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## RSC Advance

## ARTICLE

# High transparent polyimides derived from 2-phenyl-4,6-bis(4-aminophenoxy) pyrimidine and 1,3-bis(5-amino-2-pyridinoxy) benzene: preparation, characterization, and optical properties

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To investigate the structure-property relationships of polyimides containing pyrimidine or pyridine moieties, two diamine monomers, 2-phenyl-4,6-bis(4-aminophenoxy) Pyrimidine and 1,3-bis(5-amino-2-pyridinoxy) benzene, were designed and synthesized. The diamines reacted with commercially different aromatic dianhydrides to yield a series of heterocyclic polyimides via a classical two-step polymerization method. The polyimides PI-1 and PI-6 exhibited excellent solubility in strong polar solvents, such as *N,N*-dimethylacetamide, *N,N*-dimethylformamide, *N*-methyl-2-pyrrolidone. The flexible, strong and transparent polyimide films were formed with an UV-visible absorption cut-off wavelengths at 344–399nm. Glass transition temperatures ( $T_g$ ) of the polyimides PI-(1–6) derived from PBAPD and BADB with dianhydrides in the range of 212–260°C which obtained by DSC and the temperatures for 5%wt loss of polyimides in nitrogen and air atmosphere were obtained from the TGA in the range of 430–503°C and 422–465°C, respectively. Moreover, polyimide films showed low moisture absorption of 0.18–1.38% and outstanding mechanical properties with tensile strengths of 81–111MPa, an elongation at break of 4.3–8.7%, and a tensile modulus of 1.3–2.4Gpa, respectively. The coefficients of thermal expansion (CTEs) of the polyimides were ranged from 28 to 62 ppm °C<sup>-1</sup>.

## 1 Introduction

Aromatic polyimides, which were sorted out high performance polymer materials, had been applied in many fields, for example microelectronics, optical devices, integrated electronic circuits and so on, and possessed fantastic thermal and chemical stability, mechanical properties<sup>1–5</sup>. However, classical polyimides have some drawbacks, such as high melting, softening temperatures and insoluble in common organic solvents. These traits make them generally intractable or difficult to process, and ultimately limit their applications<sup>6–7</sup>. Many efforts have been made to improve their processability while maintaining their excellent thermal and mechanical properties. For example, bulky lateral pendants, flexible aryl ether linkage and noncoplanar moieties have been used to enhance the solubility and processability. Unfortunately, bulky lateral pendants, flexible aryl ether linkage and noncoplanar moieties that enhance the solubility, but these groups generally degrade the thermal properties. It is an effective way to improve thermal and mechanical properties by incorporating heterocyclic units, pyridazine<sup>8–12</sup>, pyridine<sup>13</sup>, pyrimidine<sup>14–16</sup> and so on, into polyimide backbone since these heterocycles can increase the rigidity of the polyimide.

In pyrimidine or pyridine moieties, the presence of nitrogen atoms which are similar to the nitro of nitrobenzene, leads to lowering the electron cloud densities than the benzene ring in the *ortho* and *para* positions. If the *ortho* and *para* positions have better leaving group (such as halogen, nitro), it is very prone to nucleophilic substitution reaction. Also, the presence of nitrogen atoms with a free electron, gives an opportunity for protonation to modify optical properties.

In this study, aimed at interpreting the structure-property relationships of heterocyclic high-performance polyimides, two novel diamines, 2-phenyl-4,6-bis(4-aminophenoxy)pyrimidine and 1,3-bis(5-amino-2-pyridinoxy)benzene were characterized to synthesize PIs. Meanwhile, PIs derived from 2,4-bis(4-aminophenoxy)pyrimidine (2,4-BAPD), 4,6-bis(4-aminophenoxy)pyrimidine (4,6-BAPD) and 1,3-bis(4-aminophenoxy)benzene (BAPB) with 6FDA were prepared, and the effect of different units, which were incorporated into the polymers, was studied.

## 2 Experimental

### 2.1 Materials

The aromatic bis(ether amine)s, 2,4-bis(4-aminophenoxy)pyrimidine (2,4-BAPD), 4,6-bis(4-aminophenoxy)pyrimidine (4,6-BAPD), 1,3-bis(4-aminophenoxy) benzene (BAPB), were prepared according to methods used in the literature<sup>17–19</sup>. 3,3',4,4'-oxydiphthalic anhydride (ODPA), 3,3',4,4'-

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benzophenonetetracarboxylic dianhydride (BTDA) were recrystallized from acetic anhydride before use. 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) and 2,2-bis[4-(3,4-dicarboxyphenoxy) phenyl] propane dianhydride (BPADA) and pyromellitic dianhydride (PMDA) was baked at 130°C in vacuo overnight prior to use. All commercially available dianhydrides were supplied by Sinopharm Chemical Reagent Beijing Co. Ltd. Potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) was supplied by Acros and dried in vacuum at 130°C for 1h prior to use. *N,N*-dimethylacetamide (DMAc) and *N,N*-dimethylformamide (DMF) were purified by reduced pressure distillation over calcium hydride and stored over 4Å Molecular sieves before use. 2-chloro-5-nitropyridine, 4,6-dichloro-2-phenylpyrimidine, *m*-dihydroxybenzene, *p*-nitrophenol, 10% palladium on activated charcoal/carbon (Pd/C), and 80% hydrazine monohydrate were purchased from Acros and used without further purification. The other commercially available reagents and solvents were also used without further purification.

## 2.2 Measurements

NMR was performed on a BRUKER-300 spectrometer with DMSO-d<sub>6</sub> or CDCl<sub>3</sub> as solvent at 300 MHz for <sup>1</sup>H. HRLC-MS (High Resolution Liquid Chromatograph-Mass Spectrometry) was measured by Agilent 1290-micrOTOF-QII. Inherent viscosities ( $\eta_{inh}$ ) were measured with an Ubbelohde viscometer at PAAs concentration of 0.5g/dL at 25°C in DMAc. Weight average molecular weights ( $M_w$ ) and number-average molecular weights ( $M_n$ ) were obtained via gel permeation chromatography (GPC) on the basis of polystyrene calibration on a PL-GPC 220 instrument with DMF as an eluent at a flow rate of 1.0ml/min. FT-IR (spectra Fourier transform infrared spectroscopy) was recorded on a Bruker Vector22 spectrometer with KBr (potassium bromide) pellets or about 10um thick films. Elemental analyses were obtained by a Vario EL cube CHN recorder elemental analysis instrument with the films. Glass-transition temperatures ( $T_g$ ) of polyimides were determined on a TA Instruments (DSC Q100) in a nitrogen flow of 50ml/min at a heating rate of 10°C/min, and determined by the second heating cycle. Thermo gravimetric analysis (TGA) was performed on TA 2050 with a heating rate of 10°C/min in the nitrogen or air atmosphere. Dynamic mechanical analysis (DMA) was carried out with a TA instrument (DMA Q800), and  $T_g$  was treated as the peak temperature of loss modulus (E''). Thermo mechanical analysis (TMA) was carried out with a METTLER TOLEDO instrument (TMA/SDTA841) and the coefficient of thermal expansion (CTE) was obtained on the temperature range of 50~150°C. Tensile properties of the films were measured by a Shimadzu AG-I universal testing apparatus with crosshead speed of 5mm/min at room temperature, and the film specimen sizes were at 25~30mm thick, 3mm wide and 4cm lengths. A Shimadzu UV-Vis 2501 spectrometer was used in transmittance mode to obtain the UV-Vis (ultraviolet-visible) absorption spectra with the thin films as the samples at room temperature. Water uptakes (WU) of the films were calculated from the following equation:

$$WU = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\%$$

Where  $W_{wet}$  refers to the weight of film samples after immersion in deionized water at room temperature for 24h, and  $W_{dry}$  is the initial weight of them.

## 2.3 Monomer synthesis

**2.3.1 2-phenyl-4,6-bis(4-nitrophenoxy)pyrimidine.** *P*-nitrophenol (12.34g, 88.85mmol) and 4,6-dichloro-2-phenylpyrimidine (8g, 35.54mmol) and 60ml of dried DMF were placed into a 250ml, three-necked and round-bottom flask with a mechanical stirrer, a reflux condenser under the protection of nitrogen. After the mixture was completely dissolved, potassium carbonate (12.28g, 88.85mmol) was added into it together. After stirring at room temperature for 30min, the mixture was continuously reacted at 120°C for 8h. Then cooled to room temperature, the obtained mixture was poured into 350ml of deionized water to give a precipitate, which was collected by filtration, washed with ethanol, and dried in vacuum at 110°C overnight. The light yellow solid was recrystallized from DMF/water to give the product 14.07g (92%). Melting point: 195~197°C. FT-IR (KBr): 3118, 1622, 1561, 1523, 1492, 1378, 1349, 1251, 1223, 1168, 1127. <sup>1</sup>H NMR: 6.92 (s, 1H), 7.63 (d, 4H), 8.39 (d, 4H), 7.93 (d, 2H), 7.54-7.42 (m, 2H), 7.40 (dd, 1H). Elemental Analysis Calcd: C, 61.4%; H, 3.28%; N, 13.02%. Found: C, 60.99%; H, 3.42%; N, 13.24%. HRLC-MS (ESI): 430.4 (M+H)<sup>+</sup>, Calcd 431.1 for C<sub>22</sub>H<sub>14</sub>N<sub>4</sub>O<sub>6</sub>.

**2.3.2 1,3-bis(5-nitro-2-pyridinoxy)benzene.** Under N<sub>2</sub> atmosphere, *m*-dihydroxybenzene (3.30g, 30mmol), 2-chloro-5-nitropyridine (10.47g, 66mmol) and 70ml of dried DMF were placed into a 250ml, three-necked and round-bottom flask with a mechanical stirrer, a reflux condenser. Until the reaction mixture was completely dissolved, potassium carbonate (9.12g, 66mmol) was poured into it together. After 20min of stirring at room temperature, the reaction mixture was continuously reacted at 65°C for 7h. Then cooled to room temperature, the obtained mixture was poured into 250ml of deionized water to give a solid precipitate, which was collected by filtration, washed with water, and dried in vacuum at 80°C overnight. The yellow solid was purified by recrystallization from DMF/water. The yield of the crude product (BNDB) was 10.1g (95%). Melting point: 125~127°C. FT-IR (KBr): 1605, 1572, 1518, 1465, 1388, 1349, 1253, 1163, 1118. <sup>1</sup>H NMR: 7.17 (d, 1H), 7.24-7.18 (m, 2H), 7.32-7.24 (m, 2H), 7.60-7.51 (m, 1H), 8.66-8.58 (m, 2H), 9.06 (dd, 2H). Elemental Analysis Calcd: C, 54.24%; H, 2.85%; N, 15.81%. Found: C, 54.26%; H, 2.76%; N, 15.91%. HRLC-MS (ESI): 355.1 (M+H)<sup>+</sup>, Calcd 354.3 for C<sub>16</sub>H<sub>10</sub>N<sub>4</sub>O<sub>6</sub>.

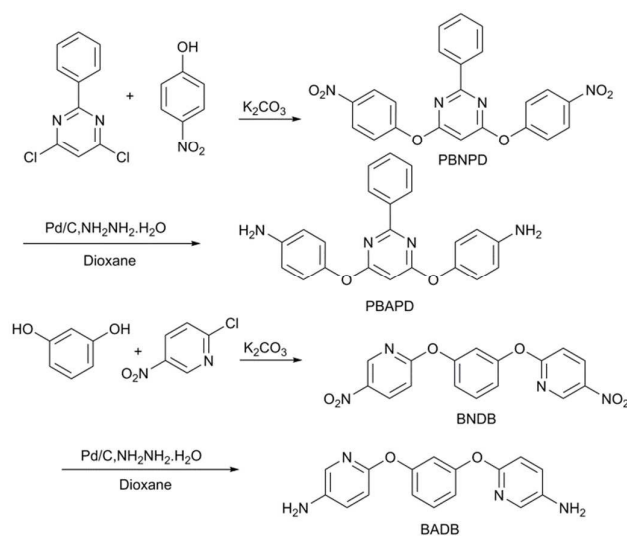
**2.3.3 2-phenyl-4,6-Bis(4-aminophenoxy)pyrimidine.** In a 250ml three-necked flask equipped with a mechanical stirrer, 10.0g (23.2mmol) PBNPD, 0.5g of 10%Pd/C, and 150ml of dioxane was placed, and heated to reflux. Then 7.0g (112.0mmol) of hydrazine monohydrate (80%) was added dropwise for 0.5h. The reaction mixture was heated to reflux for another 16h, filtered to remove Pd/C, and reduced pressure distillation to remove excess solvent to obtain the crude

product. The crude product was purified by recrystallization from DMF/water. 7.3g PBAPD was obtained. The yield was 85%. Melting point: 155~156°C. FT-IR (KBr): 3448, 3385, 3220, 1618, 1586, 1513, 1447, 1383, 1215, 1152.  $^1\text{H}$  NMR: 5.13 (s, 4H), 5.99 (d, 1H), 6.69-6.56 (m, 4H), 7.02-6.81 (m, 4H), 7.47-7.42 (m, 1H), 7.50-7.46 (m, 2H), 8.09 (dd, 2H). Elemental Analysis Calcd: C, 71.34%; H, 4.90%; N, 15.13%. Found: C, 71.44%; H, 4.93%; N, 15.06%. HRLC-MS (ESI): 371.2 (M+H) $^+$ , Calcd 370.4 for  $\text{C}_{22}\text{H}_{18}\text{N}_4\text{O}_2$ .

**2.3.4 1,3-bis(5-amino-2-pyridinoxy)benzene.** Similarly, BADB (yield: 95%) was prepared by the above-mentioned procedures. Melting point: 79~80°C. FT-IR (KBr): 3371, 3185, 1613, 1578, 1471, 1422, 1274, 1238, 1129.  $^1\text{H}$  NMR: 6.52 (s, 1H), 6.69-6.58 (m, 2H), 6.77 (d, 2H), 7.08 (dd, 2H), 7.25 (t, 1H), 7.57 (s, 2H), 5.14 (s, 4H). Elemental Analysis Calcd: C, 65.30%; H, 4.79%; N, 19.04%. Found: C, 65.24%; H, 4.86%; N, 18.96%. HRLC-MS (ESI) 295.1 (M+H) $^+$ , Calcd 294.3 for  $\text{C}_{16}\text{H}_{14}\text{N}_4\text{O}_2$ .

## 2.4 Polymer synthesis

As shown in Scheme2, the diamines were employed to react with PMDA, BTDA, ODPDA and BPADA, 6FDA, respectively, to prepare series of PIs (polyimides) via a typical two-step polymerization method. In the case of PI-1, firstly, PAAs obtained as following procedure: 0.60g 6FDA (1.35mmol) was slowly added to the solution of PBAPD (0.5g, 1.35mmol) in 6.5ml DMAc at a solid content of 15 wt%. Then, the reaction mixture was stirred at room temperature for 12h under  $\text{N}_2$  atmosphere. Finally, thin polyimide films were prepared to cast PAAs (polyamic acids) on glass plates via thermal imidization by elevated temperatures as follow: (40°C/2h; 60°C/2h; 80°C/2h; 100°C/2h; 120°C/2h; 150°C/1h) to remove the solvents in air, and then the heating imidization procedure (200°C/0.5h, 250°C/1h, 300°C/1h) under vacuum. The freestanding films were obtained by soaking in water to release from the glass plates. Similarly, PI-2~PI-9 films were obtained by the above-mentioned procedures.



Scheme 1 Preparation of monomer containing pyrimidine or pyridine

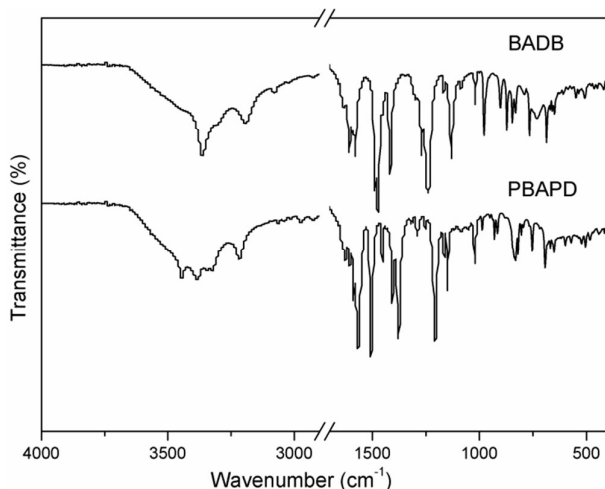


Fig. 1 FT-IR spectra of PBAPD and BADB

## 3 Result and discussion

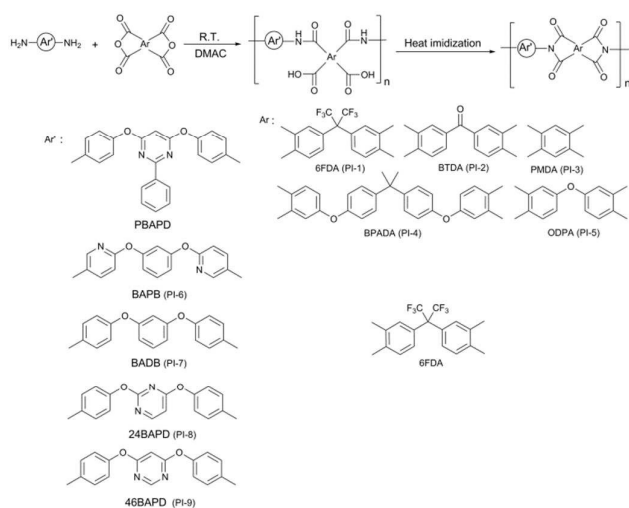
### 3.1 Monomer synthesis

Two diamine monomers, 2-phenyl-4,6-bis(4-aminophenoxy) pyrimidine, 1,3-bis(5-amino-2-pyridinoxy) benzene, was successfully prepared by aromatic nucleophilic substitution reaction starting from *p*-nitrophenol, 4,6-dichloro-2-phenylpyrimidine and *m*-dihydroxybenzene, 2-chloro-5-nitropyridine, respectively (shown in scheme1). Owing to the electron far less than that of benzene, aromatic nucleophilic substituticloud density of carbon atoms on pyrimidine or pyridine rings are on reaction occurred more easily on pyrimidine or pyridine rings, especially the *ortho* and *para* positions. The reaction which was used to synthesis nitrocompounds, was carried out readily in the presence of  $\text{K}_2\text{CO}_3$ . The reduction of nitro-compound uses hydrazine hydrate in the presence of Pd/C catalyst in refluxing dioxane to yield diamine monomer. The diamine monomer was finally purified by recrystallization in DMF/water. The structures of diamines, PBAPD and BADB, were confirmed by elemental analysis, HRLC-MS, FT-IR spectra, and  $^1\text{H}$  NMR spectroscopy. Fig.1 shows the FT-IR spectra of PBAPD and BADB, the characteristic absorptions of the nitro group disappeared, and N-H absorption peak of the amino group in the region of 3180~3450  $\text{cm}^{-1}$  were detected. As shown in Fig.2,  $^1\text{H}$  NMR spectra of the diamine monomers illustrate that the nitro groups in PBNPD and BNDB were completely reduced, and the signal of amino groups appeared at around  $\delta$ 5.0 as a singlet.

### 3.2 Polymer synthesis

The diamine PBAPD was reacted with PMDA, BTDA, ODPDA and BPADA, 6FDA, respectively, and the diamines, BADB, BABP, 2,4-BAPD and 4,6-BAPD, were reacted with 6FDA, respectively, to prepare series of polyimides (PI-1~PI-9) via a

typical two-step polymerization methods. PAAs were obtained by reacting equimolar amounts of diamine monomer with aromatic dianhydrides at a solid content of 15 wt%, and stirred for 12h at room temperature under N<sub>2</sub> atmosphere. Thin polyimide films were prepared by casting PAAs on glass plates via thermal imidization by elevated temperatures. As shown in Table 2, the inherent viscosities of the PAAs were in the range of 0.59–1.29 dL/g measured at a concentration of 0.5 g/dL in DMAc at 25°C. The molecular weights of the PIs determined by GPC in DMF relative to polystyrene standards were in the range of 48,309–68,127 for M<sub>w</sub> and 31805–45,723 for M<sub>n</sub> with M<sub>w</sub>/M<sub>n</sub> values of 1.35–1.61. In FT-IR spectra of PIs, shown in Fig. 3, the characteristic imide absorption bands were detected for 1782 cm<sup>-1</sup> (asymmetrical C=O stretching), 1726 cm<sup>-1</sup> (symmetrical C=O stretching), 1374 cm<sup>-1</sup> (C-N stretching), and N-H absorption peak among 3180–3450 cm<sup>-1</sup> disappeared because the PAAs had been full imidization. As shown in Table 1, molecular formulas were also supported for the elemental analyses (C, H, and N) of the PIs, because those found values were in agreement with the calculated ones. Two typical <sup>1</sup>H NMR spectra of the novel polyimides (PI-1 and PI-6) were measured and all the protons in the polyimides can be assigned clearly, depicted in Fig. 3.



Scheme 2 Synthesis route of the polyimides

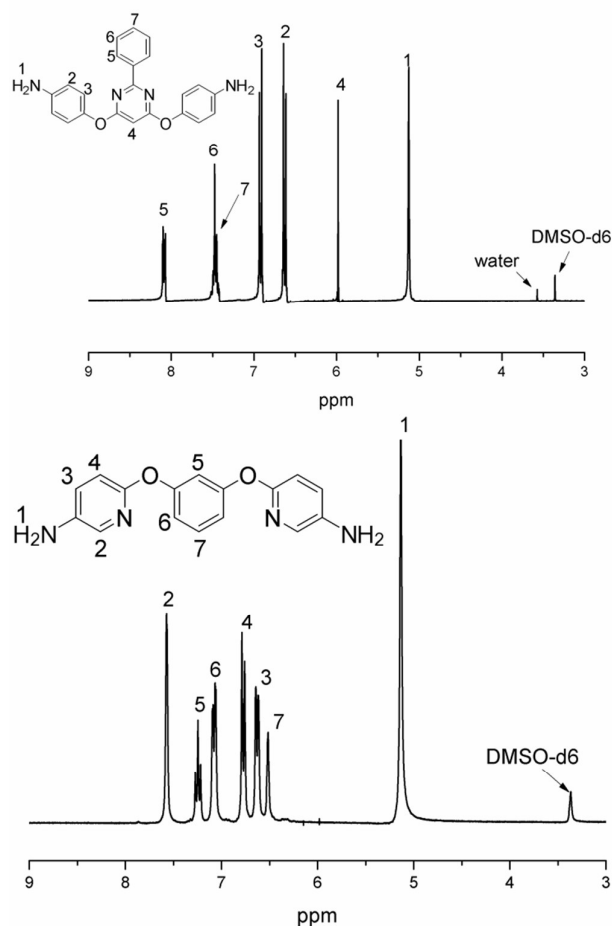


Fig. 2 <sup>1</sup>H NMR spectra of PBAPD and BADB

### 3.3 Thermal properties of the polyimides

As shown in Table 2, thermal properties of the polyimides were detected by DSC, TGA, DMA and TMA. In DMA curves,  $T_g$  was treated as the peak temperature of loss modulus ( $E''$ ). Glass transition temperatures ( $T_g$ ) of the polyimides (PI-1~PI-6) derived from PBAPD and BADB with dianhydrides in the range of 212~260°C and 220~293°C obtained by DSC in Fig. 2 and DMA in Fig. 7, respectively. From the Fig. 2, PI-3 was neither an obvious glass transition nor a melting behavior due to rigid-rod PIs derived from PMDA and the high packing density of polymer backbones<sup>20</sup>. Generally,  $T_g$  values of polymers are determined by molecular packing density and rigidity of the polymer backbones. PI-4 derived from BPADA possessed the lowest  $T_g$  due to its flexible polymer chain structure. Compared to analogous polyimides, the PI-1 shows lower  $T_g$  values than that of PI-8 and PI-9, which might be attributed to decreasing molecular packing density by incorporating the benzene pendant, and the  $T_g$  of PI-6 was higher than that of analogous polyimide PI-7, which may be due to the introduction of the rigid pyridine units into the polymer backbone<sup>21</sup>. The thermal stability properties of the polyimides were obtained by TGA in nitrogen and air at a heating rate of 10°C/min, and summarized in Table 2. The

**Table 1** Elemental analysis of the polyimides

Polyimides	Formula of repeating unit	Elemental analysis (%)							
				C		H		N	
PI-1	C <sub>41</sub> H <sub>20</sub> F <sub>6</sub> N <sub>4</sub> O <sub>6</sub>	Calcd	found	63.25	62.93	2.59	2.71	7.20	7.23
PI-2	C <sub>39</sub> H <sub>20</sub> N <sub>4</sub> O <sub>7</sub>	Calcd	found	71.34	72.21	3.07	3.38	8.53	8.73
PI-3	C <sub>52</sub> H <sub>16</sub> N <sub>4</sub> O <sub>6</sub>	Calcd	found	69.57	69.35	2.92	3.21	10.14	10.20
PI-4	C <sub>53</sub> H <sub>34</sub> N <sub>4</sub> O <sub>8</sub>	Calcd	found	74.47	74.14	4.01	3.97	6.55	6.57
PI-5	C <sub>38</sub> H <sub>20</sub> N <sub>4</sub> O <sub>7</sub>	Calcd	found	70.81	70.49	3.13	3.59	8.69	8.66
PI-6	C <sub>35</sub> H <sub>16</sub> F <sub>6</sub> N <sub>4</sub> O <sub>6</sub>	Calcd	found	59.84	59.44	2.30	2.83	7.98	7.97
PI-7	C <sub>37</sub> H <sub>18</sub> F <sub>6</sub> N <sub>2</sub> O <sub>6</sub>	Calcd	found	63.44	63.10	2.59	2.66	4.00	3.97
PI-8	C <sub>35</sub> H <sub>16</sub> F <sub>6</sub> N <sub>4</sub> O <sub>6</sub>	Calcd	found	59.84	59.42	2.30	2.54	7.98	8.02
PI-9	C <sub>35</sub> H <sub>16</sub> F <sub>6</sub> N <sub>4</sub> O <sub>6</sub>	Calcd	found	59.84	60.17	2.30	2.45	7.98	8.13

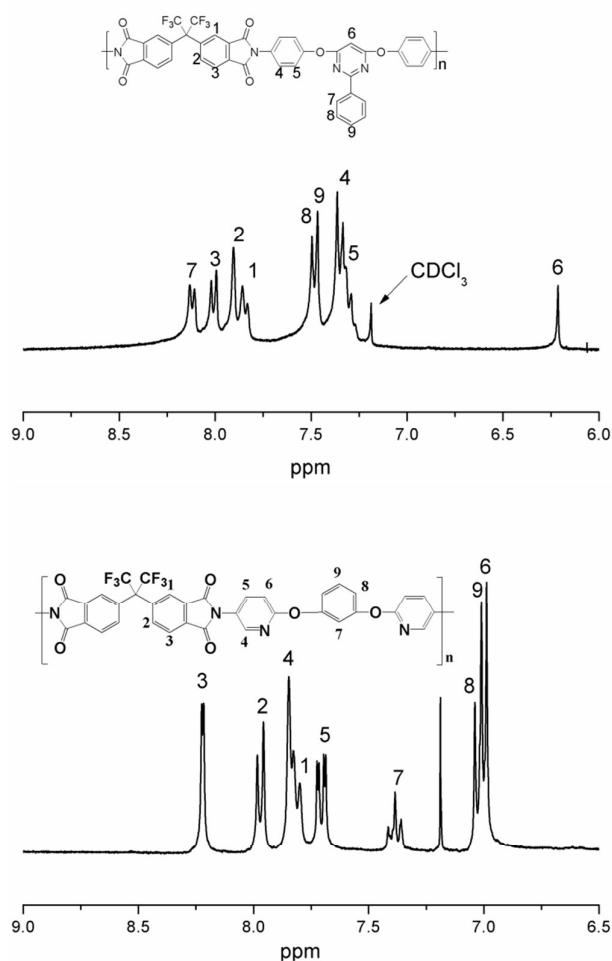
**Table 2** Physical properties and thermal properties of the PI films

Polyimides	$\eta_{inh}$ of PAA (dL/g) <sup>f</sup>	$M_n^b$	$M_w^b$	$M_w/M_n^b$	T <sub>g</sub> (°C)		T5% (°C) <sup>f</sup>		T10% (°C) <sup>g</sup>		Rw(%) <sup>h</sup>	CTE(ppm <sup>-1</sup> ) <sup>i</sup>
					DSC <sup>d</sup>	DMA <sup>e</sup>	N <sub>2</sub>	Air	N <sub>2</sub>	Air		
PI-1	1.29	45,723	68,127	1.49	260	264	44	422	477	461	54.4	61
PI-2	0.72	— <sup>c</sup>	—	—	255	261	43	427	465	464	59.9	39
PI-3	0.59	—	—	—	— <sup>j</sup>	293	43	422	469	450	59.7	28
PI-4	0.88	31,805	49,114	1.58	212	220	44	426	468	452	51.9	66
PI-5	0.76	— <sup>k</sup>	—	—	236	239	42	427	454	455	57.6	42
PI-6	1.11	40,582	65,337	1.61	245	253	50	465	529	501	40.3	62
PI-7	1.21	42,086	65654	1.56	244	253	51	495	539	523	56.3	70
PI-8	0.97	35,785	48,309	1.35	264	274	43	439	459	478	49.7	67
PI-9	1.04	38,820	57,065	1.47	267	275	44	439	464	477	49.9	46

<sup>a</sup>: Measured at PAA concentration of 0.5g/dL in DMAc at 25°C; <sup>b</sup>: Measured by GPC in DMF, polystyrene was used as standard; <sup>c</sup>: Not dissolved in DMF; <sup>d</sup>: T<sub>g</sub> obtained by DSC at the second time; <sup>e</sup>: T<sub>g</sub> measured by DMA at a heating rate of 5°C/min; <sup>f,g</sup>: T5% (5% weight loss temperatures) and T10% (10% weight loss temperatures) measured by TGA in air and nitrogen; <sup>h</sup>: Char yield at 800°C; <sup>i</sup>: CTE, coefficients of thermal expansion measured at a heating rate of 10°C/min; <sup>j</sup>: Not obviously observed; <sup>k</sup>: Appropriate concentration in DMF could not be prepared.

temperature for 5%wt loss of polyimides in nitrogen and air atmosphere were obtained from the TGA curves in the range of 430~503°C and 422~465°C, respectively. Similarly, temperatures for 10%wt loss of polyimides in nitrogen and air atmosphere were in the range of 454~529°C and 450~501°C, respectively. Meanwhile, char yields at 800°C were in the range of 40.3~59.9%. Compared with the polyimides shown in Table 2, Fig. 5 and Fig. 6, the polyimides exhibited high thermal stability due to the rigid heterocyclic groups. However, the 5% wt and 10% wt loss temperature in nitrogen and air of PI-1 was similar to that of analogous polyimides (PI-9 and PI-8) and the residue weight % at 800°C in nitrogen of PI-4 was lower than that of polyimides (PI-9 and PI-8). It was owing to incorporate benzene pendant. 5% wt and 10% wt loss temperature in nitrogen and air of PI-8 and PI-9 were lower than that of polyimides (PI-7) and the char yield at 800°C in nitrogen of PI-8 and PI-9 was higher than that of polyimides PI-7. It was owing to incorporate pyrimidine unit in the polymer backbone. From the Fig. 5 and Fig. 6, polymers, excepted for PI-6 and PI-7, showed a two decomposition stages. The former before 500°C is probably attributed to the thermal degradation of pyrimidine moiety<sup>22</sup>, and the latter was the thermal degradation of polymer backbone.

As shown in Fig. 8, TMA curves of the polyimide films were obtained at the heating rate of 10°C/min, and the results were listed in Table 2. The coefficients of thermal expansion (CTEs) of the polyimides were ranged from 28 to 62 ppm°C<sup>-1</sup>. CTEs are influenced by the rigidity and linearity of the polymer chains. PI-3 possessed the lowest CTE value owing to its highest rigidity and linearity of the polymer chain. It is understandable also from no obvious glass transition of PI-3. PI-1, PI-8, PI-9 and PI-6 exhibited higher CTE values than that of PI-7 which

**Fig. 3** <sup>1</sup>H NMR spectra of the polyimides (PI-1 and PI-6)

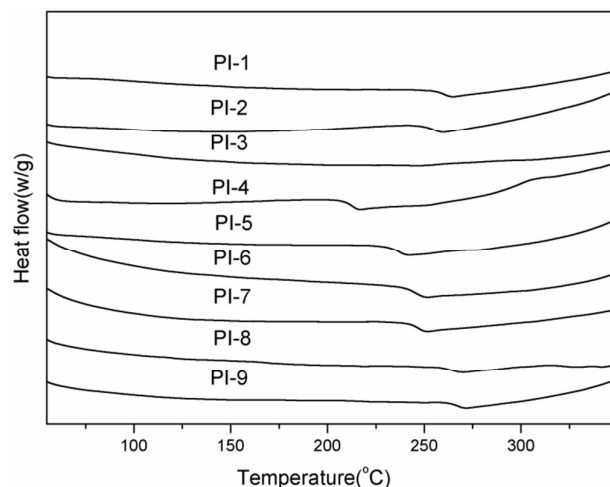


Fig.4 DSC curves of polyimide films

were probably attributed to possess higher rigidity and linearity by introducing the heterocyclic groups into the polymer chain.

### 3.4 Mechanical properties of the polyimides

The tensile properties of the polyimide films were analyzed by a Shimadzu AG-I universal testing apparatus with crosshead speed of 5mm/min at room temperature and the sizes of film specimens were at 25~30mm thick, 3mm wide and 4cm lengths, and summarized in Table3. The films had tensile strengths of 81~111MPa, an elongation at break of 4.3~8.7%, and a tensile modulus of 1.3~2.4Gpa, respectively. In a comparison of the mechanical properties of PI-6 and PI-9 with that of analogous polyimides (PI-7), PI-6 and PI-9 exhibit higher tensile strength and moduli than PI-7 which may be due to the introduction of the rigid heterocyclic rings to the polymer backbone. The PI-1 possessed lower tensile moduli than that of PI-9, but PI-1 had higher tensile strength. It may be attributed to introduce the benzene pendant increasing the rigidity of the polymer chain, simultaneously, reducing intermolecular force between the polymer chain<sup>23</sup>.

### 3.5 Solubility and X-ray diffraction of the polyimides

The solubility of the PIs was obtained by dissolving 10mg of polymers in 1ml of solvent at room temperature for 24h, and the results are listed in Table4. The PIs, excepted for PI-2 and PI-3 exhibited good solubility in polar solvents, such as NMP, DMSO, DMAc, DMF, *m*-cresol, and even in low boiling point solvents, such as THF, CHCl<sub>3</sub> at room temperature due to the introduction of the flexible -O- and -C(CF<sub>3</sub>)<sub>2</sub>- groups in polymer backbone. The former increased chain flexibility and the affinity of the polymers<sup>24</sup>, and the latter decreased the interaction between polymer chains. In a comparison of the solubility properties of PI-1 with that of analogous polyimides (PI-9), PI-1 exhibited better solubility than PI-9, which may be due to introduce the benzene pendant into the polymer chain reducing intermolecular force between the polymer chain. Furthermore, PI-6 shows better solubility than that of PI-7. It may be attributed to the presence of a nitrogen atom in the pyridine unit which produces a polarized bond rises dipole-dipole interactions in the polymer-solvent system.

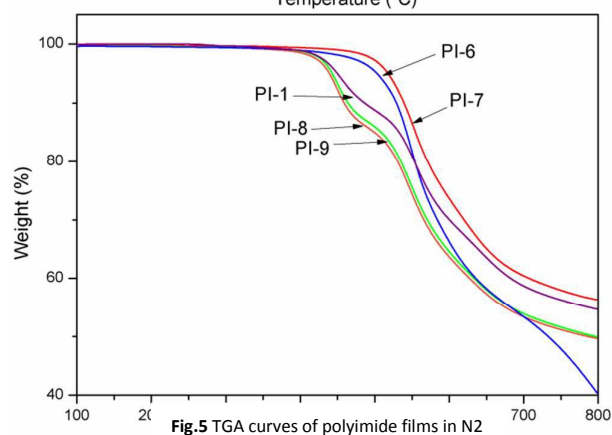
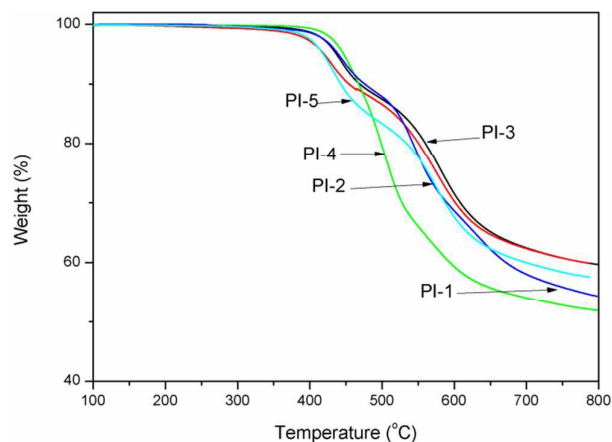


Fig.5 TGA curves of polyimide films in N<sub>2</sub>

Wide-angle X-ray diffraction analysis was shown in Fig.9. The X-ray diffraction curves of the polyimides showed a series of wide diffraction peak. It indicated the polyimides were amorphous due to introduce the flexible ether linkage and the bulk benzene pendant loosening the chain packing of the polymer.

### 3.6 Optical properties and Water uptake of the polyimides

The films with thicknesses of about 30μm as the samples were measured for optical transparency property of polyimides with UV-visible spectroscopy. Meanwhile, the UV-visible spectra are given in Fig.8, and the percentage transmittances at 450nm and cut-off wavelengths ( $\lambda_{\text{cut-off}}$ ) are listed in Table3. The cut-off wavelengths ( $\lambda_{\text{cut-off}}$ ) are in the range of 334~389nm, and the percentage transmittance at 450nm is in the range of 42%~94%. These data obtained from these spectra in Fig.8. Because the trifluoromethyl groups could inhibit the formation of the CTC between polymer chains through steric hindrance and the inductive effect the PI-1 film shows higher transparency at 450nm and lower  $\lambda_{\text{cut-off}}$  than PI-2. However, PI-1 shows lower transparency at 450nm and higher  $\lambda_{\text{cut-off}}$  than PI-9. This may be attributed to introduce the benzene pendant group.

**Table 3** Mechanical properties and Optical properties of PI films

Polyimides	$T_s$ (Mpa) <sup>a</sup>	$T_M$ (Gpa) <sup>b</sup>	$E_b$ (%) <sup>c</sup>	$\lambda_{cut-off}$ (nm) <sup>d</sup>	Transmittance(%) <sup>e</sup>	WU (%) <sup>f</sup>
PI-1	101±2.6 <sup>g</sup>	2.4±0.19	4.3±0.2	344	90	0.18
PI-2	102±3.1	2.0±0.09	6.4±0.3	389	43	0.73
PI-3	81±1.7	1.7±0.17	5.8±0.3	388	42	1.21
PI-4	84±2.2	1.3±0.16	8.6±0.4	363	91	0.20
PI-5	98±2.5	1.7±0.04	7.1±0.2	357	93	0.23
PI-6	111±3.2	1.9±0.08	8.7±0.3	334	94	1.38
PI-7	99±2.4	1.6±0.06	9.7±0.4	314	94	0.28
PI-8	108±3.5	1.6±0.16	12±0.1	302	94	0.55
PI-9	103±2.8	1.8±0.16	8.3±0.3	312	93	0.84

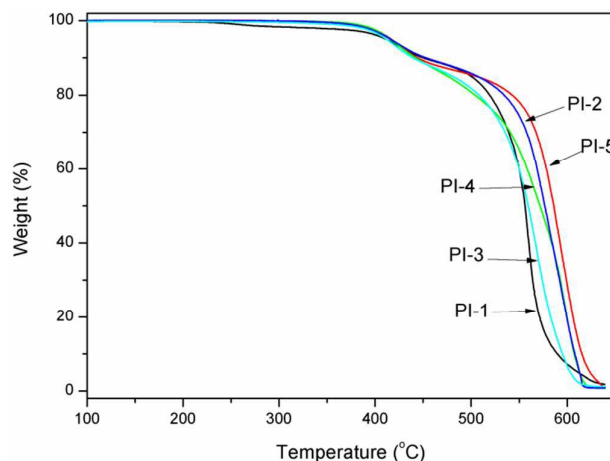
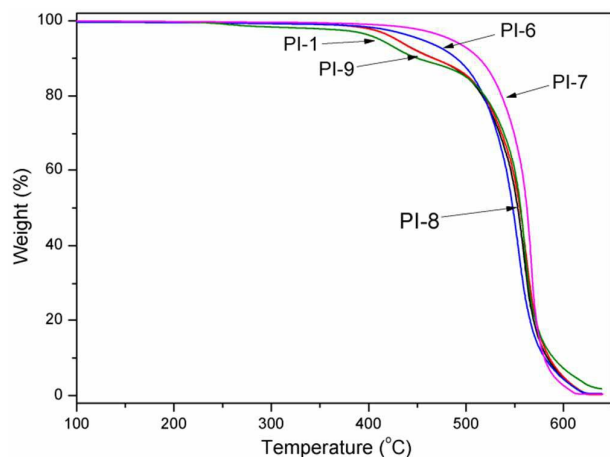
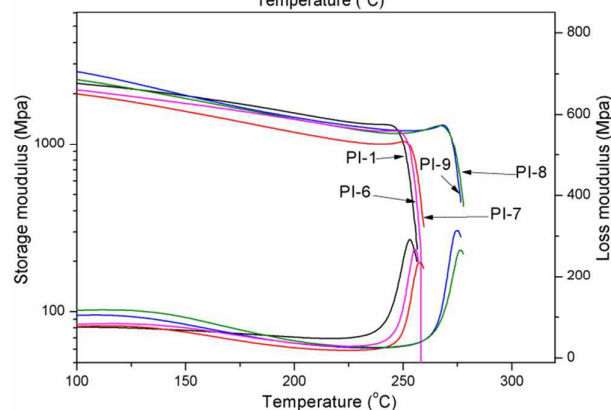
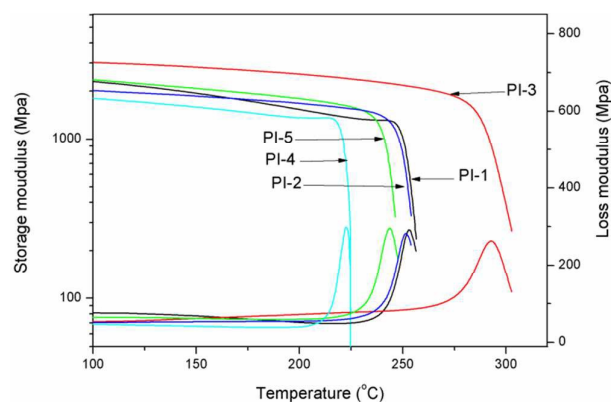
<sup>a</sup> Tensile strength( $T_s$ ); <sup>b</sup> Tensile modulus( $T_M$ ); <sup>c</sup> Elongation at break( $E_b$ ); <sup>d</sup> Cut-off wavelength( $\lambda_{cut-off}$ );

<sup>e</sup> Transmittance at 450nm; <sup>f</sup> Water uptakes(WU); <sup>g</sup>2.6, standard deviation.

**Table 4** Solubility behavior of the polyimides<sup>a</sup>

Solvents	PI-1	PI-2	PI-3	PI-4	PI-5	PI-6	PI-7	PI-8	PI-9
<i>m</i> -Cresol	+ <sup>b</sup>	--	--	--	--	--	+-	--	--
DMF	++	--	--	++	+	++	++	++	++
DMAc	++	--	--	++	+	++	++	+	+
NMP	++	--	--	+	+-	++	++	+	--
DMSO	+	--	--	+	--	+	+	--	+
THF	++	--	--	+	--	++	++	--	--
CHCl <sub>3</sub>	++	--	--	++	--	++	++	++	++
Cyclohexanone	+	--	--	--	--	+	--	--	--
CH <sub>3</sub> COOH	--	--	--	--	--	+	--	--	--
Pyridine	++	--	--	++	--	++	++	+	+

<sup>a</sup>: The solubility experiment was carried out with 10mg of PIs in 1ml of solvent at room temperature for 24h; <sup>b</sup>: ++, soluble; +-, partial soluble; --, insoluble.

**Fig.6** TGA curves of polyimide films in air**Fig.7** DMA curves of polyimide films



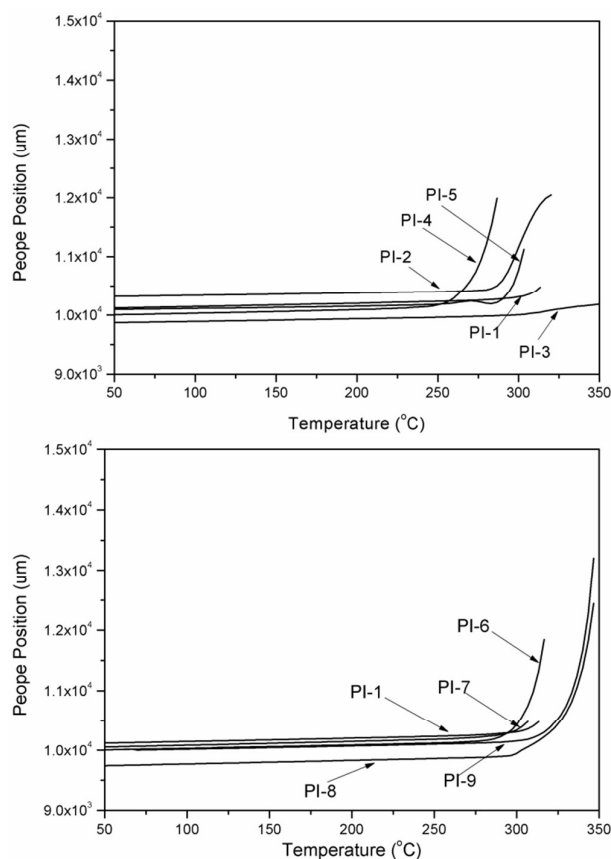


Fig.8 TMA curves of polyimide films

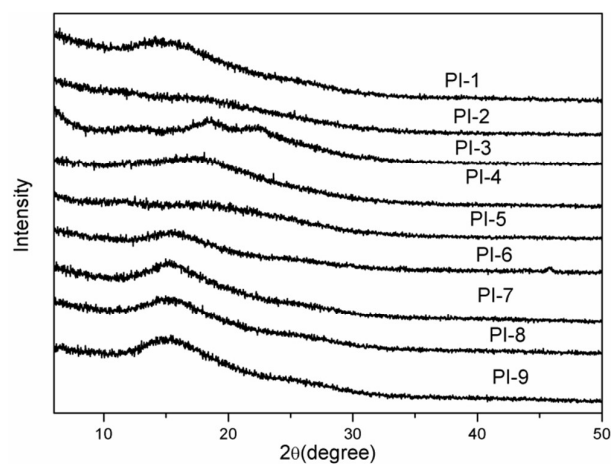


Fig.9 XRD curves of the polyimide films.

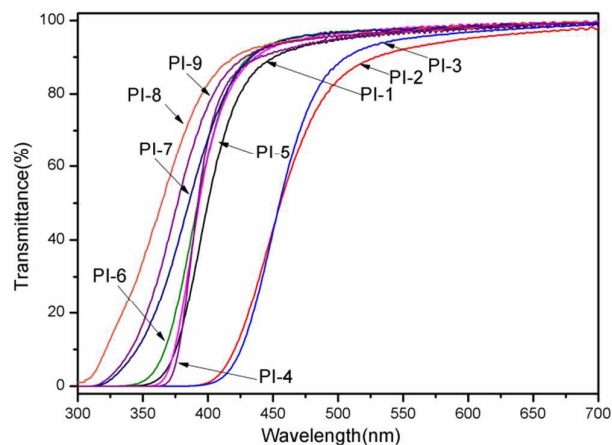


Fig.10 UV-visible spectra of the polyimides

The water uptakes of polyimides is in the range of 0.18~1.38%, and listed in Table3. PI-1 exhibited the lowest moisture absorption (0.18%), and this result may be attributed to the fact that polyimide contained the water proofing effect of the benzene pendant and trifluoromethyl groups. Meanwhile, because of the water proofing effect of the benzene pendant group, PI-1 had significantly lower moisture absorption than PI-9.

#### 4 Conclusions

For clarifying the structure-property relationships of heterocyclic high-performance Polymers, two novel diamines containing pyrimidine or pyridine moieties were designed and characterized, which were employed to react with commercially various aromatic dianhydrides to yield a series of heterocyclic polyimides via a classical two-step polymerization method. The characterized polyimides were not weakened fantastic thermal stability, mechanical property, and showed high solubility, excellent optical transparency and lower cut-off wavelength, which can be good candidates as components for advanced optical device applications.

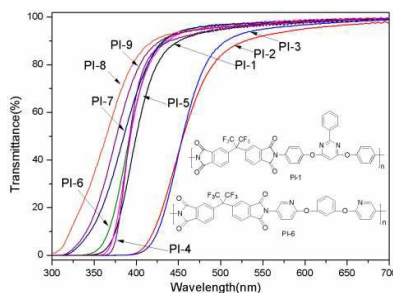
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## Graphical and Textual abstract



To investigate the structure-property relationships of polyimides containing pyrimidine or pyridine moieties, two diamine monomers, 2-phenyl-4,6-bis(4-aminophenoxy)pyrimidine and 1,3-bis(5-amino-2-pyridinoxy)benzene, were designed and synthesized. The diamines reacted with commercially different aromatic dianhydrides to yield a series of heterocyclic polyimides via a classical two-step polymerization method. The polyimides PI-1 and PI-6 exhibited excellent solubility in strong polar solvents, such as *N,N*-dimethylacetamide, *N,N*-dimethylformamide, *N*-methyl-2-pyrrolidone. The flexible, strong and transparent polyimide films were formed with an UV-visible absorption cut-off wavelengths at 344~399nm. Glass transition temperatures ( $T_g$ ) of the polyimides PI-(1~6) derived from PBAPD and BADB with dianhydrides in the range of 212~260°C which obtained by DSC and the temperatures for 5%wt loss of polyimides in nitrogen and air atmosphere were obtained from the TGA in the range of 430~503°C and 422~465°C, respectively. Moreover, polyimide films showed low moisture absorption of 0.18~1.38% and outstanding mechanical properties with tensile strengths of 81~111MPa, an elongation at break of 4.3~8.7%, and a tensile modulus of 1.3~2.4Gpa, respectively. The coefficients of thermal expansion (CTEs) of the polyimides were ranged from 28 to 62 ppm °C<sup>-1</sup>.