

Synthesis and Characterization of High-Performance Polyimides Based on 6,4'-Diamino-2-Phenylbenzimidazole

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ABSTRACT: A new synthesis route was developed to produce the diamine monomer containing benzimidazole units, 6,4'-diamino-2-phenylbenzimidazole (BIA), which was easily prepared by the reduction of 6,4'-dinitro-2-phenylbenzimidazole synthesized via a reaction between 4-nitro-1,2-phenylenediamine and 4-nitrobenzoyl chloride. The composition and structure of the products were confirmed by Fourier transform infrared, NMR, and elemental analysis. A series of polyimides were prepared by the polycondensation of BIA and various dehydrates, pyromellitic dianhydride, 3,3',4,4'-biphenyl tetracarboxylic dianhydride, 4,4'-oxydiphthalic anhydride, and benzophenone tetracarboxylic dianhydride via a traditional two-step procedure. The polyimides exhibit excellent thermal stability up to 540°C and high glass transition temperature (T_g) in the range of 382–409°C. The polyimide films are tough and flexible and possess good mechanical properties of tensile strength of 222–232 MPa and modulus of 3.1–5.6 GPa without stretching. The polyimides are amorphous state in wide-angle X-ray diffraction patterns, whereas small-angle X-ray diffraction patterns show the existence of molecular aggregation. The rigid-rod structure and intermacromolecular hydrogen bond are likely responsible for the excellent properties of the polyimides. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 145–151, 2013

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INTRODUCTION

Aromatic polyimides possess remarkable properties, such as outstanding thermal stability, excellent mechanical properties, high resistance to solvents, and great electrical properties. Because of these outstanding properties, the high-performance polymers have been extensively used in various applications, such as automobile and aircraft parts, electronic packaging, films, adhesives, and matrix materials for composites, which are supplied in the form of films, fibers, resins, or coatings.^{1–5} To further improve the properties, introduction of heterocyclic units in macromolecular chains has been developed. A series of novel polyimides containing heterocyclic units in the main chains were reported over past decades. Hsu et al.⁶ prepared a polyimide-benzoxazole with a good thermal stabilities by thermal cyclization of the precursor poly(amic acid hydroxyamide). A series of polyimide-benzbithiazole prepared via a two-step method by Kimura⁷ exhibited poor solubility and good thermal stability. Hariharan et al.⁸ reported soluble polyimides containing pyridine moiety and the polyimides exhibited good thermal stability and mechanical properties. Homo- and copolyimides containing pyrimidine units were prepared by Xia et al.,⁹ show-

ing excellent thermal stability and mechanical properties. Hergenrother and Havens¹⁰ synthesized a series of polyimide containing benzimidazole units and quinoxaline units, respectively, and the polyimides exhibit high glass transition temperature and good thermal stability. Rusu et al.¹¹ prepared copoly (peryleneimide)s containing oxadiazole rings, which exhibit a good solubility in *N*-methyl-2-pyrrolidone (NMP), a good thermal stability and relatively lower glass transition temperature.

Aromatic polybenzimidazoles (PBIs) with the excellent thermal stability were successfully prepared by Marvel and coworkers.^{12–14} The polyimides containing benzimidazole units with good thermal stability have been prepared by Preston et al.^{15,16} Polyimides containing benzimidazole moieties prepared by Berrada et al.¹⁷ and Choi et al.¹⁸ exhibited good soluble and heat-resistant properties. Recently, polyimides containing benzimidazole moieties were prepared by two-step procedure using 6,4'-diamino-2-phenylbenzimidazole (BIA) as a monomer, resulting in good mechanical properties.¹⁹

In this work, we developed a new synthesis route to produce the diamine monomer containing benzimidazole units, BIA. It was easily synthesized via formation of imidazole ring in NMP. As a

comparison, the synthesis of BIA was very complicated via amidation and ring formation, reported in the past.^{19,20} Based on BIA, a series of polyimides were prepared by the reaction of diamine with various dehydrates using a traditional two-step procedure. Tough and flexible polyimide films with good thermal stability and mechanical properties were expected to obtain by introducing benzimidazole units into the main chains of polyimides. The structure and properties of the polyimides were studied in detail.

EXPERIMENTAL

Materials

NMP, ethanol, *p*-phenylenediamine (PDA), hydrazine hydrate, and palladium–charcoal catalyst Pd/C were purchased by Sino-pharm Chemical Reagent. *N,N*-dimethylacetamide (DMAc) with the water containing <100 ppm was supplied from Shanghai Jinshan Jingwei Chemical. 4-Nitro-1,2-phenylenediamine was kindly supplied by Zhejiang Pinhu Chemical. 4-Nitrobenzoyl chloride was obtained from Jiangsu Jintan Chemical. Pyromellitic dianhydride (PMDA), 3,3',4,4'-biphenyl tetracarboxylic dianhydride (BPDA), and 4,4'-oxydiphthalic dianhydride (ODPA) were supplied by Shanghai Synthetic Resin Research Institute. 3,3',4,4'-Benzophenone tetracarboxylic dianhydride (BTDA) was purchased from Johnson Matthey Company. All the materials were used without purifying.

Monomer Synthesis

6,4'-Dinitro-2-phenylbenzimidazole. NMP (150 mL), 4-nitro-1,2-phenylenediamine (25 g), and 4-nitrobenzoyl chloride (31 g) were added into a 250-mL three-neck flask, and the temperature was heated to 190°C. The reaction kept for 6 h, and then the mixture was poured into distilled water. The precipitate was filtered, washed with distilled water, and recrystallized from DMAc to give yellow product (yield: 70%, m.p.: 356°C). Fourier transform infrared (FTIR) (KBr, cm⁻¹): 3340 (NH stretching), 1510 (NO₂ asymmetric stretching), 1340 (NO₂ stretching). ¹H NMR (DMSO-*d*₆, 400 MHz): 13.98 (br 1H H_d), 8.63 (d 1H H_a), 8.47 (dd 4H H_e H_f), 8.19 (dd 1H H_c), 7.79 (d 1H H_b). Elemental analysis: calculated for C₁₃H₈N₄O₄, (284.23), C: 54.94%, H: 2.84%, N: 19.71%. Found: C: 54.79%, H: 2.78%, N: 19.60%.

6,4'-Diamino-2-phenylbenzimidazole. The suspension of 6,4'-dinitro-2-phenylbenzimidazole (DNBI; 5.2 g) and Pd/C (0.41 g) in 150 mL ethanol was heated to refluxing, and hydrazine hydrate (41 mL) was dripped in half an hour. The mixture was stirred for 6 h, and then cooled to room temperature. The solution was poured into distilled water and neutralized with aqueous HCl to give a white precipitate, which was separated by filtration and then recrystallized from dimethylformamide (DMF)/water to give brown product (yield: 70%, m.p.: 241°C). FTIR (KBr, cm⁻¹): 3300–3500 (NH₂), 1633 (NH deformation). ¹H NMR (DMSO-*d*₆, 400 MHz): 11.85 (br 1H H_e), 7.72 (d 2H H_f), 7.19 (d 1H H_c), 6.62 (d 3H H_g H_b), 6.46 (dd 1H H_d), 5.47 (s 2H H_h), 4.83 (br 2H H_a). Elemental analysis: Calculated for C₁₃H₁₂N₄, (224.27), C: 69.54%, H: 5.21%, N: 24.95%. Found: C: 68.96%, H: 5.39%, N: 24.74%

Polymer Synthesis

The polyimides were prepared by a two-step process. Poly(amic acid)s, the precursors of polyimides, were prepared by polycon-

densation of diamines containing benzimidazole moieties with various dianhydrides. A typical polymerization process was carried out as follows: 4.220 g BIA was dispersed in 50 mL DMAc in a 100-mL three-neck flask. Under nitrogen flow, 4.104 g PMDA was slowly added into the slurry. The mixture was stirred about 8 h to form a viscous PAA solution with a solid content of 15 wt %.

The PAA film was prepared by casting the solution onto a glass plate and drying the film in a vacuum oven at 60°C for 7 h. The precursor film was heated and converted to polyimide film under vacuum at 150, 250, 300, and 400°C each for 1 h, and the products were thus obtained. The polyimide derived from BPDA and PDA was carried out the same process in DMAc.

Characterization

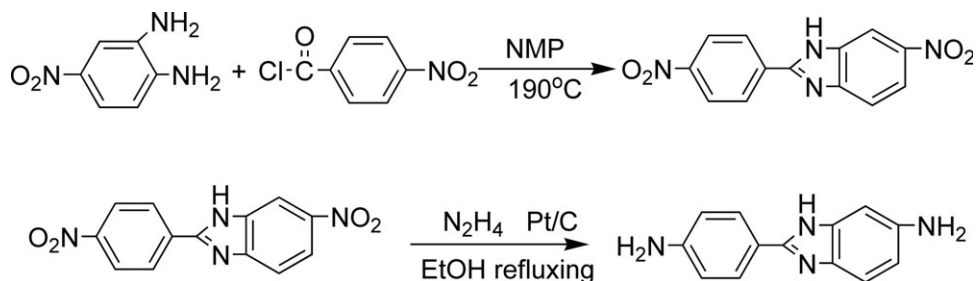
¹H NMR spectra of intermediate and monomer were recorded on a Bruker Unity Avance 400 NMR Spectrometer, in which DMSO-*d*₆ was used as a solvent. FTIR was recorded on a Nicolet 8700 infrared spectrometer using KBr pellet and film. The inherent viscosities were measured with an Ubbelohde viscometer at 25°C with DMAc as a solvent at a 0.5 g/dL. The melting point of intermediate and monomer was observed with differential scanning calorimetry (DSC) on a Mettler Toledo DSC822e at a heating rate of 10°C/min. Thermogravimetric analysis (TGA) was performed using a Netzsch TG 209F1 at a heating rate of 10°C/min in nitrogen. Dynamic mechanical analysis (DMA) was performed on thin film specimen on a TA instrument DMA Q800 at a heating rate of 5°C/min and a load frequency of 1 Hz in nitrogen. The mechanical properties were investigated by a WDW-3020 at a drawing rate of 5 mm/min. Wide-angle X-ray diffraction (WAXD) measurements were performed on a Rigaku D/Max-2550 PC X-ray diffractometer (40 kV and 100 mA), using Cu K_α with λ = 0.1514 nm. Small-angle X-ray diffraction (SAXS) experiments were carried out on Anton Paar SAXSess MC² Small-angle X-ray Scattering System using Cu K_α with λ = 0.1514 nm.

RESULTS AND DISCUSSION

Monomer Synthesis

BIA can be prepared by one-step synthesis with reduction free in polyphosphoric acid (PPA)²¹ or by the reduction of dinitro intermediate DNBI. Ayala et al.²² prepared DNBI by the reaction of 4-nitro-1,2-phenylenediamine and 4-nitrobenzoyl chloride in methanesulfonic acid (MSA) containing P₂O₅. DNBI can be prepared by a two-step procedure using 4-nitro-1,2-phenylenediamine reacted with 4-nitrobenzoyl chloride as starting materials to yield 2'-amino-4,5'-dinitrobenzimidazole and then the product was cyclodehydrated in PPA.^{19,20} In our report, NMP is used as a solvent to prepare DNBI, which is a facile route to manipulate and more safety, compared to strong acid PPA or MSA. In detail, the preparation of BIA includes two steps: First step is synthesis of the intermediate DNBI via amination reaction and cyclization of 4-nitro-1,2-phenylenediamine with 4-nitrobenzoyl chloride in NMP, and second step is that the DNBI is reduced into the corresponding diamine via hydrazine Pd/C catalyzing, as illustrated in Scheme 1.

FTIR, ¹H NMR, and elemental analysis were used to confirm the structure of the intermediate compound and the final diamine. FTIR spectrum of the dinitro compound shows an



Scheme 1. Synthesis of BIA.

absorption peak at 3340 cm^{-1} caused by NH stretching of the imidazole ring and two characteristic absorption peaks at 1510 and 1340 cm^{-1} . After the reduction, the characteristic absorption peaks of nitro group disappeared, and the absorption peaks at $3300\text{--}3500\text{ cm}^{-1}$ suggest the formation of amine groups (Figure 1).

Figure 2 gives the $^1\text{H NMR}$ spectra of DNBI and BIA. All the protons of aromatic ring are in the range of $6.4\text{--}8$. After reduction, the proton of the benzimidazole ring shifts from 13.98 to 11.85 ppm . The peaks at 5.47 and 4.83 ppm are assigned to amine protons. The assignment of proton peaks is good agreement with the chemical structure of the compounds. The elemental analysis results in Monomer Synthesis Section also agree with the calculated values for these chemical compositions, revealing the high purity products.

Polymer Synthesis

Polyimides containing benzimidazole moieties were obtained by reacting BIA with various aromatic dianhydrides via a conventional two-stage method, as shown in Scheme 2. Each of the aromatic dianhydrides (PMDA, BPDA, BTDA, and ODPA) can react with BIA to get viscous solution. The inherent viscosity and film formation of PAAs are listed in Table I. These PAA solutions were subsequently cast onto a glass plate to obtain PAA films, and the films were placed in a vacuum oven and heated at various temperatures to prepare the final polyimides. The

three films of PI-BPDA, PI-BTDA, and PI-ODPA are tough and flexible, whereas the PI-PMDA film exhibits a fragile nature. FTIR spectra confirm that the PAAs completely convert into corresponding polyimides. As shown in Figure 3, the characteristic absorption peaks around $1773\text{--}1775\text{ cm}^{-1}$ and $1715\text{--}1716\text{ cm}^{-1}$ are assigned to $\text{C}=\text{O}$ asymmetric stretching and $\text{C}=\text{O}$ stretching, respectively. The peak around $1365\text{--}1372\text{ cm}^{-1}$ is caused by $\text{C}\text{--}\text{N}$ stretching. The absorption around $726\text{--}746$

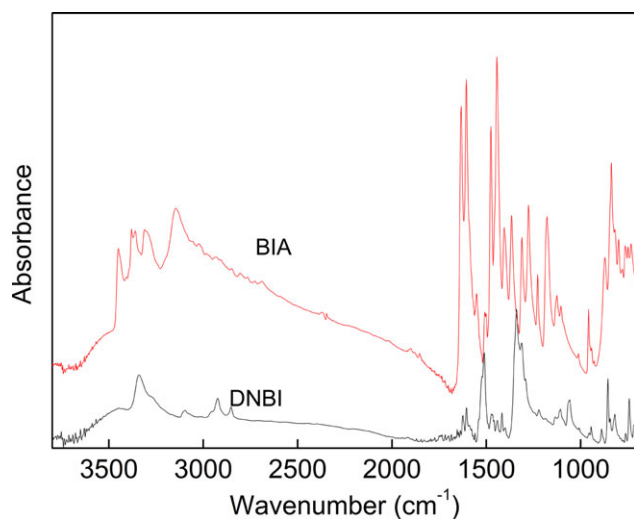


Figure 1. FTIR spectra of DNBI and BIA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

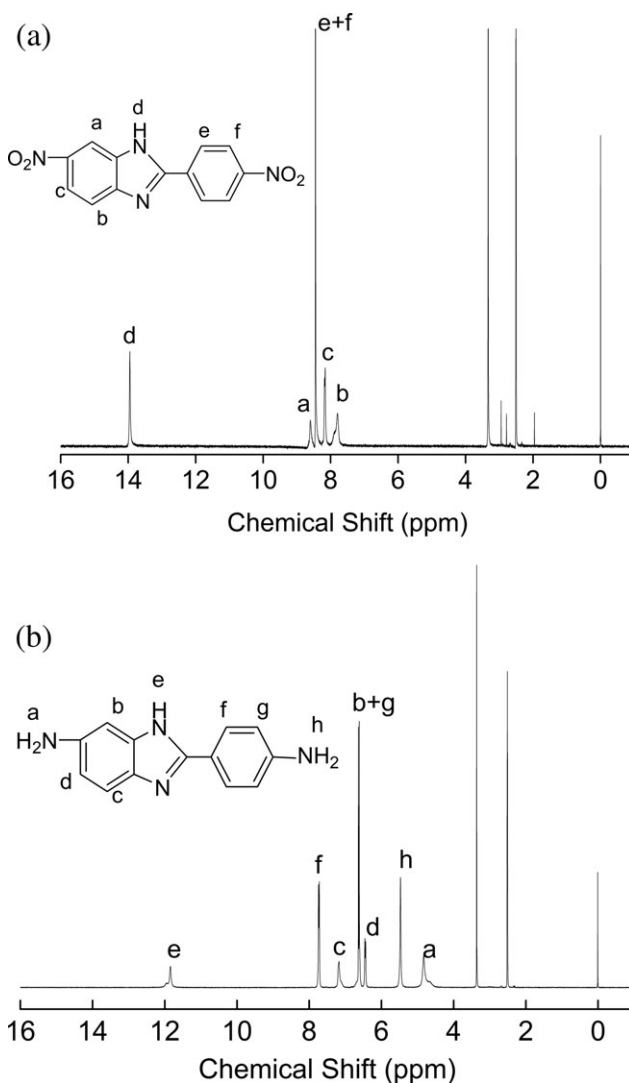
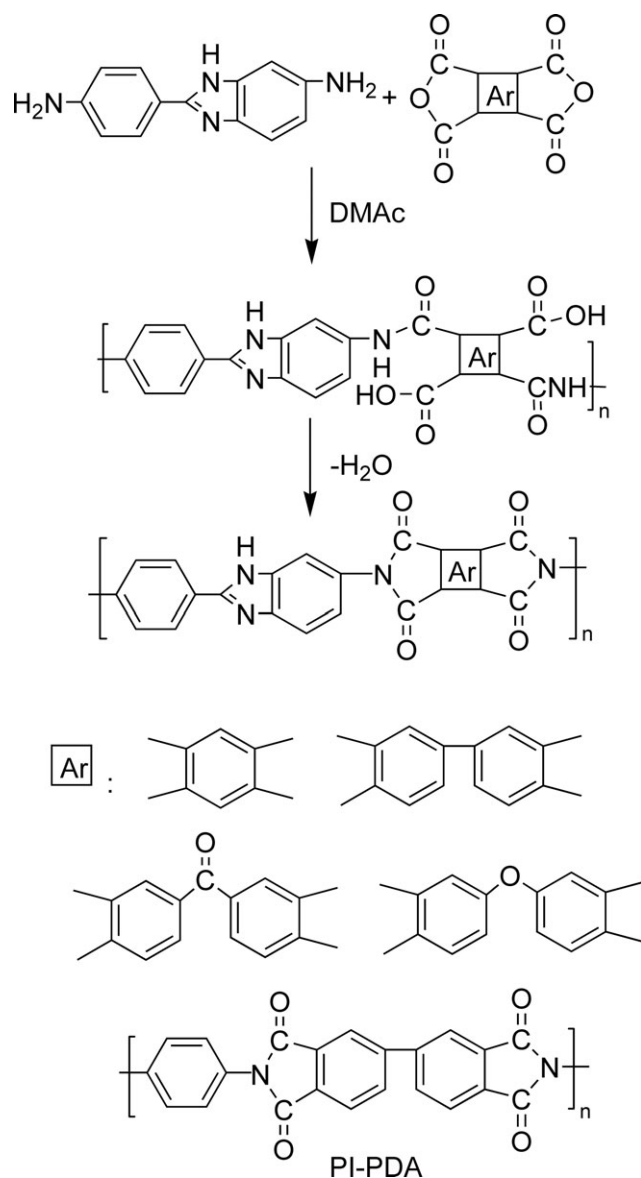


Figure 2. NMR spectra of DNBI (a) and BIA (b).



Scheme 2. Synthesis of polyimides derived from BIA.

cm^{-1} confirms the formation of imide ring. Absorption around $3345\text{--}3356\text{ cm}^{-1}$ is caused by N–H stretching of benzimidazole ring, whereas the polyimide synthesized by BPDA-PDA(PI-PDA) has no absorption in this area.

Table I. Inherent Viscosity and Film-Forming Capability of PAAs

Sample	η_{inh} (dL/g)	Film forming capability of PAA	PI film quality
PI-PMDA	1.11	Good	Fragile
PI-BPDA	1.64	Good	Tough and flexible
PI-BTDA	0.36	Good	Tough and flexible
PI-ODPA	0.69	Good	Tough and flexible

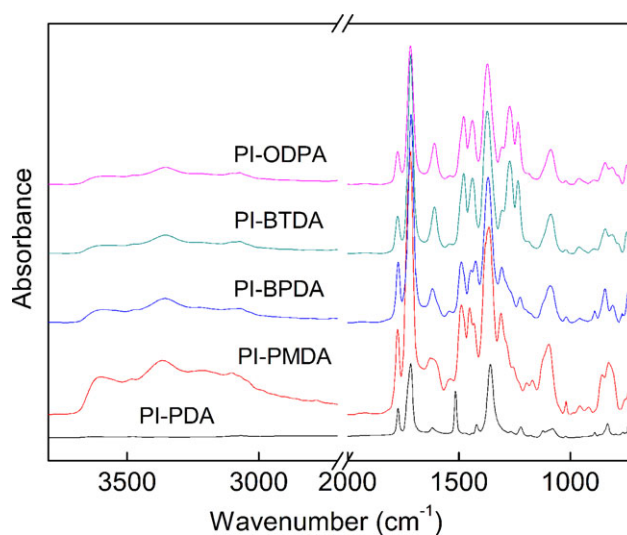


Figure 3. FTIR spectra of various polyimides. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Properties of Polyimides

Thermal properties of polyimides were investigated by DMA and TGA, and the resulting data are listed in Table II. The glass transition temperature (T_g) of the polyimides was examined by DMA (Figure 4). Generally, the peak in the plot of $\tan \delta$ versus temperature is considered as T_g . The polyimides exhibit high glass transition temperature ranging $378\text{--}408^\circ\text{C}$, depending on the various dianhydrides. Among them, PI-PDA possesses the lowest T_g . The polyimide of BPDA-BIA possesses the highest T_g up to 409°C , which is higher than PI-PDA without benzimidazole moieties in the main chain. As a comparison, the polyimides containing BTDA or ODPA exhibit the relative flexible nature with a lower T_g .

As shown in Figure 5 and Table II, TGA spectra indicate that the polyimides exhibit a good thermal stability under nitrogen. The 5% weight loss temperature (T_5) ranges from 536 to 558°C , and the 10% weight loss temperature (T_{10}) ranges from 571 to 590°C . Apparently, the polyimide of PMDA-BIA shows the best thermal stability among polyimides derived from BIA, that is, T_5 , T_{10} , and char yield are 558°C , 590°C , and 71.2%, respectively. The T_{10} of polyimides synthesized by 6,4'-diamino-2'-trifluoromethyl-2-phenylbenzimidazole and OPDA, BTDA reported by Choi et al.¹⁸ were 531°C and 548°C , respectively, which were lower than polyimides derived from BIA. PI-PDA

Table II. Thermal Properties of Polyimides

Sample	T_g ($^\circ\text{C}$) From DMA	T_5 ($^\circ\text{C}$) from TGA	T_{10} ($^\circ\text{C}$) from TGA	Char yield (%) from TGA
PI-PDA	350	590	611	64.2
PI-PMDA	-	558	591	71.2
PI-BPDA	409	546	580	68.3
PI-BTDA	378	536	571	66.4
PI-ODPA	382	539	580	66.3

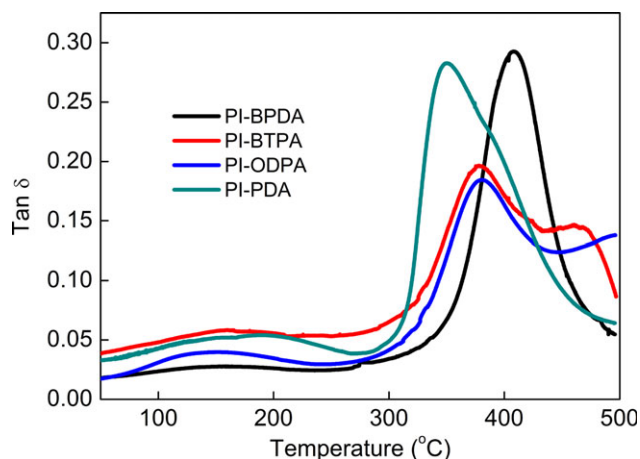


Figure 4. Plots of $\tan \delta$ versus temperature in DMA of polyimides. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

gives the best thermal stability of polyimides listed in Table II, which means the thermal stability of imide ring is better than imidazole ring.

The tensile properties are listed in Table III. The polyimides containing benzimidazole units possess good mechanical properties with a tensile strength of 222–232 MPa, tensile modulus of 3.1–5.6 GPa, and elongation at break of 6.2–9.9%. The PI-BPDA has a better tensile strength, longer elongation, comparing to the PI-PDA, which exhibits the similar mechanical properties reported by Wang et al.¹⁹ In our previous report,²³ 2,2'-p-phenylenebis(5-aminobenzimidazole) (PBABI) was synthesized, and a series of polyimides based on PBABI were prepared. Compared with the mechanical properties of polyimide derived from BIA, polyimides containing bis-benzimidazole unit exhibit relatively high modulus and lower tensile strength, which may be caused by higher polymer chain stiffness, resulting in high T_g s of polyimides based on PBABI. This result reveals that the

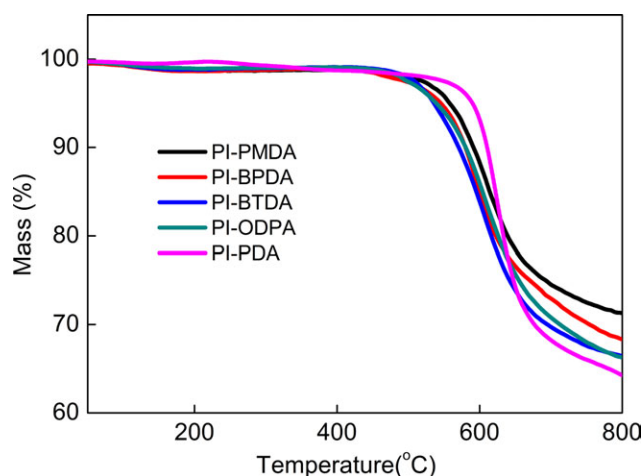


Figure 5. TGA curves of polyimides under nitrogen. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Mechanical Properties of Various Polyimide Films

Sample	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)
PI-PDA	134	5.7	4.9
PI-BPDA	232	5.6	6.2
PI-BTDA	223	3.3	9.3
PI-ODPA	222	3.1	9.9

introduction of benzimidazole units into main chain greatly improves the mechanical properties of polyimide.

The solubility of polyimides greatly depends on their chemical structures which decide the intermolecular interactions and chain density. All the polyimides are insoluble in common solvents, such as dimethyl sulfoxide (DMSO), DMF, DMAc, NMP, tetrahydrofuran (THF), or *m*-cresol. However, the products are soluble in H_2SO_4 at room temperature. The fact means that the rigid chain structure and strong intermolecular interactions give

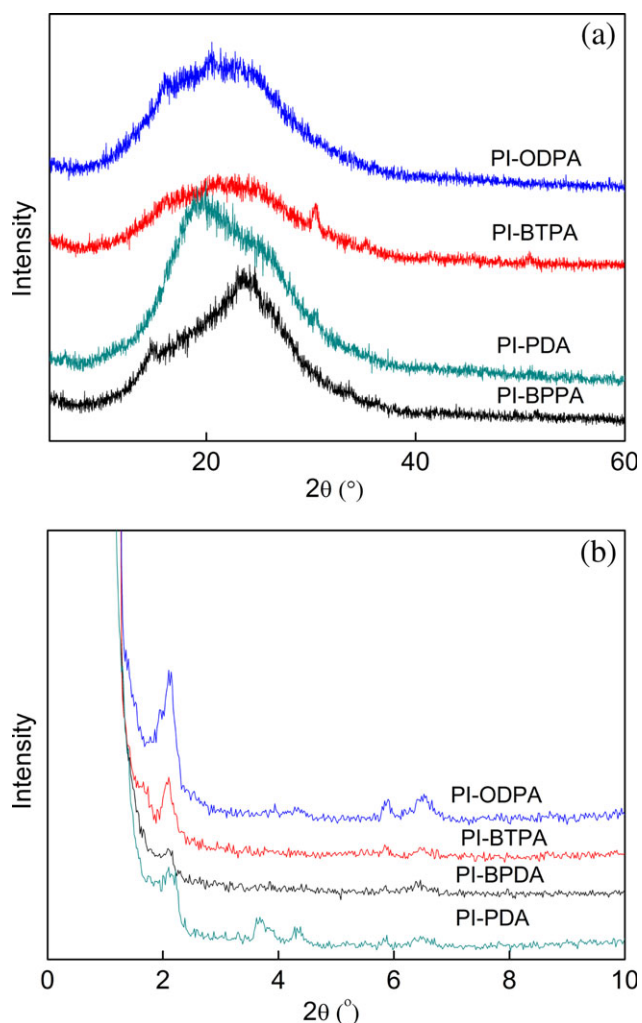


Figure 6. WAXD (a) and SAXS (b) patterns of polyimide films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

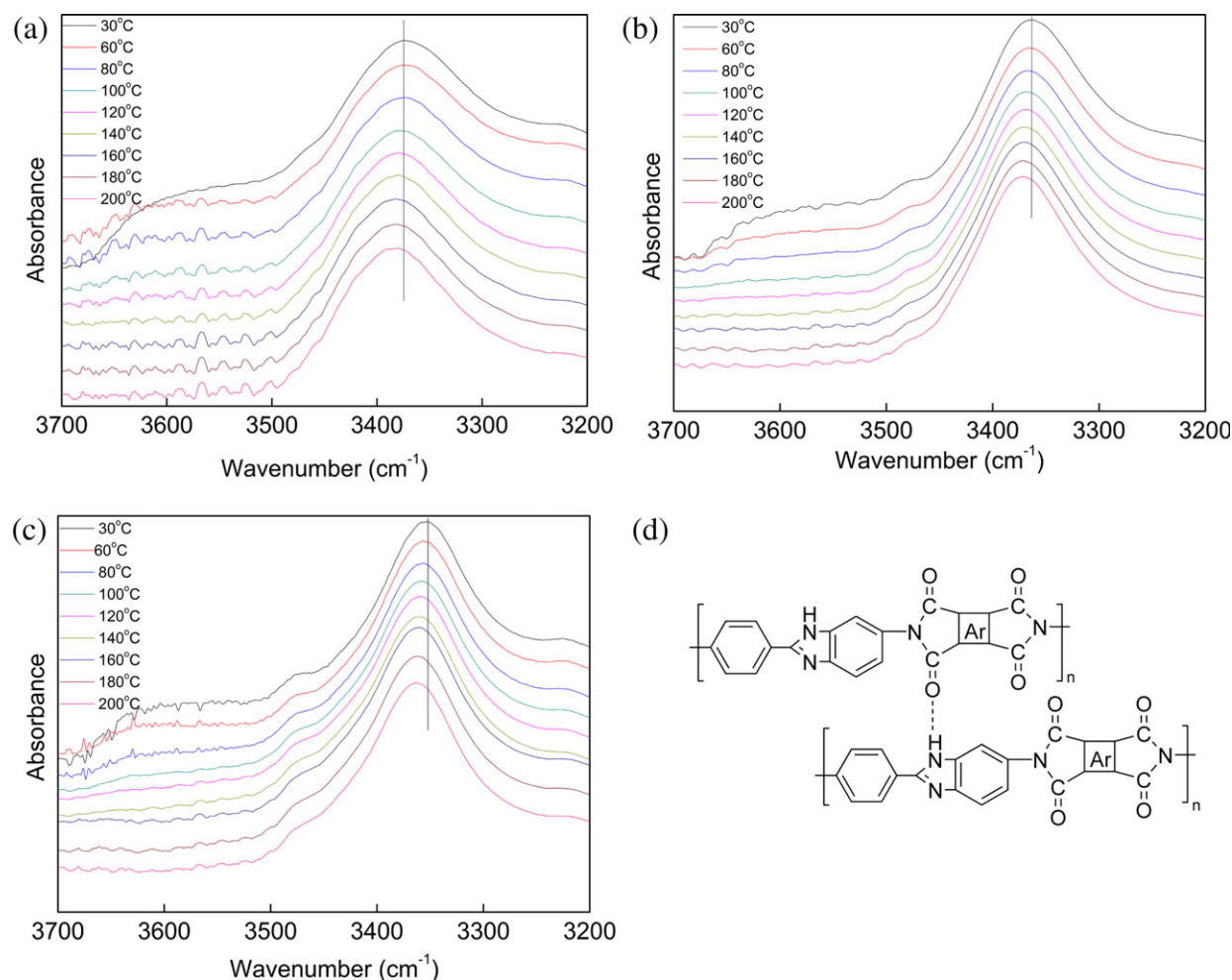


Figure 7. FTIR absorption of polyimides in the temperature range 30–200°C at 3700–3100 cm⁻¹: (a) PI-BPDA, (b) PI-BTDA, (c) PI-ODPA, and (d) proposed hydrogen-bond interaction of intermacromolecules. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

a high chain packing density and lead to a poor solubility of polyimide.

WAXD were used to investigate the aggregation state of polyimide films, as shown in Figure 6. The polyimides have a smooth peak around $2\theta = 10\text{--}30^\circ$ in WAXD patterns, revealing the amorphous state of the polyimide. The structure of polyimide films were further studied by SAXS. Apparently, the polyimides exhibit a peak at $2\theta = 2^\circ$, which confirms the existence of molecular aggregation in the polyimide films.²⁴ As it shown in Figure 6(b), PI-PDA displays a higher deflection in SAXS than PI-BPDA at $2\theta = 2^\circ$. The PI-ODPA shows a stronger deflection than PI-BPDA, PI-PDA at $2\theta = 2^\circ$, indicates a higher aggregation of the polymer chains.

Hydrogen bond between —NH— in benzimidazole and —C=O in polyimide can be easily formed, as illustrated in Figure 7(d). FTIR was used to study the hydrogen bond in the polymer blends of polybenzimidazole and polyimide.^{25–27} To confirm the existence of hydrogen bond, the polyimide film was heated and the FTIR was used to *in situ* monitor the changes of the absorbance at *ca.* 3370 cm⁻¹. As shown in Figure 7(a–c), when poly-

imides are heated to 80°C or higher temperature, the absorption peak of —NH— at $\sim 3370\text{ cm}^{-1}$ shifts to higher wavenumber. This phenomenon confirms the existence of hydrogen bond in the polyimides due to benzimidazole rings here.²⁸ This may be important to the enhanced mechanical properties, as mentioned above.

CONCLUSIONS

The benzimidazole (BIA) was successfully synthesized by a facile route. A series of polyimides were prepared by the polycondensation of BIA and one of dehydrates, PMDA, BPDA, BTDA, and ODPA. Tough and flexible polyimide films were obtained after the thermal imidization of the precursors. As a result, the polyimides exhibited the excellent thermal stability, for instance, the T_g s in the range of 382–409°C and 5% weight loss temperatures (T_5) in the range of 539–558°C in nitrogen. The polyimide films possess good mechanical properties of tensile strength of 222–232 MPa, modulus of 3.1–5.6 GPa, and elongation 6.2–9.9% without stretching. The high-performance polymers showed an amorphous state with molecular aggregation. The

introduction of benzimidazole rings into polymer backbone enhanced the rigidity and formed hydrogen bond between intermolecular chains, leading to the improved properties of polyimide. The improvement of polyimide properties makes it possible utilized as polyimide film and fiber.

ACKNOWLEDGMENTS

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