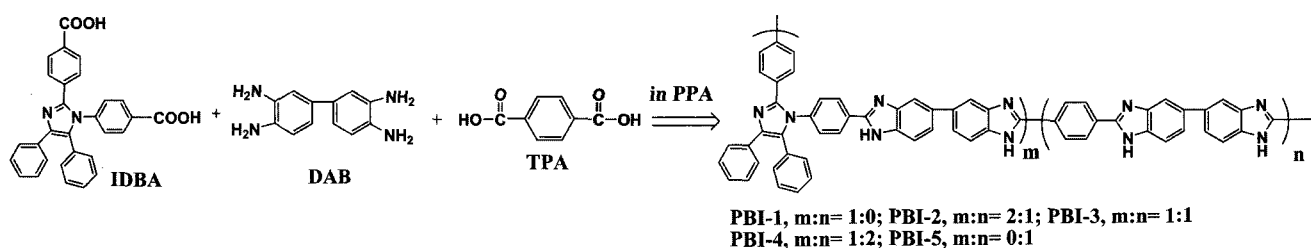

Figure 4 FT-IR spectra of PBIs

Table 1 Synthesis and molecular weight of PBIs

Polymer	IDBA:TPA		Mn^b ×10^{-4}	Mw ×10^{-4}	Mw/Mn	Viscosity ^{c}
	In feed	In polymer ^{a}				
PBI-1	1:0	1:0	2.5	4.7	1.9	0.19
PBI-2	2:1	2:1	4.0	6.6	1.7	0.32
PBI-3	1:1	1:1	2.8	4.1	1.5	0.70
PBI-4	1:2	1:2	3.2	7.0	2.2	0.48

a): Determined by ^{1}H NMR

b): Determined by GPC using PS as standard and DMF as eluent.

c): The inherent viscosities (η_{inh}) were measured at concentration of 0.5g/L in DMAc at 30°C.

PBI-1, m:n= 1:0; PBI-2, m:n= 2:1; PBI-3, m:n= 1:1
PBI-4, m:n= 1:2; PBI-5, m:n= 0:1
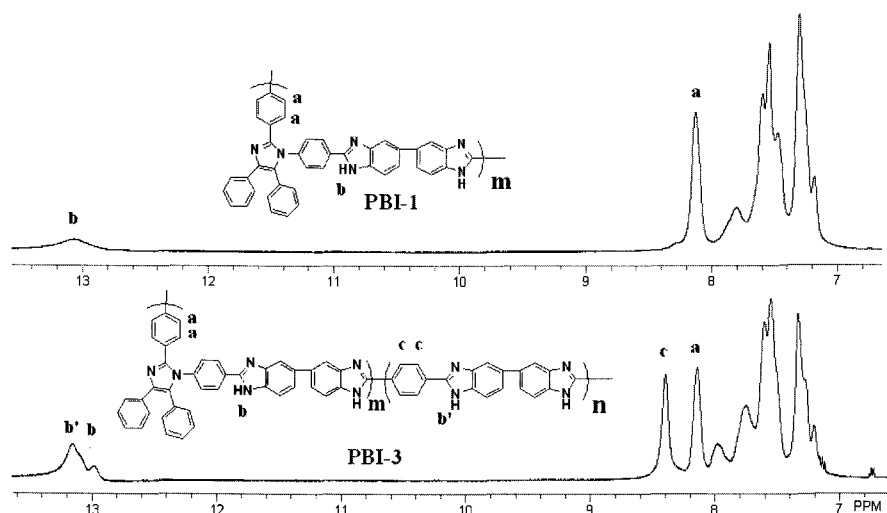
Scheme 2 Structure and synthesis of PBIs

Figure 5 ^{1}H NMR spectra of homo-polymer PBI-1 and co-polymer PBI-3 in DMSO

3.2 Preparation of PBIs

A series of polyimidazoles derived from IDBA were synthesized and their structure is shown in Scheme 2. The composition of PBIs was varied by changing the ratio of IDBA and TPA in the initiating reaction mixture. Also, homo-PBI (PBI-5) derived from DAB and TPA was prepared as reference. The obtained PBIs were fully characterized by FT-IR, ^{1}H NMR and GPC. From Fig. 4, the characteristic absorption of benzimidazole ring is present and absorption of C=O at 1720 cm^{-1} from IDBA carboxyl groups disappears, which confirms the structure of PBIs. Fig. 5 shows the ^{1}H NMR spectra of homo-polymeric PBI-1 and co-polymeric PBI-3. The signal assignment in Fig. 5 is in good agreement with the expected structure. The proton peaks assigned to imidazole rings, which are derived from IDBA and TPA, are observed at around 13.15 ppm and 13.25 ppm, respectively. In addition, two peaks denoted as Ha and Hc of different imidazole ring, which are derived form aromatic rings of IDBA and TPA, respectively, are observed. Through the integral ratio of peaks Ha and Hc, the mole ratio of IDBA and TPA units in the obtained PBIs can be determined by ^{1}H NMR, which is almost same to feeds, and the results are summarized in Table 1. Due to good solubility in DMF, the molecular weight of the obtained PBIs was determined by GPC, and the data was also summarized in Table 1. The Mn for all of the obtained PBIs shows high molecular weight beyond 2×10^4. The inherent viscosity for all PBIs is in the range of 0.19-0.70. It should be noted that the inherent viscosity is not high, which might be ascribed to noncoplanar structure of backbone.

3.3 Solubility

As one of major properties for rod-rigid aromatic polymer, solubility is very important in many applications, and polymers with good solubility are desired. The poor solubility and the consequently poor processability are the big barriers to wide applications of rod-rigid PBIs, which are only soluble in the polar aprotic solvent at extreme condition. Incorporation of noncoplanar and structure into rod-rigid polymers can enhance their solubility. It has been reported that phenyl groups on positions 1 and 2 of imidazole ring are noncoplanar [26], and the dihedral angle is less than 90° in IDBA (Fig. 1). The units derived from IDBA in PBIs chain are twisted, rigid and noncoplanr, which can inhibit the chain stacking efficiently and reduce cohesive energy, and consequently enhance the solubility of PBIs. Also, incorporation of nitrogen atom in polymer backbone is good to enhance the solubility of polymer. Both

can be reflected by the high solubility of the obtained homo-PBI, and co-PBIs, which are based on very rigid structure of TPA units. The obtained PBIs are easily soluble in polar solvents such as DMF, phenol, DMAc and DMSO at room temperature (seen in Table 2). In the strong acid such as sulfur acid, and MSA, these PBIs are also soluble. In common solvents such as THF and chloroform, however, the obtained PBIs can not be soluble, due to their polar nature. Compared with homo-PBI (PBI-5) reference derived from TPA and DAB synthesized in our lab, the solubility of obtained PBIs was enhanced obviously by incorporation of IDBA units even if the percentage of IDBA units is about 33%.

Table 2 Solubility behaviors of PBIs

Polymer	Solubility									
	DMSO	NMP	DMAc	DMF	m-Cresol	$CHCl_3$	THF	$MeSO_3H$	H_3PO_4	H_2SO_4
PBI-1	++	++	++	++	++	-	-	++	+-	++
PBI-2	++	++	++	++	++	-	-	++	+-	++
PBI-3	++	++	++	++	++	-	-	++	+-	++
PBI-4	++	++	++	+-	+-	-	-	++	+-	++
PBI-5	+-	+-	+-	+-	-	-	-	++	-	++

Key: "++", soluble at room temperature; "+-", partially soluble; "-", insoluble.

Table 3 Thermal properties of PBIs

Polymer	T_d (℃)[a]	T_5 (℃)[b]	T_{10} (℃)[c]	Residue (wt%)[d]
PBI-1	561	601	676	80
PBI-2	594	601	640	75
PBI-3	588	615	657	80
PBI-4	602	620	675	75

[a]Thermal decomposition temperature
[b]Temperature at 5% weight loss
[c]Temperature at 10% weight loss
[d]Residue at 800°C

Table 4 Optical properties of PBIs

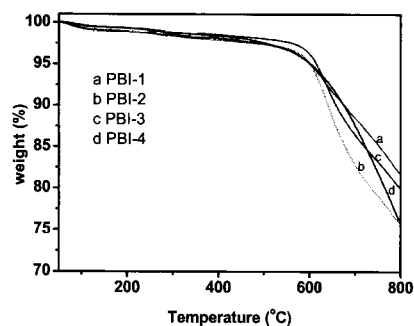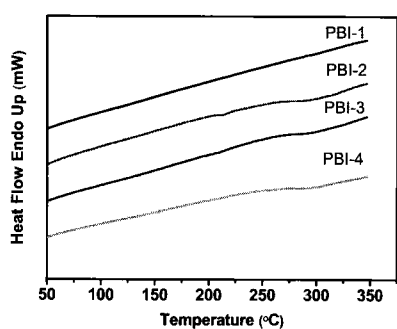| Polymer	Absorption (λ max nm)		Fluorescence emission (λ max nm)	
	Solution [a]	Solid state	Solution [a]	Solid state
PBI-1	351	352	430	488
PBI-2	362	363	433	508
PBI-3	370	372	437	517
PBI-4	376	378	440	530

a): In DMF

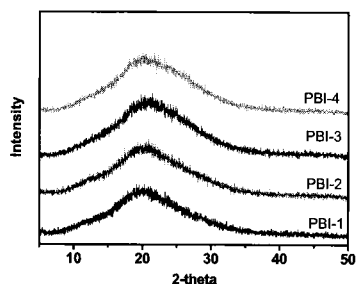Figure 6 TGA curves of PBIs

Figure 7 DSC curves of PBIs

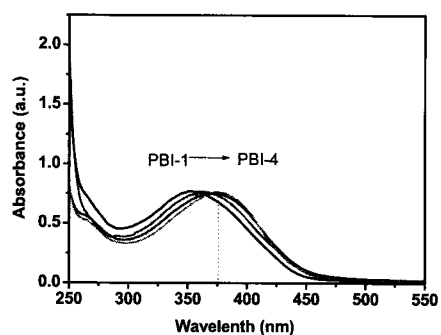Figure 8 WAXS patterns of PBIs

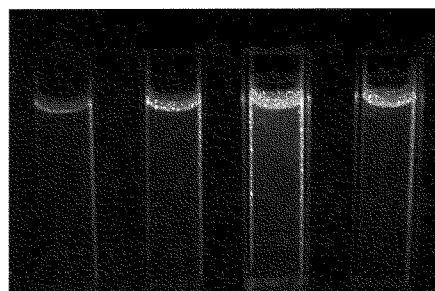Figure 9 UV-vis absorption spectra of PBIs in
DMF solution

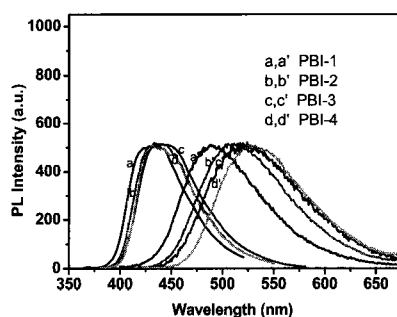Figure 10 PL images of PBIs in DMF solution

Figure 11 PL spectra of PBIs in solution and
solid state

3.4 Thermal properties and X-ray diffraction

Fig. 6 shows the represent TGA curves for the obtained PBIs, which was recorded at a heating rate of 20°C in nitrogen atmosphere. The thermal behavior data are summarized in Table 3. An initial little weight loss around 100°C is observed due to the loss of absorbed water. The other obvious weight loss for all obtained PBIs was observed above around 560°C, and temperature at 5% weight loss (T_5) was above 600 °C. These indicate that the obtained PBIs of good solubility show excellent thermo-stability. Due to the limitation of our DSC equipment, the DSC curves are recorded below 350 °C, and shown in Fig. 7. From Fig. 7, no obvious glass transition for the obtained PBIs was observed in the range of DSC measurement, indicating that the glass transition temperature for all obtained PBIs is above 350 °C. The wide angle X-ray diffraction (WAXS) patterns of the obtained PBIs are shown in Fig. 8. From the WAXS patterns, all obtained PBIs are amorphous in nature. In all cases, only a wide peak around 20° was observed and no sharp peaks were present, indicating no appearance of crystalline in the obtained PBIs. This can be reflected by the excellent solubility of the obtained PBIs, and is in agreement with DSC curves (Fig. 7), in which no crystalline melting peaks were observed.

3.5 Optical properties of PBIs

Due to the steric crowding of four phenyl groups attached to the central imidazole unit to form conjugate structure in IDBA, the obtained PBIs derived from IDBA are expected for some optical properties. The UV-vis absorption and photoluminescence (PL) of PBIs were studied from DMF solution and solid thin film. The UV-vis absorption spectra of PBIs are shown in Fig. 9. All obtained PBIs in DMF solution possess π-π* maximum absorption around 360-370nm. The maximum absorptions in solution and in thin film were summarized in Table 4. The obvious gradual red-shift of π-π* maximum absorption from PBI-1 to PBI-4 was observed (Fig. 9 and Table 4). This might be attributed to incorporation of TPA into the polymer backbone, which enhances the conjugation of PBI chains. For all obtained PBIs, the maximum absorption in thin film is red-shifted only 1-2 nm, in comparison to solution. The photoluminescence (PL) images of all obtained PBIs in DMF solution under irradiation of 365nm UV light are presented in Fig. 10, from which the obtained PBIs exhibited very strong fluorescent blue light. The PL spectra of PBIs in solution and solid state are shown in Fig. 11, and the data is summarized in Table 4. All the obtained PBIs possess the emission around 440 nm in DMF solution, which is lightly red-shifted from PBI-1 to PBI-4. Compared with PL spectra of BPIs solution, the PL spectra of all the PBIs in solid state are obvious red-shifted, this may be ascribed to the forming of excimer because of strong interaction between polymer chains.

4. Conclusions

We successfully synthesized a novel noncoplanar imidazole dibenzoic acid (IDBA), based on which a series of PBIs was prepared through polycondensation of TAB and TPA. These obtained PBIs exhibited very good solubility in polar solvents and excellent thermal properties. Furthermore, these obtained PBIs exhibited very strong fluorescent blue light.

Acknowledgements

References

1. Vogel, H.; Marvel, C. S. J Polym Sci Part A: Polym Chem 1996, 34, 1125.

2. Li, Q.; He, R.; Jensen, J. O.; Bjerrum, N. J. Fuel Cells 2004, 4, 147.

3. Savadogo, O.; Xing, B. J New Mat Electrochem Syst 2000, 3, 345.

4. Savadogo, O.; Xing, B. Electrochem Commun 2000, 2, 697.

5. Asensio, J. A.; Borros, S.; Gomez-Romero, P. J Polym Sci Part A: Polym Chem 2002, 40, 3703.

6. He, R.; Li, Q.; Xiao, G.; Bjerrum, N. J. J Membr Sci 2003, 226, 169.

7. Kim, H.-J.; Cho, S. Y.; An, S. J.; Eun, Y. C.; Kim, J.-Y.; Yoon, H.-K.; Kweon, H.-J.; Yew, K. H. Macromol Rapid Commun 2004, 25, 894.

8. Xiao, L.; Zhang, H.; Jana, T.; Scanlon, E.; Chen, R.; Choe, E.-W.; Ramanathan, L. S.; Yu, S.; Benicewicz, B. C. Fuel Cells 2005, 5, 287.

9. Bae, J. M.; Honma, I.; Murata, M.; Yamamoto, T.; Rikukawa, M.; Ogata, N. Solid State Ionics 2002, 147, 189.

10. Varma, I. K.; Veena, S. M. J Polym Sci Part A 1: Polym Chem 1976, 14, 973.

11. Varma, I. K.; Veena, S. M. J Macromol Sci Chem 1977, 11, 845.

12. Hergenrother, P. M.; Smith, J. G.; Connell, J. W. Polymer 1993, 34, 856.

13. Lakshmi Narayan, T. V.; Marvel, C. S. J Polym Sci Part A 1: Polym Chem 1967, 5, 1113.

14. Inoue, S.; Imai, Y.; Uno, K.; Iwakura, Y. Die Makromolekulare Chemie 1966, 95, 236.

15. Liou, G.-S.; Yen, H.-J. J Polym Sci Part A: Polym Chem 2006, 44, 6094.

16. Qing, S.; Huang, W.; Yan, D. J Polym Sci Part A: Polym Chem 2005, 43, 4363.

17. Asensio, J. A.; Borros, S.; Gomez-Romero, P. J Polym Sci Part A: Polym Chem 2002, 40, 3703.

18. Tae, S.-J.; J Polym Sci Part A: Polym Chem 2009, 47, 485.

19. Chen, H.; Yin, J. J Polym Sci Part A: Polym Chem 2002, 40, 3804.

20. Zhang, W.; Xu, H.-J.; Yin, J.; Guo, X.-X.; Ye, Y.-F.; Fang, J.-H.; Sui, Y.; Zhu, Z.-K.; Wang, Z.-G. J Appl. Polym Sci 2001, 81, 2814.

21. Sui, Y.; Yin, J.; Hou, Z.-J.; Zhu, N.; Lu, J.-X.; Liu, Y.-G.; Zhu, Z.-K.; Wang, Z.-G. J Polym Sci Part A: Polym Chem 2001, 39, 2189.

22. Zhang, C.-Y.; Shi, Z.-X.; Leng, W.; Yin, J.; Zhu, Z.-K. J Shanghai Jiao Tong University 2003, 37, 646.

23. Xu, H.-J.; Chen, K.-C.; Guo, X.-X.; Fang, J.-H.; Yin, J. J Polym Sci Part A: Polym Chem 2007, 45, 1150.

24. Xu, H.-J.; Chen, K.-C.; Guo, X.-X.; Fang, J.-H.; Yin, J. Polymer 2007, 48, 5556.

25. Xu, H.-J.; Chen, K.-C.; Guo, X.-X.; Fang, J.-H.; Yin, J. J Membrane Sci 2007, 288, 255.

26. Park, S.; Seo, J.; Kim, S. H.; Park, S. Y. Adv Funct Mater 2008, 18, 726.