

# Synthesis and properties of polyimides derived from diamine monomer containing bi-benzimidazole unit

Yingtao Chen · Qinghua Zhang

Received: 6 December 2013 / Accepted: 20 March 2014 / Published online: 4 April 2014  
© Springer Science+Business Media Dordrecht 2014

**Abstract** A new aromatic heterocyclic diamine monomer containing bi-benzimidazole unit, 2,2-bis(4'-aminophenyl)-5,5-bi-1H-benzimidazole, was synthesized from 2,2-bis(4'-nitrophenyl)-5,5-bi-1H-benzimidazole (BNPBBI) prepared via the reaction of 3,3',4,4'-biphenyltetramine and *p*-nitrobenzaldehyde with a high yield. Their compositions and chemical structures containing polybenzimidazole backbone were characterized by FTIR, <sup>1</sup>H NMR and elemental analysis. A series of aromatic polyimides containing the heterocyclic moiety in the main chain were prepared by the reaction of BAPBBI with various aromatic dianhydrides of 3,3',4,4'-biphenyltetracarboxylic dianhydride, 4,4'-oxydiphthalic anhydride or pyromellitic dianhydride. The polymers possess a high glass transition temperature of >415 °C and a good thermal stability up to 566 °C with a 5 % weight loss. The combination of polybenzimidazole and polyimide via introducing BAPBBI into the main chains provides the rigid structure, and macromolecular interactions are thus enhanced, resulting in the outstanding mechanical properties. These polyimides exhibit the strong tensile strength of 201 to 327 MPa, and the ultrahigh tensile moduli of 10.7 to 15.5 GPa without post stretching.

**Keywords** Polyimide · High performance polymer · Mechanical properties · Bi-benzimidazole unit

## Introduction

Aromatic Polyimides (PIs) are a kind of high performance polymers and well known for their excellent mechanical

properties, high thermal and dimensional stability, chemical resistance, dielectric and adhesive properties. Because of these properties, PIs have been widely used in aerospace industry and electronic industry in the form of films [1–9]. Meanwhile, PIs in the form of fibers possess promising application prospects in defense construction, flame-proof fabric, high-speed-transportation vehicles, ocean exploitation, and environment protection [10–15]. The outstanding properties of the high performance polymers, such as mechanical properties and thermal stability, are mainly dependent on the chemical structure and composition, molecular aggregation and intra-/inter-molecular interaction. Thus, PIs can be endowed with new functions or enhanced in the original properties by changing the chemical structure and composition. On the other hand, heterocyclic polymers, such as polybenzothiazole [16, 17], polybenzoxazole [18–21], polyquinoline [22], and polyphenylquinoxaline [23], exhibit excellent mechanical properties and thermal stability due to their inner aromatic heterocyclic chemical structures as well. Therefore, it can be predicted that the introduction of heterocyclic rings into the backbone of polyimide is helpful to enhancing the mechanical and thermal properties significantly. In the last few decades, many researches have been carried out in this field. For instance, the introduction of heterocyclic rings of pyrimidine, benzoxazole and benzoxadiazole into the backbone of polyimides led to the improved mechanical and thermal properties [24–28]. However, the synthesis of the above monomers is difficult and complicated, limiting the preparation and application of the corresponding polyimides in large scale.

As another kind of aromatic heterocyclic polymer, polybenzimidazoles (PBIs) also exhibit great physical and chemical properties and are widely used in many fields such as proton exchange membrane fuel cells, semi-conductor industry and fire-protection [29–31]. Bi-benzimidazole unit in PBI backbone have been proved as the main factor to contribute the outstanding mechanical and thermal properties to the

Y. Chen · Q. Zhang (✉)  
State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, China  
e-mail: qhzhang@dhu.edu.cn

polymer due to the high molecular aromaticity and conjugation. The aromatic diamines containing benzimidazole unit have been introduced into the backbone of polyimide, resulting in great improvements of glass transition temperature ( $T_g$ ), decomposition temperature, tensile strength and rigidity of molecular chains [32–35]. The previous researches mainly focused on partial or asymmetrical structures of PBIs.

Here, we aimed to introduce the full characteristic structure of PBIs into the backbone of polyimide to improve the mechanical properties. An intermediate of 2,2-bis(4'-nitrophenyl)-5,5-bi-1H-benzimidazole (BNPBBI) was synthesized by the reaction of biphenyltetramine and *p*-nitrobenzaldehyde, and then a new aromatic diamine 2,2-bis(4'-aminophenyl)-5,5-bi-1H-benzimidazole (BAPBBI) was prepared by the reduction of BNPBBI in an effective and environmental way with a high yield. A series of polyimides were prepared by the reaction of BAPBBI with commercial aromatic dianhydrides of pyromellitic dianhydride (PMDA), 3,3',4,4'-biphenyl tetracarboxylic dianhydride (BPDA) and 4,4'-oxydiphthalic anhydride (ODPA). The incorporation of bi-benzimidazole unit was designed to obtain tough and flexible films. The chemical structures, molecular compounds, optical property, thermal stability and mechanical properties were investigated.

## Experimental

### Materials

3,3',4,4'-Biphenyltetramine (DAB) was purchased from Chengdu Yuanda Chemicals Co., Ltd. Ethanol, *p*-nitrobenzaldehyde, hydrazine hydrate, palladium on carbon and potassium iodide were purchased from Sinopharm Chemical Reagent Co., Ltd. 3,3',4,4'-Biphenyltetracarboxylic dianhydride (BPDA), 4,4'-oxydiphthalic anhydride (ODPA) and pyromellitic dianhydride (PMDA) were purchased from Shanghai Synthetic Resin Research Institute. 4,4'-Oxydianiline (ODA) were purchased from Shandong Wanda Chemical Co., Ltd. N,N-dimethylformamide (DMF) and N,N-dimethylacetamide (DMAc) were hydrated by vacuum distillation over calcium hydride and stored over molecular sieves (0.4 nm). Other reagents from commercial institutions were used without further purification.

### Characterization

Fourier transform infrared (FTIR) spectra were captured on a Nicolet 8700 FTIR spectrometer at the range of 4,000–400  $\text{cm}^{-1}$  by averaging 32 scans.  $^1\text{H}$  NMR spectra was collected using an Avance 400 spectrometer with DMSO- $d_6$  as a solvent at 400 MHz, and TMS as internal standard. Elemental analysis was quantified with a Vario EL III elemental analyzer,

Germany Elementar. The inherent viscosities of the polyamic acids with 0.5 g/dL in DMAc were measured using an Ubbelohde viscometer at 25 °C. Dynamic mechanical analyses (DMA) of thin films were executed on a dynamic mechanical analyzer (TA Q800, USA) at a heating rate of 5 °C/min and a loading frequency of 1 Hz. The temperature corresponding to the peak in  $\tan \delta$  was confirmed to be  $T_g$  of the cured film. The coefficients of thermal expansion (CTE) of films were performed on a TA Q800 instrument with a stress of 6 MPa at a heating rate of 5 °C/min. Thermo-gravimetric analyses of the film samples were performed on a thermal analyzer (TA Q5000 IR) from 50 to 900 °C with a heating rate of 10 °C/min under  $\text{N}_2$  and air atmosphere. The mechanical properties were tested using an Instron 5969 with a drawing rate of 10 mm/min. The samples were cut to a dimension of 80×10 mm. Ultraviolet–visible (UV–Vis) spectra were obtained from a Lambda 950 UV–Vis Spectrophotometer (Pekin Elmer) via the transmittance mode. The chromaticity of the transparent films was defined as the color classification and determined by a WSL-2 Lovibond colorimeter in the transmittance mode within the color range of Y 0.1–Y 79.9 for yellow and R 0.1–R 79.9 for red, the minimum readout is 0.1 Lovibond Unit. The solubilities of the polyimides were quantitatively determined by mixing 1.0 g polyimide film in 9.0 g solvent at room temperature, i.e., 10 % solid content in the solution. The mixture was stirred at room temperature or heated in an inert atmosphere for 24 h. The resulting solution was attributed to three grades under observation: soluble at room temperature, soluble by heating and insoluble.

### Synthesis of 2,2-bis(4'-nitrophenyl)-5,5-bi-1H-benzimidazole (BNPBBI)

3,3',4,4'-Biphenyltetramine (10.71 g, 50 mmol), *p*-nitrobenzaldehyde (16.62 g, 110 mmol) (2.2 equivalents of the mole of DAB), potassium iodide (1.66 g, 10 mmol) (0.2 equivalent of the mole of DAB) and 300 mL DMF were added into a 500 mL three-neck round-bottom flask with a mechanical stirring and a condenser. The mixture was heated up to 155 °C and stirred vigorously for 25 h. The reaction mixture was cooled down to the room temperature and poured into the deionized water (6 equivalents of DMF). The resulting suspension were filtered and washed with deionized water for several times and recrystallized from ethanol. Then, the product was filtered, collected and dried in vacuum to yield the brick-red powder (26.37 g, 96.5 %). m.p. >300 °C. FTIR (KBr disc  $\text{cm}^{-1}$ ): 3,376, 3,062, 1,603, 1,515, 1,475, 1,339, and 856.  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ,  $\delta$ , ppm): 13.39 (s, 2H, NH of benzimidazole), 8.38–8.45 (m, 4H, Ar-H), 7.92–8.05 (s, 2H, Ar-H), 7.79–7.82 (d, 2H, Ar-H), 7.73 (d, 2H, Ar-H), 7.63 (m, 2H, Ar-H). Anal. Calcd. for  $\text{C}_{26}\text{H}_{16}\text{N}_6\text{O}_4$ : C, 65.54 %; H,

3.38 %; N, 17.64 %. Found: C, 65.24 %; H, 3.54 %; N, 17.28 %.

#### Synthesis of 2,2-bis(4'-aminophenyl)-5,5-bi-1H-benzimidazole (BAPBBI)

BNPBBI (23.8 g, 50 mmol) and 300 mL ethanol was added to a 500 mL three-neck round-bottom flask with a mechanical stirring and a condenser. The mixture was heated up to 78 °C to reflux and stirred, and then Pd/C powders (1 g 1 equivalent of the mole of nitro groups) was added to the system and dispersed uniformly. Hydrazine hydrate (40 mL, 4 molar equivalents of nitro groups) was added dropwise with a 50 mL constant pressure funnel in 15 min. The mixture was heated up to 90 °C with a stirring for 14 h, traced with TLC plate. The reaction mixture was filtered at high temperature to remove catalyst and concentrated with vacuum rotary evaporator. The coarse product was washed with deionized water to neutral point, and then filtered, collected and dried in vacuum to yield the champagne-colored powders. (21.74 g, 91 %). m.p. >300 °C. (KBr disc  $\text{cm}^{-1}$ ): 3,200–3,500 ( $\text{NH}_2$  NH of benzimidazole), 1,610, 1,495 ( $\text{C}=\text{C}$ ), 1,450 ( $-\text{NH}$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ,  $\delta$ , ppm): 12.49 (m, 2H, NH of benzimidazole), 7.88 (d, 4H, Ar-H), 7.71–7.77 (s, 2H, Ar-H), 7.57–7.60 (d, 2H, Ar-H), 7.50 (d, 2H, Ar-H), 6.66–6.69 (d, 4H, Ar-H), 5.64 (b, 2H,  $-\text{NH}_2$ ). Anal. Calcd. for  $\text{C}_{26}\text{H}_{20}\text{N}_6$ : C, 74.98 %; H, 4.84 %; N, 20.18 %. Found: C, 74.47 %; H, 4.99 %; N, 20.09 %.

#### Synthesis of the polyimides

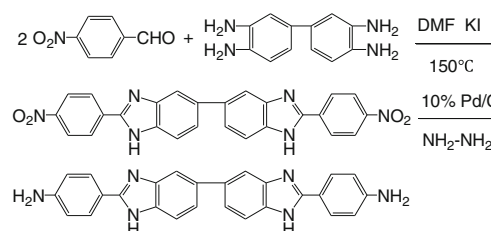
The synthesis of polyimides was carried out with a solid content of 12 % through a two-stage procedure, involving the polycondensation between the diamine and a dianhydride and then imidization process. The conventional route of PI-d is taken as example: BAPBBI (2.11 g, 5.07 mmol) and DMAc were added into a 50 mL three-neck round-bottom flask with a mechanical stirring and a nitrogen inlet. After the diamine completely dissolved, PMDA (1.11 g, 5.05 mmol) was added into the solution with a stirring under nitrogen atmosphere. Then the mixture was stirred for about 3.5 h in an ice bath to form a highly viscous polymeric solution (PAA-d, meaning PMDA used). The PAA-d solution was diluted and cast onto a glass slide uniformly, and then placed in a vacuum oven at 60 °C for 8 h to remove most of the solvents. The PAA film was heated at 80, 120, 150, 200 and 300 °C for each 1 h to obtain the completely cyclized polyimide film (PI-d). PI-b (BPDA-BAPBBI) and PI-o (ODPA-BAPBBI) were prepared by a similar route. Meanwhile, two commercial PI films, Kapton derived from PMDA and ODA and Upilex-R from BPDA and ODA were prepared with the above same method to take a comparison.

## Results and discussion

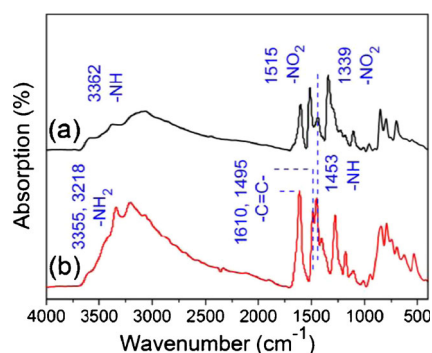
### Synthesis

BAPBBI, an aromatic diamine containing bi-benzimidazole unit, is synthesized by the reaction scheme shown in Fig. 1. The preparation of heterocyclic diamine is divided into two steps: the synthesis of the heterocyclic nitro compound and the reduction of the nitro group into amino group. The previous reports provide various preparation routes for the benzimidazole nitro compounds with a high yield [36, 37]. In this report, we optimize synthesis route for BNPBBI with mass production. The synthesis of BNPBBI is dependent on the classic imidazole ring formation, and the method of reduction of nitro groups is facile and mature. Firstly, BNPBBI is prepared by the nucleophilic substitution of 3,3',4,4'-biphenyltetramine and *p*-nitrobenzaldehyde in DMF at 155 °C, the nitro group plays a role of strong electron-withdrawing to reduce the electron cloud density in the *para* position, which causes the amino group attacking aldehyde group more easily. The KI accelerates the nucleophilic substitution as a catalyst. The intermediate is cyclized to form benzimidazole ring with 2H-bonds, subsequently, air behaves as oxidizing agent to eliminate 1H to obtain the final product. As a polar aprotic solvent, DMF is beneficial to the whole reaction procedure. For the reduction of nitro compound, hydrazine hydrate is applied as hydrogenating agent and Pd/C powder as catalyst to synthesize the BAPBBI. The pure BNPBBI recrystallized from ethanol is subsequently reduced to BAPBBI using hydrazine hydrate as the reductive agent and palladium-activated carbon (Pd/C) as the catalyst. The crude product is washed with deionized water to neutral point without any other purification. The yields of BNPBBI and BAPBBI monomer are as high as 96.5 and 91 %, respectively.

The structure information of BNPBBI and BAPBBI monomer was investigated by FTIR,  $^1\text{H}$  and elemental analysis. The FTIR spectra for both BNPBBI and BAPBBI are shown in Fig. 2. The N–H bands from imidazole ring range from 3,360 to 3,410  $\text{cm}^{-1}$ . The N–H asymmetric and symmetric stretching bands caused by the amino group can be observed at 3,355 and 3,218  $\text{cm}^{-1}$ , respectively. And the C–N stretching vibration is found at 1,610 and 1,495  $\text{cm}^{-1}$ . The nitro group of BNPBBI displays the bands at 1,515  $\text{cm}^{-1}$  (asymmetric stretch) and 1,339  $\text{cm}^{-1}$  (symmetric stretch). After reduction,



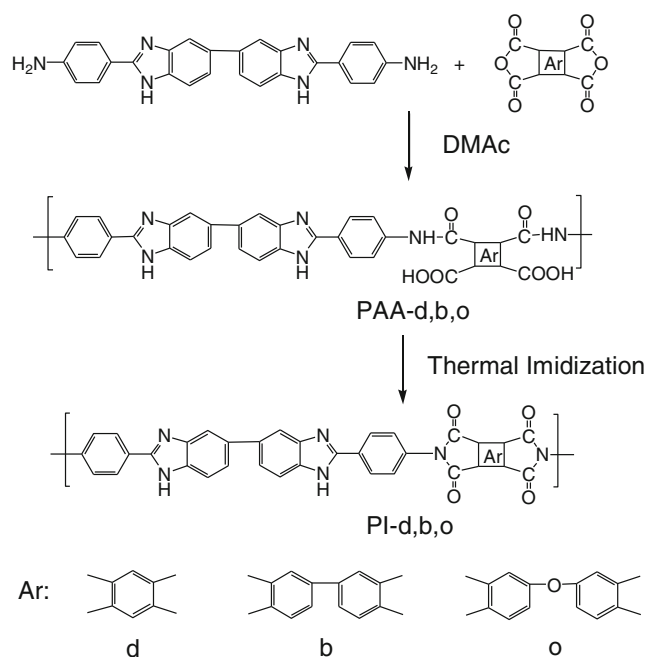
**Fig. 1** Synthesis scheme of BNPBBI and BAPBBI



**Fig. 2** FTIR spectra of BNPBBI (a) and BAPBBI (b)

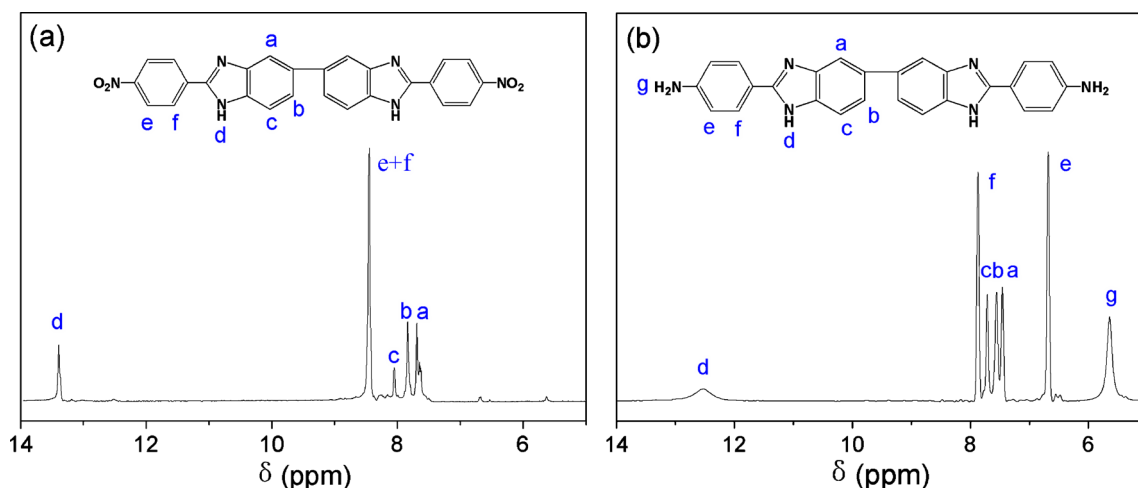
the absorption peaks for nitro groups disappear, which indicates that the nitro groups have been completely deoxidized. The  $^1\text{H}$  NMR spectra of BNPBBI and BAPBBI are shown in Fig. 3. The absorption peaks at 12.49 and 5.64 ppm are assigned to the protons of imidazole ring and amino group. The signals of aromatic protons of BNPBBI appear in the range of 7.63–8.45, while the ones of BAPBBI shift to the range of 6.69–7.88 due to deoxidization of nitro groups into amino groups and the increasing aggregation of electron cloud in biphenyl groups. According to FTIR, and  $^1\text{H}$  NMR spectra, the structure of BNPBBI and BAPBBI are consistent with the scheme, as shown in Fig. 1. The data from elemental analysis confirm the agreement with the calculated values, as described in the above. All the results indicate that the design and synthesis route of the monomer and intermediate containing bi-benzimidazole unit are reasonable, successful and feasible. Moreover, the ideal yields of each step can meet the requirements for the mass production of high molecular weight polyimides.

Polyimides containing bi-benzimidazole unit were synthesized from the diamine containing bi-benzimidazole BAPBBI and various commercial aromatic dianhydrides via a conventional two stage polymerization methodology. Polyamic acids



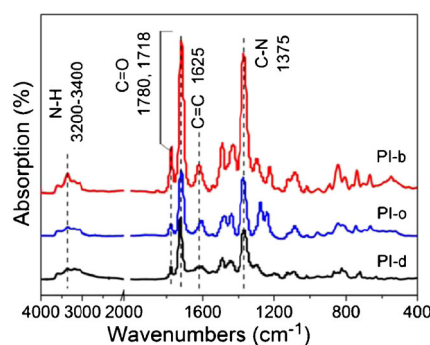
**Fig. 4** Synthesis of the polyimides

(PAAs) were first synthesized by subsequently adding aromatic dianhydride into a mixture of dissolved diamine in DMAc to yield viscous polymeric solutions. The values for inherent viscosity ( $\eta_{\text{inh}}$ ) of PAAs solution are 1.45 dL/g for PAA-d, 1.96 dL/g for PAA-b, 1.92 dL/g for PAA-o, 2.12 dL/g for PAA-PMDA-ODA and 2.64 dL/g for PAA-BPDA-ODA. Apparently, the polymerization degree is relatively high. The PAAs solutions are diluted and cast onto a glass slide and form PAA films. The films are converted to polyimides by step-by-step thermal imidization, as shown in Fig. 4. Finally, a series of polyimides containing bis-benzimidazole rings are synthesized from diamine BAPBBI with the same molar ratio of dianhydrides including PMDA, BPDA and ODPA at 12 % solid content in DMAc, respectively. In addition, PMDA-



**Fig. 3**  $^1\text{H}$  NMR spectra of BNPBBI (a) and BAPBBI (b)





**Fig. 5** FTIR spectra of polyimides

ODA and BPDA-ODA films are prepared via the same route to be tested for comparison.

The above polyimide films were characterized by FTIR. As shown in Fig. 5, the N–H stretching bands of the imidazole ring are observed at 3,200–3,400  $\text{cm}^{-1}$ . The asymmetric C=O, symmetric C=O and the C=C/C=N stretching bands appear at 1,780, 1,718 and 1,625  $\text{cm}^{-1}$  for all the polyimides. The absorption peak at 1,375  $\text{cm}^{-1}$  is usually considered as the characteristic of imide and evaluates as the criterion of imidization degree. From all the above, the complete imide cyclization is accomplished as described.

### Properties

The solubility of the prepared polyimides was tested quantitatively in various organic solvents. All the polyimides provide no solubility in common organic solvents, such as methanol, ethanol, acetic acid, ethyl acetate, methylene dichloride, chloroform, acetone, m-cresol, p-chlorophenol, DMSO, DMF, DMAc, NMP and THF. However, they are soluble slightly in concentrated sulfuric acid or only swell in methanesulfonic acid after a couple of days of immersion. Their solubility slightly increases under heating condition, but they cannot dissolve in the both solvents completely yet. The solubility of polymers depends on molecular backbone structure, polarity, inter-/intra-molecular interactions, chain packing density, for instance, rigidity or flexibility, symmetry or regularity. The insolubility is attributed to the ultra-strong

**Table 1** Thermal properties of the PI films

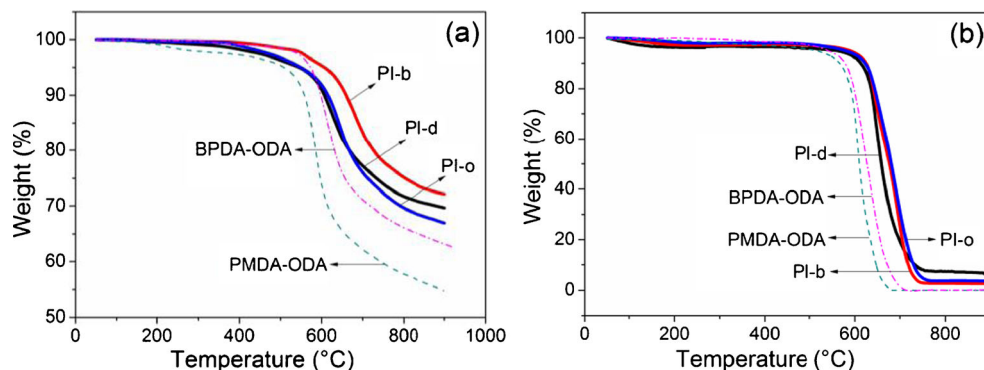
Sample	$T_d$ in $\text{N}_2$ ( $^{\circ}\text{C}$ )	$T_5$ % in $\text{N}_2$	$T_5$ % in air	$T_{10}$ % in $\text{N}_2$	$T_{10}$ % in air	Residue (%)	$T_g$ by DMA ( $^{\circ}\text{C}$ )
PI-d	581	544	560	607	613	70	439
PI-b	618	609	591	663	626	72	445
PI-o	595	549	580	616	623	67	419
PMDA-ODA	550	515	524	560	569	55	408
BPDA-ODA	570	564	547	597	581	63	320

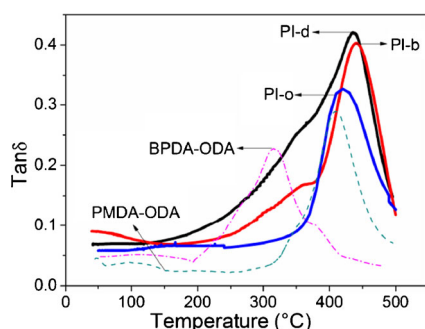
interactions between molecular chains, the rigidity and the symmetric molecular backbone. The existence of a large number of benzene rings in molecular backbone without bulky side groups tremendously improves the structure regularity, and thus reduces the solubility.

The thermal stability of the polyimides was investigated with TGA, and the curves in an air and  $\text{N}_2$  atmosphere at a heating rate of 10  $^{\circ}\text{C}/\text{min}$  are shown in Fig. 6. The decomposition-starting temperature ( $T_d$ ), the temperature at 5 % weight loss ( $T_5$  %) and the temperature at 10 % weight loss ( $T_{10}$  %) are summarized in Table 1. These polyimides exhibit superior thermal stability with a slight weight loss up to 663  $^{\circ}\text{C}$  in nitrogen and 626  $^{\circ}\text{C}$  in air. The initial decomposition temperature of the polyimides is in the range of 581–618  $^{\circ}\text{C}$  in nitrogen. The 5 % weight loss temperature is in the region of 544–609  $^{\circ}\text{C}$  in nitrogen and 560–591  $^{\circ}\text{C}$  in air, and the values for 10 % weight loss are in the region of 607–663  $^{\circ}\text{C}$  in nitrogen and 613–626  $^{\circ}\text{C}$  in air.

Moreover, the carbonized polyimides residue at 900  $^{\circ}\text{C}$  in nitrogen is 67–72 wt.%. These results demonstrate that the thermal stability of cured films is superior to that of PMDA-ODA and BPDA-ODA. In other words, the polyimides derived from symmetrical diamines containing bi-benzimidazole unit possess exceptional thermal stability. Generally, the thermal stability of the polymer depends on its composition and structure. The ether linkage from PMDA-ODA, BPDA-ODA at high temperature is relatively unstable, compared with bi-benzimidazole unit. Thus, the thermal stability of PI-o is inferior to that of PI-d and PI-b but superior to

**Fig. 6** TGA curves of PIs in  $\text{N}_2$  (a) and air (b) with a heating rate of 10  $^{\circ}\text{C}/\text{min}$

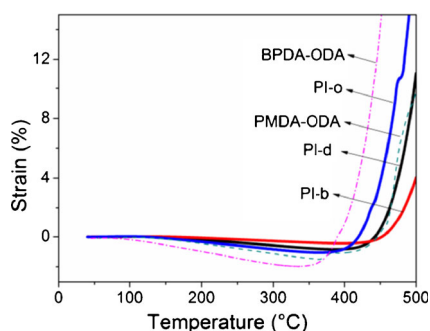




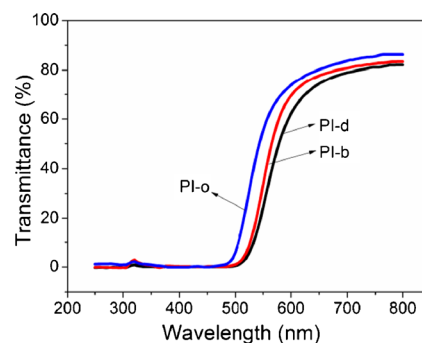
**Fig. 7** Plots of  $\tan \delta$  v.s. temperature in DMA of PI films

that of PMDA-ODA and BPDA-ODA. The increment of benzene units in main chain and the introduction of fully aromatic heterocyclic rings increase the rigidity of the molecular backbone and thus improve the thermal stability of the polymers.

$T_g$ s of the PI films were determined by DMA in nitrogen atmosphere. Fig. 7 shows the variations of the  $\tan \delta$  versus temperature, and the corresponding  $T_g$ s are listed in Table 1. The PI films possess high  $T_g$  values within the range of 419–445 °C, which are higher than that of PMDA-ODA and BPDA-ODA.  $T_g$  is affected by the main chain flexibility, polar groups, nature of side groups and other factors. Therefore, the high molecular chain rigidity and intra-/inter-molecular interactions contribute to the high  $T_g$  of the polyimides. For PI-o, the flexible ether linkage between the benzene rings reduces the rigidity of the main molecular chain, which gives the lower  $T_g$  than that of other varieties. As for PI-b, the biphenyl groups in both BPDA and BAPBBI increase the main chain rigidity, resulting in the high  $T_g$ . On the other hand, the interaction of the bi-benzimidazole unit leads to the complete rigid structure and endows the high  $T_g$  of the PI-b. The PI films exhibit slightly negative values from room temperature to 400 °C. The values obtained from Fig. 8 are  $-0.8$  ppm/°C for PI-d,  $-0.4$  ppm/°C for PI-b,  $-1.1$  ppm/°C for PI-o,  $-2.1$  ppm/°C for PMDA-ODA and  $-1.4$  ppm/°C for BPDA-ODA. As the comparison, PMDA-ODA and BPDA-ODA films exhibit more shrinkage because of the flexible ether linkage in main chains, while PI-d and PI-b films behave more stable in dimension, indicating that bi-benzimidazole unit contributes



**Fig. 8** Plots of shrinkage values v.s. temperature in TMA of PI films



**Fig. 9** UV-Vis spectra of the PI films

more rigidity and space volume to the better dimension stability at high temperature.

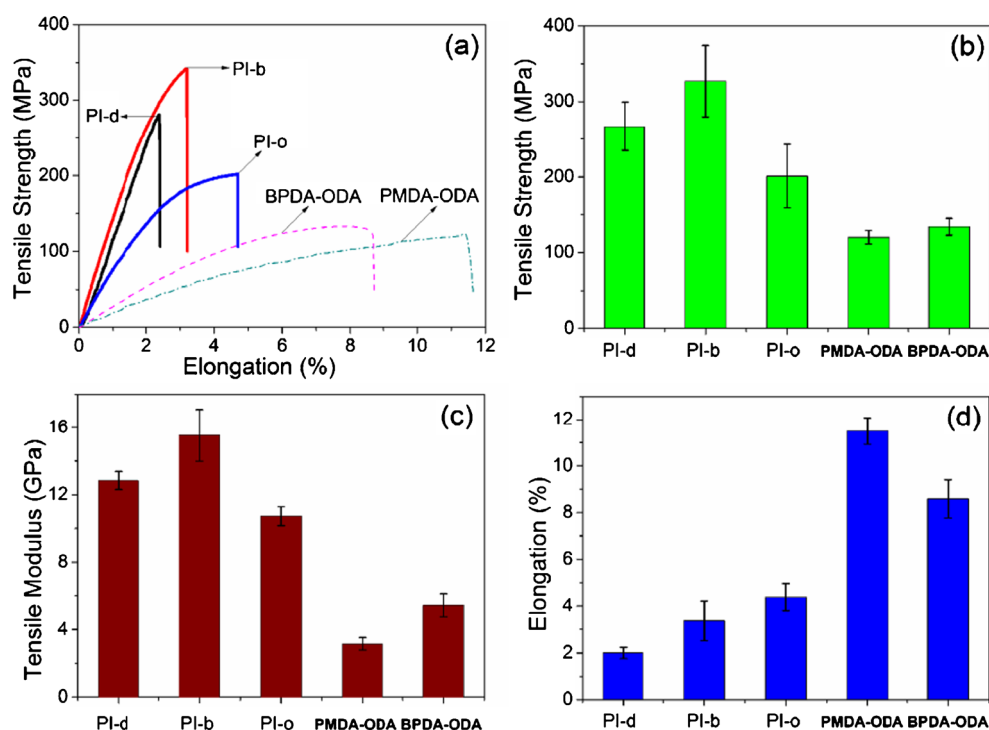
Figure 9 shows the UV-Vis spectra of the polyimide thin films with a thickness of 10–15  $\mu\text{m}$ . The minimum cut-off wavelength and the transparency at 800 nm are listed in Table 2. The PI films are light orange or brick red in color and transparent in the scale of the visible to the naked eye with the chromaticity of 4.0–5.0 lovibond unit in color red and yellow. The cutoff wavelengths range from 489 to 515 nm while the transmission at 800 nm ranges from 82.1 to 86.3 %. The spectra indicate that the films possess high capability of ultraviolet absorption due to the deep chromaticity and lower transparency, which are attributed to the more intensive charge-transfer complexes (CTC) effect between intermolecular chains. The symmetrical benzimidazole and imide rings provided by PMDA, BPDA and BAPBBI produce strong conjugative effects, which induce the CTC formation both in intra-/inter-molecules and electron-donor-acceptor. Therefore, both PI-d and PI-b have the deep color and the high cut-off wavelength. On the other hand, ODA has the lowest electron affinity with ether linkage as a flexible group, which significantly reduces the intermolecular interaction, so PI-o has the lowest cut-off wavelength and the lightest color.

As shown in Fig. 10, the polyimide films exhibit excellent mechanical properties. They possess a tensile strength of 201–327 MPa and an initial modulus of 10.7–15.5 GPa, which are several folds on those of PMDA-ODA and BPDA-ODA. The mechanical properties primarily depend on the feature polymeric structure and intermolecular interactions. The films PI-b, derived from BPDA, is superior to the other samples due to its higher molecular chain rigidity, contributed by double biphenyl repeat unit. In addition, the tensile strength of PI-b

**Table 2** Optical properties of the PI films

Samples	Color	Chromaticity (lovibond unit)	UV (%)	$\lambda_0$ (nm)
PI-d	Brick red	R 4.4–R 5.0	82.1	515
PI-b	Brick red	R 4.4–R 5.0	83.4	503
PI-o	Light orange	Y 4.0–Y 4.5	86.3	489

**Fig. 10** Mechanical properties of PI films: **a** stress–strain curves of PI films, **b** tensile strength of PI films, **c** tensile modulus of PI films, and **(d)** elongation at break of PI films



is almost three times of that of BPDA-ODA because of the substitution of BAPBBI for ODA. The bi-benzimidazole unit is a highly rigid and symmetrical structure without weak linkage, which reduces the conformational entropy to obtain more intense intermolecular interaction. Therefore, the tensile strength of PI-b is far higher than that of BPDA-ODA, almost three folds increase, while the elongation at break is accordingly lower. Similarly, the PI-o film, derived from ODA, is endowed with the highest elongation because of the relatively flexible ether linkage, along with the lowest tensile modulus. On the other hand, the PI-d films, prepared from PMDA, possess the lowest elongation at break for its complete rigid phenyl unit. The tensile modulus of these films are all above 10 GPa, which are attributed to the bi-benzimidazole structures provided by the monomer of BAPBBI.

## Conclusions

BAPBBI, an aromatic diamine containing bi-benzimidazole unit, was successfully synthesized with a high yield using a simple method. A series of polyimides were prepared by the reaction between BAPBBI with various aromatic dianhydrides of PMDA, BPDA and ODA. PAA films were prepared from the casting method, then strong and flexible polyimide films were obtained through a conventional high-temperature treatment of PAAs. As expected, the synthesized polyimides possess excellent thermal stability with high glass transition temperatures from 419 to 445 °C and initial decomposition temperatures from 581 to 618 °C in nitrogen.

Meanwhile, they exhibit outstanding thermal oxidation stability with initial decomposition temperature from 626 to 630 °C in air atmosphere. Furthermore, the polyimide films have excellent mechanical properties with tensile strength at break from 201 to 327 MPa, tensile modulus from 10.7 to 15.5 GPa and elongation at break from 2.00 to 4.38 %. These results indicated that the introduction of PBI into polyimide backbone effectively enhanced the molecular rigidity. These polyimide films show good transparency ability in visible region. Thus, the series of polyimides with excellent properties enrich the variety of aromatic polyimides and are promising for the future development of high performance materials.

**Acknowledgments** Financial support of this work is provided by NSFC (51233001, 51173024), 973 Plan (2014CB643603), 863 Plan (2012AA03A211) and the 111 Project (111-2-04).

## References

1. Wahab MA, Mya KY, He CB (2008) J Polym Sci Part A Polym Chem 46:5887–5896
2. Fukuzaki N, Higashihara T, Ando S, Ueda M (2010) Macromolecules 43:1836–1843
3. Wang C, Wang QH, Wang TM (2010) Langmuir 26:18357–18361
4. Chidambareswarapattar C, Larimore Z, Sotiriou-Leventis C, Mang JT, Leventis N (2010) J Mater Chem 20:9666–9678
5. Shoji Y, Ishige R, Higashihara T, Watanabe J, Ueda M (2010) Macromolecules 43:805–810
6. Tomikawa M, Yoshida S, Okamoto N (2009) Polym J 41:604–608
7. Xia SL, Yi LF, Sun Z, Wang YH (2013) J Polym Res 20:219

8. Dasgupta B, Sen SK, Banerjee S (2010) *Mater Sci Eng B* 168:30–35
9. Purushothaman R, Bilal IM, Palanichamy M (2011) *J Polym Res* 18: 1597–1604
10. Zhang QH, Dai M, Ding MX, Chen DJ, Gao LX (2004) *Eur Polym J* 40:2487–2493
11. Zhang QH, Dai M, Ding MX, Chen DJ, Gao LX (2004) *J Appl Polym Sci* 93:669–675
12. Zhang QH, Luo WQ, Gao LX, Chen DJ, Ding MX (2004) *J Appl Polym Sci* 92:1653–1657
13. Sukhanova TE, Baklagina YG, Kudryavtsev VV, Maricheva TA, Lednický F (1999) *Polymer* 40:6265–6276
14. Park SK, Farris RJ (2001) *Polymer* 42:10087–10093
15. Fukukawa K, Fujio I, Yamashita W, Tamai S (2008) *J Photopolym Sci Technol* 21:101–106
16. Chen CF, Juang LJ, Hsu TC, Wang JJ, Wang LF (2006) *Polym Int* 55: 1450–1455
17. Mehta VR, Kumar S (1999) *J Appl Polym Sci* 73:305–314
18. Wolfe JF, Arnold FE (1981) *Macromolecules* 14:909–915
19. Dang TD, Mather PT, Alexander MD Jr, Grayson CJ, Houtz MD, Spry RJ, Arnold FE (2000) *J Polym Sci Part A* 38:1991–2003
20. Maruyama Y, Oishi Y, Kakimoto M, Imai Y (1988) *Macromolecules* 21:2305–2309
21. Huang W, Li SJ, Du CP, Xie MR, Zhang YQ, Yin J (2009) *Eur Polym J* 45:3187–3195
22. Agrawal AK, Jenekhe SA (1993) *Macromolecules* 26:895–905
23. Rusanov AL, Belomoina NM, Bulychева EG, Yanul NA, Likhatchev DY, Dobrovolskii YA, Iojoiu C, Voytekunas VY, Abadie MJM (2008) *High Perform Polym* 20:627–641
24. Xia AX, Lu GH, Qiu XP, Gao HQ, Zhao JY, Ding MX, Gao LX (2006) *J Appl Polym Sci* 102:5871–5876
25. Hsu SLC, Luo GW, Chen HT, Chuang SW (2005) *J Polym Sci Part A* 43:6020–6027
26. Nair CPR, Sebastian TV, Nema SK, Rao KVC (1986) *J Polym Sci Part A* 24:1109–1132
27. Luo LB, Pang YW, Jiang X, Wang X, Zhang P, Chen Y, Peng CR, Liu XY (2012) *J Polym Res* 19:9783
28. Zhuang YB, Gu Y (2013) *J Polym Res* 20:168
29. Banihashemi A, Atabaki F (2002) *Eur Polym J* 38:2119–2124
30. Yang JS, He RH (2010) *Polym Adv Technol* 21:874–880
31. Hua MY, Chen HC, Tsai RY, Leu YL, Liu YC, Lai JT (2011) *J Mater Chem* 21:7254–7262
32. Liu JP, Zhang QH, Xia QM, Dong J, Xu Q (2012) *Polym Degrad Stabil* 97:987–994
33. Liu XY, Gao GQ, Dong L, Ye GD, Gu Y (2009) *Polym Adv Technol* 20:362–366
34. Gao GQ, Dong L, Liu XY, Ye GD, Gu Y (2008) *Polym Eng Sci* 48: 912–917
35. Hergenrother PM, Havens SJ (1994) *Macromolecules* 27:4659–4664
36. Sann CL, Baron A, Mann J, van den Berg H, Gunaratnam M, Neidle S (2006) *Org Biomol Chem* 4:1305–1312
37. Sakaguchi Y, Kato Y (1993) *J Polym Sci Part A* 31:1029–1033