

# Synthesis, characterization and properties of aromatic copolyimides containing Bi-benzimidazole moiety

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**Abstract** A new aromatic heterocyclic diamine monomer, 2,2-bis (4'-aminophenyl)- 5,5-bi-1H-benzimidazole (BAPBBI), was synthesized via a one-step reaction of 3,3',4,4'-biphenyltetramine and *p*-aminobenzoic acid in polyphosphoric acids with the high yield and purity. FTIR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, mass spectra and elemental analysis were employed to confirm the chemical structures. A series of copolyimide films containing the bi-benzimidazole moieties were prepared by the reaction of pyromellitic dianhydride (PMDA), 4,4'-oxydianiline (ODA) and BAPBBI with various molar ratios. The combination of polybenzimidazole and polyimide by introducing BAPBBI into the main chains brings the highly rigid structure and the enhanced macromolecular interactions, resulting in the enhancement in the thermal stability and the mechanical properties. For instance, these polyimides are endowed with a higher glass transition temperature of 408–438 °C and an initial thermal decomposition of 550–580 °C. They exhibit a strong tensile strength of 123–233 MPa, and a tensile moduli of 2.66–12.84 GPa without post stretching. Meanwhile the stretched films at 450 °C exhibited the enhanced mechanical properties with the tensile strength of 195–554 MPa and the tensile modulus of 4.69–38.57 GPa.

**Keywords** Aromatic polyimide · Thermal stability · Mechanical properties · Bi-benzimidazole unit

## Introduction

Polyimides (PI) are a kind of high-performance polymeric materials with excellent thermal stability and mechanical properties, and have been extensively used in aerospace and semiconductor industries such as inter-layer dielectrics, protection layers, and re-distribution layers for wafer level package [1–9]. As a commercial polyimide product by DuPont, Kapton® film is known as a pyromellitimide prepared by reacting pyromellitic dianhydride (PMDA) with 4,4'-oxydianiline (ODA) [10–12]. Based on the widest application of PMDA/ODA as a tough and stable substrate, a great amount of fundamental researches on the chemical and physical properties were carried out in the past few decades [12–17]. Along with the increasing varieties of polyimides and the growing demand for the mechanical properties and thermal stability, the modification for PMDA/ODA-based polyimides should be carried out to meet the further demand. For instance, Wahab et al. [18] reported the PMDA/ODA/hydroxyl functionalized silsequioxane (POSS-OH) hybrid nanocomposites films, and the introduction of POSS-OH in the hybrids effectively enhanced the thermal stability of PMDA/ODA. Gu et al. [19] prepared PMDA/ODA/2-(4-aminophenyl)-5-aminobenzimidazole (PABZ) copolyimide fibers, and PABZ with benzimidazole rings in the main chains significantly improved the mechanical and thermal properties. Therefore, the chemical modification of introducing heterocyclic moieties into the main chain can improve the properties of polyimides more significantly.

As another kind of aromatic heterocyclic polymers, polybenzimidazoles (PBIs) possess superior mechanical properties and thermal stability, and are also widely used in many fields such as flame-protection, semi-conductor industry and proton exchange membrane in fuel cells [20–24]. The characteristic structure of bi-benzimidazole

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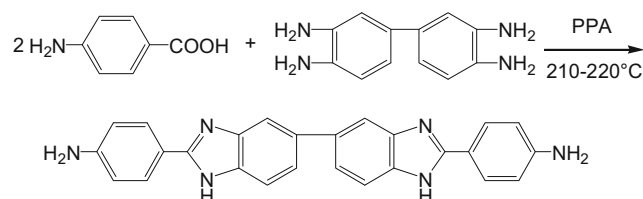
unit contributes to the high molecular rigidity and conjugation, resulting in high thermal stability and mechanical properties. Thus, the similar heterocyclic structure in the forms of aromatic diamines has been introduced into the backbone of polyimide to adjust glass transition temperature, decomposition temperature, tensile strength and rigidity of molecular chain [19, 25–27].

The aromatic diamines containing benzimidazole unit can be synthesized via a two-step procedure by preparing a nitro compound and its hydrogenation [25, 28, 29], and in our previous study, we used this method to prepare the diamine containing bi-benzimidazole unit [30]. The diamine can also be synthesized via a one-step method, and the PBIs were usually prepared in polyphosphoric acid (PPA) by this method [21, 31–33]. Compared with the reduction of nitro compound, the one-step method is a more facile and effective routine. In this report, we aimed to introduce the full characteristic structure of PBIs (bi-benzimidazole unit) into the backbone of PMDA/ODA polyimide to improve its properties. Therefore, we synthesized an aromatic diamine containing biphenyl and bi-benzimidazole unit via the one-step method in PPA [34]. The aromatic diamine, 2,2-bis (4'-aminophenyl)-5,5-bi-1H-benzimidazole (BAPBBI), was successfully synthesized with a high yield and purity. A series of PMDA/ODA/BAPBBI with various molar ratios of ODA/BAPBBI were synthesized and the corresponding films were prepared. The chemical structures, molecular compounds, optical property, thermal stability and mechanical properties were investigated in details.

## Experimental

### Materials

3,3',4,4'-Biphenyltetramine (DAB) was purchased from Chengdu Yuanda Chemicals Co., Ltd. *P*-aminobenzoic acid was purchased from Shanghai Ourchem Reagent Co., Ltd. Pyromettic dianhydride (PMDA) and 4,4'-oxydianiline (ODA) were purchased from Shanghai Synthetic Resin Research Institute and Shandong Wanda Chemical Co., Ltd, respectively. Phosphorus pentoxide, polyphosphoric acids (concentration of 80 %), phosphoric acid, sodium carbonate, ethanol, *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), *N*-methyl-2-pyrrolidone (NMP), tetrahydrofuran (THF), concentrated sulfuric acid and methanesulfonic acid were purchased from Sinopharm Chemical Reagent Co., Ltd. DMAc was dehydrated and stored over molecular sieves (0.4 nm). Other reagents from commercial institutions were used without further purification.

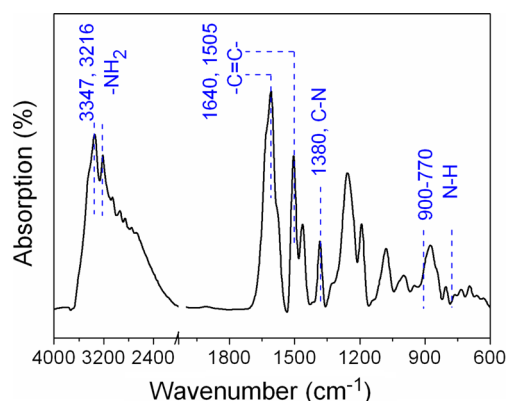


**Fig. 1** Synthetic scheme and chemical structure of BAPBBI

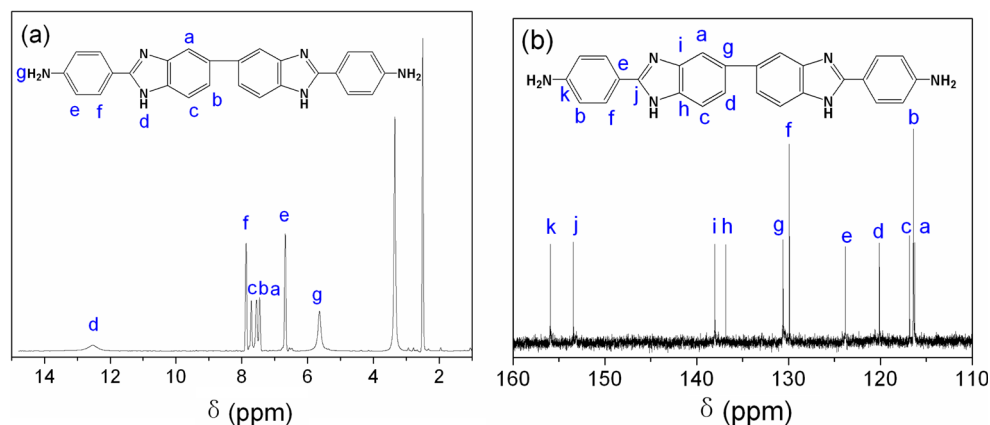
### Characterization

For diamine monomer, infrared spectra were obtained on a Nicolet 8700 FTIR spectrometer within the range of 4000–400  $\text{cm}^{-1}$  by averaging 32 scans, the powders were prepared into discs with KBr.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were obtained using an Avance 400 spectrometer with  $\text{DMSO}-d_6$  as solvent at 400 MHz and 100 MHz, respectively, and TMS as internal standard. Chemical shifts ( $\delta$ ) are labeled in per million (ppm). The chromaticity of monomer was confirmed using a WSL-2 colorimeter in transmittance mode within the color range of N 0.1 - N 3.9; the minimum readout is 0.1 lovibond unit. Mass spectra were recorded on an AXIMA-CFR spectrometer with ethanol as solvent. Elemental analysis was quantitatively confirmed using a Vario EL III elemental analyzer. Purity of refined product was recorded on a Nexera UHPLC LC-30A spectrometer, with methanol and THF as solvents.

For polymer, the inherent viscosities of the polyamic acids (PAAs) were measured using an Ubbelohde viscometer with the inner diameter of 0.5 mm at 25 °C. Infrared spectra of the casting films were obtained on a Nicolet 8700 FTIR spectrometer within the range of 4000–400  $\text{cm}^{-1}$  by averaging 32 scans in transmittance mode. Thermo-gravimetric analyses were performed on a TA Q5000 thermal analyzer from 50 to 900 °C at a heating rate of 10 °C /min under  $\text{N}_2$  and air atmosphere. The initial decomposition temperature is confirmed at the intersection point of the two tangent lines from TGA curves. Dynamic mechanical analyses (DMA) of the cured films were executed on a TA Q800 dynamic mechanical analyzer at a heating of 5 °C /min under  $\text{N}_2$  atmosphere at a



**Fig. 2** FTIR spectra of BAPBBI

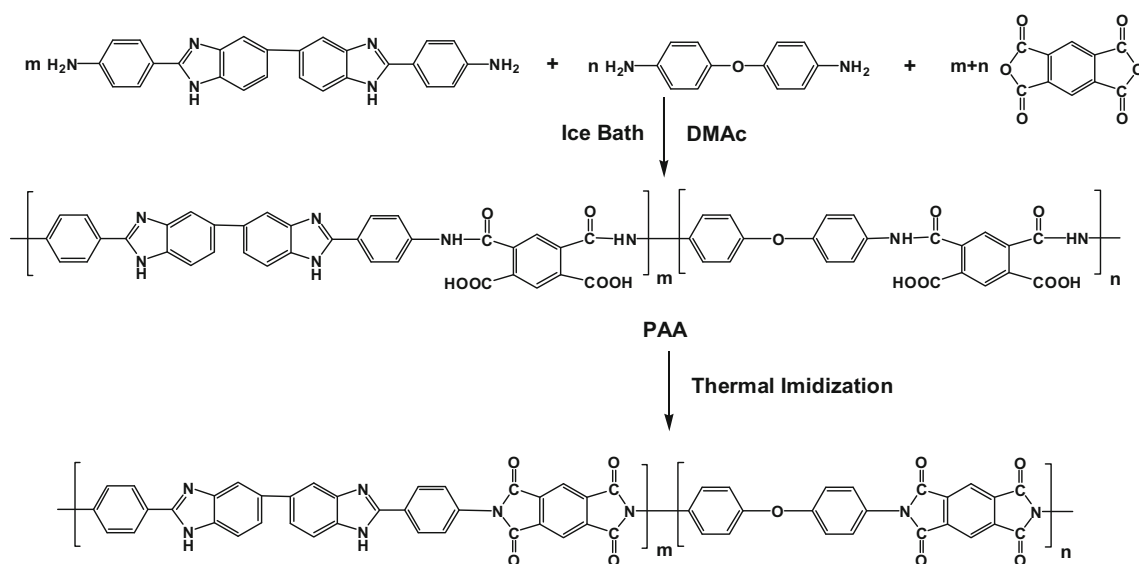
**Fig. 3** NMR spectra of BAPBBI: (a)  $^1\text{H}$  NMR, (b)  $^{13}\text{C}$  NMR

frequency of 1 Hz. The glass transit temperatures ( $T_g$ s) of the cured films were confirmed as the temperatures corresponding to the peak of  $\tan \delta$ . The coefficients of thermal expansion (CTE) of the cured films were performed on TA Q800 instrument with a stress of 6 MPa at a heating rate of 5 °C/min. The mechanical properties were tested using an Instron 5969 instrument with a drawing rate of 10 mm/min. The samples were cut to a dimension of 80 mm  $\times$  10 mm. The tensile strength, initial modulus and elongation at break were statistical average values with 10 tests for each sample. Ultraviolet–visible (UV–vis) spectra were obtained on a Lambda 950 UV–vis spectrophotometer in transmittance mode within the range of 250–800 nm. Wide-angle X-ray diffraction (WAXD) measurements for the films were conducted using a Rigaku D-max-2500 diffractometer with nickel-filtered  $\text{CuK}\alpha$  radiation with  $\lambda=0.154$  nm. The solubility of the films were quantitatively determined by mixing 1.0 g film fragments in 9.0 g solvent at room temperature, i.e., 10 % content in the solution. The mixture was stirred at room temperature or heated in an

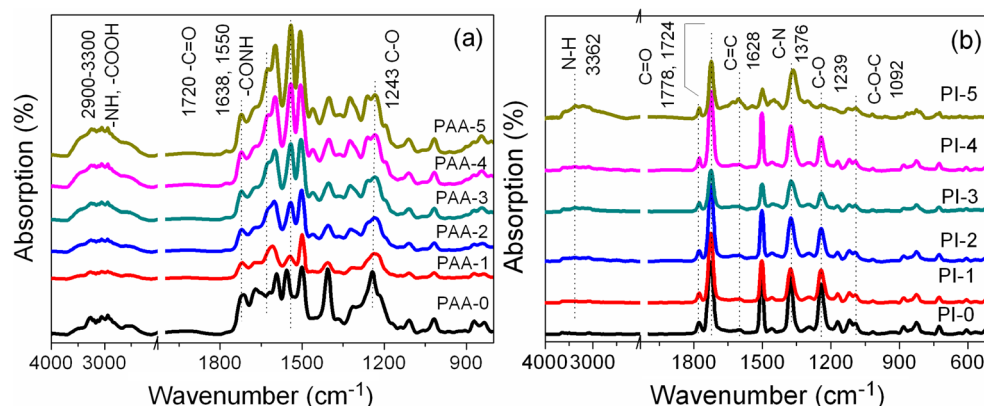
inert atmosphere for 24 h. The resulting solution was classified into three grades under observation: soluble at room temperature, soluble by heating and insoluble, respectively.

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

7.5 g Phosphorus pentoxide and 30 g PPA (80 wt.%) were added into a 100 mL three-neck round-bottom flask with a mechanical stirring, a condenser and a nitrogen inlet. The mixture was heated up in turn to 120 °C and 150 °C with stirring for each 2 h till the mixture formed a uniformly thick solution with 84 % concentration. DAB (3.214 g, 0.015 mol) and *p*-aminobenzoic acid (4.316 g, 0.0315 mol, 2.1 M equivalents of DAB) were added into the flask and left to stir for 20 h at 210–220 °C. 10–15 mL  $\text{H}_3\text{PO}_4$  was added into the mixture to promote solubilization. Then, the mixture was cooled down to 190 °C and poured into the ice bath quickly to form dark brown sediments. The sediments were

**Fig. 4** Scheme and chemical structures of the co-PI films

**Fig. 5** FTIR spectra of the co-PI films: (a) PAA films; (b) co-PI films



deacidified with a 10 % sodium carbonate solution, numerous CO<sub>2</sub> bubbles emerged and the original sediments transferred to light brown powders. The mixture was neutralized to pH=7–8 and filtered to obtain the crude product. The crude product was washed with deionized water to neutral point and recrystallized from ethanol, and then filtered and dried in vacuum to yield the light brown target powders. BAPBBI (5.581 g, yield 74.12 %). Chromaticity: N 2.2 - N 2.5 in gray. m.p. > 300 °C. FTIR (KBr disc cm<sup>-1</sup>): 3200–3500 (NH<sub>2</sub> NH of benzimidazole), 1610, 1495 (C=C), 1450 (–NH). <sup>1</sup>H NMR (ppm) δ=12.49 (m, 2H, NH of benzimidazole), δ=7.88 (d, 4H, Ar-H), δ=7.71–7.77 (s, 2H, Ar-H), δ=7.57–7.60 (d, 2H, Ar-H), δ=7.50 (d, 2H, Ar-H), δ=6.66–6.69 (d, 4H, Ar-H), δ=5.64 (b, 4H, –NH<sub>2</sub>). <sup>13</sup>C NMR (ppm) δ=116.3, 116.4, 116.8, 120.1, 123.7, 129.8, 130.6, 136.8, 138, 153.4, 156.0. m/z=417 g/mol (C<sub>26</sub>H<sub>20</sub>N<sub>6</sub>, requires 416.5 g/mol). Purity from HPLC: 98.8 %. Anal. Calcd. for C<sub>26</sub>H<sub>20</sub>N<sub>6</sub>: C, 74.98 %; H, 4.84 %; N, 20.18 %. Found: C, 74.47 %; H, 4.99 %; N, 20.09 %.

### Synthesis of the copolyimides

Polyamic acids, the precursors of the copolyimides, were synthesized by polycondensation with an equimolar of diamine and dianhydride in DMAc under a dried nitrogen atmosphere in an ice bath. The molar ratio of ODA/BAPBBI was quantified and labeled as follows: 9:1 for PI-1, 7:3 for PI-2, 5:5 for PI-3, 3:7 for PI-4, and 1:9 for PI-5, respectively. The homopolyimides of PMDA-ODA were prepared and labeled as PI-0 for comparison. For the typical preparation of PI-1, BAPBBI (1.218 g, 2.92 mmol) and ODA (5.269 g, 26.3 mmol) were dissolved in 100 mL DMAc in a 250 mL three-necked bottle, PMDA (6.378 g, 29.22 mmol) was added into the mixture. The mixture was stirred for 4–6 h in an ice bath to form a viscous PAA solution with a content of 12 wt.%. The preparation of the other PAA solutions with various ODA/BAPBBI molar ratios was similar to the above procedure. The PAA solutions were diluted and cast onto glass plates. After the solvent removal for 8 h at 60 °C in vacuum, the brown orange PAA films were obtained. The PAA films were converted to

the corresponding polyimides after successive heating at 80 °C, 120 °C, 150 °C, 200 °C and 300 °C for each 1 h. The cured polyimide films were dark brown orange with a thickness of 18±2 μm. For enhancing the mechanical properties, the original films were stretched with the drawing ratio of 150 % at 450 °C using contact-type heat tensile equipment. The stretched films were brown orange in color with the thickness of 12±1 μm.

## Results and discussion

### Monomer synthesis

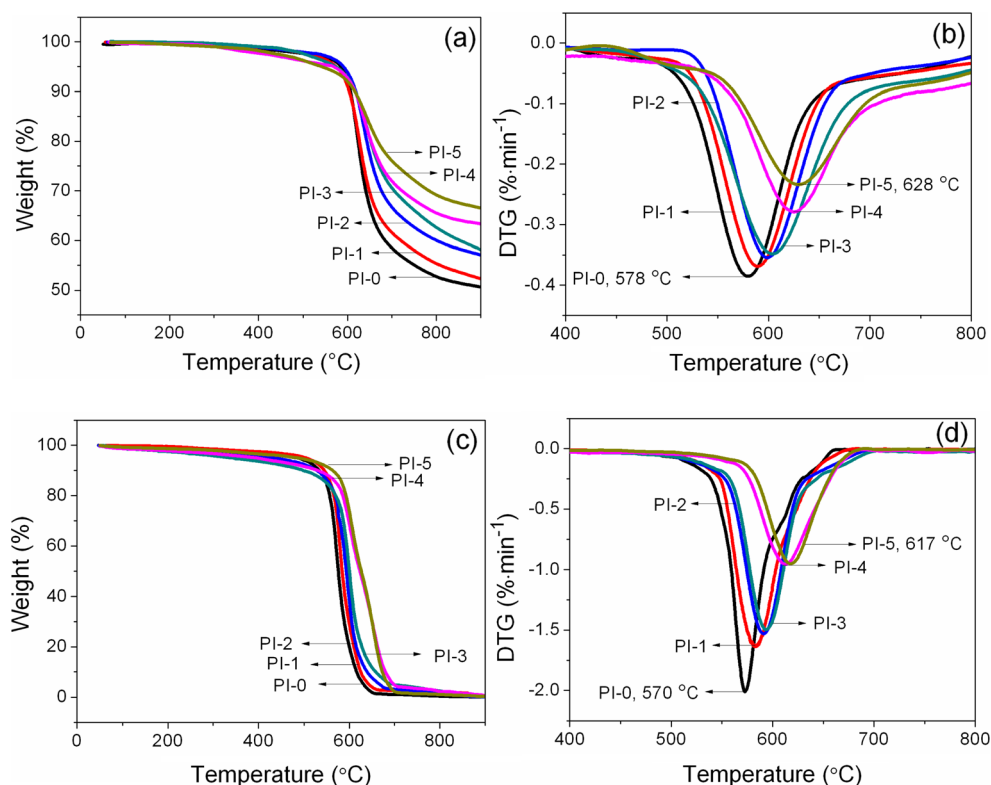
The aromatic diamine containing bi-benzimidazole unit (BAPBBI) is synthesized by the reaction of DAB and *p*-aminobenzoic acid in PPA with a concentration of 84 % mixed with P<sub>2</sub>O<sub>5</sub>, as shown in Fig. 1. PPA is widely used for catalyzing intramolecular cyclization reaction due to its high dehydration and low oxidizability. During the formation of benzimidazole ring, the reaction of amino group and carboxyl group produces the amide group firstly, and then the amide group reacts with another amino group to form an imidazole ring by dehydration of one molecule. The PPA is effective in bounding the free water molecules to keep the reaction in positive direction. Suitable amount H<sub>3</sub>PO<sub>4</sub> will lower the excessive viscosity of the mixture to accelerate the reaction.

**Table 1** Solubilities of the co-PI films

Sample	DMF	DMAc	DMSO	NMP	THF	H <sub>2</sub> SO <sub>4</sub>	MSA
PI-0	–	–	–	–	–	+	+
PI-1	–	–	–	–	–	+	+
PI-2	–	–	–	–	–	+	+
PI-3	–	–	–	–	–	+	+
PI-4	–	–	–	–	–	+	+
PI-5	–	–	–	–	–	+	+

+: soluble; ++: soluble at heating; –: insoluble

**Fig. 6** TGA curves of the co-PI films: (a) TGA in N<sub>2</sub>, (b) DTG in N<sub>2</sub>, (c) TGA in air, and (d) DTG in air



After the reaction, the mixture is neutralized and the excess acid in the mixture is removed by 10 % sodium carbonate solution, and the alkaline solutions can keep the amino group remain stable. DAB is dissolved in hot ethanol while *p*-aminobenzoic acid is dissolved in ethanol at room temperature, so ethanol is the most suitable reagent for the recrystallization of crude product. The one-step preparation is simple and facile.

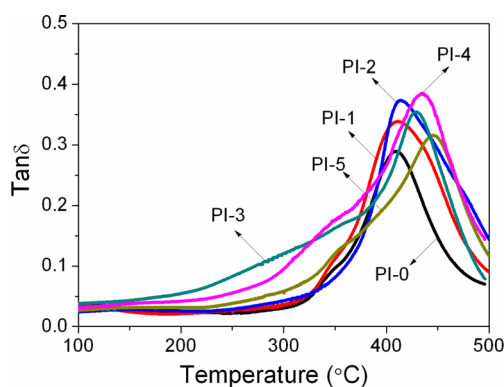
The chemical structure of BAPBBI was investigated by FTIR, <sup>1</sup>H and <sup>13</sup>C NMR, and elemental analysis. The FTIR spectra for monomer BAPBBI are shown in Fig. 2. The N-H bands from imidazole ring and the characteristic absorption peaks of amino group are observed at 3347 cm<sup>-1</sup> and 3216 cm<sup>-1</sup>, attributing to the asymmetric and symmetric stretching bands of amino groups. The skeletal vibration of C=C from benzene ring appears at 1640 cm<sup>-1</sup> and

1505 cm<sup>-1</sup>. The bending vibration of amino group also locates in this area but it is covered by the skeletal vibration of aromatic ring. The stretching vibration of C-N is observed at 1380 cm<sup>-1</sup>. The out-of-plane deformation vibration of N-H can be seen from 900 to 770 cm<sup>-1</sup>, which is an important criterion for primary amine. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra further confirm the structure of BAPBBI, as shown in Fig. 3. The peaks at 12.49 ppm and 5.64 ppm are assigned to the protons of imidazole ring and primary amino group, respectively. The aromatic protons in the skeleton of the BAPBBI molecule locate within the range of 6.69–7.28 ppm, and the attribution of each proton is labeled in Fig. 3a. The proportion for the each integral area of discharge is a:b:c:d:e:f:g = 1.12:1.08:1.05:1.2:1.2:2.23:2.30, which is in high accordance with the theoretical values of 1:1:1:1:2:2:2. The information and distribution of carbon atom in BAPBBI molecular skeleton

**Table 2** Thermal properties of the co-PI films

Sample	T <sub>d</sub> in N <sub>2</sub> (°C)	T <sub>5%</sub> (°C)		T <sub>max</sub> (°C)		T <sub>10%</sub> (°C)		Residue (%)	T <sub>g</sub> by DMA (°C)
		in N <sub>2</sub>	in air	in N <sub>2</sub>	in air	in N <sub>2</sub>	in air		
PI-0	550	508	485	558	534	578	570	55	408
PI-1	558	514	504	560	542	591	582	57	411
PI-2	560	525	509	563	552	600	590	58	414
PI-3	566	528	514	568	555	606	593	62	430
PI-4	578	538	524	572	569	625	612	65	435
PI-5	580	544	527	577	572	628	617	68	438





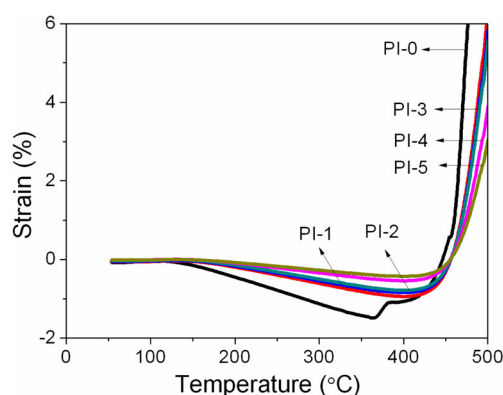
**Fig. 7** Plots of  $\tan \delta$  v.s. temperature in DMA of the co-PI films

are identifiable and marked in Fig. 3b. The proportion for the each integral area of discharge is a:b:c:d:e:f:g:h:i:j:k=1.03:2.14:1.09:1.02:0.99:2.04:1.05:1:1:1.03:1, which is in high accordance with the theoretical values of 1:2:1:1:1:2:1:1:1:1:1. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra indicate a consistent structure of the product with the target. The elemental analysis and MS tests further prove that the product possesses high purity, as listed in Experimental, which is helpful for preparing polyimides.

### Polymer synthesis

The new type copolyimides containing bi-benzimidazole unit are prepared by the reaction of PMDA and the two diamines of BAPBBI and ODA with various molar ratios (BAPBBI/ODA=1/9, 3/7, 5/5, 7/3, and 9/1), and then the casting films are produced by imidization reaction. The PMDA-ODA homopolyimide film is prepared for comparison. The equivalence between the diamines and the dianhydrides is controlled accurately during polymerization, and the synthesis conditions are the same to ensure that the practical composition of BAPBBI and ODA well matches with the molecular design. The values for inherent viscosity ( $\eta_{\text{inh}}$ ) of PAAs solution are 2.12 dL/g for PAA-0, 1.84 dL/g for PAA-1, 1.80 dL/g for PAA-2, 1.52 dL/g for PAA-3, 1.40 dL/g for PAA-4 and 1.37 dL/g for PAA-5. After dilution, the PAA solutions are cast onto glass slides to form PAA films. The PAA films are converted to corresponding polyimide films by a step-by-step thermal imidization as shown in Fig. 4. The relationship between the polymer structure and the sample code is PI-0 (ODA:BAPBBI=10:0), PI-1 (ODA:BAPBBI=9:1), PI-2 (ODA:BAPBBI=7:3), PI-3 (ODA:BAPBBI=5:5), PI-4 (ODA:BAPBBI=3:7), PI-5 (ODA:BAPBBI=1:9), respectively.

The chemical structures of the PAA films and co-PI films are confirmed by FTIR shown in Fig. 5. The wide absorption peaks at 2900–3300  $\text{cm}^{-1}$  are attributed to the -NH and -COOH groups. The C=O stretching band from -COOH group, the C=O and C-N stretching bands are observed at 1720, 1638 and 1550  $\text{cm}^{-1}$ , respectively. The C-O asymmetric



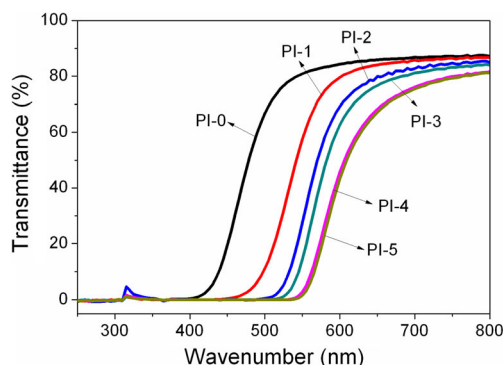
**Fig. 8** Plots of  $\delta$  v.s. temperature in TMA of the co-PI films

stretching band from ether linkage is observing at 1243  $\text{cm}^{-1}$ . After thermal imidization, the -NH stretching bands for the imidazole rings are observed at 3362  $\text{cm}^{-1}$ , while the wide absorption peaks disappear. The asymmetric C=O, symmetric C=O and the C=C stretching bands appear at 1778, 1724 and 1628  $\text{cm}^{-1}$ , while the peak at 1550  $\text{cm}^{-1}$  disappears. The C-N stretching band at 1376  $\text{cm}^{-1}$  is usually considered as the characteristic group of imide ring. Therefore, the PAAs have been converted into corresponding polyimides as described.

### Properties

The polyimides can hardly dissolve in most organic solvents, such as DMF, DMAc, NMP or THF, as listed in Table 1. They can dissolve in MSA and concentrated  $\text{H}_2\text{SO}_4$ , but the solubility decreases with the growing content of BAPBBI. Bi-benzimidazole unit, imide rings and benzene rings possess high rigidity, which reduce the solubility of polymers. The bi-benzimidazole unit has symmetric and conjugated structure, and upon increasing its content in the main chains, the content of flexible ether linkage decrease and the flexibility of molecular chain falls. The protonation effect from the N atom in benzimidazole rings enhances the interaction between the molecular chains, which weakens the interactions between solutes and solvents to reduce the solubility.

The thermal stability of the co-PI films are investigated by TGA in air and  $\text{N}_2$  at a heating rate of 10  $^{\circ}\text{C}/\text{min}$ , as shown in



**Fig. 9** UV-vis spectra of the co-PI films

**Table 3** Optical properties of the co-PI films

Sample	Cutoff Wavelength (nm)	Transparency (%)	Chromaticity (Iovibond)
PI-0	418	87.2	Y 2.0-Y 2.5
PI-1	480	86.7	Y 3.0-Y 3.5
PI-2	516	84.9	Y 3.7-Y 4.0
PI-3	529	83.9	Y 4.0-Y 4.5
PI-4	546	81.5	Y 4.8-Y 5.0
PI-5	549	81.2	Y 6.5-Y 7.0

Fig. 6. The initial decomposition temperature ( $T_d$ ) in  $N_2$ , the temperatures at 5 % weight loss ( $T_{5\%}$ ), the temperature at 10 % weight loss ( $T_{10\%}$ ), and the maximal decomposition temperature ( $T_{max}$ ) are summarized in Table 2. Compared with PI-0, the  $T_d$ s of the co-PI films range from 550 to 580 °C, the  $T_{5\%}$ s range from 508 to 544 °C in  $N_2$  and 485 to 527 °C in air, and the  $T_{max}$ s range from 578 to 628 °C in  $N_2$  and 570 to 617 °C in air. The above thermal properties are improved upon increasing content of BAPBBI in the main chains, indicating a great improvement in the thermal stability of the co-PI films. The replacement of ether linkage by bi-benzimidazole unit enhances the rigidity and the aromaticity of the polymer backbone, and thus provides stronger molecular bonds and more compact structures in the backbone. As shown in Fig. 6c, the  $T_d$ s of PI-4 and PI-5 in air are obviously higher than that of PI-0, and the  $T_{max}$  is high up to 617 °C, by 47 °C higher compared to that of PI-0. Thus, the introduction of BAPBBI into the backbone of polyimide can effectively improve the thermal stability, especially in the air atmosphere. Moreover, when the environmental temperature is up to 500–700 °C, the main thermal decomposition for polyimides is decarboxylation in  $N_2$ , i.e.,  $O_2$  free. The benzophenone in main chain is decomposed to biphenyl with the release of CO in  $N_2$ , indicating that biphenyl is more stable during the decomposition [35, 36].

The dynamic mechanical properties of the co-PI films are investigated by DMA. The plots of  $\tan\delta$  v.s. temperatures are shown in Fig. 7, and  $T_g$ s as the peak of  $\tan\delta$  are listed in Table 2. The  $T_g$ s of the co-PI films increase from 408 to

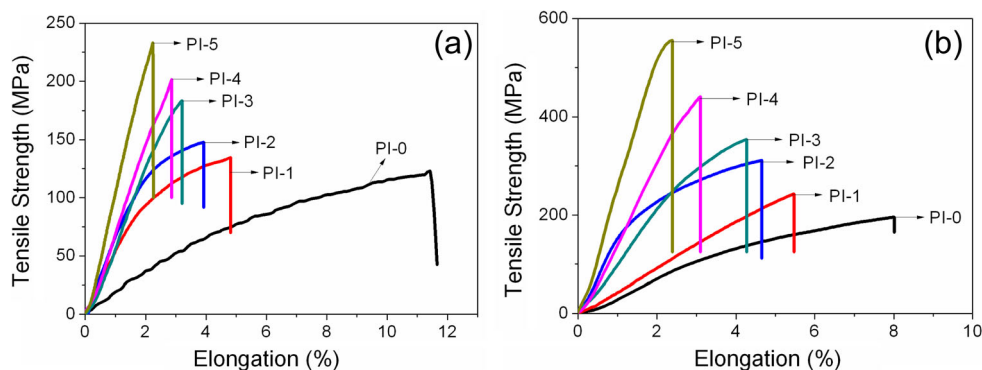
438 °C due to the addition of BAPBBI.  $T_g$ s of polymers are affected by flexibility of backbone, polar groups and nature of side groups, so the high rigidity of molecular chains and intensive inter-/intra-molecular interaction contribute to the high  $T_g$ s. For the copolyimides, the charge-transfer complexes between molecular chains improve the intermolecular interactions, and consequently, the incorporation of BAPBBI in the macromolecular chains increases the  $T_g$ s of the high performance polymers.

As indicated in Fig. 8, the co-PI films exhibit slightly shrinkage from room temperature to 430 °C. The linear coefficient thermal expansions are  $-45.5$  (371 °C),  $-27.4$  (397 °C),  $-24.2$  (412 °C),  $-21.7$  (415 °C),  $-15.4$  (428 °C) and  $-11.7$  (430 °C) ppm/°C for PI-0, PI-1, PI-2, PI-3, PI-4 and PI-5, respectively. Apparently, the thermal shrinkage degree at high temperature is sharply reduced due to the introduction of BAPBBI in the main chains. The bi-benzimidazole unit contributes more rigidity and steric hindrance to the polymer chains, lowers the movement ability of molecular chain, and thus keeps the better dimension stability.

Figure 9 shows the UV-vis spectra of the co-PI films. The values of the cutoff wavelength, the transparency at 800 nm and chromaticity are listed in Table 3. The co-PI films are light brown in color and have chromaticity of 2.0 to 7.0, which depends on the original color appearance and inner conjugative effects of BAPBBI monomer. The cutoff wavelength ranges from 480 to 549 nm while the transmission at 800 nm ranges from 81.2 to 87.2 %. The cutoff wavelength increases with the increased content of BAPBBI, associating with the gradually decreased transmission. Introducing a small quantity of BAPBBI into the backbone will drastically deepen the chromaticity of co-PI films. However, the transmissions of all samples are higher than 80 %, proving that the films possess good optical properties. The symmetrical bi-benzimidazole unit can produce strong conjugative effects which induce the formation of charge-transfer complexes in intra-/inter-macromolecules and electron-donor-acceptor. Thus the films provide lower optical transparency at higher cutoff wavelength.

The mechanical properties of the samples were measured in the film-tensile mode, and the results are shown in Fig. 10a

**Fig. 10** Mechanical properties of the co-PI films: (a) original films; (b) stretched films with the drawing ratio of 150 %



**Table 4** Mechanical properties of the co-PI films

Sample	Tensile strength (MPa)		Tensile modulus (GPa)		Elongation (%)	
	Original	Stretched	Original	Stretched	Original	Stretched
PI-0	123	195	2.66	4.69	11.42	8.01
PI-1	135	243	4.84	8.83	6.84	4.81
PI-2	148	318	7.27	28.28	5.92	4.21
PI-3	183	354	6.11	22.65	5.21	3.21
PI-4	201	441	9.84	24.21	4.87	2.87
PI-5	233	554	12.84	38.57	3.24	2.24

and Table 4. The tensile strength of the co-PI films increases from 123 to 233 MPa upon the increased content of BAPBBI, an increase by almost a 100 %. The initial modulus increases from 2.66 to 12.84 GPa, by almost 400 %, while the elongation decreases from 11.42 to 3.24 %. The mechanical properties mainly depend on the polymer structure and intermolecular interactions. The introduction of BAPBBI obviously increases the proportion of rigid heterocyclic structure, which is regarded as the main impact factor of the enhanced mechanical properties. CTC complexes derived from the bi-benzimidazole unit, imide rings and benzene rings further improve mechanical properties.

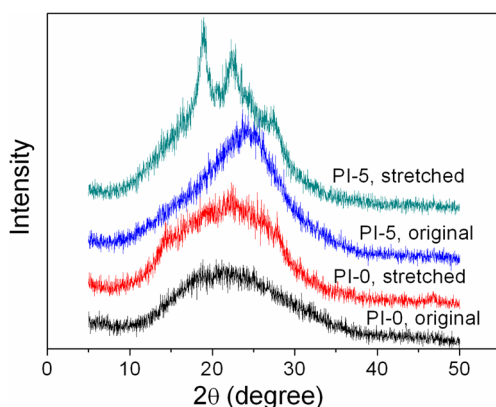
For further enhancing the mechanical properties of the films, the films were stretched with a drawing ratio of 1.5 at 450 °C. After the heat drawing, the relationship between the polymer structure and the stretched sample code is PI-0 (ODA:BAPBBI=10:0), PI-1 (ODA:BAPBBI=9:1), PI-2 (ODA:BAPBBI=7:3), PI-3 (ODA:BAPBBI=5:5), PI-4 (ODA:BAPBBI=3:7), PI-5 (ODA:BAPBBI=1:9), respectively. The mechanical properties of the drawn films are shown in Fig. 10b, and data are summarized in Table 4. Apparently, the thermal drawing process enhances the mechanical properties significantly. The tensile strength ranges from 195 to 554 MPa, the initial modulus ranges from 4.69 to 38.57 GPa, and the elongation at break decreases to 8.01 %–2.24 %. The macromolecular chains can be stretched out along the stretch direction to show a relative high orientation,

so the tensile strength and initial modulus exhibit remarkable improvement, especially in initial modulus.

The WAXD patterns of the co-PI films are shown in Fig. 11. It can be seen that the PI-0 and PI-5 original films exhibit no sharp discernible peaks but wide halos at around  $2\theta=20.5^\circ$  and  $24.5^\circ$  as the  $\pi$ - $\pi$  stack of benzene ring and heterocyclic rings, revealing that the cured films have amorphous structure [37]. The diffraction peak of PI-5 is much sharper than that of PI-0, indicating that the introduction of BAPBBI increases the packing order of the molecular chain. It is also consistent with the previous experimental results of deeper color and higher mechanical properties for PI-5. Due to the heat drawing, the diffraction peak of the sample becomes sharper and shifts towards lower scanning angle, indicating the macromolecular orientation along the stress direction and more ordered molecular chain packing. For PI-5, the sharp discernible peaks at  $2\theta=18.9^\circ$  and  $22.5^\circ$  indicates a much higher orientation or packing degree of molecular chains.

## Conclusions

BAPBBI, an aromatic diamine containing bi-benzimidazole unit, was successfully synthesized in PPA using one-step method. A series of copolyimide films were prepared via the reaction of aromatic dianhydrides of PMDA with BAPBBI and ODA with various compositions. As expected, the introduction of BAPBBI in the high performance polymer enhances the thermal stability and the mechanical properties. For instance, the  $T_g$ s of the sample PI-5 increase by 30 °C, comparing to PMDA-ODA, and the initial decomposition temperatures also increase, which expand the application temperature zone. Moreover, the films were endowed with outstanding thermal oxidation stability in air atmosphere. The films exhibited excellent mechanical properties with the tensile strength at break from 123 to 233 MPa, almost a 100 % enhancement and an initial modulus from 2.66 to 12.84 GPa. With the heat-stretching treatment, the mechanical properties were further improved substantially. The new series of polyimides enrich the variety of high performance polymers and are a promising application in the future industries.

**Fig. 11** Wide-angle X-ray diffraction patterns of the co-PI films



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