

## Synthesis of Polyimides with Low Viscosity and Good Thermal Properties via Copolymerization

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**ABSTRACT:** Novel polyimides were successfully synthesized through copolymerization of diamine monomers p-phenylenediamine (p-PDA) and 4,4'-diaminodiphenylmethane (MDA) with different proportions and 2,3,3',4'-biphenyltetracarboxylic dianhydride (a-BPDA) using 4-phenylethynylphthalic anhydride (4-PEPA) as an end-capping agent. The melt rheological properties, thermal properties, and crystallinity of PI oligomers were investigated via rheometer, dynamic mechanical analysis (DMA), thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), and X-ray diffraction (XRD). The results indicate that melt viscosity and solubility of the PI oligomers were improved, but the glass transition temperature ( $T_g$ ) and crystallinity decreased with the increasing molar ratio of MDA. PI oligomer 3 with the molar ratio of MDA/p-PDA = 2/1 shows a lower minimum melt viscosity (66 Pa.s) at 313°C and better solubility in aprotic solvents. The corresponding PI-3 exhibits a high glass transition temperature of 406°C and excellent thermal stability. This copolyimide shows good processability and thermal properties, and could become a good candidate of matrix resins for high performance composites in aerospace field. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41303.

**KEYWORDS:** copolymers; polyimides; thermal properties

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### INTRODUCTION

Owing to their excellent thermal and mechanical properties, polyimides have been widely used in the fields of aerospace and microelectronic, e.g., and as matrices for high performance composite, as thin films and coatings for microelectronic application, as structural adhesives and sealants, as insulating coatings for aircraft wire coatings, etc.<sup>1–4</sup> However, these rigid polyimides usually have poor processability that limited their widespread application. Therefore, the development of polyimides with excellent processability and high thermal properties is consistently a research goal of these fields. Phenylethynyl containing imide oligomers have been found to have unique combination of attractive properties. These oligomers exhibit good processability and their crosslinked polyimide resins have high glass transition temperature ( $T_g$ ), excellent mechanical properties, high temperature durability, and nice solvent resistance.<sup>5</sup>

On the other hand, it is well known that the processability of polyimides could be improved by decreasing the polymer backbone stiffness via introducing proper flexible linkages, bulky pendent groups or twisted and noncoplanar segments into

polyimide backbones.<sup>6–10</sup> Well, the introduction of some flexible linkages may reduce thermal properties of the corresponding polyimide. Among the flexible linkages, methylene-bridged structure in diamine is more popular due to improvement of processability with less loss of thermal properties. Another effective method for improving processability of polyimides is to introduce geometrically asymmetric unit by altering catenation patterns of dianhydrides in polyimide chain structure. Isomeric polyimides produced from isomeric dianhydrides, such as 2,3,3',4'-biphenyltetracarboxylic dianhydride (a-BPDA), exhibited broad processing windows and good thermal properties.<sup>6,11</sup> Reducing the number average molecular weight ( $M_n$ ) by adjusting the stoichiometry and chemical compositions of the reactive monomers was also an effective method to prepare polyimide matrix resins with low melt viscosity.<sup>12,13</sup> Rikio et al. reported the polyimide derived from 4,4'-oxydianiline (4,4'-ODA), a-BPDA and 4-phenylethynylphthalic anhydride (4-PEPA) with a low molecular weight exhibited a viscosity as low as 200 Pa.s at 310°C and a high  $T_g$  of 343°C.<sup>6</sup> Qu et al. reported a series of fluorinated polyimides with prepared the introduction of trifluoromethyl (-CF<sub>3</sub>) groups into polyimide backbones, and the

results showed a nice melt processability and  $T_g$  of 273°C–326°C.<sup>14</sup> However, comprehensive performances, including processability and thermal properties of these homopolyimides, could not satisfy the demands in some high-technology areas. Therefore, copolyimides bearing different diamine or dianhydride segments, which may exhibit excellent comprehensive performances, have attracted more and more attention.

In this study, a series of novel polyimides were synthesized via copolymerization of diamine monomers p-phenylenediamine (p-PDA) and 4,4'-diaminodiphenylmethane (MDA) and dianhydride monomer a-BPDA, using 4-PEPA as an end-capping agent, in order to obtain copolyimide with excellent processability and thermal properties through the combination of flexible diamine chain segment with rigid diamine chain segments. The effects of the copolyimide with different mole ratio of MDA/p-PDA on melt viscosity as well as thermal properties were investigated.

## EXPERIMENTAL

### Materials

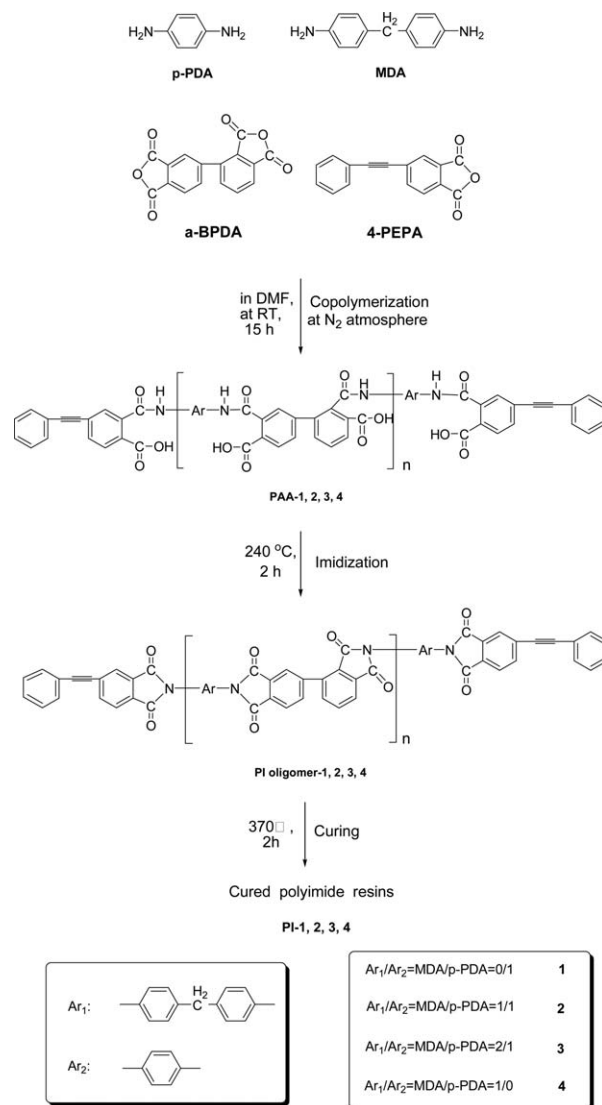
4-Phenylethynylphthalic anhydride (4-PEPA, 99%) and 2,3,3',4'-biphenyltetracarboxylic dianhydride (a-BPDA, 99.6%) were purchased from Changzhou Sunlight Pharmaceutical Co., Ltd. (Changzhou, China) and dried at 150°C for 5 hr in vacuum before use. 4,4'-Diaminodiphenylmethane (MDA, 99%) and p-phenylenediamine (p-PDA, 99%) were purchased from Sahn Chemical Technology Co., Ltd. (Shanghai, China). N,N-Dimethylformamide (DMF, analytical grade) was purchased from Tianjin Fuyu Chemical Co., Ltd. (Tianjin, China) and purified by vacuum distillation over CaH<sub>2</sub> before use. Carbon fiber (T-700, Toary Industries, Inc., Japan) was purchased from Toray industries of Japan. Other solvents were commercially available and used without further purification.

### Measurements

Infrared spectroscopy (IR) of polyimide oligomer powder sample embedded in potassium bromide (KBr) discs was performed on a PerkinElmer Spotlight 400 Fourier transform spectrophotometer. Melt viscosity of polyimide oligomer powder was measured on a TA Instruments AR2000 rheometer at a heating rate of 3°C/min and at a load frequency of 1 Hz. Dynamic mechanical analysis (DMA) was performed on moulded sample (17.5 × 8 × 1.5 mm<sup>3</sup>) on a TA instrument DMA Q800 with a heating rate of 3°C/min, and a frequency of 1 Hz in nitrogen atmosphere, the tangent of loss angle (tanδ) and storage modulus (G') were obtained as a function of temperature curves. Thermal gravimetric analysis (TGA) was conducted on a TA Instruments Q50 thermal analysis system at a heating rate of 20°C/min from 100°C to 800°C under a nitrogen atmosphere. Differential scanning calorimetry (DSC) was performed on a TA Instruments Q200 Differential scanning calorimetry at a heating rate of 20°C/min in a nitrogen atmosphere. Wide angle X-ray diffraction (XRD) was conducted on a X'Pert Pro X-ray diffractometer with Cu/Kα radiation, operated at 40 kV and 40 mA.

### Synthesis of PI Oligomers and Polyimides

A series of polyimide were successfully synthesized via copolymerization of diamine monomers (MDA and p-PDA) and



**Scheme 1.** Synthetic procedure of PI oligomers and polyimides via copolymerization.

a-BPDA using 4-PEPA as an end-capping agent according to a previously reported method.<sup>15,16</sup> Scheme 1 represents the preparation procedure of PI oligomers and the polyimides. The monomer composition is as follows: a-BPDA:(p-PDA + MDA): 4-PEPA = 2 : 3 : 2. When the molar ratio of MDA/p-PDA = 0/1, 1/1, 2/1, 1/0, the corresponding copolyimide oligomers are named as PI oligomer 1, PI oligomer 2, PI oligomer 3, and PI oligomer 4, respectively. A typical procedure is described as follows. p-PDA (1.30 g, 12 mmol), MDA (4.76 g, 24 mmol) and DMF (65 mL) were added into a 200 mL flask which was equipped with a magnetic stirrer under a nitrogen atmosphere. After p-PDA and MDA were dissolved completely, a-BPDA (7.06 g, 24 mmol) and 4-PEPA (5.96 g, 24 mmol) were added slowly to make them dissolve, additional DMF (10 mL) was used to control the solid content to 20 wt %. The reaction mixture was stirred at room temperature for 15 hr under a nitrogen atmosphere to give PAA-3 solution with a solids content of approximately 20 wt %. PAA-3 solution was heated

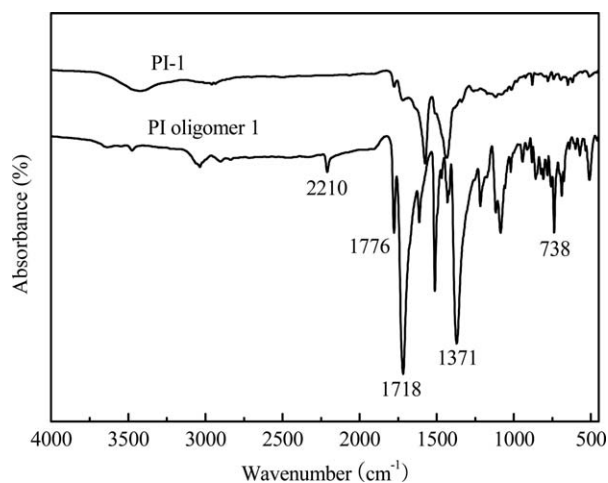


Figure 1. IR spectra of PI oligomer 1 and corresponding cured PI-1.

gradually to remove the solvent, then it was thermally imidized at 240°C for 2 hr in an oven to give PI oligomer 3 as a yellow solid. According to the above procedure, the other two PI oligomers 1, 2, and 4 were synthesized.

PI-1, PI-2, PI-3, and PI-4 were obtained after PI oligomer 1, PI oligomer 2, PI oligomer 3, and PI oligomer 4 were cured at 370°C for 2 hr, respectively.

#### Preparation of CF/PI Composites

The PAA solution was condensed to increase the solid content to 35 wt %. The prepreg was made by coating the 35 wt % PAA solution on Toray T-700 continuous carbon fiber using a brush, and dried in air at room temperature for 24 hr to remove most of solvent. The CF/PI composites were prepared through thermally curing prepreg via heated-die pressing process. The first stage of the curing process: 120°C for 3 hr and 240°C for 2 hr. Then when the temperature was increased to 290°C, a pressure of 1.5 MPa was applied. This pressure was maintained till the temperature was increased to 370°C and kept 370°C for 2 hr. After the temperature recovered to room temperature, the pressure was released, and the composites were obtained via stripping and cut into the desired sizes for testing.

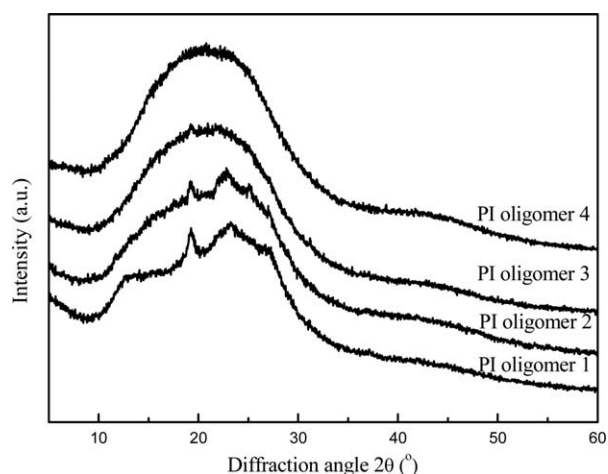


Figure 2. XRD curves of PI oligomers.

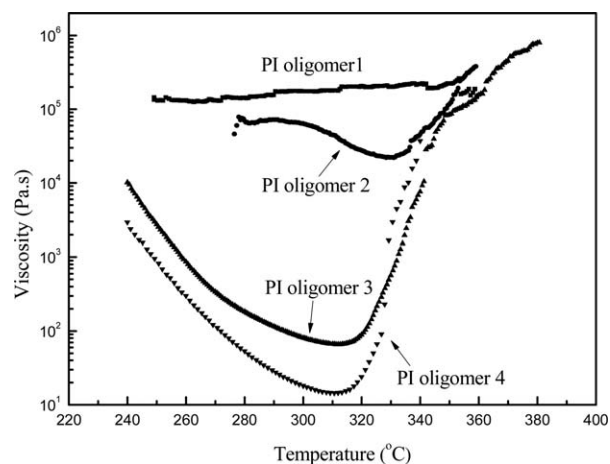


Figure 3. Melt viscosities curves of PI oligomers.

## RESULTS AND DISCUSSION

### Characterization by IR and XRD

IR spectra of PI oligomer 1 and corresponding cured PI-1 are shown in Figure 1, and were analyzed as a representative example. As shown in Figure 1, PI-1 before cured (PI oligomer 1) exhibited an absorption of terminated phenylethynyl groups ( $C\equiv C$ ) at  $2,210\text{ cm}^{-1}$ , and absorptions of imide carbonyl groups ( $C=O$ ) at  $1,776\text{ cm}^{-1}$  (symmetric stretching vibration),  $1,718\text{ cm}^{-1}$  (asymmetric stretching vibration), and  $738\text{ cm}^{-1}$  (bending vibration). The absorption at  $1,371\text{ cm}^{-1}$  was assigned to C-N stretching vibration of imides rings. The above information illustrated that PI oligomer 1 was synthesized successfully.<sup>17</sup> After the oligomer cured at 370°C for 2 hr, the absorption of triple bonds ( $C\equiv C$ ) at  $2,210\text{ cm}^{-1}$  disappeared, which indicated that the  $C\equiv C$  bonds reacted completely. IR spectra of the other two are similar.

XRD spectra of PI oligomers 1, 2, 3, and 4 are shown in Figure 2. PI oligomers 3 and 4 showed a wide and dispersed peak, which means that they are amorphous. While small amounts of sharp peaks in PI oligomers 1 and 2 were detected, which indicates they have somewhat crystalline phase. These results implies that the introduction of MDA may reduce the crystallinity of the PI oligomers, probably because the methylene group of MDA increased the flexibility of chain and reduced the interaction between chains.

### Melt Viscosity of PI Oligomers

Figure 3 shows the viscosity-temperature curves of the PI oligomers. As shown in Figure 3, melt viscosities of the PI

Table I. Solubility of PI Oligomers<sup>a</sup>

Sample	THF	Acetone	DMF	DMAc	NMP	DMSO
PI oligomer 1	–	–	–	–	–	–
PI oligomer 2	–	–	±	±	±	±
PI oligomer 3	–	–	±	+	+	±
PI oligomer 4	±	–	+	+	+	+

<sup>a</sup> Test conditions: PI oligomer/solvent = 10 mg/1 mL, room temperature, 24 hr. +, soluble; ±, partial soluble; –, insoluble.

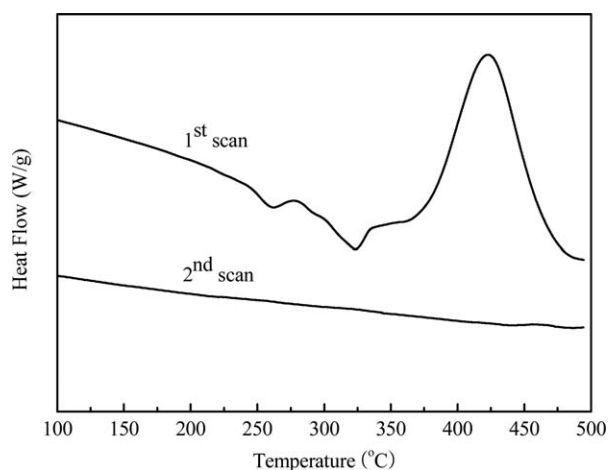
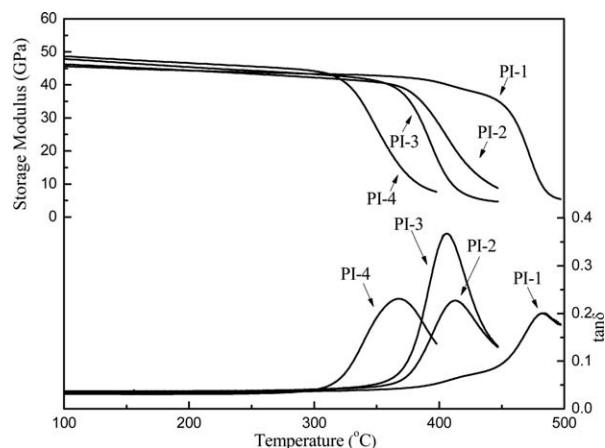
**Table II.** Glass Transition Temperature of PI Oligomers

	PI oligomer 1	PI oligomer 2	PI oligomer 3	PI oligomer 4
$T_g^1$ (°C)	249	207	188	172

$T_g^1$ : glass transition temperature of the copolyimide oligomers determined by DSC.

oligomers 2, 3, and 4 gradually decreased with the increasing of temperature at the first stage until the minimum melt viscosities were reached. Then the melt viscosities were increased due to the thermal crosslinking reaction of phenylethynyl end-caps. The results indicate that the minimum melt viscosity of PI oligomers decreased obviously with the increasing molar ratio of MDA. For example, the melt viscosity of PI oligomer 1 was about 1,00,000 Pa.s, while the minimum melt viscosity of PI oligomer 2 was 22,000 Pa.s (319°C) and those of PI oligomers 3 and 4 was 66 Pa.s (313°C) and 13 Pa.s (310°C). Usually, the lower minimum melt viscosity, the better processability. The minimum viscosity of PI oligomers 3 and 4 was much lower than the reported oligomers, such as PETI-5 exhibited a minimum melt viscosity at 60,000 Pa.s (371°C) and TriA-PI had a minimum melt viscosity at 1,000 Pa.s (320°C).<sup>4</sup> The improvement of the resin melt processability might be attributed to the introduction of methylene group of MDA in the polymer backbone, resulting in the decrease of both interactions of the chains and the backbone stiffness.

The solubility properties of the PI oligomers were investigated by dissolving 10 mg oligomer powder in 1 mL organic solvent, and the results were summarized in Table I. All oligomers were insoluble in acetone. In addition, PI oligomer 1 was insoluble in any tested solvents, probably due to its rigid diamine backbone structure (p-PDA). PI oligomer 2 was partially soluble in DMF, dimethylacetamide (DMAc), N-methyl-2-pyrrolidone (NMP), and dimethyl sulfoxide (DMSO). PI oligomer 3 with molar ratio of MDA/p-PDA = 2/1 shows better solubility than PI oligomers 1 and 2, it is soluble in DMAc and NMP. PI oligomer 4 exhibits the best solubility among the four PI oligomers, it is soluble in DMF, DMAc, NMP, and DMSO, and even soluble in tetrahydrofuran (THF). The solubility of PI

**Figure 4.** DSC curves of PI oligomer 1.**Figure 5.** DMA curves of CF/PI composites.

oligomers was greatly influenced by the content of MDA, more MDA, better solubility. The improved solubility of PI oligomers may be due to the existence of methylene group of MDA decreasing the intermolecular interactions.

#### Thermal Properties of PI Oligomer and Polyimides

The thermal properties of PI oligomers and polyimides were investigated by DSC, DMA, and TGA. The results are listed in Tables II and III, respectively.

The glass transition temperatures ( $T_g$ s) of these PI oligomers were estimated by DSC. Figure 4 shows the DSC curves of the PI oligomer 1 in the first and second scan. In the first scan, PI oligomer 1 exhibited an endothermic absorption peak at 249°C assigned as the glass transition temperature. An exothermic peak appeared at 363–487°C which attributed to the thermal curing of the phenylethynyl groups, and an endothermic peak in the range of 302–337°C may attribute to the melting of the oligomer. In the second scan, the exothermic peak of thermal curing was disappeared, and the value of  $T_g$  was not detected, probably because it is cured after the first scan and its crosslink density is too high.<sup>18</sup> The other two oligomers had similar thermal behaviors, and the  $T_g$  values of PI oligomers were summarized in Table II.  $T_g$  values of the PI oligomers decreased with the increasing molar ratio of MDA.

The thermal properties of polyimides were analyzed via DMA measurement of CF/PI composites and TGA measurement of

**Table III.** Thermal Properties of Polyimides

	DMA (N <sub>2</sub> )		TGA (N <sub>2</sub> )	
	$T_{E'}^1$ (°C)	$T_g^2$ (°C)	$T_{d,5\%}$ (°C)	Retain (%)
PI-1	391	467	555	62
PI-2	369	415	551	67
PI-3	351	406	551	67
PI-4	312	368	550	68

$T_{E'}^1$ : the onset temperature of turndown for storage modulus curve of polyimide composites;  $T_g^2$ : glass transition temperature of the polyimide composites determined by DMA;  $T_{d,5\%}$ : 5% weight loss temperatures polyimides in N<sub>2</sub> atmosphere; Retain: weight % of polyimides at 800°C in N<sub>2</sub> atmosphere.

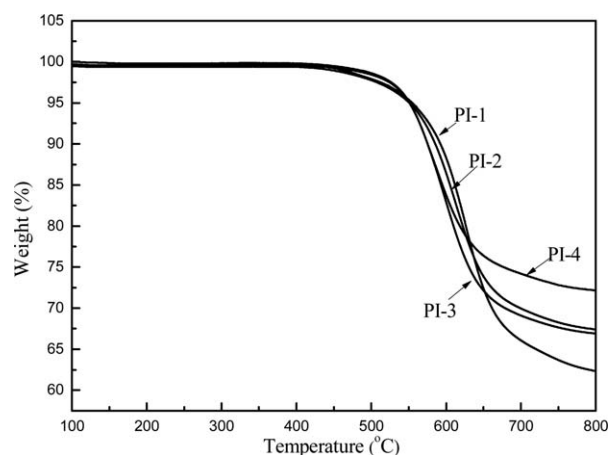


Figure 6. TGA curves of cured polyimides (in  $N_2$  atmosphere).

polyimides. The CF/PI composites were prepared by heated-die pressing process. The glass transition temperature ( $T_g$ ) of the composites were determined by DMA as shown in Figure 5. The corresponding temperature to the peak of  $\tan\delta$  represents the  $T_g$  of the composites, and the data are listed in Table III. As shown in Table III, the  $T_g$ s of these PI composites decreased with the increasing molar ratio of MDA. PI-3 composites show lower  $T_g$  value ( $406^\circ\text{C}$ ) than PI-1 composites ( $467^\circ\text{C}$ ) and PI-2 composites ( $415^\circ\text{C}$ ) due to more amount of MDA. PI-4 composites exhibit the lowest  $T_g$  value ( $368^\circ\text{C}$ ) probably because only MDA as used as diamine monomer. The  $T_g$ s of these PI-1, PI-2, and PI-3 composites are all over  $400^\circ\text{C}$ , indicating they exhibit nice heat resistance. Compared to the results of Rikio et al. (viscosity of 200 Pa.s at  $310^\circ\text{C}$  and  $T_g$  of  $343^\circ\text{C}$ ),<sup>6</sup> PIs described in this study exhibit better processability and thermal properties.

The thermal stability of the polyimides was evaluated by TGA as shown in Figure 6, and the data are also listed in Table III. The temperatures of 5% weight loss were all above  $550^\circ\text{C}$  in  $N_2$  atmosphere, the char yields at  $800^\circ\text{C}$  are all above 60% in  $N_2$  atmosphere. Therefore, the four polyimides with different molar ratio of MDA to p-PDA exhibit excellent thermal stability.

As analyzed above, considering processability and heat resistance, PI oligomer 3 and its corresponding PI-3 exhibit good comprehensive performance, which could be a good matrix resin candidate for high performance composites in aerospace field because of its excellent processability and thermal properties.

## CONCLUSIONS

Polyimides with low viscosity and good thermal properties were successfully synthesized via copolymerization of diamine monomers (MDA and p-PDA) and a-BPDA using 4-PEPA as an end-capping agent. The minimum melt viscosity and solubility of the polyimide oligomers were improved, while the glass transition temperatures and crystallinity of the polyimide oligomers decreased with the increasing molar ratio of MDA. The PI oligomer 3 with the molar ratio of MDA/p-PDA = 2 : 1 showed lower minimum melt viscosity (66 Pa.s) and better solubility in NMP and DMAc, and corresponding PI-3 exhibits a glass transition temperature of  $406^\circ\text{C}$  and excellent thermal stability.

This copolyimide could be a good matrix resin candidate for high performance composites in aerospace field because of its excellent processability and thermal properties.

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