

## The suitable itaconic acid content in polyacrylonitrile copolymers used for PAN-based carbon fibers

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**ABSTRACT:** This article was to provide some new insights into the influences of itaconic acid (IA) content in polyacrylonitrile (PAN) copolymers on polymerization, structural evolution, thermal behaviors and carbon yield relatively comprehensively. High IA containing poly(acrylonitrile-*co*-itaconic acid) (PAI) oligomers were successfully extracted from PAI copolymers with 2.0 and 3.0 mol % IA. PAI copolymers with 0.5 mol % and 1.0 mol % IA possessed more cyclized structures, conjugated carbonyl group, conjugated nitrile group, and less  $\beta$ -amino nitrile group as well as faster structural evolution rate than those of the other three PAI copolymers. Kinetic parameters indicated that excessive IA content in PAI copolymer did not have advantages in promoting cyclization reaction. The PAI copolymers with 0.5 wt % to 1.0 mol % IA possessed better crystalline parameters as well as higher carbon yield than those of the other two PAI copolymers after carbonization at 1350 °C. In summary, PAI copolymers with 0.5 mol % to 1.0 mol % IA will be more suitable for fabricating of high performance PAN-based carbon fibers. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43919.

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### INTRODUCTION

Until now, due to extensive application in high-tech sectors such as aerospace, defense areas, civil engineering, etc., polyacrylonitrile-based (PAN-based) carbon fiber has attracted significant attention by both industry and academia.<sup>1–4</sup> According to the published documents, over 90% of carbon fibers used today are made from PAN-based precursors.<sup>4–7</sup> However, PAN homopolymer has hardly been used as a carbon fiber precursor based on the current fabrication technology. As known, PAN homopolymer possesses high regularity and crystallinity (CI), but the strong intermolecular interaction makes PAN homopolymer too rigid to be solved in the spinning solvents, and thus results in poor stability of the spinning solution.<sup>8–10</sup> Moreover, during the thermal oxidative stabilization (TOS) step of PAN homopolymer, cyclization reaction between nitrile groups is initiated and transferred by free radical mechanism which can cause the centralized and sudden heat release.<sup>7,8,11–14</sup> As a result, high performance carbon fiber cannot be achieved due to the presence of many defects such as voids resulted from volatile side-products during the intense heat release.<sup>11–14</sup> To overcome

these limitations aforementioned, some kinds of comonomers, such as itaconic acid (IA) and methacrylic acid, are introduced into PAN chains.<sup>15–17</sup> Due to the presence of two carbonyl groups, IA has been mostly used to copolymerize with acrylonitrile. On the one hand, the presence of acid comonomer improves the hydrophilicity of PAN copolymers, which helps to control the double-diffusion of solvent and water during wet or jet-wet spinning, and thus gives advantages in fabricating high orientation PAN-based precursors with less defects.<sup>18,19</sup> On the other hand, during the TOS process, the acid comonomers can act as an ionic initiator to catalyze the cyclization reaction between nitrile groups at a relative low temperature, easing the concentrated heat release, enhancing the thermal stability and the aggregate of fibers, reducing the formation of defects and eventually improving carbon yield and properties of resultant carbon fibers.<sup>20–22</sup> So, the presence of vinyl acid comonomer is indispensable to produce high performance PAN-based carbon fibers. It is well known that the content of vinyl acid has great effects on the structural evolution and thermal behaviors of modified PAN copolymers during TOS, which not only decides the

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parameters of TOS and carbonization, but also decides the efficiency of products and the performance of resultant carbon fibers. However, previous reports mostly only focused on the influences of vinyl acids on the structural evolution and thermal behaviors during the TOS,<sup>11,17</sup> but less attention has been paid to evaluate the influences of vinyl acids content on the polymerization (e.g., molecular weight and/or distribution), structural evolution and thermal behaviors simultaneously. So, the best suitable contents of vinyl acid based on previous reports may be not comprehensive even not be suitable for fabricating high performance carbon fibers.

In the present work, poly(acrylonitrile-*co*-itaconic acid) (PAI) copolymers containing different content of IA comonomer were synthesized using one-step batch slurry polymerization under the same conditions to analyze the influences of IA content on polymerization and some other properties for fabricating PAN-based carbon fibers. Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) were used to track the structural evolution of PAI copolymers during TOS and carbonization. And peak-fitting analysis was adapted to understand the structural evolution quantitatively and comprehensively. Thermal behavior of PAI copolymers was investigated by differential scanning calorimetry (DSC). Based on the results of FTIR, XRD, and DSC investigations, the suitable IA content in PAI copolymers were suggested for PAN-based carbon fibers.

## EXPERIMENTAL

### Materials

Acrylonitrile was supplied by Jilin Petrochemical Company, Jilin, China, distilled under reduced pressure and restored in a freezer at  $-18\text{ }^{\circ}\text{C}$  prior to its use. IA (>99%) and ammonium persulfate (APS, >98%) were purchased from Sinopharm Chemical Reagent Co., Shanghai, China and used as received. *N,N*-dimethylformamide (DMF, >99.5%) and methanol (>99.5%) were purchased from Beijing Chemical Works, Beijing, China and used as received. Deionized water was prepared by our own laboratory and used throughout the experiments.

### Preparation of PAI Copolymers

Five samples of PAI copolymers containing about 0.5 wt %, 0.5 mol %, 1.0 mol %, 2.0 mol %, and 3.0 mol % IA were prepared by a radical polymerization in water using APS as initiator and named as PAI-0.5 wt %, PAI-0.5 mol %, PAI-1.0 mol %, PAI-2.0 mol %, and PAI-3.0 mol %, respectively. In a typical polymerization, monomer (AN + IA, 60 g) and  $\text{H}_2\text{O}$  (135 g) were charged in a three-neck, round-bottom flask equipped with a stir bar and a condenser, and subsequently the solution was degassed by bubbling with  $\text{N}_2$  for 30 min. The flask was kept in a water bath and a degassed solution of APS (0.72 g APS + 5 g  $\text{H}_2\text{O}$ ) was added into the flask to initiate the reaction. The polymerization was carried out at  $65\text{ }^{\circ}\text{C}$  for 6 h under nitrogen atmosphere. Then, the reaction mixture was added to excessive deionized water with vigorous agitation, and then washed again with deionized water for several times to remove the unreacted monomers. At last, the polymer was dried at  $60\text{ }^{\circ}\text{C}$  under vacuum to a constant weight. To separate the oligomers from PAI copolymers, the PAI copolymers were immersed in acetone at ambient temperature for 48 h, and the supernatant was removed into a surface dish to evaporate

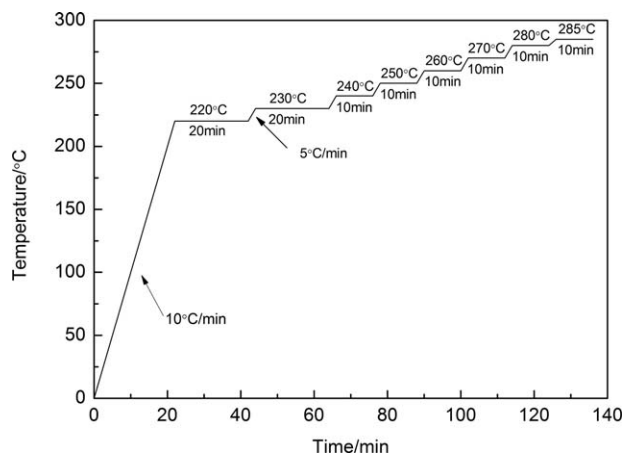


Figure 1. Program used for stabilization of PAI copolymers.

the excessive acetone. Finally, the solution was dried at  $60\text{ }^{\circ}\text{C}$  under vacuum to a constant weight.

### Preparation of PAI Films and Thermal Treatment Procedures

Thin films of the samples were prepared for heat treatments and the following FTIR analysis. The process used was as follows: First, a solution containing about 2 wt % polymers in DMF was prepared, and then the dilute solution was cast onto a horizontal glass slice, leaving a transparent thin polymer film. Second, the film was purified in methanol at  $50\text{ }^{\circ}\text{C}$  for 24 h to remove the residual DMF. Finally, the film was dried at  $75\text{ }^{\circ}\text{C}$  for 24 h under vacuum. The thickness of each film was measured by using a digital caliper (Mitutoyo 293-100). All films were prepared by casting the same volume of the dilute solution onto the same horizontal glass slice. The films for heat treatment were prepared by cutting the dried films into approximately  $2 \times 2\text{ cm}^2$ . Particular care was taken to remove the nonuniform edges from the cast film, forming a usable portion from which heat treatment samples could be cut. Thermal treatment was carried out in an air oven at a constant temperature of  $230\text{ }^{\circ}\text{C}$  with a temperature accuracy of  $1\text{ }^{\circ}\text{C}$ . The isothermal TOS was carried out at  $230\text{ }^{\circ}\text{C}$  with a constant air gas flow and sampled at some intervals. A temperature program (Figure 1) was used to stabilize the PAI films or powders with a constant air gas flow. Subsequently, carbonization of stabilized PAI powders were carried out under nitrogen condition (>99.999%) using a tube furnace. PAI powders were heated from room temperature to  $1350\text{ }^{\circ}\text{C}$  at  $10\text{ }^{\circ}\text{C}/\text{min}$  at first, and kept for 30 min at  $1350\text{ }^{\circ}\text{C}$ , subsequently cooled down to room temperature at  $10\text{ }^{\circ}\text{C}/\text{min}$ .

### Characterization of PAI Copolymers

$^1\text{H}$  NMR sample was dissolved in deuterated dimethyl sulfoxide ( $\text{DMSO-}d_6$ ) (5%, w/v polymer solution), and analysis was performed at room temperature in a 5 mm o.d. NMR tube using Bruker AVANCE III 400 Spectrometer operating at 400 MHz (See Supporting Information, Figure S1). The Nicolet iS-50 FTIR spectrometer was used to detect the structural changes during the thermal treatment in  $4000\text{--}400\text{ cm}^{-1}$  range using 32 scans at a resolution of  $4\text{ cm}^{-1}$ . Second-derivative spectra were obtained from the FTIR absorbance spectra in range of  $1800\text{--}1000\text{ cm}^{-1}$  and  $2300\text{--}2100\text{ cm}^{-1}$  using the equation  $A''_n = (A_{n-1} - 2A_n + A_{n+1})/(\Delta W)^2$ ,

**Table I.** Preparation and Characteristics of PAI Copolymers Used in this Study

Destination	In feed (mol %)		In polymer ( $F_{IA}$ , mol %) <sup>a</sup>		CI (%)	$d$ (nm)	$L_c$ (nm)	Conversion (at 15 min) (wt %) <sup>b</sup>	$M_n$ ( $\times 10^4$ ) g/mol
	AN	IA	AN	IA					
PAI-0.5 wt %	99.80	0.20	99.75	0.25	55.96	0.525	5.770	7.3	43.5
PAI-0.5 mol %	99.50	0.50	99.49	0.51	56.15	0.524	5.626	6.6	38.7
PAI-1.0 mol %	99.00	1.00	98.74	1.26	56.90	0.524	4.784	2.2	27.1
PAI-2.0 mol % <sup>c</sup>	98.00	2.00	98.08	2.10	53.93	0.525	4.412	2.0	13.6 <sup>d</sup>
PAI-2.0 mol % <sup>e</sup>	98.00	2.00	96.97	3.03	N.A. <sup>d</sup>	N.A. <sup>d</sup>	N.A. <sup>d</sup>	N.A. <sup>d</sup>	N.A. <sup>d</sup>
PAI-3.0 mol % <sup>c</sup>	97.00	3.00	96.58	3.42	53.72	0.527	4.039	1.9	7.4. <sup>d</sup>
PAI-3.0 mol % <sup>e</sup>	97.00	3.00	89.12	10.88	N.A. <sup>d</sup>	N.A. <sup>d</sup>	N.A. <sup>d</sup>	N.A. <sup>d</sup>	N.A. <sup>d</sup>

<sup>a</sup> Calculated from  $^1\text{H-NMR}$  by  $F_{IA} = [IA] \times 100 / ([AN] + [IA])$ .

<sup>b</sup> Calculated by conversion =  $100 \times \text{weight of polymer} / \text{weight of monomer}$ .

<sup>c</sup> Average IA content in PAI copolymer calculated from  $^1\text{H-NMR}$ .

<sup>d</sup> Not applicable.

<sup>e</sup> IA content in PAI oligomer calculated from  $^1\text{H-NMR}$ .

where  $A_m$ ,  $A_n''$ , and  $\Delta W$  are the absorbance at data point  $n$ , the intensity of the second derivative at data point  $n$ , and the frequency interval between data points  $n$  and  $n + 1$ , respectively. The positions of the negative peaks in the second derivatives were used to determine the position of each peak in the original spectra. PeakFit v4.12 software (SPSS/Jandel, Scientific Software) was used to deconvolute the spectra within the range of  $1800\text{--}1000\text{ cm}^{-1}$  and  $2300\text{--}2100\text{ cm}^{-1}$ . XRD patterns of the five copolymers were obtained using an X-ray diffractometer (Rigaku D/max-2550,  $\text{CuK}_\alpha$ ,  $0.154056\text{ nm}$ ,  $50\text{ kV}$ ,  $200\text{ mA}$ ) through a  $2\theta$  range of  $5\text{--}60^\circ$  at a scan speed of  $5^\circ/\text{min}$  (See XRD spectra of original polymers in Supporting Information, Figure S2). All the XRD measurements were carried out under the same conditions. The crystalline planar spacing  $d$  and crystallite size of the laterally order domains  $L_c$  of five PAI copolymers were calculated from the XRD data by the Bragg and Scherrer equation as follows,<sup>7,14</sup> respectively:

$$d = \lambda / 2 \sin \theta \quad (1)$$

$$L_c = k\lambda / \beta \cos \theta \quad (2)$$

where  $\lambda = 0.154056\text{ nm}$  is the wavelength of  $\text{CuK}_\alpha$  X-ray,  $\theta$  is the Bragg angle,  $\beta$  is the full width at half maximum intensity (FWHM) of the peak around  $2\theta = 17^\circ$  and  $2\theta = 25^\circ$ , and  $k$  is a constant 0.89. The strongest diffraction peak at around  $2\theta = 17^\circ$  is attributed to (100) crystalline plane of the pseudo-hexagonal cell.<sup>7,22</sup> The weak diffraction peak at around  $29^\circ$  is attributed to (101) crystalline plane of the pseudo-hexagonal cell.<sup>7,22</sup> The CI of five PAI copolymers was determined by Bell and Dumbleton method:

$$CI = A_c / A_c + A_a \quad (3)$$

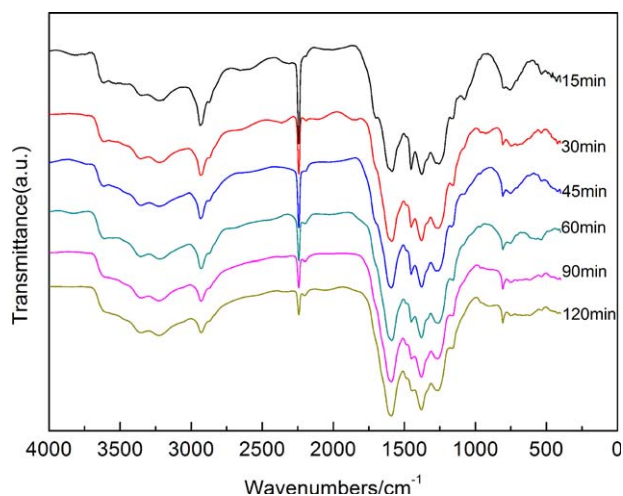
where  $A_c$  is the integral area of crystalline zone around  $2\theta = 17^\circ$  and  $29^\circ$  in XRD patterns, and  $A_a$  is the integral area of amorphous zone. XRD patterns of PAI copolymers were processed by Jade 6 software to analyze the peak center, the peak area and the FWHM.

The DSC curves of powered samples were carried out using a Mettler DSC-1 thermal analyzer. The samples were scanned under nitrogen for DSC analysis. The sample weights used for DSC measurements were about 3–5 mg. The viscosity average molecu-

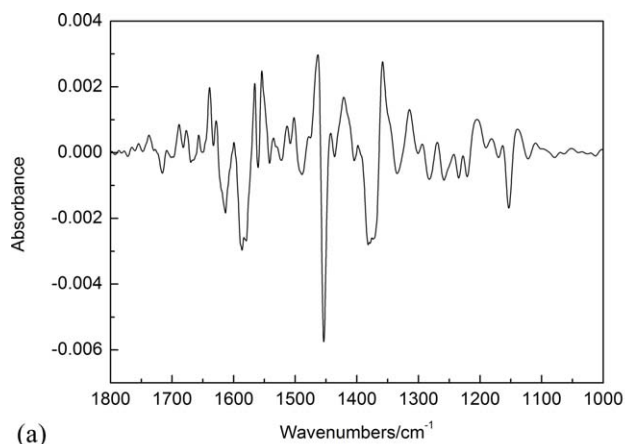
lar weights of the resultant PAI copolymers were measured using an Ubbelohde viscometer at  $30^\circ\text{C}$  using DMF as a solvent.

## RESULTS AND DISCUSSION

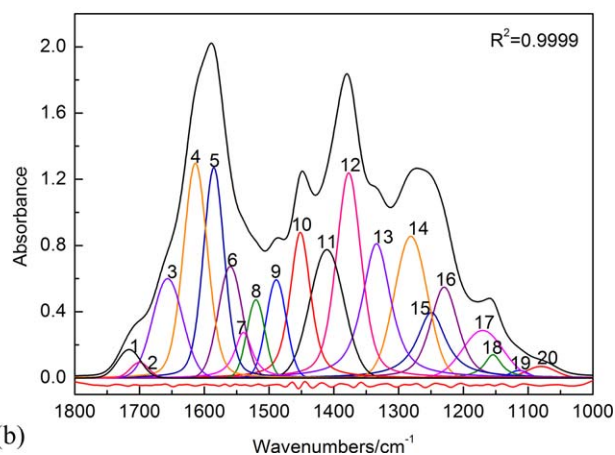
Characteristics of PAI copolymers were summarized in Table I. The content of IA in PAI copolymers are obviously higher than that in the feed, which is due to the higher reactivity of IA than that of AN. Some oligomers were extracted from PAI copolymers with 2.0 mol % and 3.0 mol % IA, but it was failed to extract oligomers from PAI copolymers with 0.5 wt % to 1.0 mol % IA. The IA contents in these oligomers were significantly higher than that in the feeds. These findings indicated that with the increasing of IA content in the feed, the penultimate effect of IA comonomer significantly decreased the molecular weight of PAI formed in the early stage<sup>23</sup> and increased the polydispersity index of the resulted copolymers, which will result in the instable flow of the spinning solution<sup>24</sup> and poor performance of PAN precursor fibers. Furthermore, the high IA containing PAI oligomers will decompose during the TOS process, which gives some kinds of volatile side-products, leaving defects such as voids in the stabilized fibers and giving the poor performance of resultant PAN-based carbon fibers.<sup>11</sup> It should be pointed out that the XRD spectrum of PAI-3.0 mol % exhibited two narrow peaks at approximately  $28^\circ$  and  $38^\circ$ , respectively. But, after extraction in boiling acetone for 8 h, these two narrow peaks at approximately  $28^\circ$  and  $38^\circ$  disappeared. So, we inferred these two peaks may be related to the presence of high IA containing oligomers. As shown in Table I, the polymerization rate were significantly decreased as the IA content increasing, especially when the IA content over 1.0 mol % in the feed. So, taking the influences of IA on polymerization into account, the IA content in the feeds should be decreased appropriately. In the following sections, the structural evolution and thermal behaviors were characterized to evaluate the suitable IA content in PAI copolymers used for PAN-based carbon fiber, and kept the influences of IA on the polymerization was kept in mind at all times.



**Figure 2.** FTIR spectra of PAI-1.0 mol % copolymer thermal treated at 230 °C for different time. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

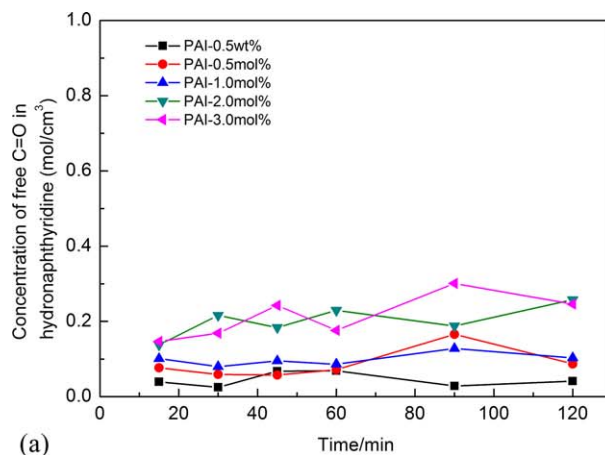


(a)

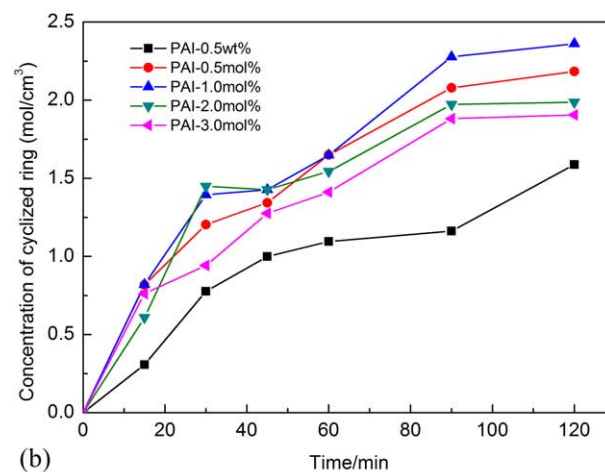


(b)

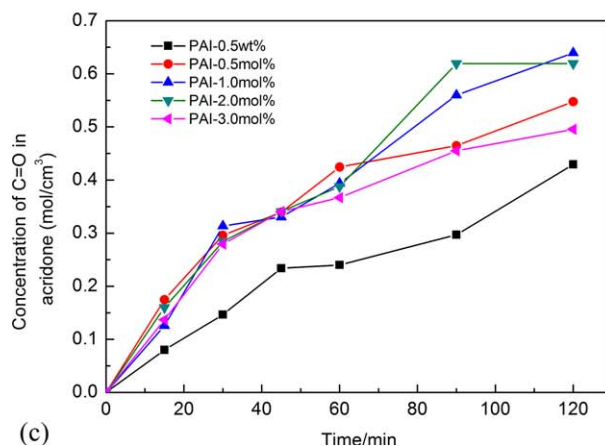
**Figure 3.** Typical second-derivative and corresponding deconvolution spectra of PAI-1.0 mol % copolymer thermal treated at 230 °C for 60 min (Peak fitting by Gauss + Lor area by fixing the peak position and varying the peak width and intensity). The curve at the bottom of deconvolution spectra is the different spectrum between the experimental spectrum and simulated spectrum. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



(a)



(b)

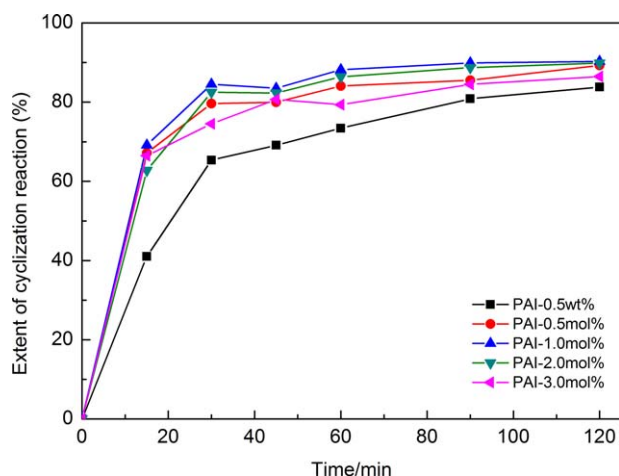


(c)

**Figure 4.** Evolution of stabilized structures: (a), free carbonyl group in hydronaphthyrindine ( $1715\text{ cm}^{-1}$  in Supporting Information Table 1S), (b), cyclic ring structures ( $1610$  and  $1580\text{ cm}^{-1}$  in Supporting Information Table 1S), and (c), conjugated carbonyl group in an acridone ring ( $1660\text{ cm}^{-1}$  in Supporting Information Table 1S) during thermal treatment at 230 °C. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

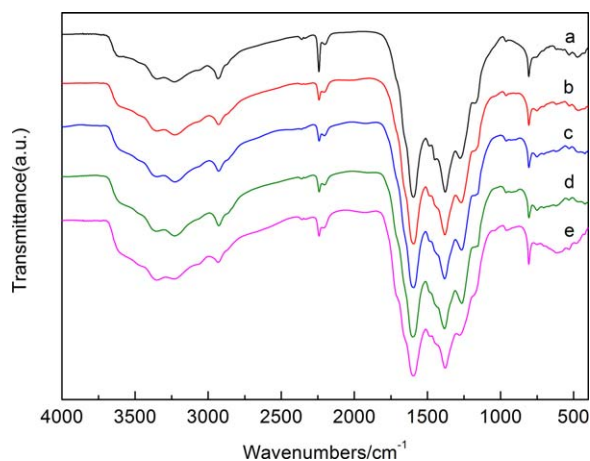
### Structural Evolution of PAI Copolymers during TOS

It is well known that TOS is an indispensable step for the formation of carbon materials from PAN-based precursors. Figure

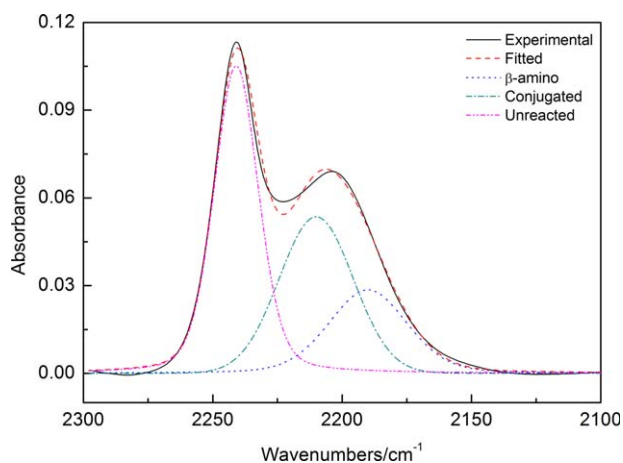


**Figure 5.** Extent of cyclization reaction of PAI copolymers during thermal treatment at 230 °C as determined by the evolution of peaks 4 + 5. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

2 presented the structural evolution of PAI-1.0 mol % copolymer isothermal treated at 230 °C in air for different time (See the other spectra in Supporting Information, Figure 3S). The characteristic changes are those: The intensity of peak of CN group at 2240  $\text{cm}^{-1}$  decreased gradually as a function of thermal treatment time<sup>7,8,11</sup>; The appearance of broad and overlapped peak at the range of 1620–1580  $\text{cm}^{-1}$  presented the formation of cyclic  $\text{—C=N—}$ ,  $\text{—C=C—}$ , and  $\text{=N—H}$  groups<sup>7,8,14,21</sup>; The peaks of  $\text{CH}_2$  at 2940, 2870, and 1450  $\text{cm}^{-1}$  had some decreased intensities,<sup>7,8,11,14</sup> whereas the peak of out-of-plane bending of  $\text{=C—H}$  in unsaturated ring (810  $\text{cm}^{-1}$ ) appeared with a increased intensity as a function of thermal treatment time<sup>11</sup>; The peak at 1715  $\text{cm}^{-1}$  presented the carbonyl group in hydronaphthyridine rings (free carbonyl group),<sup>11,25–27</sup> which mainly evolved from IA, whereas the peak at 1660  $\text{cm}^{-1}$  presented the carbonyl group in acridone rings (conjugated carbonyl group),<sup>25–27</sup> which originated from



**Figure 6.** FTIR spectra of PAI copolymers thermal treated under programmed temperature: (a) PAI-0.5 wt %, (b) PAI-0.5 mol %, (c) PAI-1.0 mol %, (d) PAI-2.0 mol %, (e) PAI-3.0 mol %. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 7.** Nitrile band peak fitting results of PAI-1.0 mol % copolymer thermal treated under programmed temperature. (Peak fitting by Gauss + Lor area by fixing the peak position and varying the peak width and intensity). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

oxygen-uptake reaction from air. All these findings demonstrated the success of TOS reactions of PAI copolymers during thermal treatment in air. However, the influences of IA content on the TOS reactions cannot be discussed in details here due to the insignificant differences of structural evolution of PAI copolymers.

As well known, for quantitative analysis, the peaks should be resolved to identify each individual contribution according to Beer–Lambert law. However, the overlapped peaks of 1800–1000  $\text{cm}^{-1}$  make the quantitative analysis of TOS reactions very difficult and unreliable. Second derivative and curve-fitting procedures have been applied to the structural evolution of PAN polymers to overcome those problems.<sup>14,26,29</sup> The minima of the second-derivative spectrum provided the numbers and positions of the overlapping peaks in the original spectrum. The positions and destinations of the peaks were summarized in Table IS (See Supporting Information). Subsequently, the corresponding deconvolution spectrum was achieved on the basis of the number and position determined from the second-derivative spectrum. Typical representative second-derivative and corresponding deconvolution spectra are presented in Figure 3.

To quantitatively investigate the contribution of the cyclic ring and carbonyl groups during the TOS, the Beer–Lambert equation was used. The equation of Beer–Lambert law is as follows:

$$A = \epsilon \cdot L \cdot C \quad (4)$$

where  $\epsilon$  and  $C$  are the molar absorption coefficients and concentration of specific groups, respectively.  $L$  is the path length and was measured by using a digital caliper.  $A$  stands for the absorbance of a specific group. In the present work, 55.2 and 65.8  $\text{cm}^2\text{mmol}^{-1}$  was used as the molar absorption coefficient of cyclic ring and carbonyl groups,<sup>26</sup> respectively.

Based on the results of peak fitting, the evolution of the carbonyl group in hydronaphthyridine ring [Figure 4(a), peak 1 in Supporting Information Table IS], cyclized ring [Figure 4(b),

**Table II.** Nitrile Band Peak Fitting Results of FTIR Spectra for PAI Copolymers

Destination	Area fraction by peak fitting			S2/S3
	Unreacted nitrile: S1 (%)	Conjugated nitrile: S2 (%)	$\beta$ -amino nitrile: S3 (%)	
PAI-0.5 wt %	66.49	16.02	17.49	0.912
PAI-0.5 mol %	46.08	34.99	18.93	1.848
PAI-1.0 mol %	44.62	34.58	20.80	1.663
PAI-2.0 mol %	49.00	32.90	18.10	1.817
PAI-3.0 mol %	44.58	34.13	21.29	1.603

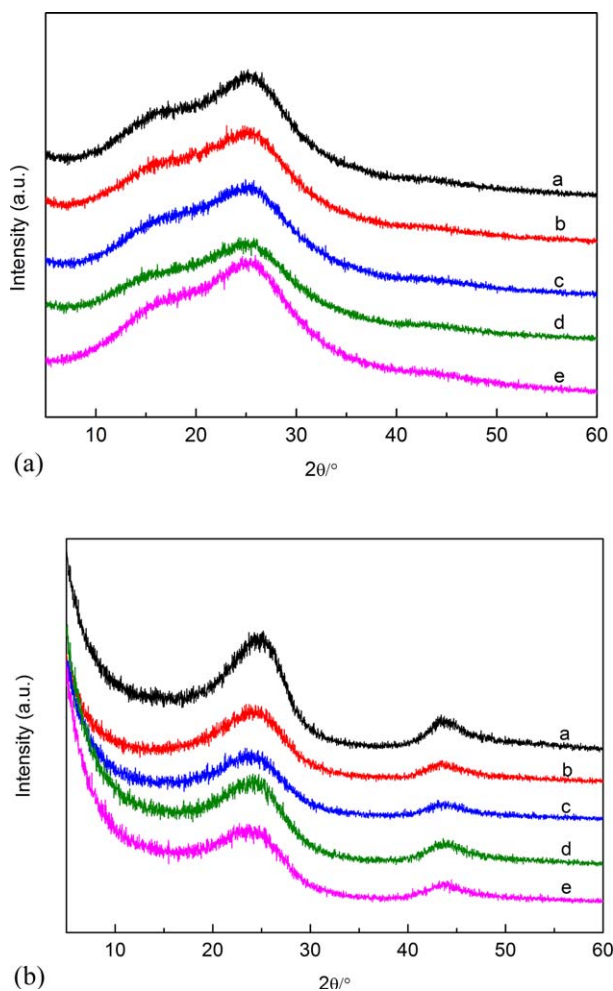
peaks 4 + 5 in Supporting Information Table 1S], and carbonyl group in acridone ring [Figure 4(c), peak 2 + 3 in Supporting Information Table 1S] were shown in Figure 4. The concentration of free ketone in hydronaphthridine ring increased with IA content increasing and was kept almost constant concentration during the TOS, which due to the carbonyl group in

hydronaphthridine ring mainly originated from the IA comonomer.<sup>26</sup> However, PAI copolymers containing 2.0 mol % and 3.0 mol % IA had almost the same concentration of carbonyl group in hydronaphthridine ring. This may be attributed to a part of IA comonomer, for 3.0 mol % even 2.0 mol % IA content, failed to initiate the cyclization reaction and decomposed during the isothermal TOS process. Moreover, as discussed in the above section, the presence of excessive IA comonomer significantly decreased the molecular weight of PAI polymers and formed low molecular weight, high IA containing oligomers, which significantly decreased the thermal oxidative stability of PAI copolymers. As shown in Figure 4(b,c), the synchronized evolution of cyclized ring and carbonyl group in acridone as a function of TOS time were observed. For PAI containing 0.5 wt % IA, the concentration of cyclized ring and carbonyl group in acridone was lowest among PAI copolymers, which suggests that the too less IA content could not promote the formation of large number of cyclized structure, as well as not generated high concentration of carbonyl group in acridone. PAI copolymers with 1.0 mol % IA exhibited the most efficient cyclization and oxygen-uptake reactions followed by 0.5 mol % and 2.0 mol % IA. It is well known that the cyclic structure is the intermediate products to form the two dimensional turbostratic graphite-like structures during the high temperature carbonization. And on the one hand, the carbonyl groups promote the interchain hydrogen bonding between C=O and N-H of PAI copolymer chains, which significantly improve the thermal stability of the stabilized PAI copolymers. On the other hand, the presence of carbonyl groups (mainly carbonyl group in acridone) promotes the conversion of ladder structures into the two dimensional turbostratic graphite-like structures during the high temperature carbonization.

Due to a part of the nitrile groups failed to participate in the cyclization reaction during the TOS process, the extent of cyclization reaction is another useful characteristic parameter to evaluate the TOS reactions. The extent of cyclization reaction was calculated by using the data of peak fitting above and the following equation<sup>26,30</sup>:

$$\text{Extent of cyclization reaction} = \frac{f \times \text{ABS}(1610 + 1580)}{\text{ABS}(2240) + f \times \text{ABS}(1610 + 1580)} \quad (5)$$

where  $\text{ABS}(2240)$  = absorbance of nitrile groups,  $\text{ABS}(1610 + 1580)$  = absorbance of  $\nu_{\text{C}=\text{C}} + \nu_{\text{C}=\text{N}} + \delta_{\text{N}-\text{H}}$  (cyclic structure



**Figure 8.** XRD spectra of PAI copolymers thermal oxidatively stabilized (a) and carbonized (b) under programmed temperature: (a) PAI-0.5 wt %, (b) PAI-0.5 mol %, (c) PAI-1.0 mol %, (d) PAI-2.0 mol %, (e) PAI-3.0 mol %. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Table III.** Parameters of Stabilized and Carbonized PAI Copolymers

Destination	Stabilized under programmed temperature					Carbonized under programmed temperature				
	$2\theta/^\circ$	FWHM/ $^\circ$	$d$ (nm)	CI (%) <sup>a</sup>	Yield (%)	$2\theta/^\circ$	FWHM/ $^\circ$	$d$ (nm)	$L_c$ (nm)	Yield (%) <sup>b</sup>
PAI-0.5 wt %	15.69	8.11	0.564	28.46	89.4	25.480	5.69	0.349	1.47	52.1
PAI-0.5 mol %	15.29	7.43	0.579	22.17	86.3	24.879	6.67	0.358	1.19	42.6
PAI-1.0 mol %	15.37	7.93	0.576	24.00	83.7	24.296	6.17	0.366	1.39	43.9
PAI-2.0 mol %	14.85	8.32	0.596	22.69	81.0	24.786	6.88	0.359	1.16	41.1
PAI-3.0 mol %	15.51	8.23	0.571	27.15	68.2	24.512	6.91	0.363	1.19	40.5

<sup>a</sup>Calculated from the peak at ca.  $15^\circ$ .

<sup>b</sup>Calculated based on the stabilized PAI copolymers.

originated from cyclization and dehydrogenation reactions),  $f =$  ratio of  $\nu_{CN}$  and  $\nu_{C=C} + \nu_{C=N} + \delta_{N-H}$  group absorptivity constants = 0.29.

From Figure 5, the extent of cyclization reaction increased as a function of thermal treatment time and reached a constant at thermal treatment time of about 60 min, except the PAI with 0.5 wt % IA. Moreover, the cyclization rate of PAI with 0.5 wt % was the lowest. Those findings indicated that too low IA content in PAN polymer did not promote the cyclization reaction with a fast rate and a high extent of cyclization reaction. PAI with 1.0 mol % IA possessed the fastest cyclization reaction rate and the highest extent of cyclization reaction, followed by PAI copolymers with 2.0 mol %, 0.5 mol %, and 3.0 mol % IA in sequence.

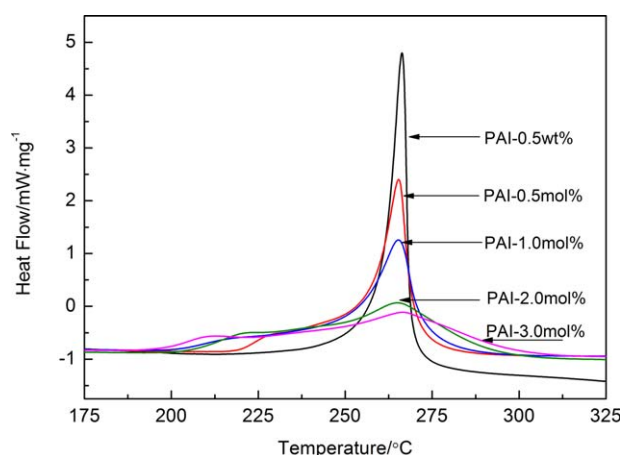
The structural evolution of PAI copolymers thermal treated under programmed temperature (as shown in Figure 1) was presented in Figure 6. The unreacted nitrile group ( $2240\text{ cm}^{-1}$ ) in PAI with 0.5 wt % IA was obviously higher than that in the PAI copolymers. And this unreacted nitrile group will be lost in the step of high temperature carbonization, giving poor performance of the resultant carbon fibers.<sup>11</sup> For the other PAI copolymers with 0.5 mol % to 3.0 mol % IA, the differences of

structural evolution were too small to be distinguished. So, we attempted to analyze the unreacted nitrile group ( $2240\text{ cm}^{-1}$ ), conjugated nitrile group ( $2210\text{ cm}^{-1}$ ), and  $\beta$ -amino nitrile ( $2190\text{ cm}^{-1}$ ) by peak fitting to obtain some fine information about the formed structures. The optimum peak fitting of various nitrile groups for PAI-1.0 mol % copolymer was shown in the Figure 7 (See the other results in Supporting Information, Figure 4S), and the corresponding data were listed in Table II. It should be noted that PAI with 0.5 mol % to 2.0 mol % IA possessed less unreacted nitrile group and  $\beta$ -amino nitrile group or higher conjugated nitrile group than that for the two other PAI copolymers with 0.5 wt % and 3.0 mol % IA. More importantly, the ratio of  $S_2$  to  $S_3$  for PAI with 0.5 mol % to 2.0 mol % IA possessed higher values compared to PAI copolymers with 0.5 wt % and 3.0 mol % IA. These results indicated that PAI copolymers with 0.5 mol % to 2.0 mol % IA possessed longer cyclized structure and fewer cyclization terminations compared to PAI copolymers with 0.5 wt % and 3.0 mol % IA, and this is very important for improving the performance of carbon fibers.

Figure 8 presented the XRD spectra of PAI copolymers thermal oxidative stabilized and carbonized under programmed temperature and corresponding parameters were summarized in Table III. It was found out that the peak at ca.  $17^\circ$  has a reduced intensity, whereas, a new broad peak at ca.  $25^\circ$  appeared after TOS process. This finding indicated that the crystalline was destroyed due to the TOS reactions, and some new structures have formed. However, there was still a weak peak at ca.  $15^\circ$  even thermal treated after  $285^\circ\text{C}$ , which was inferred that a small fraction of linear PAI chains failed to converted in cyclized structures. It should be pointed out that the yield of stabilized and carbonized PAI copolymers decreased as a function of IA content, especially that of PAI with 3.0 mol % IA, which indicated that, to obtain high carbon yield, IA content should be reduced appropriately. As shown in Table III, after carbonization at  $1350^\circ\text{C}$ , the PAI copolymers with 0.5 wt % to 1.0 mol % IA possessed better crystalline parameters than that of the other PAI copolymers.

#### Thermal Behaviors of PAI Copolymers

Figure 9 presented the DSC curves of PAI copolymers heated at  $5^\circ\text{C}/\text{min}$  from ambient temperature to  $325^\circ\text{C}$  under  $\text{N}_2$  atmosphere. And the primary corresponding parameters obtained from the exotherms, including the temperature of



**Figure 9.** DSC curves of PAI copolymers at  $5^\circ\text{C}/\text{min}$  under nitrogen atmosphere. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Table IV.** Parameters for DSC Curves of PAI Copolymers under Nitrogen atmosphere at 5 °C/min

Destination	$T_i$ (°C)	$T_{p1}$ (°C)	$T_{p2}$ (°C)	$T_f$ (°C)	$\Delta T$ (°C)	$\Delta H$ (J g <sup>-1</sup> )	$\Delta H/\Delta T$ (J g <sup>-1</sup> °C <sup>-1</sup> )
PAI-0.5 wt %	212.8	232.0	266.2	290.1	77.3	2243.91	29.02
PAI-0.5 mol %	205.6	228.0	265.2	306.9	101.9	2063.23	20.25
PAI-1.0 mol %	192.5	216.0	265.0	307.9	115.4	2026.35	17.56
PAI-2.0 mol %	186.3	220.0	265.0	315.9	129.6	1865.02	14.39
PAI-3.0 mol %	181.2	210.0	266.3	320.8	139.6	1668.31	11.95

initiation ( $T_i$ ), the temperature of peak ( $T_p$ ), the temperature of termination ( $T_f$ ), and their difference ( $\Delta T = T_f - T_i$ ), the released heat ( $\Delta H$ ), and the velocity of releasing heat ( $\Delta H/\Delta T$ ), are listed in Table IV. As shown in Figure 9, there were two peaks of DSC curves to be observed obviously except that of PAI with 0.5 wt % IA, which indicated that too less IA content in PAI copolymer could not ease the concentration of heat releasing during the thermal treatment. But the DSC curve of PAI-0.5 wt % is still broader than that of PAN homopolymer compared to our previous report.<sup>29</sup> The DSC experiments of PAI copolymers were carried out under nitrogen condition without the presence of oxygen, so the DSC exotherms were attributed to the only cyclization reaction. The lower exothermic peak (peak 1,  $T_{p1}$ ) was assigned to cyclization reaction initiated by IA comonomer through an ionic mechanism, whereas the higher exothermic peak (peak 2,  $T_{p2}$ ) was assigned to cyclization reaction initiated through a free radical mechanism.<sup>7,11</sup>

As shown in Table IV, the values  $T_i$  and  $T_{p1}$  of PAI copolymers were shifted to low temperature as the IA content increasing, which indicated that the cyclization reaction was easier to be initiated by ionic mechanism. Furthermore, it is easy to be found out that the fraction of cyclization reaction initiated by ionic mechanism increased as a function of IA content, because with increasing of IA content in PAI copolymers, the intensity of exothermic peak around 225 °C became stronger with a more and more weak exothermic peak around 265 °C. The increased  $\Delta T$  and reduced  $\Delta H$  resulted in significantly reduced

the values of heat release rate  $\Delta H/\Delta T$ , indicating that the thermal behaviors were significantly improved by increasing the IA content in PAI copolymers.

Another useful parameter to value the thermal behaviors is the apparent activation energy of cyclization reaction ( $E_a$ ). It is well known that to calculate the value of  $E_a$ , the DSC curves measured under different rates were needed. Figure 10 presented the DSC curves of PAI-1.0 mol % measured under different rates ( $\phi$ ) (See the other curves in Supporting Information, Figure 5S), and the corresponding parameters were obtained from these curves as listed in Table V. The values of  $E_a$  were calculated from the Kissinger and Ozawa method as following equations,<sup>31,32</sup> respectively:

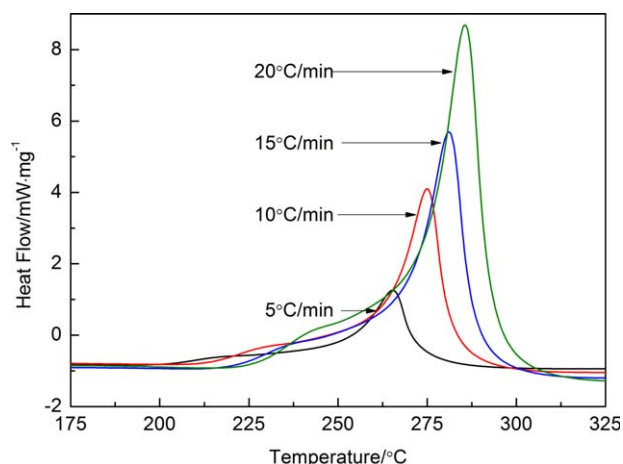
$$-\frac{E_a}{R} = \frac{d[\ln(\phi/T_p^2)]}{dT_p} \quad (6)$$

$E_a$  was calculated from the slope of the linear plot of  $\ln(\phi/T_p^2)$  versus  $1000/T_p$ .

$$-2.15 \frac{E_a}{R} = \frac{d \log \phi}{dT_p} \quad (7)$$

$E_a$  was calculated from the slope of the linear plot of  $\log \phi$  versus  $1000/T_p$ .

For PAI copolymers, the  $E_a$  was split into two parts. The first part was attributed to the cyclization reaction initiated by an ionic mechanism, whereas the second part was attributed to the cyclization reaction initiated by a free radical mechanism. The values of  $E_a$  were summarized in Table VI. The values calculated from Kissinger and Ozawa methods showed almost the same values, which indicated the results were reliable. The values of  $E_{a1}$  were reduced as the IA content increasing, which indicated the initiation of cyclization through an ionic mechanism became easier for PAI copolymer with higher IA content, whereas, the values of  $E_{a2}$  increased as the IA content increasing, which indicated the initiation of cyclization through a free radical mechanism became harder for PAI copolymer with higher IA content. This may be attributed to that as increasing of IA content in PAI, the formed cyclized structures by ionic mechanism increased, which increased the energy of configuration rotation of PAN macromolecules, and consequently increased the values of  $E_{a2}$ . Interestingly, the value of  $E_{a1}$  for PAI containing 3.0 mol % IA was not the lowest in PAI copolymers as theoretical predication. As aforementioned, there were high IA containing PAI oligomers in PAI copolymers with IA 2.0 and 3.0 mol %, especially PAI with 3.0 mol %, and it is reasonable to infer that a part of the high IA containing PAI



**Figure 10.** DSC curves of PAI-1.0 mol % copolymer heated at different rates under nitrogen atmosphere. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Table V.** Parameters for DSC Curves of PAI Copolymers under Nitrogen Atmosphere

Heating rate (°C/min)	PAI-0.5 wt %		PAI-0.5 mol %		PAI-1.0 mol %		PAI-2.0 mol %		PAI-3.0 mol %	
	$T_{p1}$ (°C)	$T_{p2}$ (°C)	$T_{p1}$ (°C)	$T_{p2}$ (°C)	$T_{p1}$ (°C)	$T_{p2}$ (°C)	$T_{p1}$ (°C)	$T_{p2}$ (°C)	$T_{p1}$ (°C)	$T_{p2}$ (°C)
5	232.0	266.2	228.0	265.2	216.0	265.0	220.0	265.0	210.0	266.3
10	243.0	276.5	240.0	275.5	228.6	274.8	234.0	275.0	223.0	275.8
15	250.0	283.7	248.0	282.2	236.2	281.0	240.0	279.7	231.5	281.4
20	256.0	290.5	253.0	287.0	242.3	285.6	249.0	285.0	236.0	284.2

**Table VI.** Activation Energy Calculated by Kissinger and Ozawa Methods

Destination	$E_{a1}$ calculated by Kissinger method (kJ/mol)	$E_{a1}$ calculated by Ozawa method (kJ/mol)	$E_{a2}$ calculated by Kissinger method (kJ/mol)	$E_{a2}$ calculated by Ozawa method (kJ/mol)
PAI-0.5 wt %	120.7	120.8	136.3	135.9
PAI-0.5 mol %	112.1	112.7	150.3	148.8
PAI-1.0 mol %	102.7	103.7	159.4	157.3
PAI-2.0 mol %	96.0	98.0	167.0	164.5
PAI-3.0 mol %	98.1	99.3	180.6	177.2

$E_{a1}$  was calculated from the first peak of DSC exothermic peak.

$E_{a2}$  was calculated from the second peak of DSC exothermic peak.

oligomers were decomposed at some relative low temperatures during the thermal treatment.

## CONCLUSIONS

In summary, PAI copolymers containing different content of IA comonomer were synthesized using one-step batch slurry polymerization under the same conditions. The structural evolution and thermal behaviors were studied by using FTIR, XRD, and DSC technologies in detail. High IA containing PAI oligomers were found in PAI copolymers with 2.0 and 3.0 mol % IA but were not found in the other three PAI copolymers. PAI copolymer with 0.5 and 1.0 mol % IA possessed more cyclized structures, conjugated carbonyl group, conjugated nitrile group concentration, and less  $\beta$ -amino nitrile group as well as faster structural evolution rate than those of the other three PAI copolymers. Furthermore, the kinetic parameters proved that excessive IA, such as 3.0 mol %, in PAI did not have advantages in promoting cyclization reaction. After carbonization at 1350 °C, the PAI copolymers with 0.5 wt % to 1.0 mol % IA possessed better crystalline parameters as well as higher carbon yield than those of the other PAI copolymers. In a word, PAI copolymers with 0.5 mol % to 1.0 mol % IA possessed a larger room to adjust manufacture parameters to fabricate the high performance PAN-based carbon fibers.

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## REFERENCES

- Liu, Y.; Kumar, S. *Polym. Rev.* **2012**, *52*, 234.
- Chand, S. *J. Mater. Sci.* **2000**, *35*, 1303.
- Morgan, P. In *Carbon Fibers and Their Composites*; CRC press, Taylor & Francis Group: Boca Raton, FL, **2005**.
- Frank, E.; Steudle, L. M.; Ingildeev, D.; Spörl, J. M.; Buchmeiser, M. R. *Angew. Chem. Int. Ed.* **2014**, *53*, 5262.
- Rahaman, M. S. A.; Ismail, A. F.; Mustafa, A. *Polym. Degrad. Stabil.* **2007**, *92*, 1421.
- Figueiredo, J. L.; Bernardo, C. A.; Baker, R. T. K.; Hüttinger, K. J. In *Carbon Fibers Filaments and Composites*; Springer Science & Business Media: GX Dordrecht, **2013**.
- Ju, A. Q.; Guang, S. Y.; Xu, H. Y. *Carbon* **2013**, *54*, 323.
- Xue, Y.; Liu, J.; Liang, J. Y. *Polym. Degrad. Stabil.* **2013**, *98*, 219.
- Devasia, R.; Reghunadhan, N. C. P.; Ninan, K. N. *Polym. Int.* **2005**, *54*, 381.
- Devasia, R.; Nair, C. P.; Ninan, K. N. *Polym. Adv. Technol.* **2008**, *19*, 1771.
- Ouyang, Q.; Cheng, L.; Wang, H. J.; Li, K. X. *Polym. Degrad. Stabil.* **2008**, *93*, 1415.
- Gupta, A. K.; Paliwal, D. K.; Bajaj, P. *Polym. Rev.* **1991**, *31*, 1.
- Fu, Z. Y.; Gui, Y.; Liu, S.; Wang, Z.; Liu, B. J.; Cao, C. L.; Zhang, H. X. *J. Appl. Polym. Sci.* **2014**, *131* DOI: 10.1002/app.40834.
- Nguyen-Thai, N. U.; Hong, S. C. *Carbon* **2014**, *69*, 571.
- Chae, H. G.; Newcomb, B. A.; Gulgunje, P. V.; Liu, Y.; Gupta, K. K.; Kamath, M. G.; Lyons, K. M.; Ghoshal, S.; Pramanik, C.; Giannuzzi, L.; Sahin, K.; Chasiotis, I.; Kumar, S. *Carbon* **2015**, *93*, 81.

16. Chai, X.; Mi, H.; Zhu, C.; He, C.; Xu, J.; Zhou, X.; Liu, J. *Polymer* **2015**, *76*, 131.
17. Bajaj, P.; Sreekumar, T. V.; Sen, K. *Polymer* **2001**, *42*, 1707.
18. Du, W.; Chen, H.; Xu, H.; Pan, D.; Pan, N. *J. Polym. Sci. Polym. Phys.* **2009**, *47*, 1437.
19. Tan, L.; Liu, S.; Pan, D. *Colloids Surf. A: Physicochem. Eng. Asp.* **2009**, *340*, 168.
20. Fu, Z. Y.; Gui, Y.; Cao, C. L.; Liu, B. J.; Zhou, C.; Zhang, H. X. *J. Mater. Sci.* **2014**, *49*, 2864.
21. Hideto, K.; Kohji, T. *Polym. J.* **1997**, *29*, 557.
22. Yu, M. J.; Bai, Y. J.; Wang, C. G.; Xu, Y.; Guo, P. Z. *Mater. Lett.* **2007**, *61*, 2292.
23. Wang, J.; Zhang, M. Y.; Fu, Z. Y.; Zhou, T. T.; Xu, X. H.; Liu, B. J. *Fiber. Polym.* **2015**, *16*, 2505.
24. Tan, L. J.; Pan, J. P.; Wan, A. *Colloids Polym. Sci.* **2012**, *290*, 289.,
25. Gupta, A. K.; Paliwal, D. K.; Bajaj, P. *J. Appl. Polym. Sci.* **1995**, *58*, 1161.
26. Nguyen-Thai, N. U.; Hong, S. C. *Macromolecules* **2013**, *46*, 5882.
27. Silverstein, R. M.; Webster, F. X.; Kiemle, D.; Bryce, D. L. In *Spectrometric Identification of Organic Compounds*, 8th ed.; Wiley, **2014**.
28. Shimada, I.; Takahagi, T.; Fukuhara, M.; Morita, K.; Ishitani, A. *Polym. Chem.* **1986**, *24*, 1989.
29. Fu, Z. Y.; Ma, J. Y.; Deng, Y. J.; Wu, G. F.; Cao, C. L.; Zhang, H. X. *Polym. Adv. Technol.* **2015**, *26*, 322.
30. Collins, G. L.; Thomas, N. W.; Williams, G. E. *Carbon* **1988**, *26*, 671.
31. Kissinger, H. E. *Anal. Chem.* **1957**, *29*, 1702.
32. Ozawa, T. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 1881.