

Study on synthesis and characterization of novel polyimides derived from 2,6-Bis(3-aminobenzoyl) pyridine

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Abstract

A new kind of aromatic diamine monomer containing pyridine unit, 2,6-Bis(3-aminobenzoyl)pyridine (BAPB), was synthesized by the Friedel–Crafts acylation of benzene with 2,6-pyridinedicarbonyl chloride to form 2,6-Dibenzoylpyridine (DBPY), the nitration of DBPY with nitric acid (99%) to form dinitro compound (BNBP), and the deoxidization of BNBP using SnCl₂ in ethanol, successively. The diamine monomer BAPB reacted with various aromatic dianhydrides to prepare a series of poly(amic acid), meanwhile, corresponding polyimides were obtained via the thermal or chemical imidization procedures of the resulting poly(amic acid). The poly(amic acid) solutions in *N,N*-dimethylacetamide (DMAc) would be coated onto a plane-glass and could be thermally converted into transparent and tough polyimides films. The compositions, structures of the resulting monomer including corresponding intermediates, as well as the structure, physical property, thermostability, thermal behavior, solubility and solution viscosity of the resulting polyimides were characterized by means of FT-IR, ¹H-NMR, ¹³C-NMR, MS (EI), DSC, TGA, wide-angle X-ray diffraction, elemental analysis methods, and the effects of reactive conditions on the above structures and properties were studied, too.

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1. Introduction

Polyimides (PI) based on aromatic ring structures or their copolymers are well known as high performance polymers due to their excellent thermal and thermooxidative stabilities, outstanding mechanical and electrical

properties, therefore, all kinds of polyimides have been widely used in the fields of adhesives, composite matrices, fibers, films, foams, as well as microelectronic materials [1–4]. With enhancement of the requirements of the microelectronics devices for increasing signal propagation speed and wiring line density, as well as reliability and moisture resistance, for examples, polyimide materials have been widely employed in the microelectronics industry and have shown excellent combined properties including easy processing and pattern making, low curing temperatures, low dielectric constants and

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dissipation factors, low stress and ionic impurity levels, high electric insulation, good mechanical properties, as well as moisture and hydrothermal resistance [5–7]. Although significant improvements in the performances of polyimide materials have been made in recent years [8–10], the further development of polyimides is still required to meet increasing demands and reduce production costs.

For the polyimides materials, synthesis of newly heteroaromatic monomers and corresponding polyimides that have both good processability and maintained thermal stability would be very interesting, e.g. new kinds of heteroaromatic diamine or dianhydride monomers are always focused and employed in the synthesis of polyimides, in other words, newly aromatic monomers would play very important roles in synthesis of advanced polyimide materials [11,12]. In general, the heteroaromatic structures in the main chain of a polymer would impart certain properties to it, while pyridine with heteroaromatic structure would have excellent stabilities derived from its molecular symmetry and aromaticity, as well as polarizability resulting from nitrogen atom in pyridine ring [13,14], so new kinds of heteroaromatic diamine, dianhydride or other monomers holding pyridine unit should have contributions for the thermal stability, chemical stability, retention of mechanical property of the resulting polymer at elevated temperature [15], meanwhile, the resulting polymer holding pyridine ring should also exhibit a good solubility during processing. Consequently, some researchers have been also focused on the adoption monomers containing pyridine nucleus structures to synthesize novel heteroaromatic polymers that have good thermostability and processability [16–19].

In this work, 2,6-Bis(3-aminobenzoyl)pyridine, a new kind of heteroaromatic diamine monomer, has been synthesized successfully, and novel polyimides have been also prepared by the polycondensation of 2,6-Bis(3-aminobenzoyl)pyridine with different commercially available aromatic tetracarboxylic dianhydrides. Meanwhile, the composition and structure of 2,6-Bis(3-aminobenzoyl)pyridine and the corresponding intermediates, as well as the structures and properties of the resulting polyimides were studied by means of FT-IR, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, MS (EI), DSC, TGA, X-diffraction and elemental analysis methods.

2. Experimental

2.1. Materials

2,6-pyridinedicarboxyl chloride (from TCI), 4,4'-oxydiphthalic anhydride (ODPA, Shanghai Nanxiang Chemical Co., China), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA, Beijing Chemical Reagents

Corp., China) and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA, from Aldrich) were recrystallized from acetic anhydride before use. *N,N*-dimethylacetamide (DMAc) were purified by distillation under reduce pressure over calcium hydride and stored over 4 Å molecular sieves. All other solvents were obtained from various commercial sources and used without further purification.

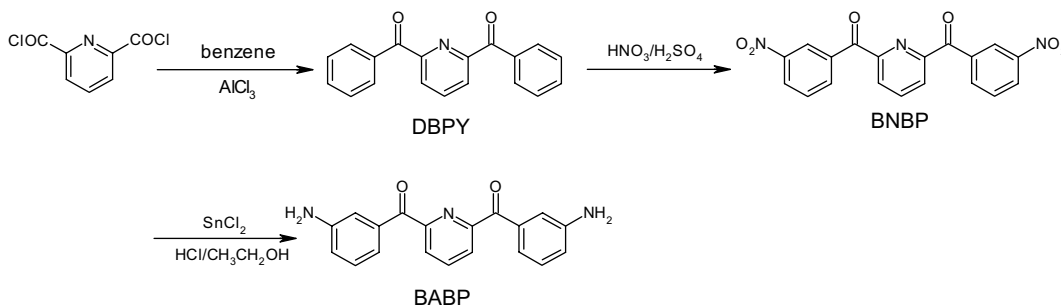
3. Measurements

The inherent viscosities of the resulting poly(amic acid)s and polyimides were measured with an Ubbelohde viscometer at 30 °C. FT-IR spectra (KBr) were recorded on a Nicolet NEXUS 670 fourier transform infrared spectrometer. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were measured on a JEOL EX-300 spectrometer using tetramethylsilane as the internal reference. Elemental analyses were determined by a Perkin–Elmer model 2400 CHN analyzer. Analyses of differential scanning calorimetry (DSC) were performed on a Perkin–Elmer differential scanning calorimeter DSC 7 or Pyris 1 DSC at a scanning rate of 20 °C min^{-1} in flowing nitrogen (30 $\text{cm}^3 \text{min}^{-1}$), glass transition temperatures (T_g) were read at the DSC curves at the same time. Thermogravimetric analysis (TGA) was conducted with a TA Instruments TGA 2050, and experiments were carried out on approximately 10 mg of samples in flowing air (flowing rate = 100 $\text{cm}^3 \text{min}^{-1}$) at a heating rate of 20 °C min^{-1} . Wide-angle X-ray diffraction measurements were performed at room temperature (about 25 °C) on a Siemens Kristalloflex D5000 X-ray diffractometer, using nickel-filtered CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$, operating at 40 kV and 30 mA).

3.1. Monomer synthesis

3.1.1. 2,6-Dibenzoylpyridine (DBPY)

Two hundred milliliters of benzene and 190 g (1.5 mol) of anhydrous aluminum chloride were put into a 500 mL flask to obtain a mixture, with stirring, then 90 g (0.44 mol) of 2,6-pyridinedicarboxyl chloride was gradually added into the flask and the temperature was maintained at 12–18 °C during the addition of 2,6-pyridinedicarboxyl chloride, and then it was kept over 2 h at 12–18 °C. After the addition was complete, the reaction would be continued at 18 °C for another 4 h. The mixture was slowly heated to 40 °C and kept at that for 2 h, finally, the reaction mixture was cooled and poured into 500 mL of a water solution of hydrochloric acid, some white solids were precipitated out, filtering, washing with ethanol, and the crude product obtained was recrystallized from petroleum ether (bp 60–90 °C), the related yield is 81%, melting point is 106–108 °C.



Scheme 1. Synthesis procedure of diamine monomer containing pyridine unit.

FT-IR spectrum exhibited absorption peaks at 3065 cm^{-1} (aromatic C–H), 1671 cm^{-1} (C=O stretching) and 1326 cm^{-1} (C–N stretching); $^1\text{H-NMR}$ (300 MHz, $\text{DMSO-}d_6$, ppm): $\delta = 8.30\text{--}8.28$ (m, 3H), $8.16\text{--}8.12$ (d, 4H), $7.55\text{--}7.60$ (d, 2H), $7.44\text{--}7.39$ (d, 4H); $^{13}\text{C-NMR}$ (300 MHz, $\text{DMSO-}d_6$, ppm): $\delta = 192.8$, 153.2 , 139.3 , 135.6 , 133.1 , 130.6 , 128.1 , 126.2 ; MS(EI): 287 (M^+); elemental analysis: Calcd. C 79.43, H 4.56, N 4.87, while Found C 78.26, H 4.39, N 4.42.

3.1.2. 2,6-Bis(3-nitrobenzoyl)pyridine (BNBP)

22 g (77 mmol) of the above DBPY was first dissolved in 40 mL sulfuric acid in a flask equipped with a thermometer and stirrer, 15 mL of nitric acid (99%) was gradually added at $15\text{ }^\circ\text{C}$ with stirring. The mixture was stirred at $25\text{ }^\circ\text{C}$ for 4 h before being poured into 400 mL of ice to keep the temperature below $15\text{ }^\circ\text{C}$, and white solids precipitated out from the mixture solution. After filtration, the crude product obtained was recrystallized from acetone. The reaction yield is 76% and melting point of the resulting product is at $296\text{--}297\text{ }^\circ\text{C}$.

FT-IR spectrum exhibited characteristic absorptions of the product at 3092 cm^{-1} (aromatic C–H), 1671 cm^{-1} (C=O stretching), 1524 cm^{-1} , 1317 cm^{-1} (C–NO₂ stretching) and 1317 cm^{-1} (C–N stretching), respectively; $^1\text{H-NMR}$ (300 MHz, CD_3COCD_3 , ppm) indicates resonance signals resulting in different protons: $\delta = 8.71$ (s, 2H), $\delta = 8.43\text{--}8.33$ (m, 7H), 7.71 (t, 2H); $^{13}\text{C-NMR}$ (300 MHz, $\text{DMSO-}d_6$, ppm): $\delta = 190.3$, 151.9 , 147.1 , 139.8 , 137.0 , 136.5 , 129.7 , 127.7 , 126.9 , 125.1 ; MS (EI): 377 (M^+); elemental analysis: Calcd. C 60.48, H 2.94, N 11.14, while Found C 59.34, H 2.46, N 10.78.

3.1.3. 2,6-Bis(3-aminobenzoyl)pyridine (BABP)

A mixture consisting of 7.5 g (20 mmol) of the above dinitro compound, 27 g (120 mmol) of anhydrous SnCl_2 and 500 mL of 95% $\text{C}_2\text{H}_5\text{OH}$ was put into a reaction flask and stirred, while 60 mL of concentrated HCl was added slowly. After addition of hydrochloric acid was finished, the mixture was refluxed for 12 h. Excess ethanol was evaporated, and the remaining solution was poured into 400 mL of distiller water, the mixing

solution was basified with 10% NaOH solution to form a precipitate, and it was filtrated off, washing with water and methanol, recrystallized from methanol to get a yellow product, successively. The reaction yield is 62% while melting point of the resulting product is at $156\text{--}158\text{ }^\circ\text{C}$.

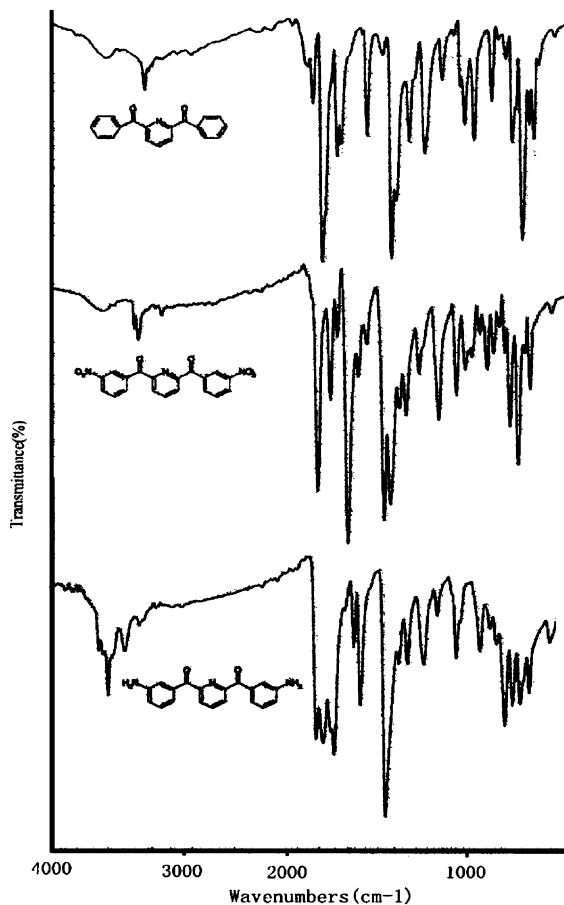


Fig. 1. FT-IR spectra of DBPY, BNPB and BABP.

FT-IR spectrum exhibited characteristic absorptions of the product at 3454–3415, 3368, 3204 cm^{-1} (NH_2), 3063 cm^{-1} (aromatic C–H), 1668 cm^{-1} (C=O stretching), 1642–1580, 1486 cm^{-1} (aromatic C=C) and 1332 cm^{-1} (C–N); $^1\text{H-NMR}$ (300 MHz, $\text{DMSO-}d_6$, ppm) illustrates resonance signals of different protons: $\delta = 8.26\text{--}8.23$ (m, 1 H), 8.10–8.07 (d, 2H), 7.18–7.05 (m, 6H), 6.84–6.81 (d, 2H), 5.36 (s, 4H, NH_2); $^{13}\text{C-NMR}$ (300 MHz, $\text{DMSO-}d_6$, ppm): $\delta = 193.8, 154.3, 148.7, 138.9, 136.2, 128.8, 126.1, 118.8, 118.6, 115.2$; MS (EI): 317 (M^+); elemental analysis: Calcd. C 71.91, H 4.76, N 13.24, while Found: C 69.32, H 4.35, N 12.53.

3.2. Polyimide synthesis

3.2.1. Thermal cyclodehydration

A typical example of polymerization is as follows. 0.6444 g (2.00 mmol) of BTDA was added gradually to a stirred solution of 0.6347 g (2.0 mmol) BABP of in 8 mL of DMAc. The mixture was stirred at room tem-

perature for 24 h under nitrogen atmosphere, forming a solution of poly(amic acid) (PAA) in DMAc. The inherent viscosity of the poly(amic acid) in DMAc was 0.64 dL/g, measured at a concentration of 0.50 g/dL at 30 °C. The poly(amic acid) solution obtained was spread on a glass plate and the solvent was removed slowly at 80 °C overnight. Imidization was carried out by thermal cyclodehydration of the poly(amic acid) film by sequential heating at 110, 150, 180, 210, 230 and 280 °C for 30 min each.

3.2.2. Chemical cyclodehydration

Chemical cyclodehydration was carried out by adding a mixture of acetic anhydride and pyridine (volume ratio 2:1) into the above-mentioned poly(amic acid) solution with stirring at room temperature for 1 h, and then heating at 100 °C for 3 h. The polymer solution was poured into methanol to form a precipitate. The precipitate was collected by filtration, washed thoroughly with methanol and hot water, and dried at 100 °C under vacuum.

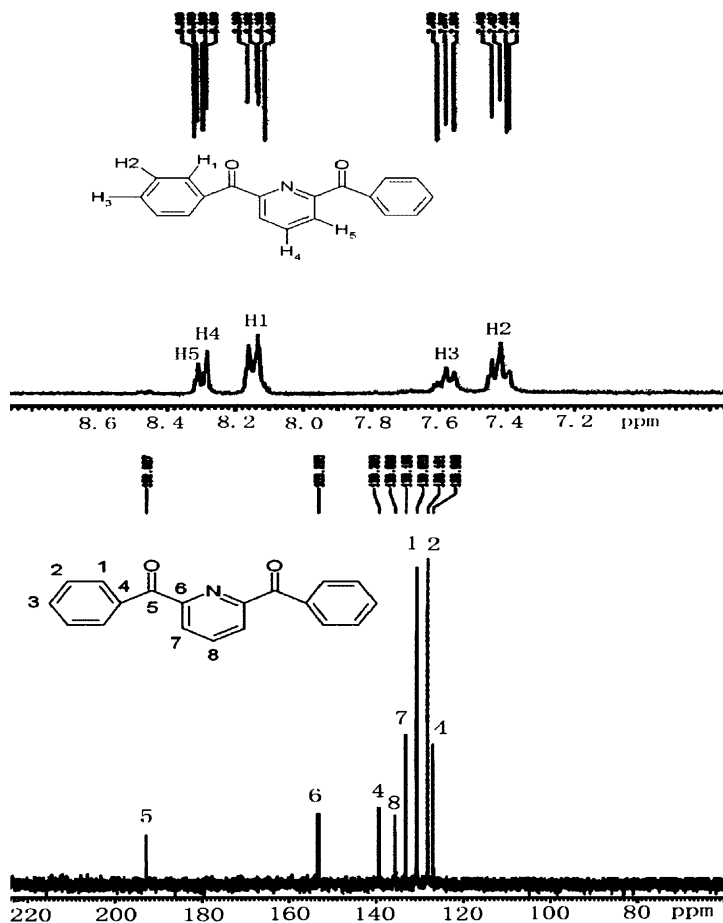


Fig. 2. ^1H and ^{13}C -NMR spectra of DBPY in $\text{DMSO-}d_6$.

4. Results and discussion

4.1. Composition and structure of diamine monomers (BABP)

Novel diamine monomer, i.e. 2,6-bis(3-amino-benzoyl)pyridine (BABP), were synthesized by a three step procedure, respectively, as shown in Scheme 1. Firstly, 2,6-dibenzoylpyridine (DBPY) was formed by Friedel–Crafts acylation of benzene with 2,6-pyridinedi-carbonyl chloride using anhydrous aluminum chloride as a catalyst, then dinitro compound, 2,6-bis(3-nitro-benzoyl)pyridine (BNBP), was synthesized by the nitric acid (99%), and BNBP was converted to BABP by the reduction of the nitro groups into NH_2 groups by reaction with SnCl_2 and HCl in ethanol.

FT-IR, NMR, and elemental analysis were used to confirm the structures of the intermediate BABP, DBPY and the diamine monomer (BABP). Fig. 1 shows FT-IR spectra of the diamine monomer BABP, and its intermediate BNBP and DBPY. The phenyl and pyridine rings of DBPY gave three characteristic bands at 3065 cm^{-1} (aromatic C–H symmetric stretching), 1671 cm^{-1} (C=O symmetric stretching), and 1626 cm^{-1} (pyridine C–N stretching). After nitration of DBPY, the resulting nitro compound BNBP gave two characteristic bands indicating asymmetric and symmetric stretching of NO_2 group

at 1524 and 1326 cm^{-1} , especially, the diamine monomer BABP obtained by the reduction of BNBP illustrates that there are the characteristic absorption of the amino group showed a pair N–H stretching bands in the region of 3369 – 3203 cm^{-1} , however, the corresponding absorption bands of the nitro group have disappeared. The analysis results from FT-IR spectra confirm the reaction mechanism shown by Scheme 1.

Figs. 2–4 represent the ^1H -NMR and ^{13}C -NMR spectra of DBPY, BNBP and BABP, respectively. The resonance signals of aromatic protons of DBPY appeared in the region of 8.35 – 7.30 ppm, and those of the dinitro compound BNBP shifted to a downfield between 8.71 and 7.69 ppm, while the ^1H -NMR spectrum of BNBP shows that the protons of H_1 and H_2 resonated at the farthest downfield because of the induction effect of electron with drawing $-\text{NO}_2$ and $-\text{CO}$ groups, meanwhile, the resonance signals of diamine monomer BABP shifted to a higher field 8.27 – 6.80 ppm because of the electron-donating property of the amino groups. The ^1H -NMR spectra confirm that the nitro groups in BNBP have been completely deoxidized into amino groups, and so the resonance signals of the primary aromatic amino protons are presented at 5.35 ppm. As to the ^{13}C -NMR spectra presented in the above figures, the resonance signals of all carbon –13 atoms of DBPY showed eight main signals, which resonated in the regions of 126.9 – 192.8 ppm, while those of BNBP and BABP

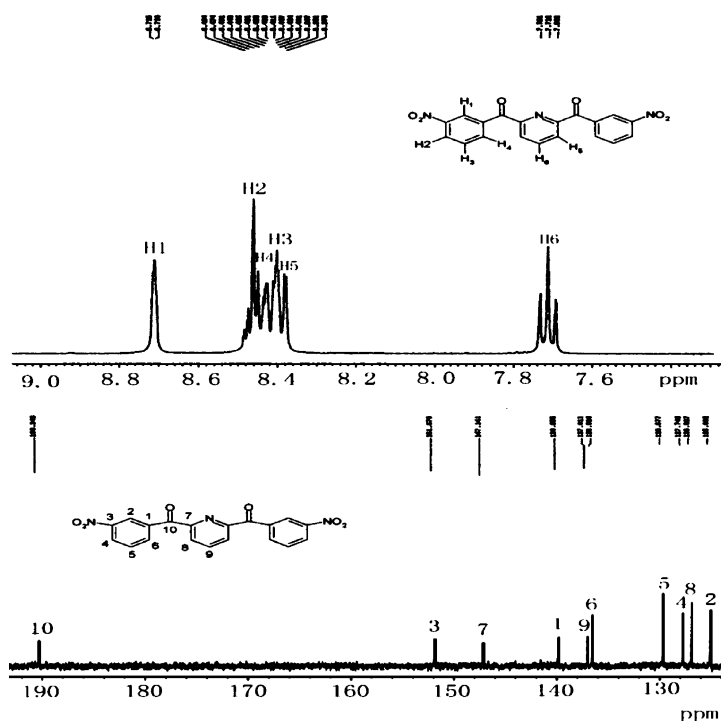
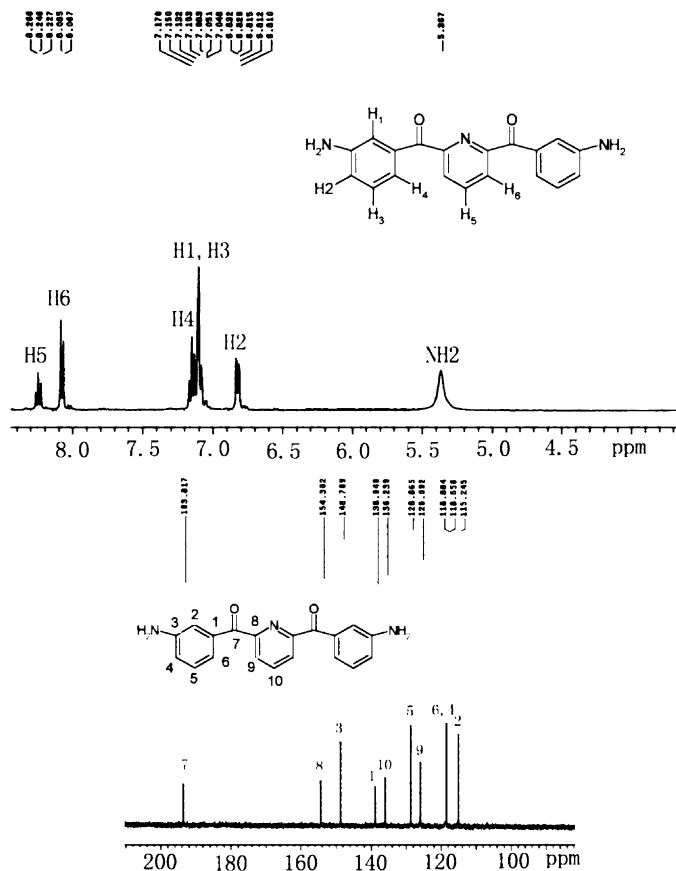
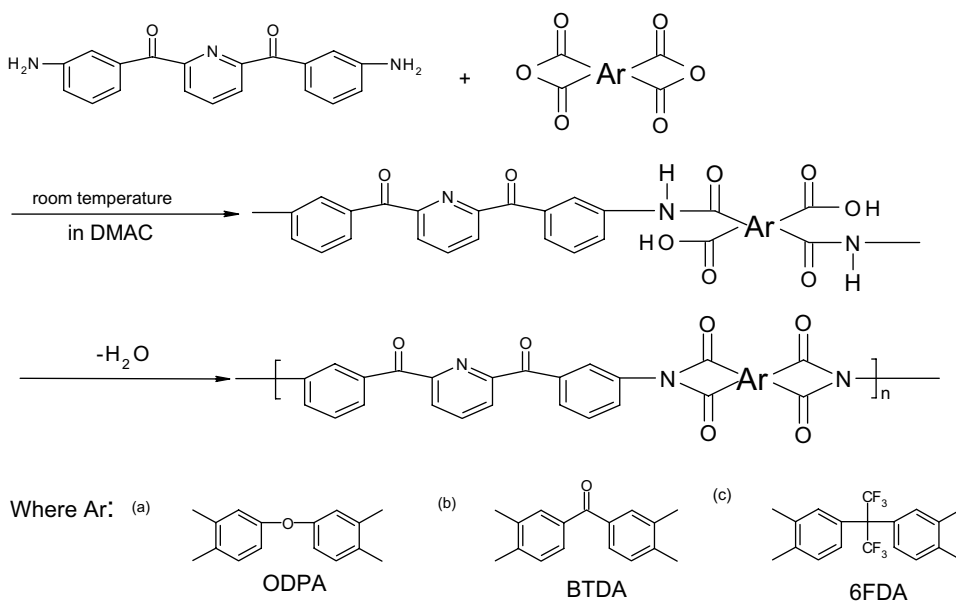


Fig. 3. ^1H and ^{13}C -NMR spectra of BNBP in $\text{DMSO-}d_6$.

Fig. 4. ^1H and ^{13}C -NMR spectra of BABP in $\text{DMSO-}d_6$.

Scheme 2. Synthesis of the polyimides.

showed 10 main signals that resonated in the region 125.1–190.3 and 115.2–193.8 ppm, respectively. The analysis results from the above $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra would also sustain the reaction mechanism shown by Scheme 1. Furthermore, the data of the MS and elemental analyses to have mentioned in experimental section could agree with the analysis results from FT-IR, $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra, in other words, the novel diamine monomer BABP expected, i.e. 2,6-bis(3-aminobenzoyl)pyridine, should have been synthesized successfully.

4.2. Synthesis chemistry of polyimides

The new polyimides were prepared by polycondensation of diamine monomer BABP with dianhydride monomers ODP, BTDA, and 6FDA, as shown in Scheme 2. The synthesis of polyimides usually were carried out via poly(amic acid)s or derivatives thereof. Two different procedures were chosen to achieve imidization at the final stage of the reaction forming polyimides, one of those is using thermal imidization of poly(amic acid) solution to form polyimide films. Initially, the diamine BABP was reacted with equimolar amounts of BTDA, ODP, or 6FDA in DMAc at room temperature to form a poly(amic acid) solution. BABP was first dissolved in a given amount of dry DMAc, and the solid dianhydride monomer was added to it slowly, the reaction mixture became highly viscous within 10–15 min, the reactions were continued for 24 h. The inherent viscosities of the polyimides are listed in Table 1. The η_{inh} values of the polyimides were about 0.37–0.58 dL/g, indicating moderate molecular weights. When the poly(amic acid) solutions were coated on clean glass plates, the novel polyimide films were obtained by heating through various stages up to 280 °C in order to remove solvent and water formed during the imidization process, transparently, the polyimide films with pale-yellowish and holding tough property were obtained by the imidization process.

Fig. 5 illustrates FT-IR spectra of poly(amic acid) and polyimide derived from BABP–BTDA polycondensation. The FT-IR spectrum of the polyimides exhibits

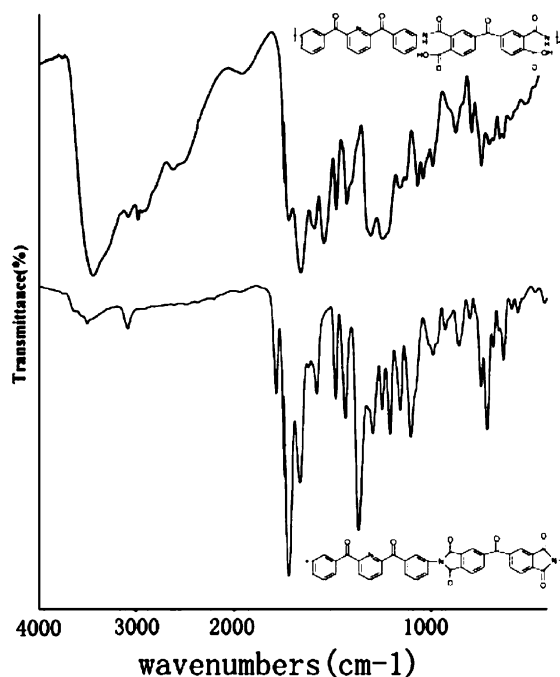


Fig. 5. FT-IR spectra of the poly(amic-acid) and corresponding polyimide from BABP–BTDA.

characteristic absorptions of imide group at 1780 and 1725 cm^{-1} (typical of imide carbonyl and symmetrical stretching), 1380 cm^{-1} (C–N stretching), and 1100 and 730 cm^{-1} (imide ring deformation), together with some strong absorption bands in the region of 1100–1300 cm^{-1} due to the C–O stretching, especially, the characteristic absorptions indicating N–H ($\sim 3400 \text{ cm}^{-1}$) and $=\text{NH}_2^+$ (2200 \sim 2700 cm^{-1}) of amide and carboxyl groups in FT-IR spectrum of the poly(amic acid) precursor have been disappearance in that of the polyimide. The analysis results of the FT-IR spectra demonstrate that the novel polyimide has been synthesized by the polycondensation BABP with BTDA. Data of elemental analyses of all polyimides obtained by thermally curing are also listed in Table 1. The data presented in Table 1 show that C, H and N values were

Table 1
Experimental data of polyimides prepared by two-step

Polyimide	$\eta_{\text{inh}}(\text{g/dL})^{\text{a,b}}$	Elemental analysis of polyimides (%)					
		C		H		N	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
BABP–BTDA	0.37	71.64	71.18	2.84	2.44	6.96	6.54
BABP–ODPA	0.58	71.07	70.77	2.90	2.69	7.10	6.87
BABP–6FDA	0.44	62.91	61.36	2.36	2.18	5.79	5.89

^a Measured on solutions of 0.5 g/dL in NMP at 30 °C.

^b Measured by chemical imidization from the corresponding poly(amic acid)s.

Table 2
Solubility data of the polyimides^a

No.	Polyimide	Solvent ^b				
		NMP	DMAc	DMF	DMSO	H ₂ SO ₄
1	BABP–BTDA	--	--	--	--	--
2	BABP–ODPA	--	--	--	--	--
3	BABP–6FDA	--	--	--	--	--
4 ^c	BABP–BTDA	+	--	--	--	++
5 ^c	BABP–ODPA	+	+	+	--	++
6 ^c	BABP–6FDA	++	++	+	--	++

(++): soluble at room temperature; (+) soluble on heating; (--) insoluble even on heating.

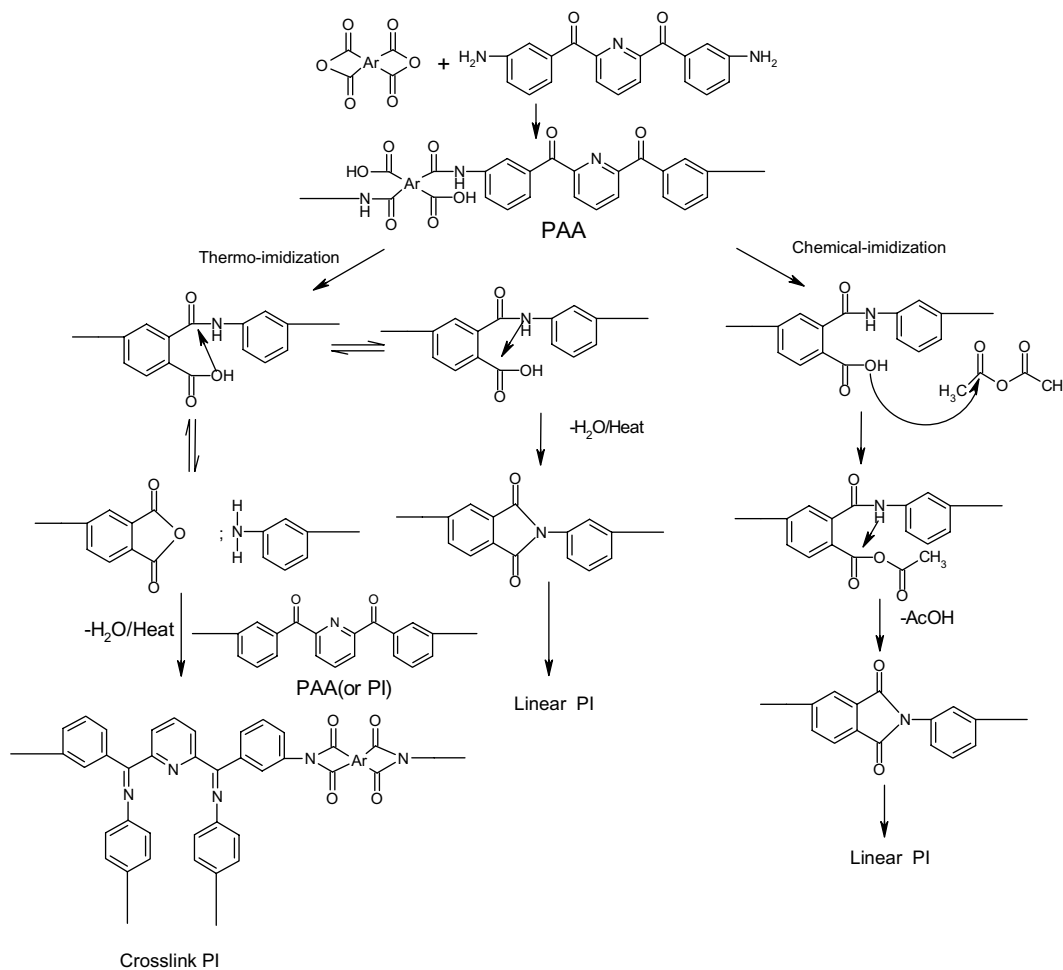
^a Qualitative solubility was determined with 10 mg of polymer in 1 mL of solvent.

^b NMP, *N*-methylpyrrolidone; DMAc, *N,N*-dimethylacetamide; DMF, *N,N*-dimethylformamide; DMSO, dimethyl sulfoxide.

^c Measured by chemical cyclization from the corresponding poly(amic acid)s.

generally in good agreement with those calculated according to the structures proposed in Scheme 2. So complete imidization was achieved when the curing tem-

perature of thermal imidization reached 300 °C. Moreover, 100% chemical imidization could be obtained at lower temperature [10].



Scheme 3. Mechanism of thermal and chemical imidization.

4.3. Solubility of the resulting polyimides

The solubility of these polyimides was tested qualitatively, and the results are summarized in Table 2. PI (1–3) series obtained via thermal imidization were insoluble in all test solvents, while PI (4–6) series prepared via chemical imidization had better solubility than those prepared thermally. The PI (6) had better solubility than others because of the presence of a bulky CF_3 group of 6FDA inhibiting close packing and reducing the inter-chain interactions to enhance solubility.

The difference in solubility between PI from thermal and chemical imidization could be explained by the imidization reaction mechanism shown in Scheme 3. PAA should be a linear polymer with both aromatic amido and carboxyl groups obtained by polycondensation of aromatic dianhydride and diamine in a polar solvent at room temperature, but this kind of PAA was an unstable polymer. The hydroxy group of the carboxylic acid and the amino group of amide in PAA either form aromatic imide by further dehydration or form aromatic anhydride and amine groups again by a nucleophilic substitution reaction between each other. The aromatic amine formed, however, could react with the electrophilic carbonyl group presented in PAA chain during the heating process to form an imine structure which makes the polyimide crosslinking, in other words, the polyimides obtained by thermal imidization will show insolubility in organic solvents at room temperature because there are some crosslinkages in them [20,21]. When PAA was treated via chemical imidization using $\text{Ac}_2\text{O}/\text{Py}$ as dehydrating reagent, the Ac_2O would react with carboxyl group in PAA to form another anhydride group, then this kind of anhydride group will react with amide group in PAA to form linear polyimide structure via a nucleophilic reaction removing acetic acid in it, the structure without both amine ends and crosslinking structure in PAA chains were formed, therefore, the most of polyimides obtained by chemical imidization will exhibit good solubilities, comparing with the polyimides obtained by thermal imidization.

4.4. X-Ray diffraction of the polyimides

Fig. 6 is wide-angle X-ray diffraction curves of the polyimides obtained by thermal imidization. The X-ray diffraction curves of the polyimides express a set of wider diffraction peaks, these should be evidences that indicate the polyimides holding heterogenous morphology, and should also be a reason that could obtain transparent films from these polyimides. However, the X-ray diffraction curves presented in Fig. 6 show that there are small crystal peaks in those wider diffraction peaks. These show a little of crystalline morphologies in the resulting polyimides (peak around 27°), which maybe relate to rigidity and planar structure of the polymer

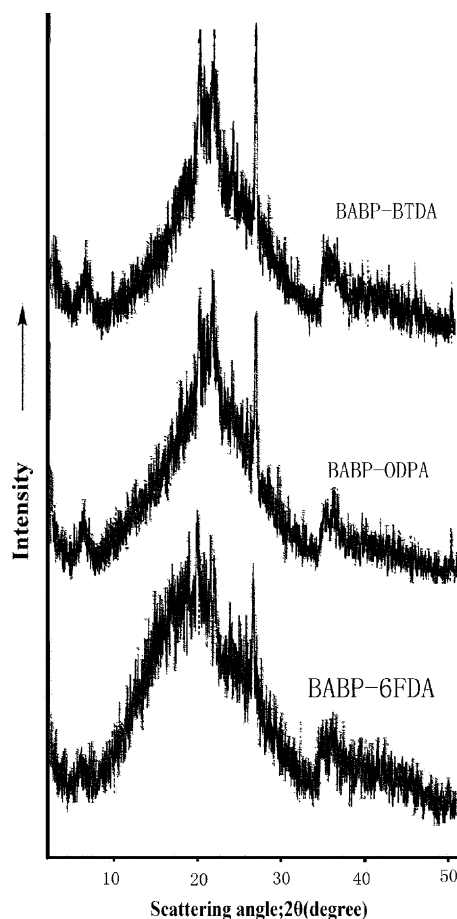


Fig. 6. Wide-angle X-ray diffraction curves of the polyimides(thermal imidization).

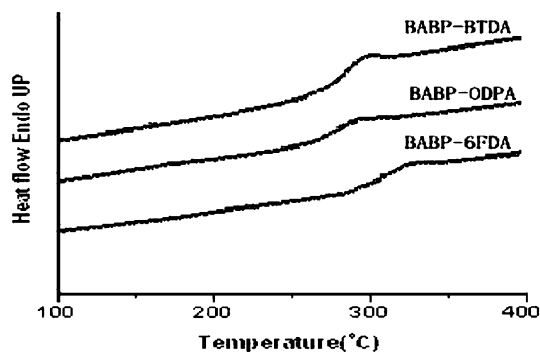


Fig. 7. DSC thermograms of PIs at heating rate of $20\text{ }^\circ\text{C min}^{-1}$ in nitrogen.

chains. In contrast, the polyimide based on BABP-6FDA exhibits a relative fewer crystalline peak than that of others, this maybe results from contribution of two

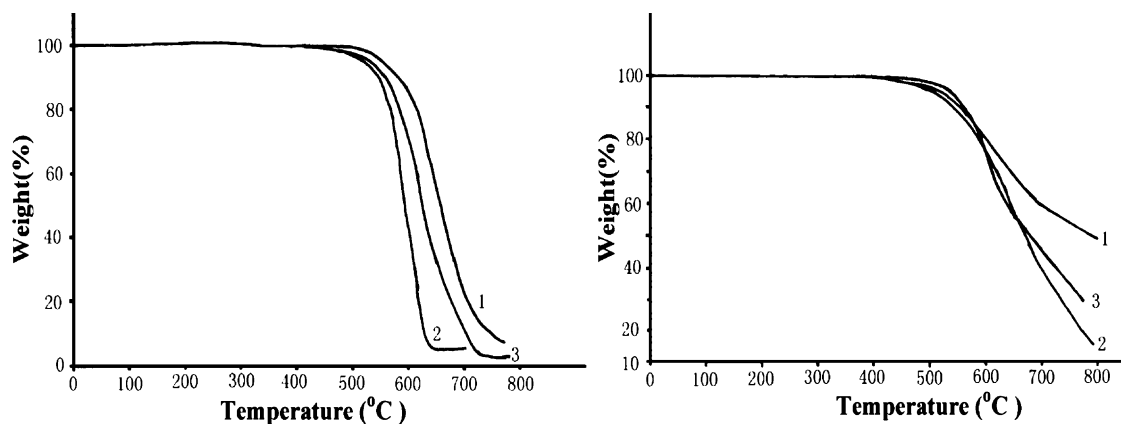


Fig. 8. TGA curves of PIs at a heating rate of 20 °C/min in air and N₂.

bulky trifluoromethyl in 6FDA monomer for flexibility of the polyimide.

4.5. Thermal properties of the resulting polyimides

DSC and TGA were used to evaluate the thermal properties of the polyimides, DSC and TGA curves of the polyimides are shown in Fig. 7 and 8 respectively, and thermal analysis data from the TGA and DSC curves of the polyimides are summarized in Table 3. The data in Table 3 represents that T_g values of these PIs are in the range of 284–310 °C. As we expected, the T_g value of these PIs both depended on the structure of the dianhydride component and decreased with increasing flexibility of the polyimides backbones. The polyimide derived from BABP–BTDA, for examples, exhibits the highest T_g because of the rigid backbone, and one derived from BABP–ODPA exhibits a lower T_g because of the presence of a flexible ether linkage between the phthalimide units. According to Fig. 6, T_m values of the resulting PIs that should exhibit in DSC curves were not observed in the DSC curves presented

Table 3
Data of thermal analysis of the resulting polyimides

Polyimide	T_g (°C) ^a	In air ^b		In N ₂ ^b		Char yield (%) ^c
		T_5 (°C)	T_{10} (°C)	T_5 (°C)	T_{10} (°C)	
BABP–BTDA (1)	292	549	578	522	558	64
BABP–ODPA (2)	284	495	536	506	554	42
BABP–6FDA (3)	310	496	538	555	561	53

^a T_g measured by DSC at a heating rate of 10 °C min⁻¹ in N₂.

^b Temperature at a 5% or 10% weight loss at a 20 °C/min heating rate.

^c Residual weight (%) at 700 °C in nitrogen.

in Fig. 7, these probably be that the T_m values of the resulting polyimides could overstep measure range of used DSC [22,23].

For the thermal stability of the polyimides, Table 3 gives the temperature of 5% and 10% weight loss in nitrogen and in air, respectively, i.e. T_5 and T_{10} values. The T_5 and T_{10} values of the polyimides were in the range 496–549 °C and 526–580 °C in air, while those of them were in the range 522–555 °C and 558–561 °C in nitrogen, and the amount of residue of all polyimides at 700 °C in nitrogen atmosphere was higher than 42%, especially, the polyimide derived from BABP–BTDA had the highest residue yield up to 64%. The data from thermal analysis show that the resulting polyimides have fairly high thermal stability.

5. Conclusions

A new kind of diamine monomer, i.e. 2,6-Bis(3-amino-benzoyl)pyridine(BABP), was successfully prepared in high purity and high yields in this work, and the resulting BABP was employed to react with various aromatic dianhydrides to form a series of aromatic polyimides by two-step thermal or chemical imidization methods. Experimental results indicate that the novel polyimides obtained have higher T_g values, excellent thermal and thermooxidative stabilities, as well as good solubility in organic solvents. Meanwhile, the resulting poly(amic acid)s could all be thermally converted into polyimide films with transparent and tough properties.

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