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Synthesis and properties of novel polyimides derived from 2,6-bis(4-aminophenoxy-4′-benzoyl)pyridine with some of dianhydride monomers

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Abstract

A new kind of aromatic diamine monomer containing pyridine unit, 2,6-bis(4-aminophenoxy-4′-benzoyl)pyridine (BABP), was synthesized successfully. The Friedel–Crafts acylation of phenyl ethyl ether with 2,6-pyridinedicarbonyl chloride formed 2,6-bis(4,4′-dihydroxybenzoyl)-pyridine (BHBP), BHBP was changed into 2,6-bis(4-nitrophenoxy-4′-benzoyl)-pyridine (BNBP) by the nucleophilic substitution reaction of it and *p*-chloronitrobenzene, and BNBP was reduced with $SnCl_2$ and HCl in ethanol to form the diamine monomer BABP finally, the diamine monomer BABP could be obtained in quantitative yield. A series of novel polyimides were prepared by polycondensation of BABP with various aromatic dianhydrides in *N*-methy-2-pyrrolidone (NMP) via the conventional two-step method. Experimental results indicated that some of the polyimides were soluble both in strong dipolar solvents (*N*-methy-2-pyrrolidone or *N*,*N*-dimethylacetamide) and in common organic solvents tetrahydrofuran. The resulting polyimides showed exceptional thermal and thermooxidative stability, no weight loss was detected before a temperature of 450 °C in nitrogen, and the values of glass-transition temperature of them were in the range of 208–324 °C. Wide-angle X-ray diffraction measurements revealed that these polyimides were predominantly amorphous.

Keywords: Pyridine-containing polyimides; Synthesis; Thermostablity

1. Introduction

It is well known that the polyimides with aromatic heterocyclic structures play important roles in the development of advanced technologies because of their excellent thermal and thermooxidative stabilities, outstanding mechanical and electrical properties, so they have been employed in the adhesives, matrices of composites, fibers, films, foams, microelectronic materials and so on [1–4]. However, the further applications of the polyimides are often limited by their poor solubility and high processing temperature partly due to the rigidity and strong interaction among their chains. In order to overcome these limitations, some significant and synthetic efforts were focused, and improving solubilities in organic solvents without sacrificing the above excellent properties should be research objectives regarded, especially, the design and synthesis of new monomers would be one of approaches improving the processability and solubility of the polyimides [5–10].

Pyridine is a heteroaromatic molecule with rigidity and polarizability. New kinds of heteroaromatic diamine, dianhydride or other monomers holding pyridine unit have been designed and synthesized, and the novel heteroaromatic polymers with good thermostability and processability have been obtained derived from those monomers containing pyridine nucleus structures at the same time [11–17]. Considering the rigidity based on symmetry and aromaticity of pyridine ring would have contributions for the thermal stability, chemical stability, retention of mechanical property of the resulting polymer at elevated temperature, as well as polarizability resulting from nitrogen atom in pyridine ring could be suitable to improve their solubility in organic solvents [18,19], the polyimides with good themostability and

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processability have been prepared by polycondensation of 2,6-bis(3-aminobenzoyl) pyridine with some aromatic dianhydride monomers [20].

In this paper, the synthesis and characterization on a new kind of aromatic diamine containing pyridine was described, i.e. 2,6-bis(4-aminophenoxy-4′-benzoyl)pyridine, which was derived from 2,6-bis(4,4′-dihydroxybenzoyl)pyridine. Meanwhile, the resulting diamine monomer was employed in preparation of the polyimides with several aromatic dianhydrides by a tow-step procedure, and the polyimides obtained were characterized detailedly.

2. Experimental

2.1. Materials

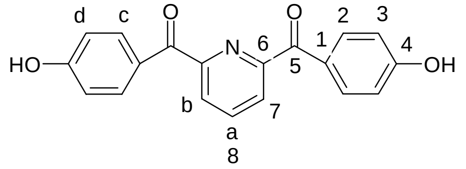
2,6-Pyridinedicarboxyl chloride (TCI). Phenyl ethyl ether (Chemspec Inc. Shanghai, China) was purified by distillation from calcium hydride prior to use. 4,4′-Oxydiphthalic anhydride (ODPA, Shanghai Nanxiang Chemical Co., China), 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA, Beijing Chemical Reagents Corp., China) and 4,4′-(hexaflouroisopropylidene)diphthalic anhydride (6FDA, Aldrich) were recrystallized from acetic anhydride before use. Pyromellitic dianhydride (PMDA, Beijing Chemical Reagents Corp., China) was purified by sublimation at 200–220 °C. *N*,*N*-dimethylacetamide (DMAc) and *N*-methy-2-pyrrolidone (NMP) were purified by distillation under reduce pressure over calcium hydride and stored over 4 Å molecular sieves. Reagent-grade potassium carbonate was dried in vacuo at 130 °C for 12 h before use. All other solvents were obtained from various commercial sources and used without further purification.

2.2. Monomer synthesis

2.2.1. 2,6-Bis(4,4′-dihydroxybenzoyl)pyridine (BHBP)

Sixty milliliter of benzene, 48 mL (0.32 mol) of phenyl ethyl ether and 64 g (0.48 mol) of anhydrous aluminum chloride was placed into a 250 mL three-necked flask equipped with a mechanical stirrer, thermometer and condenser, resulting a mixture with stirring, then 32 g (0.15 mol) of 2,6-pyridinedicarboxyl chloride was gradually added into the three-necked flask during the addition the temperature was maintained at 10–12 °C. After the addition was complete, the reaction would be continued at 12 °C for 4 h, then 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 (5%), some white solids were precipitated out, filtrating, washing with ethanol, the crude product obtained was recrystallized from methanol to get 2,6-bis(4,4′-dihydroxybenzoyl)pyridine (BHBP), the related yield is 81%, melting point is 278–280 °C.

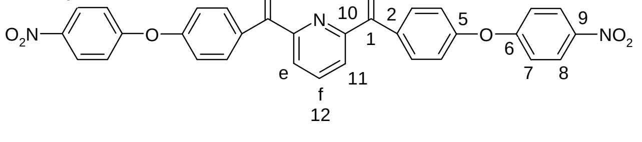
FT-IR (KBr): 3352–3251 (O–H stretching), 3065 (aromatic C–H stretching), 1645 (C=O stretching), 1326 (C–N stretching); ^{1}H NMR (300 MHz, DMSO-d_6,): δ (ppm) 10.50 (s, 2H, –OH), 8.20–8.28 (t, $J=8.4$ Hz, 1H, H$_a$), 8.06–8.09 (d, $J=7.4$ Hz, 2H, H$_b$), 7.90–7.95 (d, $J=8.6$ Hz, 4H, H$_c$), 6.82–6.86 (d, $J=8.4$ Hz, 4H, H$_d$); ^{13}C NMR (300 MHz, DMSO-d_6): δ (ppm) 190.9 (C^5), 162.4 (C^4), 154.2 (C^6), 138.8 (C^8), 133.3 (C^2), 126.7 (C^1), 125.8 (C^7), 115.0 (C^3); MS (EI): 319 (M$^+$); Elem. Anal. Calcd for $C_{19}H_{13}NO_4$ (319.08): C 71.47, H 4.10, N 4.39. Found: C 71.26, H 4.20, N 4.32.



2.2.2. 2,6-Bis(4-nitrophenoxy-4′-benzoyl)pyridine (BNBP)

In a three-necked flask equipped with a nitrogen inlet and a condenser, 15.9 g (50 mmol) of BHBP was first dissolved in 80 ml of DMAc, 17 g (108 mmol) of *p*-chloronitrobenzene and 16.6 g (120 mmol) of potassium carbonate were added subsequently. The mixture was heated at 160 °C for 12 h with stirring under nitrogen, then was poured into 400 mL of solution consisting of equal volumes of ethanol and water, and yellowish solids precipitated out of the solution overnight. After filtration, the residual reactants and potassium carbonate were eliminated from the solids by washing with water, methanol and ethanol consecutively. Finally, 2,6-bis(4-nitrophenoxy-4′-benzoyl)pyridine (BNBP) with solids was collected and dried at 100 °C for 12 h. The crude BNBP was purified by recrystallized from acetone to afford an 85% yield of a white powder, melting point is 196–198 °C.

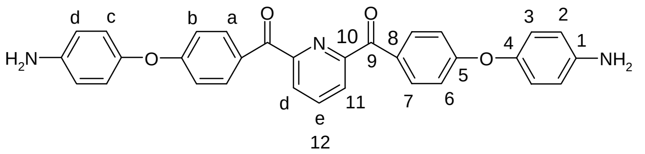
FT-IR (IR): 3106, 3075 (C–H stretching), 1659 (C=O stretching), 1582, 1345 (C–NO$_2$ stretching), 1326 (C–N stretching). ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 8.37–8.33 (m, 3H, H$_f$, He), 8.28–8.24 (d, $J=5.6$ Hz, 4H, H$_d$), 8.16–8.12 (d, $J=9.6$ Hz, 4H, H$_a$), 7.27–7.22 (d, $J=8.4$ Hz, 4H, H$_c$), 7.20–7.15 (d, $J=11.6$ Hz, 4H, H$_b$). ^{13}C NMR (300 MHz, DMSO-d_6,): δ (ppm) 191.1 (C^1), 161.3 (C^9), 158.3 (C^{10}), 153.0 (C^2), 142.9 (C^{11}), 139.4 (C^{12}), 133.5 (C^8), 132.2 (C^6), 127.0 (C^5), 126.1 (C^3), 119.2 (C^7), 118.5 (C^4). MS (EI): 562 (M$^+$); Elem. Anal. Calcd for $C_{31}H_{19}N_3O_8$ (561.51): C 66.31, H 3.41, N 7.48. Found: C 65.86, H 3.46, N 7.28.



2.2.3. 2,6-Bis(4-aminophenoxy-4′-benzoyl)pyridine (BABP)

A mixture consisting of 25.3 g (45 mmol) of BNBP, 41.0 g (216 mmol) of anhydrous SnCl$_2$ and 500 mL of 95% C_2H_5OH was put into a reaction flask, with stirred while 20 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 15% NaOH solution to form a precipitate, and the precipitate was filtrated off, washing with water and methanol, recrystallized from toluene to get a yellow product, i.e. 2,6-bis(4-aminophenoxy-4′-benzoyl)pyridine (BABP). The reaction yield is 76% while melting point of the resulting product is at 186–188 °C.

FT-IR (IR): 3418, 3345 (N–H stretching); 3043, 3014 (C–H stretching); 1652 (C=O stretching); 1333 (C–N stretching). ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 8.27–8.25 (t, $J=7.6$ Hz, 1H, H$_e$), 8.16–8.14 (d, $J=8.0$ Hz, 2H, H$_d$), 7.98–7.96 (d, $J=6.8$ Hz, 4H, H$_a$), 6.89–6.87 (d, $J=6.8$ Hz, 4H, H$_b$), 6.81–6.80 (d, $J=4.4$ Hz, 4H, H$_c$), 6.62–6.12 (d, $J=4.4$ Hz, 4H, H$_d$), 5.11 (s, 4H, –NH$_2$). ^{13}C NMR (300 MHz, DMSO-d_6): δ (ppm) 191.2 (C^9), 163.3 (C^5), 153.7 (C^{10}), 146.2 (C^4), 144.0 (C^1), 138.6 (C^{11}), 133.2 (C^{12}), 129.0 (C^7), 126.4 (C^8), 121.3 (C^6), 115.2 (C^2), 114.9 (C^3); MS (EI): 501 (M$^+$); Elem. Anal. Calcd for $C_{31}H_{23}N_3O_4$ (501.55): C 74.24, H 4.62, N 8.38. Found: C 73.87, H 4.49, N 8.24.



2.3. Synthesis of polyimides

The typical tow-step method was applied to polycondensation of objective polyimides. 0.6444 g (2.0 mmol) of ODPA was added gradually to a solution consisting of 1.002 g (2.0 mmol) BABP dissolving in 9 mL of NMP with stirring, and the solid content of the mixture solution was approximately 15%. The mixture was stirred at room temperature for 24 h under nitrogen atmosphere, forming a viscous solution of poly(amic acid) (PAA) in NMP. The inherent viscosity of the poly(amic acid) in DMAc was 0.87 dL/g, measured at a concentration of 0.50 g/dL at 30 °C. The poly(amic acid) was subsequently converted into polyimide by either a thermal or chemical imidization process. For the thermal imidization, the obtained poly(amic acid) was poured into a glass culture dish, which was placed overnight in a 90 °C oven for the slow release of the solvent. The semidried poly(amic acid) film was further dried and transformed into polyimide by sequentially heated at 110, 150, 180, 210, 230 and 280 °C for 30 min each, then the fully imidized polymer film was stripped from the glass substrate by being soaked in water. The inherent viscosity of the thermally cured polyimide was 0.64 dL/g in DMAc at a concentration of 0.50 g/dL at 30 °C. Meanwhile, chemical imidization was carried out via the addition of 3 mL of an acetic anhydride/pyridine (5:4, v/v) mixture into the PAA solution (with mechanical stirring) at ambient temperature, then the mixture was stirring at 100 °C for 4 h to yield a homogeneous polyimide solution, which was poured slowly into mixture of water/ethanol(1:2, v/v) to give a fibrous precipitate, which was collected by filtration, washed thoroughly with methanol, dried at 100 °C in vacuum.

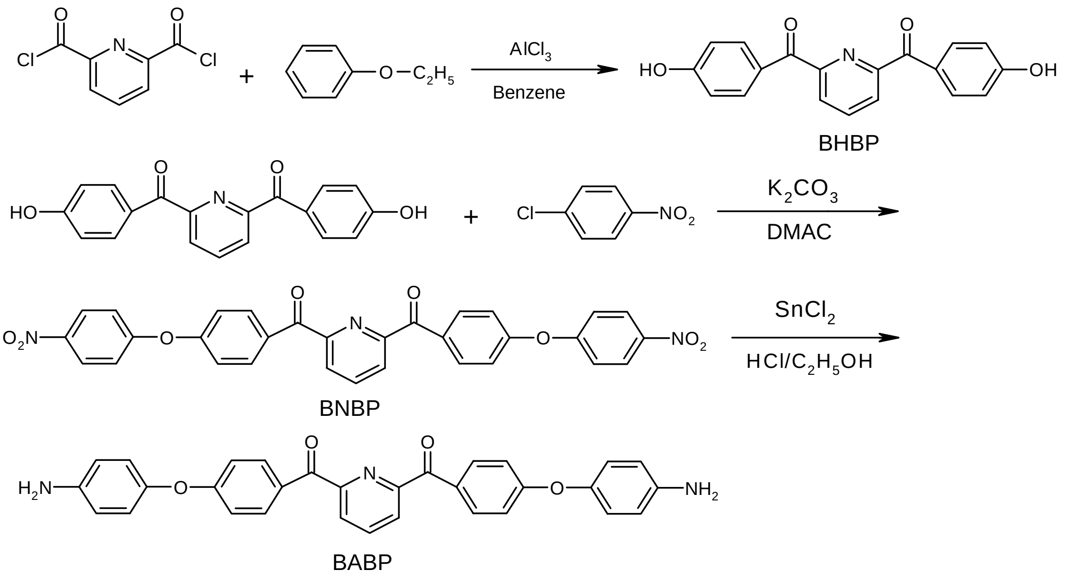
2.4. Measurements

Melting temperatures were determined on an electrothermal melting point apparatus IA6304. 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 NEXUS670 fourier transform infrared spectrometer. ^{1}H NMR and ^{13}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. Testing 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 in flowing nitrogen (30 cm^3/min), and 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 cm^3/min) at a heating rate of 20 °C/min.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 CuKα, radiation ($\lambda=1.5418$ Å, operating at 40 kV and 30 mA).

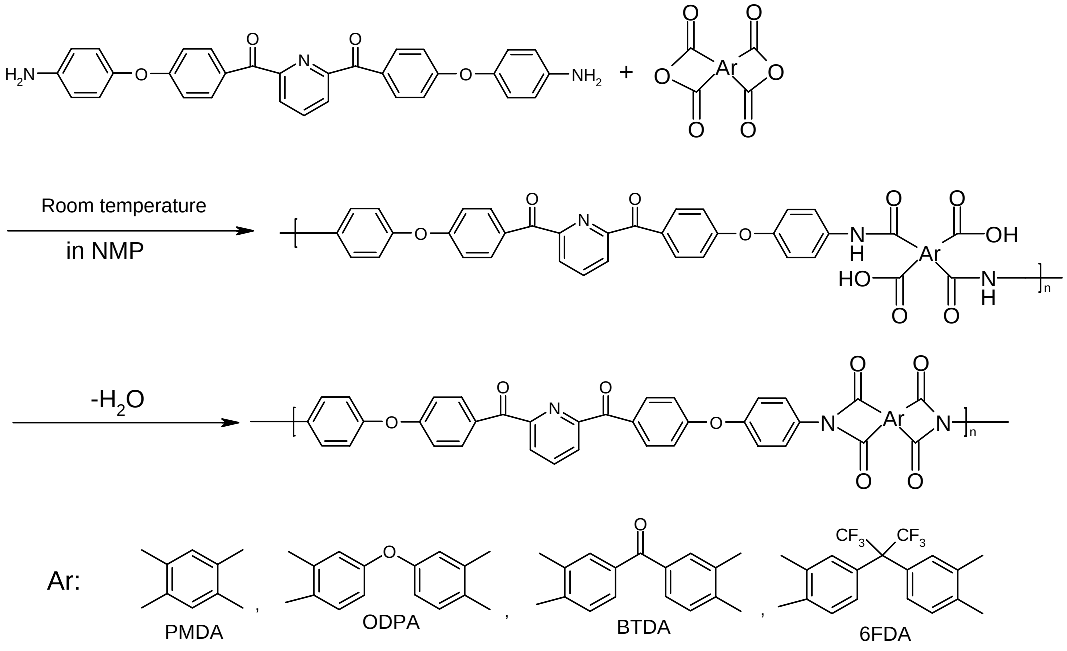
3. Results and discussion

3.1. Monomer synthesis

As shown in Scheme 1, 2,6-bis(4-aminophenoxy-4′-benzoyl)pyridine, i.e. novel diamine monomer BABP, was synthesized via consecutive reactions by three step procedures. Firstly, 2,6-bis(4,4′-dihydroxybenzoyl)pyridine (BHBP) was formed by Friedel–Crafts acylation of phenyl ethyl ether with 2,6-pyridinedicarbonyl chloride using anhydrous aluminum chloride as a catalyst, secondly, 2,6-bis(4-nitrophenoxy-4′-benzoyl)pyridine, i.e. dinitro compound BNBP, was obtained by the nucleophilic substitution reaction of BHBP with *p*-chloronitrobenzene in the presence of potassium carbonate, and finally, the novel diamine monomer BABP, i.e. 2,6-bis(4-aminophenoxy-4′-benzoyl)pyridine, was prepared by reduction of BNBP using $SnCl_2$ and HCl in ethanol. According to the analytic results from FT-IR, ^{1}H NMR, ^{13}C NMR and MS (EI) presented in the above mononmer synthesis (2.2), the diamine monomer BABP, intermediate BHBP and BNBP holds structure as uniform as that shown in Scheme 1, respectively, the results found of elemental analysis were also inosculated with those calculated by theoretics. The results indicate that the design and synthesis of novel diamine monomer BABP should be successful and feasible in this work. On the other hand, the yield of the BHBP, BNBP and BABP was 81, 85 and 76%, successively, this is to say that the novel diamine monomer BABP obtained in this work could satisfy requirement of polycondensation for the monomer dosage.



Scheme 1. Synthesis of 2,6-bis(4-aminophenoxy-4′-benzoyl)pyridine (BABP).



Scheme 2. Synthesis of the polyimides.

Table 1
Inherent viscosity and element analysis of the polyimides

Polyimides code	PAA η_{inh}[a] (dL/g)	PI η_{inh}[a] (dL/g)	Elemental analysis (%) of polyimides[c]				
			Formula of PI (formula weight)		C	H	N
BABP-PMDA	1.37	–	$(C_{41}H_{25}N_3O_9)n$	Calcd	72.03	3.10	6.15
			$(683.64)n$	Found	71.89	3.05	6.18
BABP-ODPA	0.87	0.64	$(C_{47}H_{25}N_3O_9)n$	Calcd	72.77	3.25	5.42
			$(775.74)n$	Found	72.25	3.14	5.37
BABP-BTDA	1.27	0.81[b]	$(C_{48}H_{25}N_3O_9)n$	Calcd	73.19	3.20	5.33
			$(787.75)n$	Found	73.13	3.09	5.48
BABP-6FDA	0.76	0.58	$(C_{50}H_{25}N_3O_9F_6)n$	Calcd	67.20	2.80	4.70
			$(893.34)n$	Found	67.04	2.45	4.50

[a] Inherent viscosity (η) determined on 0.5% solutions in a solvent (DMAc) at 30 °C.

[b] Obtained by chemical cyclization from the corresponding poly(amic acid)s.

[c] Obtained by thermal cyclization from the corresponding poly(amic acid).

3.2. Synthesis chemistry of polyimides

The new polyimides (PI) were prepared by polycondensation of diamine monomer BABP with aromatic dianhydride monomers through two-step imidization methods, and polyimides usually were carried out by poly(amic acid)s (PAA) or related derivatives, as shown in Scheme 2. The diamine BABP was dissolved in a given amount of anhydrous NMP, and was firstly reacted with equimolar amounts of PMDA, ODPA, BTDA or 6FDA in NMP to form a poly(amic acid) solution at room temperature for 24 h, while the solid dianhydride monomer should be a slowly added into the solution of BABP dissolved in anhydrous NMP. The either thermal or chemical imidization procedures were chosen to achieve imidization at the final stage of the reaction forming polyimides, merits of the former were ease for the synthesis, whereas the latter was suited for the preparation of soluble PI. The chemical conversion also enabled us to more easily characterize the resulting polyimides. Despite the presence of electron-withdrawing –C=O substituents in diamine structure, BABP still holds excellent reactivity so that getting high-molecular-weight poly(amic acid)s by allowing for a longer polymerization time. The inherent viscosities presented in Table 1 show that those of the poly(amic acid)s from BABP are 0.76–1.37 dL/g. The molecular weights of all these poly(amic acid)s would be suitable to gain good flexible and tough poly(amic acid) films [20,21], subsequently, the poly(amic acid) films could be converted into tough polyimide films by extended heating at elevated temperatures or chemical imidization. Meanwhile, the elemental analysis data of the resulting polyimides also agreed well with the calculated values (Table 1).

FT-IR spectra of PAA, PIs prepared by the above two imidization methods based on BABP-ODPA are illustrated in Fig. 1. The absorption at 1600–1700 cm^{-1} and ~2500 cm^{-1} presented in IR spectrum of PAA should be assigned to the C=O vibration of amide bands and the –OH vibration of carboxyl bands in PAA, and they disappear after thermal or chemical imidization, however, there exist strong absorptions that represent imide ring at 1777 and 1721 cm^{-1}after forming polyimides. The results show that the polyimides have formed. Comparing with IR spectra of polyimides, there exist similar IR absorption bands for the polyimide either from thermal or chemical imidization, these indicate that the conversion from PAA to PI were basically complete by using two kinds of imidization methods. Fig. 2 shows the high-resolution ^{1}H NMR spectrum of PI derived from BABP and ODPA by chemical imidization. The assignments of the NMR spectrum agree well with the proposed polymer structure. The above results demonstrate that the diamine monomer BABP holds a good polymerization activity to form polyimides, meanwhile, 100% chemical imidization could be achieved at lower temperatures, and this should be suitable to get soluble polyimide.

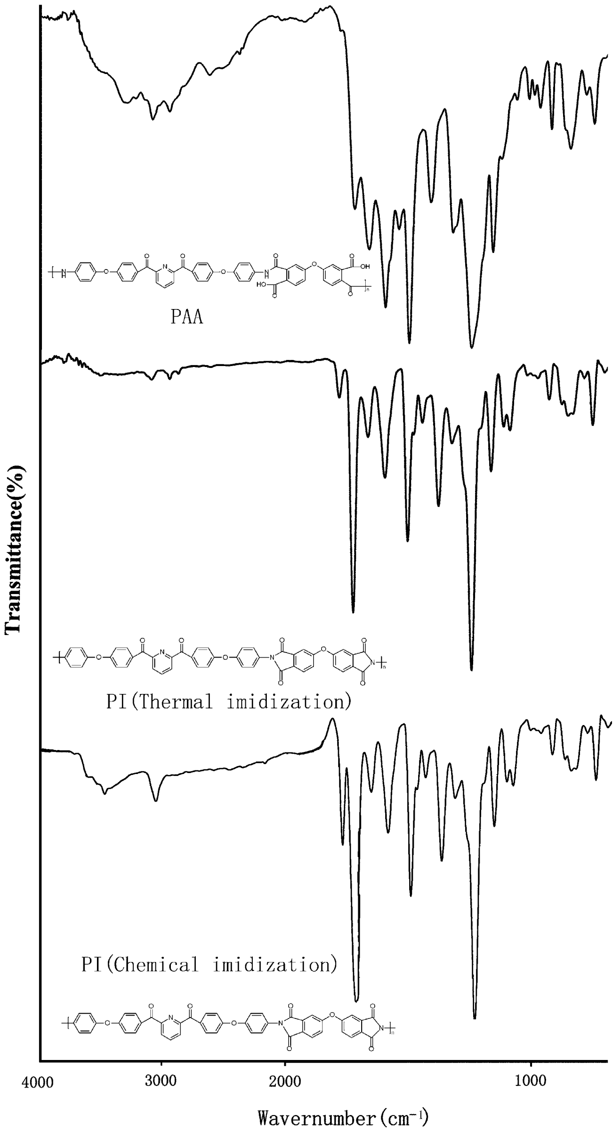


Fig. 1. FT-IR spectra of poly(amic acid) and polyimides.

3.3. Solubility of the resulting polyimides

The solubilities of the resulting polyimides in several organic solvents at 3.0% (w/v) are summarized in Table 2. Most of the polyimides obtained by chemical imidization, except PI from PMDA-BABP, were soluble in the test solvents including NMP, DMAc, dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and tetrahydrofuran. The good solubility should be result from both the flexibility of ether groups and

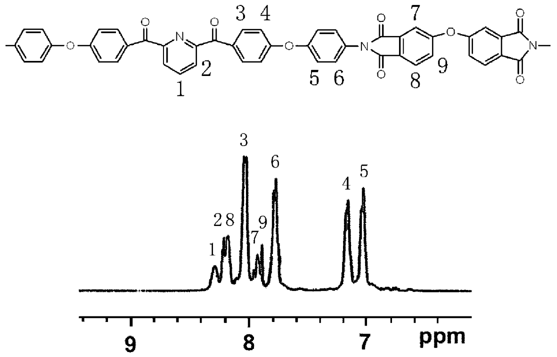


Fig. 2. ^{1}H NMR spectrum of PI (Chemical imidzation) in DMSO-d_6 solution.

Table 2
Soubility date of the polyimides

Polyimides		Solvent^a				
Number	Structure	NMP	DMAc	DMF	DMSO	THF
1	BABP-PMDA	−−	−−	−−	−−	−−
2	BABP-BTDA	+	+	−−	−−	−−
3	BABP-ODPA	++	+	+	−−	−−
4	BABP-6FDA	++	+	+	−−	−−
5^b	BABP-PMDA	+	−−	−−	−−	−−
6^b	BABP-BTDA	++	++	+	+	−−
7^b	BABP-ODPA	++	++	++	++	++
8^b	BABP-6FDA	++	++	++	++	++

Qualitative solubility was determined at 3.0% (w/v); ++, soluble at room temperature; +, soluble on heating, and −−, insoluble even on heating.

[a] NMP, *N*-methy-2-pyrrolidone; DMAc, *N*,*N*-dimethylacetamide; DMF, *N*, *N*-dimethylformamide; DMSO, dimethyl sulfoxide.

[b] Measured by chemical cyclization from the corresponding poly(amic acid)s.

polarizability of nitrogen atom in pyridine ring in the polyimide structure. The solubility data listed in Table 2 show that the polyimides obtained by thermal imidization method also hold a better solubility in NMP, DMAc and DMF. Comparing with those obtained by chemical imidization, the poor solubility of PI obtained by thermal imidization was possibly due to the presence of partial inter molecular crosslinking during the thermal imidization stage [21,22].

3.4. X-Ray diffraction of the polyimides

The crystallinity of the polyimides was examined by wide-angle X-ray diffraction analysis with graphite monochromatized CuKα radiation, 2θ ranging from 0 to 60°, and the results were shown in Fig. 3, using the polyimide films obtained by thermal cyclodehydration as samples. 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. The polyimides based on BABP-PMDA and BABP-BTDA show some crystalline character and exhibit two peaks around 15 and 25°, which show a little of crystalline morphologies in the resulting polyimides. These should relate to rigidity and planar structure of the polymer chains, as well as due to the more efficient packing of polymer chains containing pyromellitimide unit. The polyimides based on BABP-ODPA and BABP-6FDA show amorphous patterns, this is because the presence of flexible ether link induces looser chain packing and reveals a large decrease in crystallinity. Therefore, the amorphous nature of the resulting polyimides would endow them a good solubility.

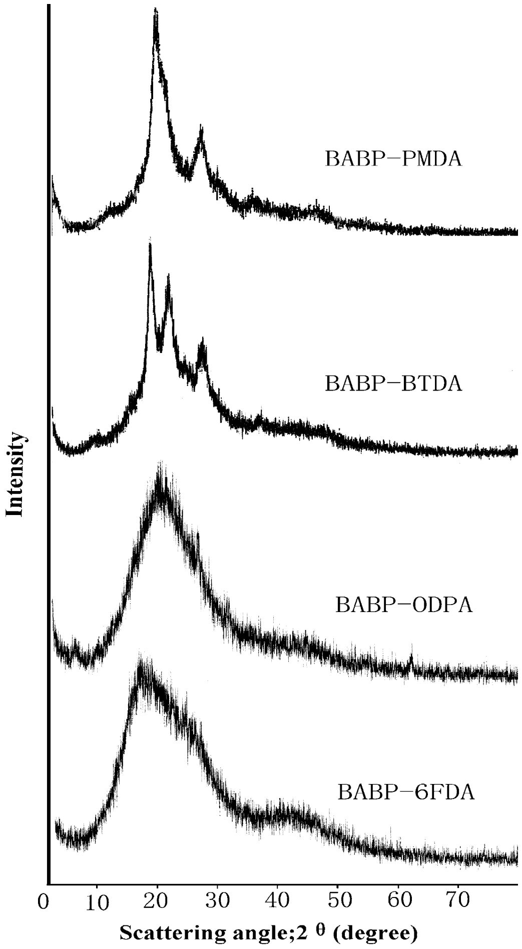


Fig. 3. Wide-angle X-ray diffraction curves of the polyimides (thermal imidization).

3.5. Thermal properties of the resulting polyimides

DSC and TGA methods were applied to evaluate the thermal properties of the polyimides, DSC and TGA curves of the polyimides are shown in Figs. 4 and 5, 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 208–324 °C. As we expected, the T_g values of these PIs depended on the structure of the dianhydride component, and decreased with increasing flexibility of the polyimides backbones based on applied the structure of dianhydride. The ployimide derived from BABP-PMDA, for examples, exhibits

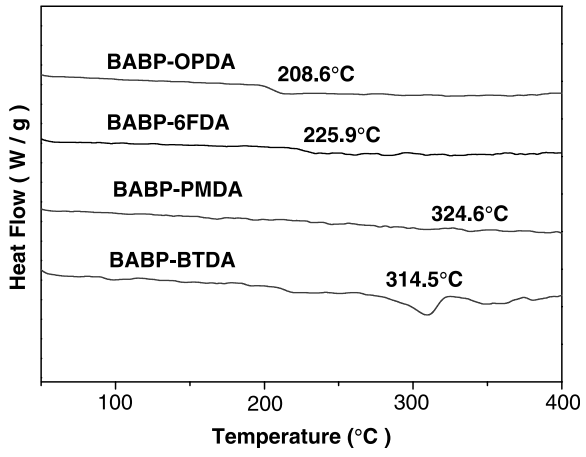
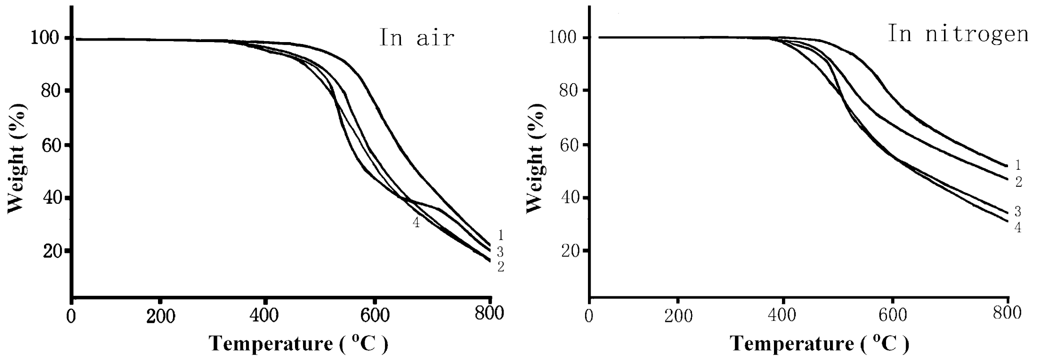


Fig. 4. DSC thermograms of PIs at heating reat of 20 °C/min in nitrogen.



1.BABP-ODPA, 2.BABP-BTDA, 3.BABP-6FDA, 4.BABP-PMDA.

Fig. 5. TGA curves of PIs at a heating reat of 20 °C/min in air and N_2.

Table 3
Data of thermal analysis of the 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-ODPA	208.6	509	531	512	548	54
BABP-6FDA	226.9	477	516	505	532	42
BABP-BTDA	314.5	451	513	491	529	51
BABP-PMDA	324.6	439	478	452	503	37

[a] T_g measured by DSC at a heating rate of 10 °C/min in N_2.

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

[c] Residual weight (%) at 800 °C in nitrogen.

the highest T_g because of the rigid backbone based on PMDA, 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. 3, some of the resulting PIs should exhibit melting peaks from the crystalline morphology in DSC curves, but no melting peaks were observed in the DSC curves presented in Fig. 4, the T_m values represented the crystalline morphology were not obtained from the DSC curves certainly. These probably be that the T_m values of the resulting polyimides were too high to have overstepped measure range of used DSC meter [23,24].

For the thermal stability of the polyimides, Table 3 gives the temperature of 5 and 10% weight loss in air and in nitrogen, respectively, i.e. T_5 and T_{10} values. The T_5 and T_{10} values of the polyimides were in the range 439–509 and 478–531 °C in air, while those of them were in the range 452–512 and 503–548 °C in nitrogen, and the amount of residue of all polyimides at 800 °C in nitrogen atmosphere was higher than 37%, especially, the polyimide derived from BABP-OPDA had the highest residue yield up to 54%. The data from thermal analysis show that the resulting polyimides have fairly high thermal stability.

4. Conclusions

A new heteroaromatic diamine monomer containing pyridine unite, i.e. 2,6-bis(4-aminophenoxy-4′-benzoyl)pyridine (BABP), was successfully prepared in high purity and high yields in this work, and the resulting BABP could be employed in preparation of the novel polyimides with aromatic dianhydride monomer PMDA, BTDA, ODPA and 6FDA by two-step procedures and thermal or chemical imidization methods. Experimental results indicate that the resulting diamine monomer BABP holds a good polymerizability, and 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, and 100% chemical imidization could be achieved at lower temperatures.

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