



# Synthesis and characterization of novel polyimides derived from 2,4-bis(4-aminophenoxy)pyrimidine

High Performance Polymers

2014, Vol. 26(8) 978–985

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DOI: 10.1177/0954008314536216

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## Abstract

A novel heterocyclic diamine monomer based on pyrimidine ring, 2,4-bis(4-aminophenoxy)pyrimidine, was successfully synthesized. The obtained heterocyclic diamine was fully characterized and employed to synthesize a series of polyimides (PIs) by polycondensation with commercially available aromatic dianhydrides via the conventional two-step method. The effects of the pyrimidine rings into the main chain of the PIs were evaluated through the study of their solubility, thermal, mechanical, and optical properties. The inherent viscosities of the resulting poly(amic acid)s were in the range of 0.58–1.45 dL g<sup>-1</sup>. Meanwhile, the PIs had good thermal stability with the 5% weight loss temperatures of 445–475°C under nitrogen atmosphere as well as outstanding mechanical properties with tensile strength of 93–105 MPa and elongation at break of 3.6–4.2%. The cutoff wavelength of the PI films were in the range of 348–413 nm.

## Keywords

Polyimide synthesis, pyrimidine, heterocyclic diamine

## Introduction

Aromatic polyimides (PIs) constantly attract wider interest because of their high mechanical strength, excellent electrical properties, high thermal stability, and good chemical resistance.<sup>1–5</sup> Therefore, PIs have been widely applied in the fields of aerospace, microelectronics, functional membranes and composites, and so on.<sup>6–9</sup> However, the vigorous development of these high-tech fields has imposed increasingly stringent requirements on the PI materials employed in these fields.

It is effective to improve thermal, mechanical, and optical properties of PIs by incorporating heterocyclic units into the main chains, because such groups tend to increase the rigidity of the polymer backbones and provide a relatively high molar refraction.<sup>10,11</sup> Recently, some studies have focused on incorporating aromatic nitrogen-containing heterocyclic units into PI backbones to modify their properties, such as pyridazine,<sup>12</sup> pyrimidine,<sup>10,13,14</sup> benzimidazole,<sup>15,16</sup> and phthalazine.<sup>17,18</sup> It is of particular interest to design and synthesize new monomers to incorporate into PIs backbones while maintaining the desirable properties.

In this work, a novel pyrimidine-containing diamine, 2,4-bis(4-aminophenoxy)pyrimidine (BAPD), was synthesized and characterized. A series of new PIs were prepared based on BAPD and commercial dianhydrides. The thermal,

mechanical, optical properties, and solubilities of the resulting PIs were investigated. Meanwhile, PI derived from 1,3-bis(4-aminophenoxy)benzene (BAPB) was prepared, and the effect of pyrimidine unit on the properties of PIs was studied by comparing the properties of BAPD and BAPB-derived PIs.

## Experimentation

### Starting materials

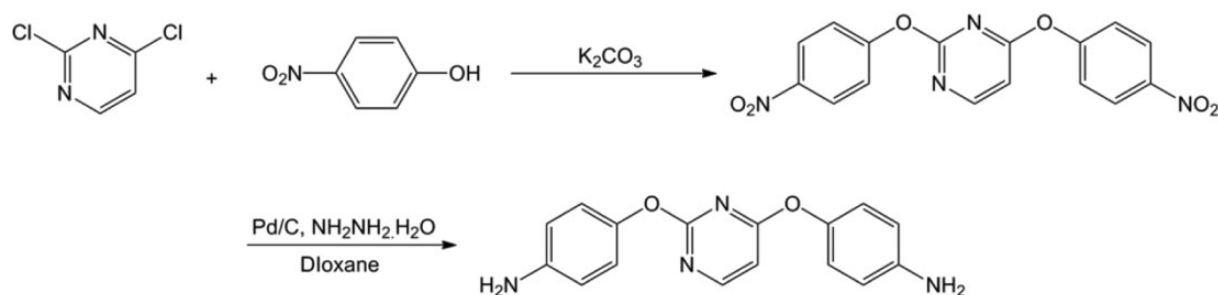
Pyromellitic dianhydride (PMDA), 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA), 3,3',4,4'-oxydiphthalic anhydride (ODPA), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), and 2,2'-bis(3,4-dicarboxyphenyl)-hexafluoropropane dianhydride (6FDA) were supplied by Sinopharm Chemical Reagent Beijing Co. Ltd (Beijing, China), and these aromatic dianhydrides were all recrystallized from acetic anhydride and then dried in vacuum at

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**Figure 1.** Preparation of BAPD monomer. BAPD: 2,4-bis(4-aminophenoxy)pyrimidine.

150°C for 10 h prior to use. BAPB (Acros, Beijing InnoChem Science & Technology Co. Ltd., Beijing, China), 2,4-dichloropyrimidine (Acros), and 4-nitrophenol (Acros) were used without further purification. Potassium carbonate ( $K_2CO_3$ ) (Acros), 10% palladium on activated charcoal/carbon (Pd/C) (Acros), and 80% hydrazine monohydrate (Acros) were used as received. Toluene and *N,N*-dimethylacetamide (DMAc) were purified by vacuum distillation over calcium hydride and stored over 4 Å molecular sieves prior to use. The other commercially available reagents and solvents were used without further purification.

### Measurements

Fourier transform infrared (FTIR) spectra were recorded on a Bruker Vector 22 spectrometer (Germany) at a resolution of  $2\text{ cm}^{-1}$  in the range of  $400\text{--}4000\text{ cm}^{-1}$ . All spectra were measured at room temperature and represented an average of 128 scans. Nuclear magnetic resonance (NMR) spectra were determined on a Bruker-300 spectrometer at 300 MHz for proton NMR ( $^1\text{H}$  NMR) and 75 MHz for carbon-13 NMR ( $^{13}\text{C}$  NMR) in deuterated chloroform ( $CDCl_3$ ) or deuterated dimethyl sulfoxide ( $DMSO-d_6$ ). High-resolution liquid chromatography–mass spectroscopy (HRLC-MS) data were obtained using micrOTOF-QII (model 1290; Agilent, Santa Clara, California, USA). Elemental analyses were performed on a Vario EL cube CHN recorder (Elementar Analysensysteme GmbH, Germany). Inherent viscosities ( $\eta_{inh}$ ) of poly(amic acid)s (PAA) were measured with an Ubbelohde viscometer with  $0.5\text{ g dL}^{-1}$  of DMAc solution at 25°C. Differential scanning calorimetric (DSC) analysis was performed on a DSC Q100 (TA Instruments, New Castle, Delaware, USA) at a scanning rate of  $10^\circ\text{C min}^{-1}$  under  $N_2$  atmosphere at  $50\text{ mL min}^{-1}$ . Thermogravimetric analysis (TGA) was conducted with a thermogravimetric analyzer (model 2050; TA Instruments) at a heating rate of  $10^\circ\text{C min}^{-1}$  under  $N_2$  atmosphere. Dynamic mechanical analysis (DMA) was carried out with a DMA Q800 (TA Instruments) at a heating rate of  $5^\circ\text{C min}^{-1}$  and a load frequency of 1 Hz in film tension geometry; glass transition temperature ( $T_g$ ) was considered as the peak temperature

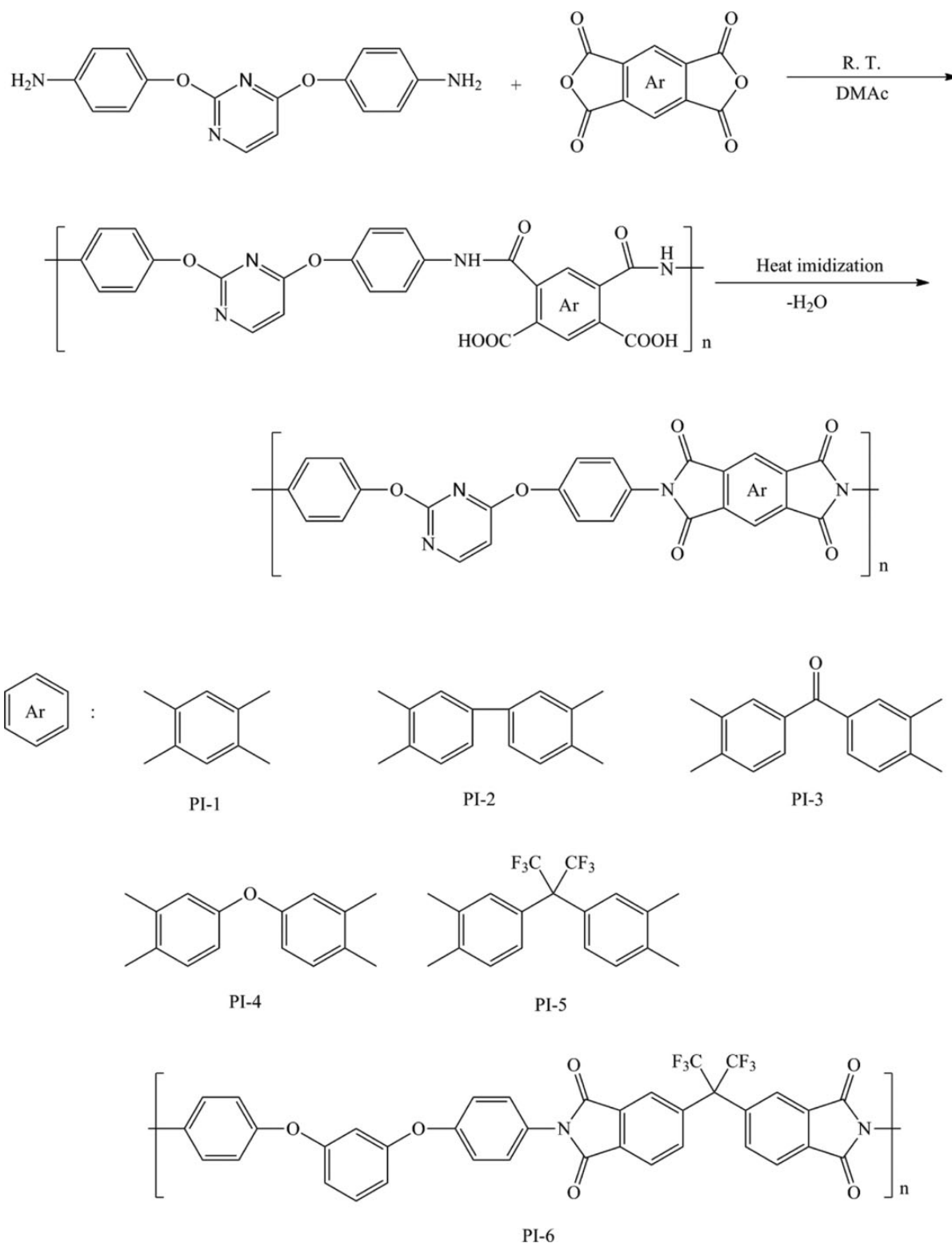
of loss modulus ( $E''$ ). Mechanical properties of the films were measured at room temperature on an AG-I universal testing apparatus (Shimadzu, Tokyo, Japan) with a cross-head speed of  $5\text{ mm min}^{-1}$ , while tensile modulus ( $T_M$ ), tensile strength ( $T_S$ ), and elongation at break ( $E_B$ ) were calculated as the average of five strips. Ultraviolet–visible (UV-Vis) spectra of PI films were recorded with a UV-Vis spectrometer (model 2501; Shimadzu) in transmittance mode at room temperature. The cutoff wavelength ( $\lambda_{cut-off}$ ) was used as the parameter to evaluate the transparency of the films. Water uptake (WU) of the films was measured by the weight differences before and after immersion in deionized water at room temperature for 24 h, using the following equation:

$$WU = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\%, \quad (1)$$

where  $W_{wet}$  is the weight of the film samples after immersion in deionized water and  $W_{dry}$  is the initial weight of the film samples.

### Synthesis of the monomers

**2,4-Bis(4-nitrophenoxy)pyrimidine.** 2,4-Dichloropyrimidine (10.7 g, 71.9 mmol) and 4-nitrophenol (25 g, 179.7 mmol) were charged into a 250-mL flask equipped with a mechanical stirrer, thermocouple, heating/cooling capacity, and  $N_2$  inlet/outlet. The mixture was heated until it melts and subsequently cooled to room temperature. After that, the powdered anhydrous  $K_2CO_3$  (24.8 g, 179.7 mmol) was added, and the mixture was heated to  $160^\circ\text{C}$  for 1 h and cooled to  $80^\circ\text{C}$ , then 5% aqueous potassium hydroxide solution 150 mL was added and refluxed for 1 h with stirring. The crude product was collected by filtration, washed with water, and dried in vacuo at  $80^\circ\text{C}$  for 10 h. After recrystallization from chloroform, 23.6 g was obtained (93%).<sup>19</sup> Melting point:  $180\text{--}181^\circ\text{C}$  (DSC at a heating rate of  $10^\circ\text{C min}^{-1}$  under  $N_2$  atmosphere). FTIR (potassium bromide, KBr): 3111, 3082, 1617, 1567, 1518, 1486, 1248, 1213,  $1138\text{ cm}^{-1}$ ;  $^1\text{H}$  NMR ( $CDCl_3$ , ppm): 8.40 (m, 1H), 8.36–8.33 (m, 2H), 8.31 (t, 2H), 7.38–7.35 (m, 2H), 7.35–7.32 (m, 2H), 6.63 (m, 1H);  $^{13}\text{C}$  NMR ( $CDCl_3$ , ppm): 170.4,



**Figure 2.** Preparation of the PIs. PIs: polyimides.

158.0, 157.1, 145.2, 125.5, 122.2, 94.2, 90.2; HRLC-MS (ESI): 355.2 ( $M + H$ )<sup>+</sup>, calculated (Calcd) 354.3 for  $C_{16}H_{10}N_4O_6$  (Figure 1).

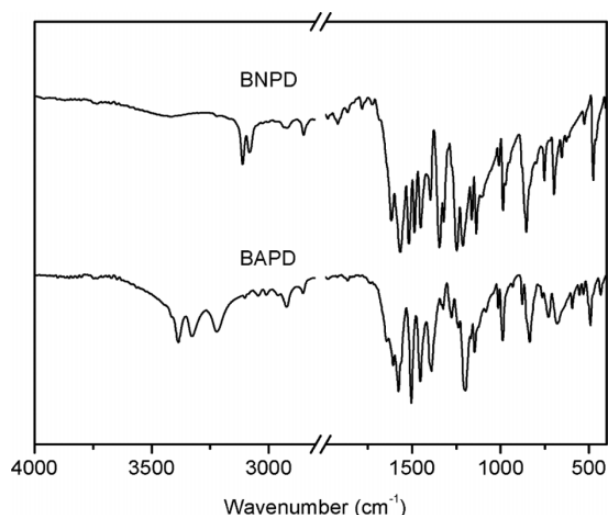
**2,4-Bis(4-aminophenoxy)pyrimidine.** Under  $N_2$  atmosphere, 15.0 g (42.3 mmol) of 2,4-bis(4-nitrophenoxy)pyrimidine (BNPD) and 0.7 g of Pd/C (10%) were suspended in 150 mL

**Table 1.** Physical properties and elemental analysis of the PIs.

PIs	$\eta_{inh}$ of PAA (dL g <sup>−1</sup> ) <sup>a</sup>	Composition of repeating unit	Elemental analysis (%)			
				C	H	N
PI-1	0.58	C <sub>26</sub> H <sub>12</sub> N <sub>4</sub> O <sub>6</sub>	Calculated	65.55	2.54	11.76
			Found	65.66	2.62	11.72
PI-2	1.26	C <sub>32</sub> H <sub>16</sub> N <sub>4</sub> O <sub>6</sub>	Calculated	69.57	2.92	10.14
			Found	69.61	2.98	10.06
PI-3	0.62	C <sub>33</sub> H <sub>16</sub> N <sub>4</sub> O <sub>7</sub>	Calculated	68.28	2.78	9.65
			Found	68.08	2.82	9.74
PI-4	1.45	C <sub>32</sub> H <sub>16</sub> N <sub>4</sub> O <sub>7</sub>	Calculated	67.61	2.84	9.86
			Found	67.50	3.04	9.94
PI-5	0.99	C <sub>35</sub> H <sub>16</sub> F <sub>6</sub> N <sub>4</sub> O <sub>6</sub>	Calculated	59.84	2.30	7.98
			Found	59.72	2.42	8.08
PI-6	1.24	C <sub>37</sub> H <sub>18</sub> F <sub>6</sub> N <sub>2</sub> O <sub>6</sub>	Calculated	63.44	2.59	4.00
			Found	63.52	2.62	4.02

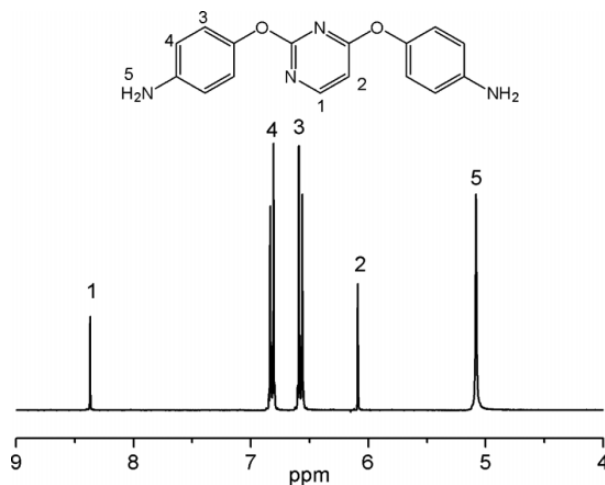
PI: polyimide;  $\eta_{inh}$ : inherent viscosity; PAA: poly(amic acid); PI-1: polyimide derived from pyromellitic dianhydride; PI-2: polyimide derived from 3,3',4,4'-biphenyltetracarboxylic dianhydride; PI-3: polyimide derived from 3,3',4,4'-benzophenonetetracarboxylic dianhydride; PI-4: polyimide derived from 3,3',4,4'-oxydiphthalic anhydride; PI-5: polyimide derived from 2,2'-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride; PI-6: polyimide derived from 2,2'-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride and 1,3-bis(4-aminophenoxy)benzene; DMAc: *N,N*-dimethylacetamide.

<sup>a</sup> $\eta_{inh}$  values of PAA were measured at 25°C with a concentration of 0.5 g dL<sup>-1</sup> in DMAc.



**Figure 3.** FTIR spectra of the BNPD and BAPD monomers. FTIR: Fourier transform infrared; BNPD: 2,4-bis(4-nitrophenoxy)pyrimidine; BAPD: 2,4-bis(4-aminophenoxy)pyrimidine.

of anhydrous dioxane. After heating to reflux with stirring, 52.9 g (846.0 mmol) of 80% hydrazine monohydrate was added dropwise for 1 h. The hot darkened solution was filtered to remove Pd/C after further refluxing for 10 h. The filtrate was distilled to remove some solvent. After being poured into 500 mL of deionized water, the gray precipitate was collected by filtration and dried under vacuum at 60°C overnight. After purifying the crude product by recrystallizing from ethanol/water, 9.7 g of BAPD was obtained. Yield: 78%. Melting point: 133–135°C (DSC at a heating rate of 10°C min<sup>-1</sup> under N<sub>2</sub> atmosphere). FTIR (KBr): 3386, 3328, 3224, 1607, 1577, 1504, 1455, 1278, 1195, 1147 cm<sup>-1</sup>; <sup>1</sup>H NMR (deuterated DMSO, DMSO-*d*<sub>6</sub>, ppm): 8.37 (m, 1H), 6.87–6.82 (m,



**Figure 4.** <sup>1</sup>H NMR spectra of BAPD. <sup>1</sup>H NMR: proton nuclear magnetic resonance; BAPD: 2,4-bis(4-aminophenoxy)pyrimidine.

2H), 6.82–6.78 (m, 2H), 6.61–6.58 (m, 2H), 6.58–6.54 (m, 2H), 6.09 (m, 1H), 5.08 (s, 4H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, ppm): 172.0, 158.1, 145.5, 142.2, 121.7, 114.4, 90.3; HPLC–MS (ESI): 295.3 (M+H)<sup>+</sup>, Calcd 294.3 for C<sub>16</sub>H<sub>14</sub>N<sub>4</sub>O<sub>2</sub>. Elemental analysis: Calcd for C<sub>16</sub>H<sub>14</sub>N<sub>4</sub>O<sub>2</sub>: C, 65.30%, H, 4.79%, N, 19.04%; found: C, 65.26%, H, 4.84%, N, 18.98%.

### Synthesis of the polyimides

PIs were prepared by polycondensation of aromatic dianhydrides with BAPD in DMAc to form soluble PAA precursors, followed by thermal imidization at elevated temperatures (as shown in Figure 2). PIs based on PMDA, BPDA, BTDA, ODPA, and 6FDA were designated as PI-1,

PI-2, PI-3, PI-4, and PI-5, respectively. The general procedure for the preparation of the PIs was shown as follows: 0.8725 g PMDA (4 mmol) was added to a solution of 1.1772 g BAPD (4 mmol) in 5 g DMAc in two portions. Extra 6.61 g DMAc was added to adjust the solid content of the reaction system to 15% by weight. The reaction mixture was stirred at room temperature for 24 h to give a viscous PAA solution. The values of  $\eta_{inh}$  of the PAA solutions were in the range of 0.58–1.45 dL g<sup>-1</sup>, as shown in Table 1. PI films were prepared by cast PAA solutions onto glass plates, followed by a preheating program (60°C/1 h, 80°C/3 h, 120°C/0.5 h, and 150°C/0.5 h) and an imidization procedure under vacuum (200°C/0.5 h, 250°C/0.5 h, and 300°C/1 h). The freestanding films were released from the glass substrates by soaking in water.

PI-6 derived from 6FDA and BAPB, which has the same skeletal structure without pyrimidine group as compared to PI-5, was prepared by the similar method for comparison of properties.

## Results and discussion

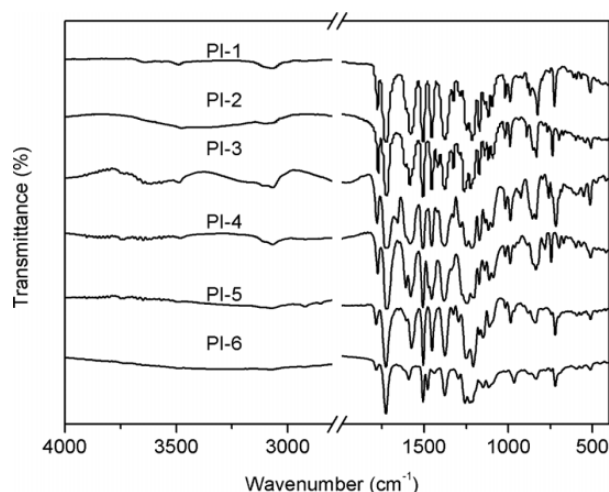
### Monomer synthesis

A novel aromatic diamine, BAPD, was synthesized via a two-step procedure, as shown in Figure 1. First, the intermediate dinitro compound, BNPD, was prepared by a nucleophilic chloro-displacement reaction of 4,6-dichloropyrimidine with 4-nitrophenol in the presence of K<sub>2</sub>CO<sub>3</sub>. Second, the diamine monomer, BAPD, was synthesized by the hydrazine reduction reaction of BNPD catalyzed with Pd/C in dioxane. The structures of BNPD and BAPD were confirmed by FTIR spectroscopy (Figure 3), NMR spectroscopy (Figure 4), and elemental analysis. All the results are in good agreement with the ones of the proposed structures.

### Polyimides synthesis

The diamine monomer, BAPD, was reacted with five commercially available aromatic dianhydrides, PMDA, BPDA, BTDA, OPA, and 6FDA, to give the corresponding PIs as shown in Figure 2. The new PIs were synthesized using a two-step method, which was carried out via PAA intermediate. The polymerization was carried out by the reaction of equimolar amounts of BAPD and aromatic dianhydrides at a concentration of 15% solids in DMAc. The PAAs were prepared by the polycondensation process at room temperature for 24 h. As shown in Table 1, the values of  $\eta_{inh}$  of the PAA precursors were 0.58–1.45 dL g<sup>-1</sup>. Tough and flexible PI films were obtained by casting the PAA solutions onto glass plates followed by thermal curing process.

The chemical structures of the PIs were characterized using FTIR spectroscopy, as shown in Figure 5. There was no existence of the characteristic absorption bands of the amide group near 3220–3400 cm<sup>-1</sup> (N–H stretching), indicating the polymers had been fully imidized. The data of



**Figure 5.** FTIR spectra of the PIs. FTIR: Fourier transform infrared; PIs: polyimides.

the elemental analyses of the PIs are listed in Table 1. The results are in good agreement with the calculated values.

### Thermal properties of the polyimides

Thermal properties of the PIs were determined by DSC, DMA, and TGA, and the results are listed in Table 2. DSC curves are shown in Figure 6, and neither an obvious glass transition nor a melting behavior was observed from the thermograms of PI-1 and PI-2. This may be due to the low thermal response of rigid-rod PIs during the transition and the high-packing density of polymer chains.<sup>20</sup> DMA curves are shown in Figure 7, as determined by the peak temperatures of  $E''$ . The slight differences of  $T_g$  values obtained by DSC and DMA are mainly attributed to the different responses of polymers to these two measurements. Generally,  $T_g$ s of polymers are determined by molecular packing and chain rigidity of the polymer backbones. As a result, PI-1 derived from BAPD-PMDA exhibits the highest  $T_g$ , whereas PI-4 derived from BAPD-ODPA possessed a lower  $T_g$  owing to the presence of flexible ether linkage. From Table 2, it can be seen that  $T_g$  of PI-5 (266°C, derived from 6FDA and BAPD) was higher (245°C) than PI-6 (derived from 6FDA and BAPB, with the same skeletal structure without pyrimidine unit as compared to BAPD). This result indicating the rigidity of pyrimidine ring was higher than that of benzene ring.

Thermal stabilities of the pyrimidine-based PIs were evaluated by TGA under N<sub>2</sub> atmosphere (as shown in Figure 8), and the results are summarized in Table 2. As can be seen from Figure 8, the PIs did not show obvious weight loss before 400°C, and the onset decomposition temperature was as high as 431°C. The values of 5% weight loss temperature ( $T_{5\%}$ ) and 10% weight loss temperature ( $T_{10\%}$ ) were in the range of 445–475°C and 459–500°C, respectively. The residual weight retentions at 800°C were 50.9–66.1%. TGA results indicated that the obtained PIs possessed fairly



**Table 2.** Thermal properties of the PI films.

PIs	$T_g$ (°C)		$T_d$ (°C) <sup>c</sup>	$T_{5\%}$ (°C) <sup>d</sup>	$T_{10\%}$ (°C) <sup>d</sup>	$R_w$ (%) <sup>e</sup>
	DSC <sup>a</sup>	DMA <sup>b</sup>				
PI-1	— <sup>f</sup>	— <sup>g</sup>	456	475	500	66.1
PI-2	— <sup>f</sup>	267	440	457	474	57.8
PI-3	262	281	431	451	485	55.7
PI-4	243	256	433	445	459	52.3
PI-5	266	264	438	455	475	50.9
PI-6	245	247	513	522	543	57.3

PI: polyimide;  $T_g$ : glass transition temperature;  $T_d$ : onset decomposition temperature;  $T_{5\%}$ : 5% weight loss temperature;  $T_{10\%}$ : 10% weight loss temperature;  $R_w$ : residual weight retention; DSC: differential scanning calorimetry; DMA: dynamic mechanical analysis; PI-1: polyimide derived from pyromellitic dianhydride; PI-2: polyimide derived from 3,3',4,4'-biphenyltetracarboxylic dianhydride; PI-3: polyimide derived from 3,3',4,4'-benzophenonetetracarboxylic dianhydride; PI-4: polyimide derived from 3,3',4,4'-oxydiphthalic anhydride; PI-5: polyimide derived from 2,2'-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride; PI-6: polyimide derived from 2,2'-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride and 1,3-bis(4-aminophenoxy)benzene; TGA: thermogravimetric analysis;  $N_2$ : nitrogen.

<sup>a</sup>Obtained at the baseline shift in the second heating DSC traces at a heating rate of  $10^\circ\text{C min}^{-1}$  under  $N_2$  atmosphere.

<sup>b</sup>Obtained at a heating rate of  $5^\circ\text{C min}^{-1}$  and a load frequency of 1 Hz in film tension geometry.

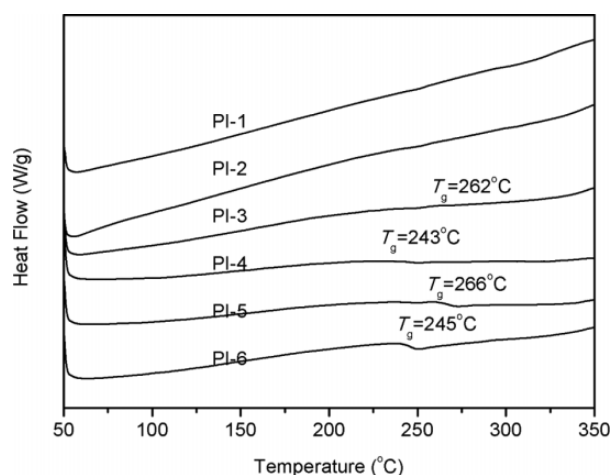
<sup>c</sup>Obtained by TGA at a heating rate of  $10^\circ\text{C min}^{-1}$  under  $N_2$  atmosphere.

<sup>d</sup>Obtained by TGA at a heating rate of  $10^\circ\text{C min}^{-1}$  under  $N_2$  atmosphere.

<sup>e</sup>Obtained at  $800^\circ\text{C}$  by TGA at a heating rate of  $10^\circ\text{C min}^{-1}$  under  $N_2$  atmosphere.

<sup>f</sup>Not obviously observed.

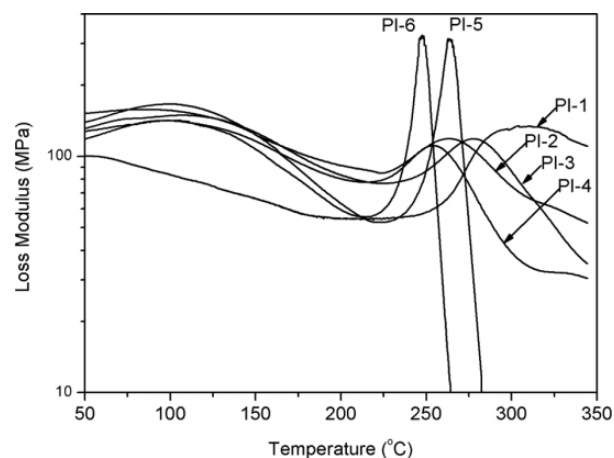
<sup>g</sup>Can not be determined due to broadened peak.

**Figure 6.** DSC curves of PI films. DSC: differential scanning calorimetry; PI: polyimide.

good thermal stability. For comparison,  $T_{5\%}$  and residual weight at  $800^\circ\text{C}$  of PI-5 were remarkably smaller than those of PI-6, indicating that the thermal stability of PIs-based pyrimidine is inferior to the wholly aromatic PI structure.

### Mechanical properties of the polyimides

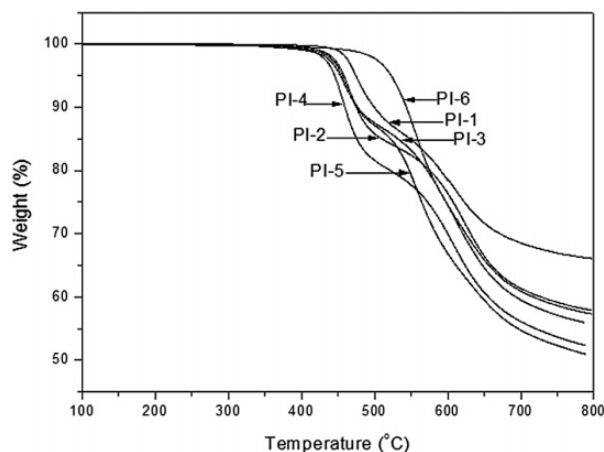
High-quality PI films could be prepared by casting the PAA solution onto glass plates followed by thermal curing. Table 3 summarizes  $T_S$  and  $T_M$  of the PI films. The value of  $T_S$  was as high as 105.7 MPa, with the  $T_M$  in range of 3.1–3.5 GPa. These results indicate that the obtained PI films are strong and tough. From Table 3, it can be seen that

**Figure 7.**  $E''$  curves of the PI films in DMA.  $E''$ : loss modulus; PI: polyimide; DMA: dynamic mechanical analysis.

the mechanical properties of PI-5 (6FDA/BAPD) were slightly higher than that of PI-6 (6FDA/BAPB). This might be attributed to the more rigid pyrimidine ring incorporated into the PI backbone.

### Optical properties and WU of PIs

The optical transparency of PI films (approximately 26–33  $\mu\text{m}$  thick) was measured by UV-Vis spectroscopy, the value of  $\lambda_{\text{cutoff}}$  was used as the parameter to evaluate transparency. As listed in Table 2,  $\lambda_{\text{cutoff}}$  values were in the range of 348–413 nm. Figure 9 shows UV-Vis absorption spectra of the PI films. Both 6FDA and ODA produce fairly transparent PI films in contrast



**Figure 8.** TGA curves of PI films. TGA: thermogravimetric analysis; PI: polyimide.

**Table 3.** Mechanical and optical properties and WU of PI films.

PIs	$T_S^a$ (MPa)	$T_M^b$ (GPa)	$E_B^c$ (%)	$\lambda_{\text{cutoff}}^d$ (nm)	WU <sup>e</sup> (%)
PI-1	105.7	3.4	4.2	392	0.75
PI-2	100.1	3.5	3.9	408	0.79
PI-3	99.3	3.1	3.7	413	0.72
PI-4	93.3	3.3	3.9	366	0.62
PI-5	101.9	3.3	3.6	348	0.45
PI-6	97.9	3.1	6.7	369	0.15

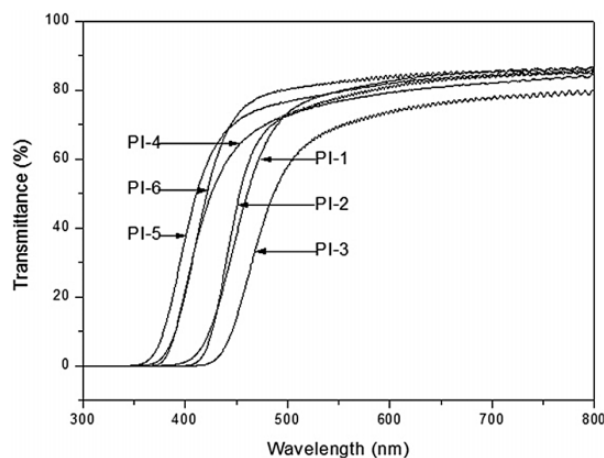
WU: water uptake; PI: polyimide;  $T_S$ : tensile strength;  $T_M$ : tensile modulus;  $E_B$ : elongation at break;  $\lambda_{\text{cut-off}}$ : cutoff wavelength; PI-1: polyimide derived from pyromellitic dianhydride; PI-2: polyimide derived from 3,3',4,4'-biphenyltetracarboxylic dianhydride; PI-3: polyimide derived from 3,3',4,4'-benzophenonetetracarboxylic dianhydride; PI-4: polyimide derived from 3,3',4,4'-oxydiphthalic anhydride; PI-5: polyimide derived from 2,2'-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride; PI-6: polyimide derived from 2,2'-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride and 1,3-bis(4-aminophenoxy)benzene.

to other dianhydrides.<sup>21,22</sup> When the diamine structures are fixed, the values of  $\lambda_{\text{cutoff}}$  are directly related to the color intensity of PI films. The deep color of the PI prepared from BTDA can be due to the occurrence of cross-linking reactions at benzophenone C=O groups, and the cross-linked portion usually shows a deep yellow color.

The PI films exhibited WU of 0.45–0.79% as shown in Table 2. Since water absorption rate of Upilex<sup>®</sup>-75S (Ube Industries Ltd, Japan) was measured to be 1.49% under the same conditions,<sup>23</sup> these results implied that introducing pyrimidine moiety into PI backbones did not deteriorate the water absorption behavior of the PIs.

### Solubility of PIs

Solubility of the PIs was determined at room temperature, and the results are summarized in Table 4. The obtained PIs exhibited good chemical resistance, and most of them were insoluble in common solvents such



**Figure 9.** UV-Vis spectra of PIs. UV-Vis: ultraviolet–visible; PIs: polyimides.

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

Solvent	PI-1	PI-2	PI-3	PI-4	PI-5	PI-6
<i>m</i> -Cresol	—	—	—	—	—	—
DMF	—	—	—	—	+-	++
DMAc	—	—	—	—	+-	++
NMP	—	—	—	—	+-	+-
DMSO	—	—	—	—	—	+-
THF	—	—	—	—	—	+-
Chloroform	—	—	—	+-	+-	++
Cyclohexanone	—	—	—	—	—	—
CH <sub>3</sub> COOH	—	—	—	—	—	—
Pyridine	—	—	—	—	+-	+-

PI: polyimide; PI-1: polyimide derived from pyromellitic dianhydride; PI-2: polyimide derived from 3,3',4,4'-biphenyltetracarboxylic dianhydride; PI-3: polyimide derived from 3,3',4,4'-benzophenonetetracarboxylic dianhydride; PI-4: polyimide derived from 3,3',4,4'-oxydiphthalic anhydride; PI-5: polyimide derived from 2,2'-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride; PI-6: polyimide derived from 2,2'-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride and 1,3-bis(4-aminophenoxy)benzene; DMF: *N,N*-dimethylformamide; DMAc: *N,N*-dimethylacetamide; NMP: *N*-methyl-2-pyrrolidone; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran; CH<sub>3</sub>COOH: acetic acid; ++: soluble at room temperature; +-: partially soluble; —: insoluble.

<sup>a</sup>Solubility was determined with 10 mg of PIs in 1 mL of solvent at room temperature for 24 h.

as NMP, DMF, DMAc, and DMSO at room temperature. PI-5 showed better solubility than other polymers, due to their distinguishing backbone structures: bulky pendant trifluoromethyl group derived from 6FDA inhibited close packing of the polymer chains,<sup>24</sup> making PI-5 easier to be dissolved. Besides, PI-5 (derived from 6FDA/BAPD) showed worse solubility compared with PI-6 (derived from 6FDA/BAPB) in aprotic polar solvents. This weakening in the organosolubility of the PI-5 might be attributed to the incorporation of nitrogen-containing pyrimidine ring into PI main chains, which increase the intermolecular interactions of macromolecular chains.

## Conclusions

PIs were prepared based on a novel pyrimidine-containing diamine and various aromatic dianhydrides via a two-step polymerization process. The resulting PAAs showed  $\eta_{\text{inh}}$  values in the range of 0.58–1.45 dL g<sup>-1</sup>. Tough and flexible PI films could be obtained by PAA solution cast on a clean glass plate, followed by thermal curing process. The PI films showed a good combination of properties. Thermal stabilities denoted by  $T_{5\%}$ s varied from 445°C to 475°C under N<sub>2</sub> atmosphere. The PI films also had good mechanical properties, with  $T_S$  values of 93–105 MPa,  $T_M$  of 3.1–3.5 GPa, and  $E_B$  of 3.6–4.2%. The values of  $\lambda_{\text{cut-off}}$  of the PI films were in the range of 348–413 nm.

## Funding

This research received no specific grant from any funding agency in the public, commercial, or not-for-profit sectors.

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