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# High performance polyimides with good solubility and optical transparency formed by the introduction of alkyl and naphthalene groups into diamine monomers†

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Three kinds of naphthalene-containing diamines with –H, –CH<sub>3</sub> or –CH(CH<sub>3</sub>)<sub>2</sub> substituents at the *ortho*-positions of the aniline ring including 4,4'-(naphthalen-1-ylmethylene)dianiline (BAN-1), 4,4'-(naphthalen-1-ylmethylene)bis(2,6-dimethylaniline) (BAN-2) and 4,4'-(naphthalen-1-ylmethylene)bis(2,6-diisopropylaniline) (BAN-3) were synthesized *via* a simple one-step electrophilic substitution reaction. These diamines were then reacted with three commercial dianhydrides, *via* chemical imidization under microwave irradiation, to obtain nine types of polyimide (PI). It was found that the introduction of alkyl side groups can improve the solubility and optical transparency of PIs. Moreover, compared with BAN-2 based PIs containing –CH<sub>3</sub> groups, BAN-3 based PIs containing –CH(CH<sub>3</sub>)<sub>2</sub> groups exhibited better solubility and optical transparency (transmittances at 450 nm of over 86%). Meanwhile, due to the presence of the rigid naphthalene side groups, all the PIs possessed high thermal stability with a glass transition temperature ( $T_g$ ) of over 290 °C and a decomposition temperature at 5% weight loss of over 510 °C under nitrogen. Furthermore, the  $T_g$  of PI-2B composed of BAN-2 and 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) was found to be as high as 387 °C, which is comparable to that of the commercial and conventional PI material (Kapton®,  $T_g$  = 390 °C).

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## Introduction

Polyimides (PIs) are a class of important high performance materials because of their excellent thermal stability, high mechanical strength and good electrical properties. However, conventional aromatic PIs display deep coloration and show low transparency due to the formation of charge transfer complexes (CTC).<sup>1</sup> Furthermore, fully aromatic PIs are generally insoluble in common organic solvents which seriously limits their application. Therefore, the preparation of soluble and transparent PIs with excellent properties for flexible display devices remains a challenge.<sup>2</sup>

The introduction of side groups into the PI backbone is a commonly applied approach to improving the solubility and optical transparency of PIs.<sup>3</sup> A variety of side groups have been used including halogens,<sup>4</sup> halogenated units,<sup>5</sup> aliphatic,<sup>6</sup> aromatic<sup>7</sup> and sulfur groups.<sup>8</sup> Among them, aliphatic units such

as methyl, ethyl and isopropyl are often introduced into the diamine or dianhydride monomers. However, the incorporation of aliphatic units generally reduces thermal stability which is a crucial factor for PIs. More and more research has been focused on the simultaneous introduction of aliphatic and aromatic units into a single monomer unit to balance the final properties of PIs, as aromatic groups such as benzene, anisole and naphthalene are rigid and helpful in improving thermal stability.<sup>9,10</sup> Nevertheless, the reported synthetic routes for the preparation of diamines or dianhydrides containing different groups generally involved several synthetic steps, making them difficult to consider practical application.<sup>10</sup>

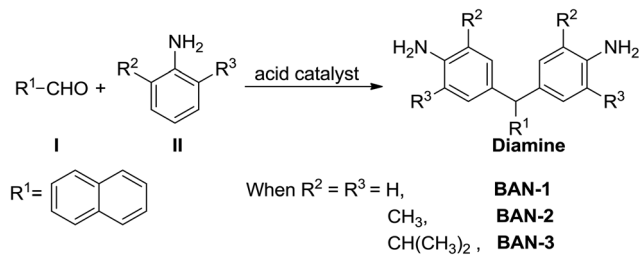
In recent decades, some groups have utilized a one-step reaction of aldehyde **I** and aniline **II**, catalyzed by strong protonic acids, to prepare various diamines with side groups as shown in Scheme 1.<sup>6,11,12</sup> Using this reaction pathway, it is relatively easy to introduce various aliphatic units into the R<sup>2</sup> and R<sup>3</sup> positions and aromatic units into R<sup>1</sup> position of the diamine. Moreover, most of the aldehydes and anilines are commercially available and relatively inexpensive. It is therefore anticipated that this synthetic route to diamines containing side groups could be extremely useful in the development of high performance PIs of low-cost. Sarojadevi,<sup>13</sup> Huang<sup>14</sup> and Li groups<sup>15</sup> have previously used this reaction to prepare various diamines, discovering that most of the resulting PIs were

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Scheme 1 Synthetic route of diamine monomer *via* a one-step reaction of aldehyde I and aniline II.

soluble in common organic solvents. However, some PIs were found to still exhibit deep color. Furthermore, the glass transition temperature ( $T_g$ ) of these PIs was much lower than that of commercial PI (Kapton®,  $T_g = 390$  °C). Cheng *et al.* studied the effect of  $R^2$  and  $R^3$  groups on the thermal properties of PIs and found that methyl groups at the *ortho*-positions of the aniline ring can increase the  $T_g$  of PIs. This was because the introduced methyl group can hinder rotation of the two aromatic rings around the C–N bond. Nevertheless, they did not introduce an aromatic group into the  $R^1$  position, and the  $T_g$  of the resulting PIs was not high enough.<sup>16</sup> Meanwhile, it remained unclear how the  $R^2$  and  $R^3$  alkyl groups of diamines affected the solubility and optical transparency of PIs.

In this paper, we prepare three different diamines whose  $R^2$  and  $R^3$  groups are –H, – $\text{CH}_3$  and – $\text{CH}(\text{CH}_3)_2$  *via* a simple one-step reaction of aldehyde I and aniline II (Scheme 1). Our main purpose was to investigate how alkyl groups at the *ortho*-positions of the aniline ring affected the solubility and optical transparency of PIs. Meanwhile, naphthalene was used as the  $R^1$  group because this group is known to enhance the solubility and thermal stability of materials.<sup>7,13</sup> The diamines were reacted with three commercial dianhydrides including 4,4'-oxydiphthalic anhydride (ODPA), BPDA and (4,4'-hexafluoroisopropylidene)-diphthalic anhydride (6FDA) *via* a one-step microwave assisted method to yield a series of PI films as

shown in Scheme 2. The solubility, transparency, thermal stability and mechanical properties of these PIs were studied.

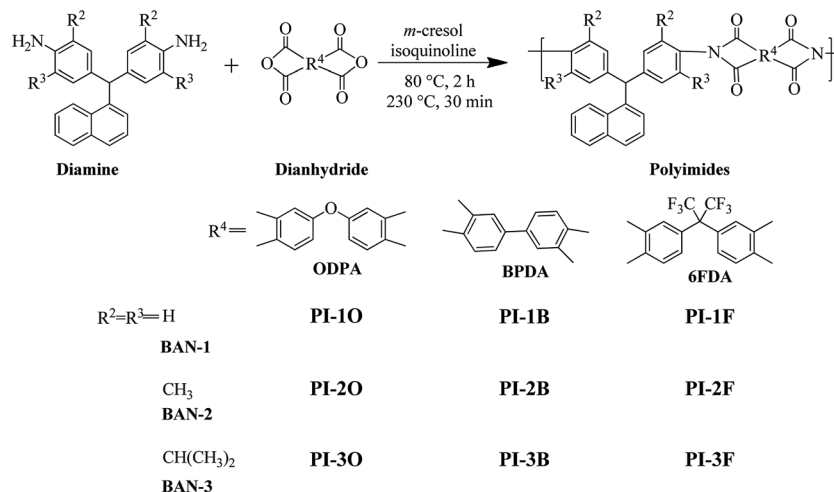
## Experimental

### Materials

ODPA (98%), BPDA (98%) and 6FDA (98%) were purchased from TCI and dried at 120 °C for 1 day under vacuum prior to use. 1-Naphthaldehyde (97%), aniline (99%), 2,6-dimethylaniline (99%), 2,6-diisopropylaniline, *m*-cresol (99%), isoquinoline (98%) and triethylamine (99%) were purchased from Aladdin and used as received. Sulfuric acid (98%), concentrated hydrochloric acid, sodium hydroxide (AR) and 1-methyl-2-pyrrolidinone (NMP, 98%) were purchased from Aladdin. Other solvents including *N,N'*-dimethylacetamide (DMAc), *N,N'*-dimethylformamide (DMF), tetrahydrofuran (THF), dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), chloroform ( $\text{CHCl}_3$ ) and dimethyl sulfoxide (DMSO) were chemical pure grade from Guangzhou Chemical Reagent Factory and used as received.

### Characterization

NMR spectra were recorded on a Bruker Avance 400 spectrometer at resonant frequencies of 400 MHz for  $^1\text{H}$  and 100 MHz for  $^{13}\text{C}$  nuclei using  $\text{DMSO}-d_6$  or  $\text{CDCl}_3$  as the solvent. Elemental analysis was performed on a CHNS element analyzer. Melting points were obtained on a polarizing microscope (Shang Hai SGW X-4). The PIs were synthesized by microwave-assisted polymerization with a microwave synthesizer using Biotage Initiator<sup>+</sup> instrument. Fourier-transform infrared spectra (FT-IR) and attenuated total reflection Fourier-transform infrared spectra (ATR FT-IR) were measured on a Bruker Vector 22 spectrometer in the range of 400–4000  $\text{cm}^{-1}$ . Inherent viscosities were performed with an Ubbelohde viscometer placed in water at 35 °C after the PI was dissolved in NMP completely. The number-average molecular weight ( $M_n$ ) and polydispersity index (PDI) were tested by gel permeation chromatography (GPC) on a Waters equipped with a set of Waters



Scheme 2 Synthetic route of naphthalene-containing PIs.



Styragel HT-2, HT-4 and HT-6 columns, monitored by 2414 refractive index detectors. The columns were maintained at 50 °C in an oven. DMF containing 0.01 M lithium bromide was used as an eluent at 1.0 mL min<sup>-1</sup>. Calibration was performed using polystyrene as standards. Wide-angle X-ray diffraction (WXR) patterns were obtained with a RIGAKU D-MAX 2200 VPC, using graphite monochromated Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) and a 0.5 mm collimator at room temperature.

The thermal decomposition behaviors were recorded by thermogravimetric analysis (TGA) under N<sub>2</sub> using Pyris TG 2000 equipment with about 3–5 mg of film sample at a heating rate of 10 °C min<sup>-1</sup>. Measurements of  $T_g$  were performed by differential scanning calorimetry (DSC) using a PerkinElmer DSC-7 instrument with a heating rate of 20 °C min<sup>-1</sup> under N<sub>2</sub> from 40 to 400 °C. The thickness of films was measured by digital display thickness gauge (exploit 220200, the resolution was 1  $\mu\text{m}$ ). The coefficients of thermal expansion (CTEs) were conducted by thermo mechanical analysis (TMA) using TA Q400 equipment with a heating rate of 10 °C min<sup>-1</sup> in the range from 100 to 200 °C. Ultraviolet-visible (UV-vis) spectra of the films (about 20  $\mu\text{m}$ ) were evaluated by a Thermo Evolution 201 spectrometer in transmittance mode, with spectrometer width of 200–800 nm at room temperature. Tensile properties were measured with universal testing measurement (UTM) of Xinsansi Company. Materials were tested with 4 mm  $\times$  25 mm at a strain rate of 10 mm min<sup>-1</sup> at room temperature and the minimal strength was 50 N.

### Monomer synthesis

**Synthesis of BAN-1 and BAN-2.** The two monomers BAN-1 and BAN-2 were synthesized *via* a reaction between 1-naphthaldehyde and aniline or 2,6-dimethylaniline, respectively, according to the methodology in the literature.<sup>17</sup> Elemental analysis: calc. for C<sub>23</sub>H<sub>20</sub>N<sub>2</sub> of BAN-1: C, 85.2; H, 6.2; N, 8.6%. Found: C, 84.9; H, 5.9; N, 8.8%. Calc. for C<sub>27</sub>H<sub>28</sub>N<sub>2</sub> of BAN-2: C, 85.2; H, 7.4; N, 7.4%. Found: C, 85.1; H, 7.5; N, 7.5%.

**Synthesis of BAN-3.** A 250 mL three-neck flask equipped with a reflux condenser was charged with 2,6-diisopropylaniline (22.33 g, 126 mmol), 1-naphthaldehyde (7.80 g, 50 mmol), concentrated sulfuric acid (16 mL) and deionized H<sub>2</sub>O (100 mL). The reaction system was stirred at 100 °C under a nitrogen atmosphere for 20 h during which a yellow solid was formed. An aqueous solution of sodium hydroxide (60 mL, 20 wt%) was added to the resulting suspension when the reaction mixture had cooled to 60 °C. The mixture was poured into deionized H<sub>2</sub>O and stirred for 5 hours. A pale yellow solid was filtered and washed repeatedly with deionized H<sub>2</sub>O. The product was recrystallized from methanol to produce white crystals. Yield: 11.32 g, 46%. Melting point: 174–175 °C. Elemental analysis: calc. for C<sub>35</sub>H<sub>44</sub>N<sub>2</sub>: C, 85.3; H, 9.0; N, 5.7%. Found: C, 85.4; H, 9.0; N, 5.6%.

### Polymer synthesis

All PIs were synthesized *via* chemical imidization under microwave irradiation. A typical synthetic procedure of PI-1O is demonstrated as follows: two monomers BAN-1 (0.6488 g, 2.0 mmol) and ODP (0.6226 g, 2.02 mmol), isoquinoline (*ca.* 5 drops) and 5 mL of *m*-cresol were added to a unique tube

used for microwave reaction, and then sealed. The solid content of the reaction system was about 20 wt%. All operations were completed inside a glovebox purged with nitrogen before the reaction. The homogeneous mixture was irradiated at 80 °C for 2 h, 230 °C for 30 min and a yellow and transparent viscous liquid was obtained. After cooling to room temperature, the solution was diluted with CHCl<sub>3</sub> and slowly poured into an excess of ethanol. Pure PI-1O was obtained by repeating the re-precipitation from CHCl<sub>3</sub> into ethanol and drying at 80 °C under vacuum. The PIs based on BAN-3 were prepared with a similar experimental procedure to those of the PIs based on BAN-1 and BAN-2, except that the catalyst was triethylamine.

### Film preparation

The PI powder was firstly dissolved in DMAc with the content of about 10% (w/v, g mL<sup>-1</sup>) and then filtered through a 0.45  $\mu\text{m}$  PTFE filter. After casting onto clean glass plates, the solution was heated at 60 °C for 12 h and 200 °C for 12 h under vacuum to thoroughly remove the solvent. TGA (Pyris TG 2000) was used to confirm that the dried film contained no residual solvent. It is worth mentioning that NMP was used to dissolve PI-1B as it cannot be dissolved in DMAc.

## Results and discussion

### Synthesis and characterization of diamines

Three kinds of naphthalene-containing diamines, including BAN-1, BAN-2 and BAN-3, were synthesized to study the influence of aliphatic groups at the *ortho*-positions of the aniline ring on the physical properties of PIs. All three compounds were prepared through a one-step electrophilic substitution reaction of aldehyde I and aniline II, as shown in Scheme 1. After the reaction, recrystallization was used to purify BAN-3 while a simple precipitation was used to purify BAN-1 and BAN-2. The three diamines were tested by <sup>1</sup>H and <sup>13</sup>C NMR, which are provided in ESI (Fig. S1 and S2<sup>†</sup>). All spectral data of the monomers were in accordance with their molecular structures.

**Table 1** Inherent viscosities and molecular weights of naphthalene-containing PIs

PIs	$\eta_{\text{inh}}^a$ (dL g <sup>-1</sup> )	$M_n^b$ ( $\times 10^4$ g mol <sup>-1</sup> )	PDI
PI-1O	0.67	<sup>c</sup>	<sup>c</sup>
PI-2O	0.99	19.18	1.44
PI-3O	0.61	9.57	1.46
PI-1F	0.54	<sup>c</sup>	<sup>c</sup>
PI-2F	0.87	<sup>c</sup>	<sup>c</sup>
PI-3F	0.78	13.35	1.44
PI-1B	0.66	<sup>d</sup>	<sup>d</sup>
PI-2B	1.03	<sup>c</sup>	<sup>c</sup>
PI-3B	0.68	9.18	1.34

<sup>a</sup> Measured at PI concentration of 0.5 g dL<sup>-1</sup> in NMP at 35 °C.

<sup>b</sup> Measured by GPC in DMF. <sup>c</sup> There was no GPC peak of PI sample.

<sup>d</sup> The PI did not dissolve in DMF.



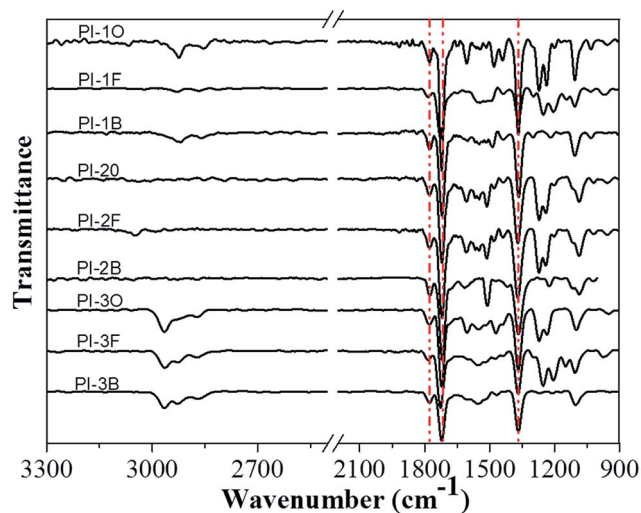


Fig. 1 ATR FT-IR spectra of all naphthalene-containing PI films.

### Synthesis and characterization of naphthalene-containing PIs

Recently, microwave-assisted polymerizations are being frequently adopted as compared with conventional heating, microwave reactions have obvious advantages such as shorter reaction time, reduced side reactions and higher yields.<sup>18</sup> Nevertheless, report on microwave-assisted polymerization of PIs remain relatively unusual. Herein, all polymerizations of naphthalene-containing PIs were carried out using a Biotage® Initiator<sup>+</sup> synthesizer in a sealed tube. The diamines, dianhydrides, *m*-cresol solvent and isoquinoline or triethylamine catalyst were added to the reaction tube together under nitrogen inside a glove box. The monomer contents were 20–25 wt%. The reaction tube was heated at 60–80 °C for 2 h to form poly(amic acid) (PAA), then at 240 °C for 30 min for chemical imidization under stirring in the microwave reactor. The yields of all PI products were higher than 90%.

The inherent viscosity of all PIs was measured in NMP solvent at 35 °C, and the result listed in Table 1. It was found that the inherent viscosities ( $\eta_{inh}$ ) of all PIs were rather high and more than 0.6 dL g<sup>-1</sup>, except for PI-1F. Moreover, the  $\eta_{inh}$  values of BAN-2 series PIs were obviously higher than those of BAN-1 and BAN-3 based PIs with the same dianhydride. This should be due to the electronic effects of the methyl groups at the *ortho*-positions of the aniline ring, which can enhance the nucleophilic activity of the amino unit, thus increasing the reactivity of BAN-2. Additionally, it was discovered that the  $\eta_{inh}$  value (0.87 dL g<sup>-1</sup>) of PI-2F was higher than that of PI composed of the same monomer prepared by conventional heating within the literature (0.54 dL g<sup>-1</sup>).<sup>19</sup> This may be related to microwave-assisted polymerization, which is favorable in increasing the molecular weight of polymers. The molecular weights of some PIs can be characterized by GPC. It was found that the samples had a high  $M_n$  ranging from  $9.18 \times 10^4$  to  $19.18 \times 10^4$  g mol<sup>-1</sup>, as well as a relatively small PDI (lower than 1.50) (Table 1). It is worth noting that some PIs such as PI-10 and PI-1F had no GPC peak. This means that the polymers cannot be eluted from the columns of GPC probably due to the strong interaction between polymers and the columns.

The chemical structures of naphthalene-containing PIs were confirmed by ATR FT-IR and NMR spectra. Fig. 1 presents the ATR FT-IR spectra of all the PIs. Typical absorption bands of imide groups appeared at 1778 cm<sup>-1</sup> (C=O asymmetrical stretching), 1727 cm<sup>-1</sup> (C=O symmetrical stretching) and 1365 cm<sup>-1</sup> (C–N stretching), which reflected the formation of the imide structure. Meanwhile, the characteristic absorptions of amide groups in the region of 3220–3440 cm<sup>-1</sup> (N–H stretching) were no longer detectable, clearly indicating that all the PIs had been fully imidized.

All the PIs were characterized by <sup>1</sup>H NMR spectra using CDCl<sub>3</sub> as solvent except for PI-1B (BAN-1/BPDA) polymer, due to poor solubility. Fig. 2 showed the <sup>1</sup>H NMR spectrum of PI-30. The proton signals of the isopropyl side group were observed in the upfield region of 0.96 ppm and 2.67 ppm. The signal of

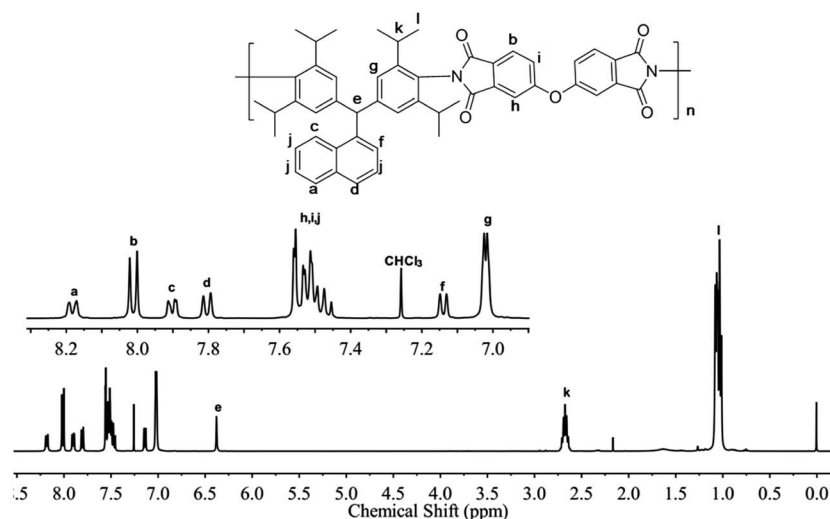


Fig. 2 <sup>1</sup>H NMR spectrum of PI-30 polymer (CDCl<sub>3</sub>, 400 MHz).



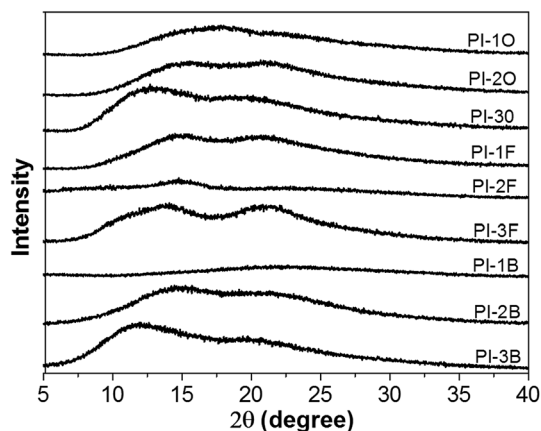


Fig. 3 X-ray diffraction profiles of naphthalene-containing PI films.

the CH group of the backbone was located at 6.25 ppm, and the signals of the phenyl and naphthalene protons appeared in the downfield region ranging from 7.02 ppm to 8.27 ppm. Additionally, as shown in the  $^{13}\text{C}$  NMR spectrum of PI-3O (Fig. S3†), a very strong imide carbon peak appeared at 165 ppm, while a carboxylic peak at approximately 200 ppm was not detectable, also confirming complete imidization reaction.  $^1\text{H}$  NMR spectra of other PIs are offered in Fig. S4–S6.† All the spectral data of the PIs matched with the expected structure of the PI polymers.

The morphology of naphthalene-containing PI films (thickness of around 20  $\mu\text{m}$ ) was studied by X-ray diffractometer and the diffraction spectra displayed in Fig. 3. In their X-ray diffraction curves, there are no sharp scattering signals and only very broad peaks, which reflect that all the PI films exhibit amorphous patterns. This indicated that the naphthalene and aliphatic pendant groups at the *ortho*-positions of the aniline ring disturbed the well-packed PI chains and decreased the packing density.

### Solubility of naphthalene-containing PIs

The solubility of all the PIs was tested by dissolving PI films in common organic solvents with a concentration of 10  $\text{mg mL}^{-1}$ , and the results collected in Table 2. Two series of PIs composed

of ODPA or 6FDA dianhydride are not only soluble in polar solvents such as *m*-cresol, NMP, DMSO and DMAc, but are also soluble in solvents of low boiling point like  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$ , at room temperature or upon heating. It was additionally found that PI-2O and PI-3O are soluble in non-polar THF solvent at room temperature, but that PI-1O is only partially soluble in THF even upon heating to reflux. These results reflect that the introduction of side groups at the *ortho*-positions of the imide ring can enhance the solubility of PIs. When rigid BDPA dianhydride is used, the side group of the diamines also has a great effect on the solubility of PIs. PI-1B is only able to be soluble in *m*-cresol and NMP, while PI-2B and PI-3B are soluble in some solvents of low boiling point.

Furthermore, compared with the solubility of PIs composed of the same dianhydride in acetone, it was clearly found that the solubility of PIs with BAN-3 was better than that of PIs with BAN-1 or BAN-2 diamine. This indicates that an isopropyl group is more beneficial than a methyl group for the solubility of PIs, presumably because the free volume of the PI polymeric chains is increased due to the bulky isopropyl unit. Thereof, the ability of the diamines to improve the solubility of PIs follows the order: BAN-3 > BAN-2 > BAN-1. As thus, PI-3F polymer composed of BAN-3 and 6FDA has the most optimal solubility of our system owing to the presence of two bulky isopropyl and  $\text{CF}_3$  groups, leading to an efficient reduction of the interactions among polymeric chains.

### Thermal properties of naphthalene-containing PIs

Thermal properties of PIs including  $T_g$ , thermal decomposition and CTE were evaluated by DSC, TGA and TMA, respectively, and the data summarized in Table 3. Fig. 4 and 5 display TGA curves and DSC second heating scan curves of all PI films, respectively.

As shown in Table 3, the decomposition temperatures of all PIs at 5% and 10% weight loss ( $T_{d5}$  and  $T_{d10}$ ) are over 510 and 525  $^\circ\text{C}$ , respectively. Meanwhile, the PIs have high char yields (>55%). These results firmly indicate that all the PIs possess excellent thermal stability, regardless of the aliphatic substituent used in the system. In previous literature based on similar PIs with methylbenzene, *tert*-butyl benzene, morpholinyl or anthracene as the pendant substituents, the  $T_{d10}$  data of the PIs

Table 2 Solubility of naphthalene-containing PI films<sup>a</sup>

PIs	<i>m</i> -Cresol	NMP	DMSO	DMAc	$\text{CH}_2\text{Cl}_2$	$\text{CHCl}_3$	THF	Acetone
PI-1O	++	+	+	++	++	++	+–	–
PI-2O	++	++	+	++	++	++	++	–
PI-3O	++	++	+	++	++	++	++	+–
PI-1F	++	++	+	++	++	++	++	+–
PI-2F	++	++	+	++	++	++	++	+–
PI-3F	++	++	+	++	++	++	++	++
PI-1B	++	++	+–	+–	+–	+–	+–	–
PI-2B	++	++	+–	+	+	++	+–	–
PI-3B	++	++	+–	++	++	++	++	+–

<sup>a</sup> ++: soluble at room temperature; +: soluble upon heating at 100  $^\circ\text{C}$ ; +–: partially soluble upon heating at 100  $^\circ\text{C}$  or the boiling point; –: insoluble upon heating. Solubility was measured with the concentration of 10  $\text{mg mL}^{-1}$  for 24 h.

Table 3 Thermal properties of naphthalene-containing PI films

PIs	$T_{d5}^a$ ( $^\circ\text{C}$ )	$T_{d10}^a$ ( $^\circ\text{C}$ )	$R_w^b$ (%)	$T_g^c$ ( $^\circ\text{C}$ )	CTE <sup>d</sup> ( $\text{ppm } ^\circ\text{C}^{-1}$ )
PI-1O	523	539	55	301	56.50
PI-2O	528	540	63	343	56.10
PI-3O	516	528	56	296	75.23
PI-1F	519	532	59	322	54.30
PI-2F	536	555	64	343	52.40
PI-3F	511	526	60	294	83.10
PI-1B	538	555	63	341	52.10
PI-2B	550	567	68	387	48.03
PI-3B	526	542	65	339	65.68

<sup>a</sup> Temperature at 5% and 10% weight loss determined by TGA with 10  $^\circ\text{C min}^{-1}$  under nitrogen. <sup>b</sup> Residual weight percentage at 800  $^\circ\text{C}$ . <sup>c</sup> Measured by DSC with 20  $^\circ\text{C min}^{-1}$ . <sup>d</sup> Measured by TMA from 50 to 200  $^\circ\text{C}$  with 10  $^\circ\text{C min}^{-1}$ .



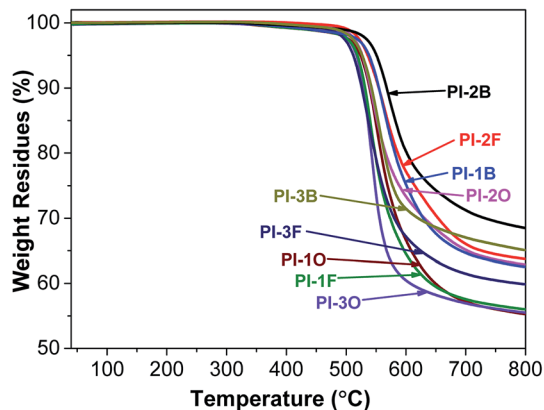


Fig. 4 TGA curves of naphthalene-containing PI films.

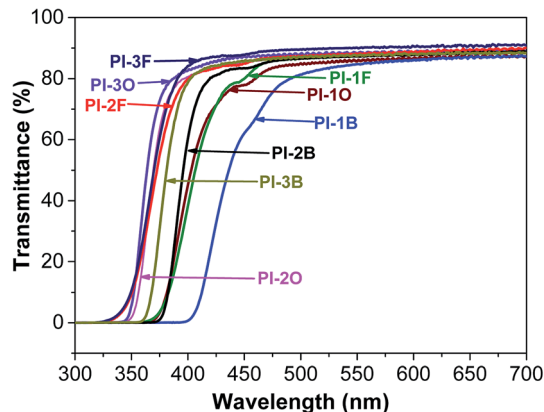


Fig. 6 UV-vis absorption spectra of naphthalene-containing PI films.

were less than 500 °C.<sup>11,12,20</sup> This indicates that the use of stiff and aromatic naphthalene as a pendant group can enhance the thermal properties of PIs. Additionally, it was discovered that the  $T_{d5}$  and  $T_{d10}$  data of BAN-2 based PIs are higher than those of BAN-1 and BAN-3 based PIs when the same dianhydride is used. This indicates that the methyl substituent can increase the thermal stability of PIs. This is because a methyl group at the *ortho*-position of the imide nitrogen limits the rotation of the C–N bond, thus leading to increase rigidity within the molecular chains. However, the isopropyl group of relatively large steric hindrance would weaken the intermolecular interaction of PI chains. Thus, the thermal stability of naphthalene-containing PIs follows this order: BAN-2 > BAN-1 > BAN-3.

The  $T_g$  values of the PIs was discovered to be in line with the decomposition data. BAN-2 based PI showed the highest  $T_g$  value, while BAN-3 based PI exhibited the lowest value when compared with PIs of the same dianhydride. All the  $T_g$  data of BAN-2 based PI series are over 340 °C, even in the presence of a flexible ether bond in the PI-2O backbone. Moreover, PI-2B composed of BAN-2 diamine and a stiff BPDA dianhydride exhibits an especially high  $T_g$  value (387 °C), comparable to that of the commercial and fully

aromatic PI named Kapton® (390 °C). As discussed above, BAN-2 based PI series also have excellent solubility and are soluble in multiple common organic solvents at room temperature. Thus, BAN-2 based PIs may be considered attractive and promising materials from an industrial standpoint because they possess excellent thermal stability and solubility, and in addition the synthesis of their diamines is relatively simple and inexpensive.

In addition, CTE data of PIs was tested by TMA which estimates the size stability of the material upon heating. The CTE value is related to the rigidity and the intermolecular interactions of the polymeric chain. Obviously, BAN-2 based PIs showed relatively lower CTE data than BAN-1 and BAN-3 based PIs did. This may be because the methyl group limits the rotation of the C–N bond, thus leading to increase the rigidity. Especially, PI-2B composed of rigid BDPA dianhydride and BAN-2 diamine had the lowest CTE value of 48.03 ppm °C<sup>-1</sup>. However, the bulky isopropyl group of BAN-3 would decrease the intermolecular interactions, which is harmful to the CTEs. So, the CTE value of naphthalene-containing PIs follows this order: BAN-3 > BAN-1 > BAN-2 when using the same dianhydride. This is accordance with the above DSC and TGA results of PIs.

### Transparency of naphthalene-containing PIs

The optical transparency of PI films in the visible region is considered to be a crucial factor in optoelectronic applications.

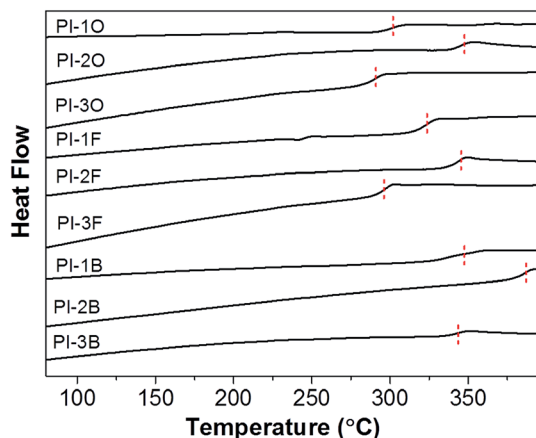


Fig. 5 DSC second heating scan curves of naphthalene-containing PI films with 20 °C min<sup>-1</sup>.

Table 4 Optical properties of naphthalene-containing PI films

Pis	Thickness (μm)	$\lambda_{\text{cut-off}}^a$ (nm)	$T_{400 \text{ nm}}^b$ (%)	$T_{450 \text{ nm}}^c$ (%)
PI-1O	21	371	41	78
PI-2O	17	345	80	85
PI-3O	24	346	83	87
PI-1F	24	368	38	80
PI-2F	20	330	80	85
PI-3F	24	326	85	88
PI-1B	23	401	0	62
PI-2B	25	376	60	84
PI-3B	18	361	79	86

<sup>a</sup> Cut-off wavelength. <sup>b</sup> Transmittance at 400 nm. <sup>c</sup> Transmittance at 450 nm.



Table 5 Mechanical properties of naphthalene-containing PI films<sup>a</sup>

PIs	$T_S$ (MPa)	$T_M$ (GPa)	$E_B$ (%)
PI-1O	53.8	2.3	3.2
PI-2O	77.2	2.5	3.9
PI-3O	64.9	1.7	4.6
PI-1F	64.8	2.5	3.4
PI-2F	78.1	2.7	3.7
PI-3F	87.4	2.2	5.9
PI-1B	70.3	2.7	3.4
PI-2B	91.9	2.8	4.7
PI-3B	68.9	2.7	3.2

<sup>a</sup>  $T_S$ : tensile strength,  $T_M$ : tensile modulus,  $E_B$ : elongation at break.

Generally, due to intra- or intermolecular CTC formation, aromatic PI films exhibit pale yellow to deep brown coloration, depending on the molecular structure. Fig. 6 shows the UV-vis absorption spectra of all the PI films, and the data present in Table 4. The cut-off wavelength ( $\lambda_{\text{cut-off}}$ ) of all the PIs derived from BAN-2 and BAN-3 was below 400 nm, which explains why these films were almost colorless. Meanwhile, BAN-2 and BAN-3 based PIs exhibited good optical transparency, whose transmittances exceeded 84% at 450 nm. Obviously, when compared with PIs derived of the same dianhydride, the transmittance data of BAN-3 based PIs was the highest while the data of BAN-1 based PIs was the lowest. These results clearly indicate that the introduction of side groups into the *ortho*-positions of the imide nitrogen significantly improve the transparency of PI films. Moreover, the transmittances were enhanced with increasing the steric hindrance of the aliphatic substituent. Therefore, the optical transparency of naphthalene-containing PIs follows this order: BAN-3 > BAN-2 > BAN-1.

### Mechanical properties of naphthalene-containing PIs

The mechanical properties of the PI films including tensile strength, tensile modulus as well as elongation at break are summarized in Table 5. All the PIs exhibited good tensile strengths above 64 MPa except for the PI-1O polymer, and modulus values of 1.7–2.8 GPa. The elongations at break of the PIs are between 3.2–5.9%. Compared with BAN-1 and BAN-3 based PIs of the same dianhydride, BAN-2 based PIs exhibits stronger tensile strength, higher modulus and longer elongation at break. This is related to the relatively high intrinsic viscosity of BAN-2 based PIs as listed in Table 1.

## Conclusions

In conclusion, this work demonstrates the synthesis of soluble and optically transparent PIs without sacrificing their excellent thermal properties by simultaneously introducing a suitable alkyl group and a naphthalene unit into the diamine monomer. Three kinds of naphthalene-containing diamines with  $-H$ ,  $-CH_3$  or  $-CH(CH_3)_2$  groups substituted at the *ortho*-positions of the aniline ring were obtained in a simple, inexpensive and high-yielding way. Following this, a series of PIs with an intrinsic

viscosity above  $0.6 \text{ dL g}^{-1}$  were prepared under a highly efficient microwave-assisted polymerization between the diamines and three commercial dianhydrides. Most of these PIs were readily soluble in various polar or non-polar solvents at room temperature, and BAN-2 and BAN-3 based PIs possessed good optical transparency ( $T_{450 \text{ nm}} > 84\%$ ). Moreover, it was found that the ability of the alkyl groups to improve the solubility and optical transparency of the PIs followed this order:  $-CH(CH_3)_2 > -CH_3 > -H$ . In addition, all the PIs exhibited high thermal stability ( $T_g > 290 \text{ }^\circ\text{C}$  and  $T_{5\% \text{ weight loss}} > 510 \text{ }^\circ\text{C}$ ). What is more, PI-2B composed of BAN-2 and BPDA maintained excellent thermal properties which was comparable with the conventional PI material, as well as possessed good solubility and optical transparency. Therefore, the simultaneous introduction of suitable aliphatic and aromatic units into the same monomer can offer an opportunity to prepare high-temperature PI materials with excellent solution processability and optical transparency.

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## Notes and references

- 1 T. Hasegawa and K. Horie, *Prog. Polym. Sci.*, 2001, **26**, 259–335.
- 2 H. J. Ni, J. G. Liu, Z. H. Wang and S. Y. Yang, *J. Ind. Eng. Chem.*, 2015, **28**, 16–27.
- 3 L. Yi, W. Huang and D. Y. Yan, *J. Polym. Sci., Part A: Polym. Chem.*, 2017, **55**, 533–559.
- 4 F. W. Harris, S.-H. Lin, F. Li and S. Z. D. Cheng, *Polymer*, 1996, **37**, 5049–5057.
- 5 M. G. Dhara and S. Banerjee, *Prog. Polym. Sci.*, 2010, **35**, 1022–1077.
- 6 W. Huang, D. Y. Yan and Q. H. Lu, *Macromol. Rapid Commun.*, 2001, **22**, 1481–1484.
- 7 D.-J. Liaw, F.-C. Chang, M.-k. Leung, M.-Y. Chou and K. Muellen, *Macromolecules*, 2005, **38**, 4024–4029.
- 8 P. K. Tapaswi, M.-C. Choi, K.-M. Jeong, S. Ando and C.-S. Ha, *Macromolecules*, 2015, **48**, 3462–3474.
- 9 Y. Z. Guo, H. W. Song, L. Zhai, J. G. Liu and S. Y. Yang, *Polym. J.*, 2012, **44**, 718–723.
- 10 G. C. Eastmond, J. Paprotny, R. A. Pethrick and F. Santamaria-Mendia, *Macromolecules*, 2006, **39**, 7534–7548.
- 11 R. Hariharan, S. Bhuvana, N. Amutha and M. Sarojadevi, *High Perform. Polym.*, 2006, **18**, 893–905.
- 12 X. H. Huang, W. Huang, J. Y. Liu, L. L. Meng and D. Y. Yan, *Polym. Int.*, 2012, **61**, 1503–1509.
- 13 R. Hariharan and M. Sarojadevi, *J. Appl. Polym. Sci.*, 2006, **102**, 4127–4135.
- 14 X. H. Huang, M. Mei, C. J. Liu, X. L. Pei and C. Wei, *J. Polym. Res.*, 2015, **22**, 1–9.



- 15 C.-Y. Wang, G. Li, X.-Y. Zhao and J.-M. Jiang, *J. Polym. Sci., Part A: Polym. Chem.*, 2009, **47**, 3309–3317.
- 16 L. Y. Wang, P. L. Chang and C. L. Cheng, *J. Appl. Polym. Sci.*, 2006, **100**, 4672–4678.
- 17 C.-S. Wang, T.-S. Leu and K.-R. Hsu, *Polymer*, 1998, **39**, 2921–2927.
- 18 K. Kempe, C. R. Becer and U. S. Schubert, *Macromolecules*, 2011, **44**, 5825–5842.
- 19 C.-S. Wang and T.-S. Leu, *Polymer*, 2000, **41**, 3581–3591.
- 20 C. J. Liu, X. L. Pei, X. H. Huang, C. Wei and X. Y. Sun, *Chin. J. Chem.*, 2015, **33**, 277–284.

