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Structure Evolution Mechanism of Poly(acrylonitrile/itaconic acid/acrylamide) during Thermal Oxidative Stabilization Process*

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Abstract Polyacrylonitrile (PAN) polymers with different compositions were prepared by an efficient aqueous free-radical polymerization technique. Thermal properties of polyacrylonitrile homopolymer (PAN), poly(acrylonitrile/itaconic acid) [P(AN/IA)] and poly(acrylonitrile/itaconic acid/acrylamide) [P(AN/IA/AM)] were studied by Fourier transform infrared spectroscopy, X-ray diffraction, differential scanning calorimetry and thermogravimetry in detail. It was found that AM had the ability to initiate and accelerate thermal oxidative stabilization process, which was confirmed by the lower initiation temperature and broader exothermic peak in P(AN/IA/AM) as compared with that in P(AN/IA) and PAN. The intensity of heat releasing during the thermal treatment was relaxed due to the presence of two separated exothermic peaks. Accompanied by DSC analysis and calculation of the apparent activation energy of cyclization reaction, two peaks were assigned to the ionic and free radical induction mechanisms, respectively. The higher rate constant in P(AN/IA/AM) indicated that the ionic mechanism actually had a kinetic advantage at promoting thermal stability over the free radical mechanism. This study clearly show that the synthesized P(AN/IA/AM) terpolymers possess larger room to adjust manufacture parameters to fabricate high performance of PAN-based carbon fibers.

Keywords PAN terpolymers; Structural evolution; Thermal oxidative stabilization; Thermal analysis; Kinetics

INTRODUCTION

Carbon fibers, due to their superior properties, such as lightweight, low density, very high specific strength and stiffness, excellent thermal, as well as fatigue characteristics, have been widely used in industry as engineering and structural materials[1−3]. It is well known that carbon fibers can be made from various precursors, but 90% of the carbon fibers worldwide are obtained from polyacrylonitrile (PAN). In general, PAN-based fibers are considered the most suitable precursors for producing high performance carbon fibers (compared to pitch, rayon, *etc.*) because of its low cost, good processibility, and higher carbon yield[4, 5]. However, PAN homopolymer (named PAN in the following section) has hardly ever been used as carbon precursor because of its high regularity and crystallinity (CI). PAN cannot dissolve in the spinning solvents due to the strong intermolecular interaction, which thus results in its poor liquidity and spinnability. To overcome these limitations aforementioned, some kinds of comonomers, such as itaconic acid (IA), vinyl acetate (VAc) and methacrylic acid (AA), are usually introduced into PAN chains[6−9] to obtain PAN co-/terpolymers containing a small amount of comonomers and exhibiting superior performance, especially easing the concentrated heat release during thermal oxidative stabilization process[10, 11]. As known, PAN-based carbon fibers are usually produced by the

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following steps: (1) preparation of PAN copolymers and spinning of precursors; (2) oxidative stabilization and carbonization of fiber precursors. Thermal stabilization reaction of PAN typically occurs at the temperature of 200–300 °C in air, which converts the linear structure of PAN to an intermediate cyclic structure for the succeeding carbonization process and graphitization.

Thermal oxidative stabilization process results in the formation of a ladder polymer in stabilized fiber, which plays a key role for the physical properties and the microstructure of the resultant carbon fibers[12, 13]. Thermal oxidative stabilization is a complicated and overlapped process, since it involves a variety of exothermic chemical reactions, primarily dehydrogenation, oxidation and cyclization[2, 5]. Among them, the cyclization reactions which lead to the formation of a ladder-like structure in the PAN molecular chains are of most importance[14, 15]. Dehydrogenation reactions produce the carbon-carbon double bond and conjugated structures in PAN macromolecules, which may be affected from oxidation, where oxygen-containing groups such as carbonyl groups are introduced to the chains and hydrogen is eliminated in the form of H_2O[16].

In the foregoing description, a lot of literatures clearly indicate that the comonomers have significant impact on the thermal stabilization process. Thus, the effects of comonomers on the physicochemical properties of PAN copolymers are always highly attractive to researchers. Two types of comonomers, carboxylic acid and vinyl esters, are mainly adopted during the copolymerization of AN[17]. IA is preferred and widely used due to its two carboxylic groups, which provides more probability for the interaction between carboxyl and nitrile groups than acrylic acid with only one acid group during thermal oxidative stabilization process[18, 19]. On the other hand, the bulky side groups of vinyl esters such as methyl acrylate (MA) assist in lowering the structural regularity and disrupting the dipole-dipole interactions in the AN sequence, thereby enhancing the melt processability of macromolecules and improving the quality of spinning and stretching[20]. It has been seen that a critical comonomer composition and amount are essential in ensuring superior mechanical properties and adequate plasticity of PAN fibers[21]. Zhang *et al.*[22] noted that compared to IA-containing copolymers, the copolymers with acrylamide (AM) were more effective in separating the exothermic reactions corresponding to peroxidation stages in DSC curves. The similar result was also reported by Wu *et al*[23]. In contrast, Grassie[24] and coworkers studied the effects of various comonomers on reducing the cyclization temperature and found that the cyclization of AM-containing copolymer was same sharp one as that of PAN. Watt and Johnson[25] studied the thermal properties of PAN and its copolymer with carboxylic acid comonomer in oxidative atmosphere. They found that the oxygen uptake at 230 °C was greater for acid-containing copolymer. Sivy[26] reported that the acyl group in AM might accelerate the next stabilization process. The AM units acted as the initiation sites for nitriles oligomerization through an ionic mechanic pathway, leading to a relaxed exothermic reaction. However, most previous reports only targeted on PAN copolymers or terpolymers individually, without the comparison between co- and terpolymers. To our knowledge, the influences of the comonomers of IA and AM simultaneously on structural evolution and thermal behaviors have been rarely investigated. In this study, IA and AM are used as comonomers to prepare P(AN/IA) and P(AN/IA/AM) polymers by an aqueous suspension polymerization method. The effects of AM on the stabilization of PAN copolymers were examined. The structural evolution during stabilization and stabilization mechanism of PAN, P(AN/IA) and P(AN/IA/AM) are studied quantitatively and comprehensively by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), dynamic mode and isothermal mode (DSC) and thermogravimetry (TGA).

EXPERIMENTAL

Materials

AN (analytical grade) was provided by Sinopharm Chemical Reagent Co., Ltd., Shanghai, China and purified by CaH_2 washing, distilled twice between 76–78 °C under reduced pressure before polymerization. IA (analytical grade) was purchased from Shanghai Boer Chemical Reagent Co., Ltd., Shanghai, China and separated from the inhibitor in standard manner, dried over anhydrous magnesium sulphate and then distilled under pressure. AM (analytical grade) was received from Shanghai Huadong Reagent Company, Shanghai, China and recrystallized twice before use. Ammonium persulfate (APS) and deionized water (H_2O) were adopted as initiator and reaction

medium, respectively. Suspension aid was principally hydrolyzed polyvinyl alcohol (PVA). The purity of both APS and PVA were analytical-grade and commercially supplied by Sinopharm Chemical Reagent Co., Ltd., Shanghai, China, and they were freshly distilled before use. Dimethyl sulfoxide (DMSO, analytical grade) was purchased from Shanghai Huadong Reagent Company, Shanghai, China and distilled by reduced pressure before use.

Preparation of PAN Polymers

Copolymerization of AN with comonomers (IA and/or AM) was carried out in a 250 mL three-necked, round-bottom flask equipped with a stir bar and a condenser. In a typical polymerization reaction system, monomers AN, IA and/or AM in a given weight fraction in the feed with 0.2 wt% (on the basis of total monomers) of dispersant PVA dissolved in H_2O beforehand were charged into the reactor. The mixture was thoroughly stirred and degassed by bubbling with N_2 for 30 min, and subsequently APS (0.22 wt% on the basis of total monomers) solution was added to initiate the polymerization for synthesizing P(AN/IA) and P(AN/IA/AM) polymers, respectively. The flask was kept in an oil bath at 65 °C and the whole polymerization process under nitrogen atmosphere was stopped after 3 h. The white precipitated polymer was filtered, washed successively with an excess of water and acetone to remove unreacted products, and then dried in a vacuum oven at 50 °C for 24 h to a constant weight. Similar polymerization conditions were used to prepare PAN with 22 wt% of total monomer concentration. In addition, a solution containing about 3 wt% polymers in DMSO was prepared and thin films with the thickness about 5 μm (approximately 2 cm × 2 cm) were obtained prior to subsequent analysis. 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[27]. The details of PAN polymers used in this study were given in Table 1.

Table 1 Experimental and calculated parameters of PAN polymers with different compositions

Polymer [a]	f_{IA} [b] (wt%)	f_{AM} [b] (wt%)	$F_{IA, NMR}$ [c] (wt%)	$F_{AM, NMR}$ [c] (wt%)	Conversion (%)	M_w [d] (g·mol^{-1})	PDI [d]
PAN	0	0	0	0	79.40	28.90 × 10^4	2.07
P(AN/IA)	2.0	0	4.22	0	71.50	24.50 × 10^4	2.35
P(AN/IA/AM)	0.7	1.45	2.38	1.82	75.20	25.70 × 10^4	2.21

[a] The values of initial pH of PAN, P(AN/IA) and P(AN/IA/AM) were 5.60, 3.55 and 4.28, respectively; [b] f_{IA} = [IA] × 100/([AM] + [IA] + [AN]) in feed, f_{AM} = [AM] × 100/([AM] + [IA] + [AN]) in feed; [c] F_{IA} = [IA] × 100/[AM + IA + AN] in polymer calculated from ^{1}H-NMR, F_{AM} = [AM] × 100/[AM + IA + AN] in polymer calculated from ^{1}H-NMR; [d] Weight average molecular weight (M_w) and polydispersity index (PDI) determined by GPC

Characterization

The weight-average molecular weight (M_w) and polydispersity index (PI) of PAN polymers were determined with a Waters GPC/ALC 150C (Japan). GPC measurement was performed in dimethylformamide (DMF) at 30 °C. The amount of polymer solution injected was 0.3 g·dL^{-1} × 0.2 mL and the elution rate was 1 mL·min^{-1}. The GPC was calibrated with the standard polystyrene ultra styragel columns. ^{1}H-NMR sample was dissolved in deuterated dimethylsulfoxide (DMSO-d_6) (10%, *W*/*W* 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 100 MHz, with a recycle time of 10 s. The thin films of the three samples prepared beforehand were used for the following heat treatment process. FTIR spectra of initial and stabilized PAN polymers were recorded on a Nicolet-8700 (Nicolet) in 4000–400 cm^{-1} range using 32 scans at a resolution of 4 cm^{-1}. 1 mg of powder sample was mixed thoroughly with 200 mg of KBr and pelletized for FTIR characterization at room temperature. XRD patterns of P(AN/IA) and P(AN/IA/AM) during thermal oxidative stabilization process were measured using a Rigaku D/max-2550 diffractometer through a 2θ range of 3°–50° at a scan speed of 3 (°)·min^{-1}. All the XRD measurements were carried out under the same conditions. XRD calibration was performed using silicon (Si) and the obtained pattern was compared with standard pattern of Si. A NETZSCH STA 409PC thermal analyzer was used to observe the thermal behaviors of PAN, P(AN/IA) and P(AN/IA/AM) samples with mass 5–10 mg. A heating ramp in temperature range of 40–400 °C was performed for DSC analysis at different heat rates under air

or nitrogen atmosphere (40 mL·min^{-1}). The parameters obtained from the DSC exotherms including initiation temperature (T_i), final temperature (T_f), their difference ($\Delta T = T_f - T_i$), peak temperature (T_{pk}), evolved heat (ΔH), and velocity of heat evolution ($\Delta H/\Delta T$) were listed in corresponding tables. Isothermal studies at different temperatures ranging from 200 °C to 240 °C were performed on Mettler FP-84 HT DSC along with central processor Settler PF-90. The studies were conducted in air for 1 h at a flow rate of 3.5 L·min^{-1}. Weight loss of PAN polymers weighing 1–5 mg during thermal oxidative stabilization process was conducted on a TGA 209F1 thermal analyzer (NETZSH). Three samples were heated from ambient temperature to 600 °C with a heating rate of 10 K·min^{-1} in air atmosphere. For the stabilization of PAN polymers, the fine powder samples were heated in an air oven at a constant temperature with a temperature accuracy of 1 °C for 30 min.

RESULTS AND DISCUSSION

Investigation of Structure Evolution of PAN Polymers by FTIR Spectroscopy

The structural changes related to the thermal history of thermal oxidative stabilization process were measured by means of FTIR technology. Figure 1 shows the spectra change of PAN heated at different temperatures in air for 30 min. Of particular interest is the band at 2244 cm^{-1} assigned to the vibrations characteristic of CN nitrile group, and the bands at 2939, 1454 and 1360 cm^{-1} assigned to the aliphatic CH group vibrations of different modes in CH_3, CH_2 and CH, respectively[8, 28, 29]. It should be pointed out that a weak absorption at 1635 cm^{-1} ($\nu_{C=C}$) probably originated from termination by disproportionation which can be confirmed by the discoloration of very dilute bromine water[30]. In case of PAN, the stabilization reactions do not occur obviously below 240 °C, since the intensity of bands at 2244 cm^{-1} is still high in Fig. 1 (original ~240 °C). As stabilization temperature increases, the intensity of C≡N stretching band at 2244 cm^{-1} decreases. In the meanwhile, a new band at 1590 cm^{-1} appears which is due to the combination vibrations of C=C and C=N stretching, and NH in-plane bending of the ladder-frame structure of the stabilized PAN[17, 27]. Moreover, the intensity of band at 1590 cm^{-1} increases with increasing the temperature. All of these indicate the occurrence of cyclization and dehydrogenation in PAN during thermal oxidative stabilization process. By careful observation of Fig. 1, it can be seen that the band of 1718 cm^{-1} shifts to 1620 cm^{-1} gradually and a combined shoulder-like peak shows up at 1640 cm^{-1} as temperature increasing, indicating that some conjugation structures have been formed and the stabilization reactions start progressing to a small extent.

Figure 2 shows the IR spectra of P(AN/IA) heated at different temperatures for 30 min. A strong band at 1735 cm^{-1} is presented in the PAN copolymers before heating due to the C=O stretching of carboxyl group (COOH) in IA comonomer[8, 17, 28, 30]. Moreover, it can be found that the peak at 1735 cm^{-1} has completely disappeared after treated at 220 °C for 30 min. At the same time, a shoulder-like peak attributed to the C=O

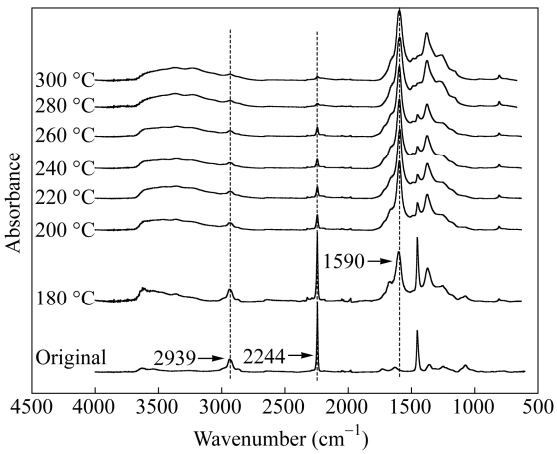


Fig. 1 FTIR spectra of PAN heated at different temperatures for 30 min

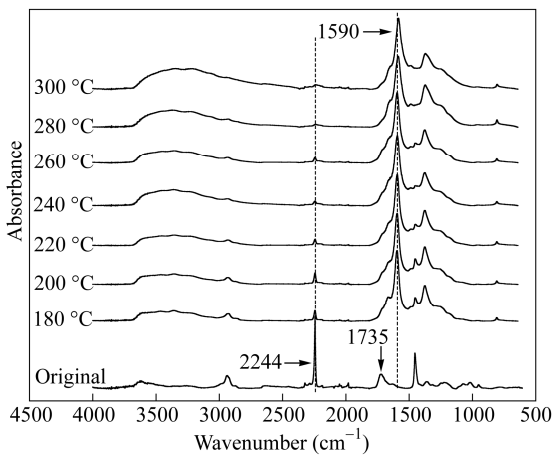


Fig. 2 FTIR spectra of P(AN/IA) heated at different temperatures for 30 min

group in hydronaphthyridine ring of cyclized PAN appears at 1715 cm^{-1}. In addition, a shoulder-like peak emerges near the characteristic absorption of CN at 2197 cm^{-1}, which may be attributed to the formation of amino-substituted unsaturated nitriles and aminonitriles from partial cyclization or thermal degradation[27]. The bands at 1620 and 810 cm^{-1}, attributed to C=N, C=C, N−H and the out-plane bending of C=C−H, present and increase as a function of temperature. However, the spectra change in PAN seems to be slower than that of P(AN/IA), especially the bands of 1620 and 810 cm^{-1}, indicating that the cyclization and dehydrogenation reactions have been promoted by the comonomer IA.

FTIR spectra of P(AN/IA/AM) show similar changes during stabilization process, as shown in Fig. 3. These changes include a decrease in the intensity of C≡N stretching band at 2244 cm^{-1} especially after 200 °C, and simultaneous growth of a band at 1590 cm^{-1}, attributed to the combination effect of C=N, C=C, N−H groups. In addition, other significant changes include a decrease in intensity of the bands of 2939 and 1456 cm^{-1}, assigned to the stretching and bending vibrations of aliphatic methylene groups, respectively. The results further confirm the conversion of linear structure of PAN to a partially cyclized structure containing C=O, C=C, C=N and N−H groups in cyclized parts and C≡N groups in linear parts of the chains. By comparing the spectra of P(AN/IA) (Fig. 2) and P(AN/IA/AM) (Fig. 3), it can be seen that the band intensity at 2244 cm^{-1} (stretching vibration of C≡N) decreases initially at 220 °C for P(AN/IA) and 200 °C for P(AN/IA/AM), and the initiation temperature of PAN terpolymer reduces significantly as compared with copolymer. Besides, the band at 2244 cm^{-1} almost disappears at 240 °C in P(AN/IA/AM), implying that the cyclization reactions have progressed to a large content. However, in P(AN/IA), the band at 2244 cm^{-1} is still high due to residual isolated CN groups in the molecular chains at 240 °C, which are difficult to convert into a ladder-like polymer structure and will be lost at higher temperature during carbonization, resulting in the poor performance of resultant PAN-based carbon fibers. Moreover, the intensity of 1595 cm^{-1} (stretching vibration of C=N conjugated with C=C) goes up gradually as a function of temperature above 200 °C in P(AN/IA/AM), whereas in P(AN/IA) it does not show obvious change at temperatures below 220 °C. The result further demonstrates that the cyclization and dehydrogenation reactions of P(AN/IA/AM) occur at lower temperature than that of P(AN/IA). It also can be inferred that the introduction of AM comonomer into P(AN/IA) chains results in a lower cyclization temperature as well as more nitriles being oligomerized. A similar phenomenon was also observed from the following dynamic and isothermal DSC studies. The results obtained as mentioned above are also in good accordance with the report of Bajaj[17].

In order to evaluate the extent of stabilization, a parameter (CN fraction unreacted) which has been previously derived in the literatures is defined as follows[27, 31]:

$$\text{CN fraction unreacted} = \frac{\text{ABS}(2240)}{\text{ABS}(2240) + f \times \text{ABS}(1590)} \tag{1}$$

where ABS(2240) is the absorbance of nitrile groups, ABS(1590) is the absorbance of −C=N− groups, and f is the ration of CN and −C=N− group absorptivity constants, which equals 0.29.

The extents of thermal stabilization of PAN, P(AN/IA) and P(AN/IA/AM) as a function of temperature are shown in Fig. 4. With increasing temperature, unreacted CN fraction decreases and reaches a constant level at last. From the cyclization data, we can see that as temperature increases, the rate of cyclization reaction becomes faster and the extent of cyclization is higher, hinting that the reaction of nitriles depends significantly on temperature. As displayed in Fig. 4, the existence of AM units in P(AN/IA/AM) chains greatly promotes the cyclization reactions during the thermal oxidative stabilization process, which can be clearly evidenced by the lowest value of CN fraction, particularly above 220 °C. For PAN, there is a distinct induction period at relatively low temperature (below 220 °C). However, the induction period is less distinct or not present in the cyclization for P(AN/IA) and P(AN/IA/AM). The presence of an induction period during cyclization suggests the formation of intermediates. The difference in the length and presence of the induction period between PAN and PAN copolymer may be indicative of the different mechanistic behavior in these polymers during cyclization. There is

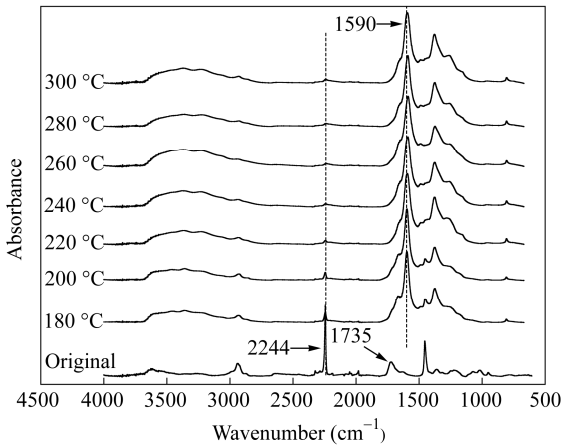


Fig. 3 FTIR spectra of P(AN/IA/AM) heated at different temperatures for 30 min

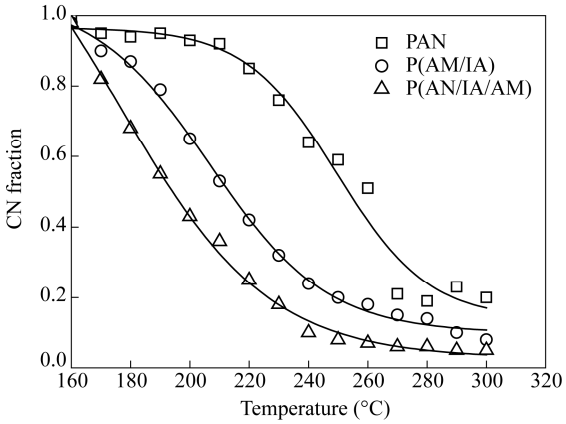
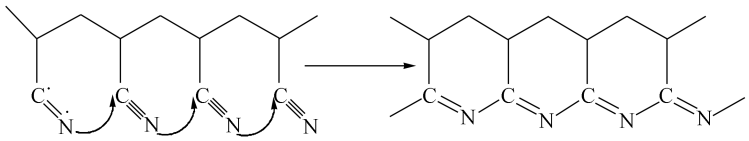
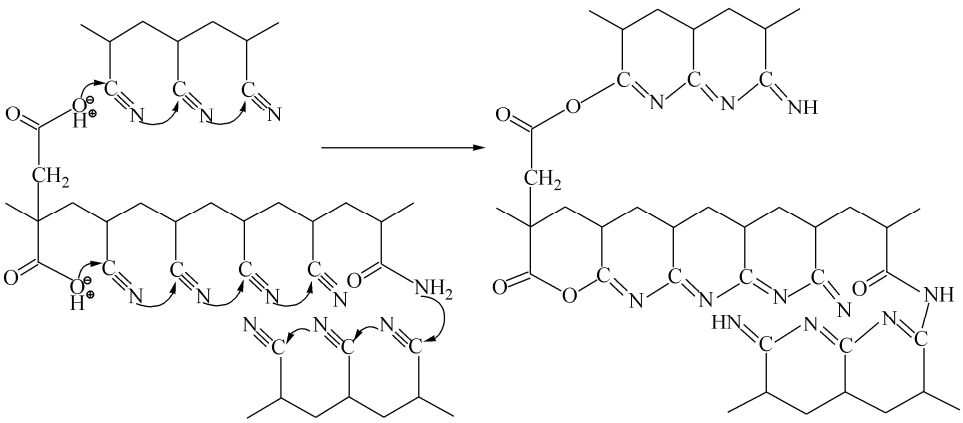


Fig. 4 CN fraction of PAN polymers at different temperatures for 30 min

no clear decrease in CN fraction of PAN even when the temperature reached at 220 °C for 30 min, while for P(AN/IA) and P(AN/IA/AM), CN fraction decreases to near 0.42 and 0.25, respectively. It can be seen clearly that the rate of cyclization reaction is markedly dependent on the compositions of PAN polymers with the following order: PAN < P(AN/IA) < P(AN/IA/AM). It has been widely accepted that the cyclization of nitrile groups in PAN can be initiated through a free radical mechanism (Scheme 1)[29], whereas in our case the cyclization in P(AN/IA) and P(AN/IA/AM) is initiated through both a radical mechanism and an ionic mechanism (Scheme 2)[17, 23]. As can be seen in Scheme 2, the hydroxyl oxygen of —COOH in the IA units and amino nitrogen of —NH_2 in AM units make a nucleophilic attack on the carbon atom of an adjacent nitrile group and induce it to be cycled. Such an oxygen uptake reaction can be confirmed with the appearance of two shoulders at 1718 cm^{-1} assigned to C=O stretching vibrations of a free ketone, and 1660 cm^{-1} assigned to stretching vibrations of a conjugated ketone by FTIR analysis (Fig. 3). Thus, based on the above results, it can be inferred that the thermal stability of P(AN/IA/AM) is superior to P(AN/IA).



Scheme 1 Cyclization in PAN initiated through a free radical mechanism



Scheme 2 Cyclization in PAN co-/terpolymer initiated through an ionic mechanism

XRD Studies of P(AN/IA) and P(AN/IA/AM) Stabilized at Different Temperatures

In order to investigate the crystal evolution of PAN co- and terpolymers during thermal oxidative stabilization process, WXRD analysis was performed. The XRD patterns of P(AN/IA) and P(AN/IA/AM) stabilized after stepwise temperatures are shown in Figs. 5 and 6, respectively. In both figures, the strongest diffraction peak at about $2\theta = 17°$ corresponds to a crystalline planar spacing $d = 0.53$ nm, which is assigned to (100) crystalline plane of the pseudo hexagonal cell. In the meanwhile, a weak diffraction peak at around $2\theta = 29°$ ($d = 0.30$ nm) is attributed to (101) crystalline plane of the pseudo hexagonal cell[29, 32, 33]. The stabilization is a process to convert linear structure into ladder structure, and thus the structure transformation during the stabilization agrees well with the intensity change of the peak around $2\theta = 17°$. Therefore, the extent of stabilization can also be evaluated according to the intensity changes around $2\theta = 17°$. The equation for the evaluation of stabilization index (SI) using X-ray diffraction is displayed as follows[29, 32]:

$$\mathrm{SI} = (I_0 - I_s)/I_0 \tag{2}$$

where I_0 is the peak intensity around $2\theta = 17°$ from the polymer at room temperature (RT), and I_s is the peak intensity around $2\theta = 17°$ from the polymer stabilized at different temperatures for 30 min. SI values calculated by Eq. (2) are listed in Table 2.

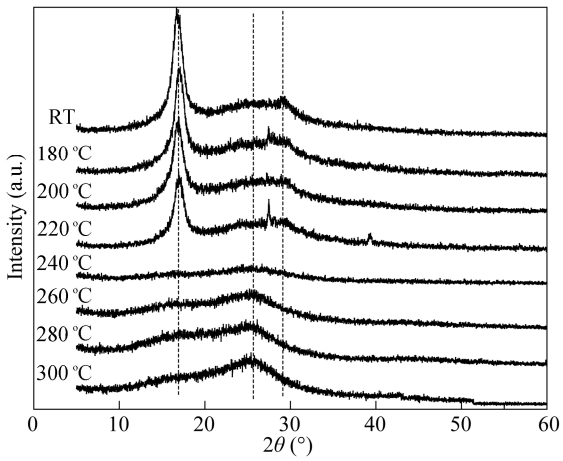


Fig. 5 XRD patterns of P(AN/IA) at various stages

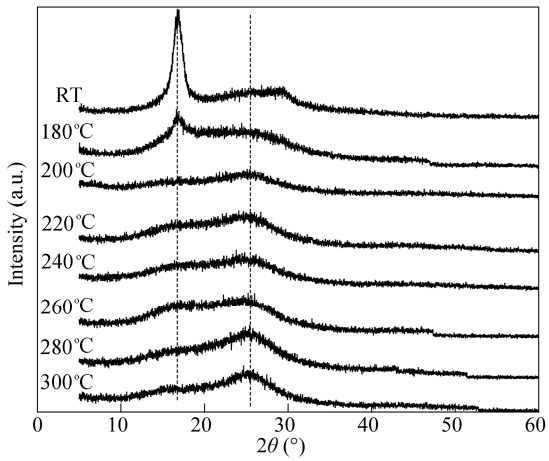


Fig. 6 XRD patterns of P(AN/IA/AM) at various stages

Table 2 XRD data related to PAN polymers and the polymers stabilized at various stages

P(AN/IA)	2θ (°)	I (CPS)	SI (%)	P(AN/IA/AM)	2θ (°)	I (CPS)	SI (%)
RT	17.42	1055	0	RT	16.94	1420	0
180 °C	17.15	1540	–45.97	180 °C	16.80	1637	–15.28
200 °C	16.89	1200	–13.74	200 °C	16.82	1150	19.01
220 °C	16.96	945	10.43	220 °C	16.85	970	31.69
240 °C	16.89	880	16.59	240 °C	16.94	558	60.70
260 °C	16.90	614	41.80	260 °C	16.89	192	86.48
280 °C	16.87	499	52.70	280 °C	25.50	0	100
300 °C	16.89	227	78.48	300 °C	25.52	0	100

For both P(AN/IA) and P(AN/IA/AM), the value of SI is negative at first, then it turns positive at 220 °C for P(AN/IA) and 200 °C for P(AN/IA/AM). Although cyclization reactions have not yet started remarkably at the temperatures lower than 204.3 °C for P(AN/IA) and 198.7 °C for P(AN/IA/AM) based on the following DSC data (Fig. 7), the energy obtained from heating breaks boundaries between crystalline zones and amorphous zones. Hence, the SI is negative due to further crystallization as well as increase of peak intensity. When the temperature is higher than 220 °C for P(AN/IA) and 200 °C for P(AN/IA/AM), the peaks at $2\theta = 17°$ and $2\theta = 29°$ gradually become weak and broad, respectively. Linear structures vanishes, whereas ladder structure in

PAN polymers dominates the intensity of (100) peak, hence the SI value is positive and becomes larger with the increase of temperature. As shown in Figs. 5 and 6, the linear structures still exist and no new peaks appear even at 240 °C for P(AN/IA). However, for P(AN/IA/AM), the peak around $2\theta = 17°$ almost disappears at 220 °C and a wide, flat peak at $2\theta = 25.5°$ attributed to ladder structure appears obviously. Similar observations have been reported in the literature[29, 32]. It should be pointed out that both P(AN/IA) and P(AN/IA/AM) still show weak diffraction even by heat-treatment at 260 °C for 30 min, suggesting that the incorporated AM comonomers are able to sustain the crystal structure of the polymers. In addition, for P(AN/IA/AM), the conversion temperature of SI from negative to positive is 200 °C, much lower than that of P(AN/IA) (220 °C). The results further confirm that the thermal stability of P(AN/IA/AM) has been successfully promoted with larger extent of stabilization by the introduction of AM comonomer as compared with P(AN/IA).

Effect of Acrylamide on Oxidative Reactions

The DSC curves of PAN, P(AN/IA) and P(AN/IA/AM) heated at 10 K·min^{-1} from ambient temperature to 400 °C under air atmosphere are shown in Fig. 7. It can be seen that the curve exhibits a three-peak DSC exotherm which begins at about 208, 204 and 199 °C for PAN, P(AN/IA) and P(AN/IA/AM), respectively. According to the literatures report[34–36], the first peak is assigned to the dehydrogenation and cyclization reactions, and the second peak is attributed to the oxidative reactions, while the middle peak at about 280 °C may be due to the concurrence of both reactions. The conversion of C—C structure to C=C structure and the formation of a condensed naphthyridine ring structure are accomplished by dehydrogenation and cyclization reactions, while the generation of oxygen-containing groups such as —OH and >C=O, *etc.*, are caused by oxidative reactions. Oxygen-containing groups can promote intermolecular crosslinking and formation of stabilized structure so as to endure the high temperature with less cleavage during carbonization process[37]. The rate of cyclization reaction is fast, especially the free radical cyclization reactions, while the oxidative reactions are always stumbled by the diffusion speed of oxygen and limit the stabilization treatment[25, 38]. It can be seen that the first peak and second peak become weak and strong respectively, suggesting that AM is able to balance the rates of these reactions and improve the thermal stability.

As can be seen from Table 3, the T_{pk1} of P(AN/IA/AM) shifts to lower temperature compared with those of P(AN/IA) and PAN, which suggests that the exothermic reactions become easier to process at lower temperature. In addition, the ΔH of P(AN/IA/AM) significantly increased, hinting that AM can accelerate stabilization treatment. The lower T_i, larger ΔT and smaller $\Delta H/\Delta T$ further confirm the better thermal stability of PAN terpolymer than copolymer.

TGA was also carried out to get an estimate of the carbon yield for three types of PAN polymers. Typical TGA curves of PAN, P(AN/IA) and P(AN/IA/AM) recorded under air atmosphere from ambient temperature to 600 °C with a heating rate of 10 K·min^{-1} are shown in Fig. 8. By comparing three TGA curves of PAN

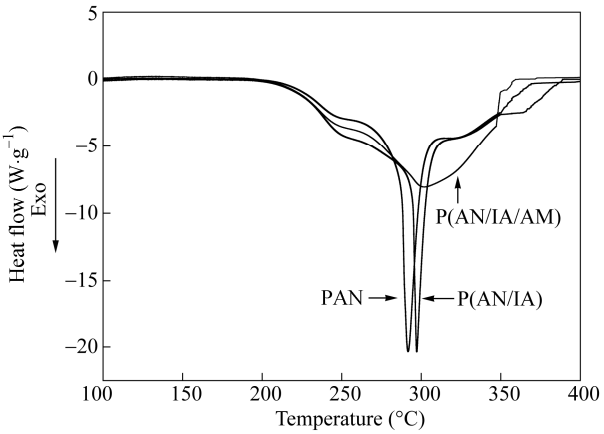


Fig. 7 DSC curves of PAN polymers heated at 10 K·min^{-1} in air

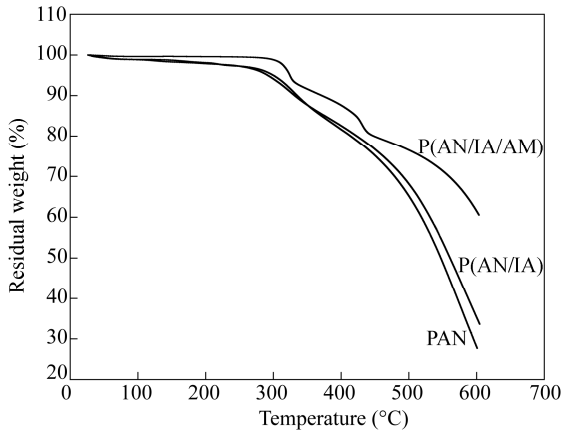


Fig. 8 TG curves of PAN polymers heated at 10 K·min^{-1} in air

Table 3 DSC parameters of PAN polymers in air atmosphere

Code	T_i (°C)	T_f (°C)	ΔT (°C)	T_{pk1} (°C)	T_{pk2} (°C)	T_{pk3} (°C)	ΔH ($J\cdot g^{-1}$)	$\Delta H/\Delta T$ ($J\cdot(g\cdot°C)^{-1}$)
PAN	207.8	380.7	172.9	228.7	288.6	330.5	1780	10.29
P(AN/IA)	204.3	382.0	177.7	226.1	297.4	332.4	1820	10.24
P(AN/IA/AM)	198.7	380.5	181.8	225.7	299.5	342.3	1850	10.18

polymers, we find that the overall trends are similar during the heat treatment. The curves can be roughly divided into three steps according to the rate of weight loss. The first stage is up to *ca.* 260 °C with a slow rate of weight loss. In combination of DSC results, it can be concluded that the dominant reaction in this temperature range is cyclization which is enhanced in air atmosphere. It can also be inferred that the weight loss may be mainly due to the dehydrogenation reactions, since cyclization reaction theoretically does not cause any weight loss[17]. Furthermore, during the first stage, the weight loss of P(AN/IA/AM) is smaller than that of P(AN/IA) and PAN at the same temperature. Based on the FTIR data above, unreacted CN fraction of P(AN/IA/AM) decreases to a very small value (approximately 0.07) below 260 °C, indicating that P(AN/IA/AM) is more stable by the aid of AM comonomer. The second step is up to *ca.* 450 °C and the rate of mass loss becomes rapid in this stage, which mainly ascribes to the dehydrogenation, the evolution of hydrogen cyanide (HCN), aliphatic species and the moieties containing —CN or CN structures, resulting in weight loss sharply. It should be pointed out that the weight loss in the second step for P(AN/IA/AM) is smaller compared to that of PAN and P(AN/IA). This is probably due to the improved thermal stability of stabilized P(AN/IA/AM) by IA and AM through an ionic mechanism during thermal oxidative stabilization process. The last stage is above 450 °C with a quite steady rate of weight loss. During the third step, it is apparent that the mass loss of P(AN/IA/AM) is the smallest among three types of PAN polymers at a given temperature, implying that AM successfully facilitates the stabilization process which transfers the structure from linear to ladder by cyclization reactions at higher temperatures. The higher weight residual of P(AN/IA/AM) shows that the incorporation of AM into P(AN/IA) molecular chains increases the possibility of forming longer chain structure and decreases the defects in the ladder structure against high temperature treatment.

Effect of Acrylamide on Cyclization Reactions

Theoretically, there are no oxidative reactions during thermal oxidative stabilization process. When DSC curves of PAN polymers are obtained in nitrogen atmosphere, the exothermic peaks are only attributed to the cyclization reactions[39]. As shown in Fig. 9, in the case of PAN, only one sharp exothermic peak can be observed, which implies that only one fast reaction occurs with a high exothermic rate (Table 4). Thus, the single exothermic peak in PAN is attributed to the overlapping of the free radical cyclization reactions and other exothermic reactions at the higher temperature. Moreover, in P(AN/IA), the DSC curve also exhibits one peak,

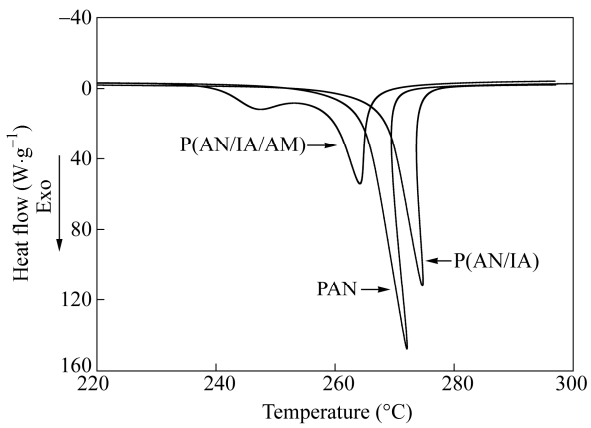


Fig. 9 DSC curves of PAN polymers heated at 10 $K\cdot min^{-1}$ in N_2

Table 4 DSC parameters of PAN polymers in nitrogen atmosphere

Code	T_i (°C)	T_f (°C)	ΔT (°C)	T_{pk1} (°C)	T_{pk2} (°C)	ΔH (J·g^{-1})	$\Delta H/\Delta T$ (J·(g·°C)$^{-1}$)
PAN	234.8	277.7	42.9	–	272.1	520.6	12.1
P(AN/IA)	232.1	283.4	51.3	–	274.7	528.0	10.3
P(AN/IA/AM)	231.3	285.4	54.1	246.9	264.2	534.6	9.9

but the initiation temperature is lower compared with that of PAN. According to the literature[17, 30], the broadening of the exothermic peak is probably contributed to the IA comonomer that initiates cyclization at a lower temperature through an ionic mechanism. By careful observation of Fig. 9 and Table 4, one can see that the heat release of PAN copolymer is still concentrative and expeditious because of only one exothermic peak in DSC curve of P(AN/IA), indicating that the function of IA for promoting thermal oxidative stabilization process is not ideal, and it is also not beneficial for making high-performance carbon fibers. However, in P(AN/IA/AM), the DSC curve demonstrates that PAN terpolymer has the broadest exothermic peak compared with that of PAN and P(AN/IA), as evidenced by the appearance of two exothermic peaks. Considering the same total comonomer content in the synthesized PAN copolymers, the appearance of two separated peaks in DSC curves of P(AN/IA/AM) implies that the cyclization reactions are initiated by ionic mechanism at a lower temperature and the sharp exothermic reactions are decreased to an extent with the introduction of AM comonomer into P(AN/IA) molecular chains.

Evaluation of Kinetic Parameters of Cyclization Reactions

To quantitatively investigate the contribution of AM for promoting the thermal oxidative stabilization process, the apparent activation energy of cyclization reaction (E_a), which is another useful parameter to value the thermal behaviors, is adapted[17, 23, 27, 29, 30]. Figures 10, 11 and 12 give the DSC curves of PAN, P(AN/IA) and P(AN/IA/AM) heated at different rates (5, 10, 15, 20 and 30 K·min^{-1}) from ambient temperature to 320 °C under nitrogen atmosphere, respectively. It can be found that as increasing the heating rate, the exothermic curves of all PAN polymers shift to higher temperature and the exothermic peaks become stronger. Interestingly, in Fig. 12, the first exothermic peak almost disappears when the heating rate is higher than 20 K·min^{-1}. As mentioned above, the former is mainly contributed to the cyclization induced by ionic mechanism and the latter is related to the cyclization induced by radical mechanism. However, according to the above DSC analysis results, the cyclization initiated by ionic mechanism is slower than that by radical mechanism. Thus, the cyclization induced by radical mechanism is more sensitive to the changes of heating rate[40]. Moreover, from the above discussion, it follows that high heating rate facilitates the reaction with higher activation energy in the case of the coexistence of several reactions.

Ozawa[41] and Kissinger[42] methods are frequently used in the literature to calculate E_a. In our study, we quantify E_a by a series of DSC curves obtained at different heating rates without prior knowledge of reaction mechanism. The mathematical expression of the Ozawa method is defined as follow:

$$-\frac{E_a}{R} = \frac{\mathrm{d}\ln\phi}{\mathrm{d}\left(\frac{1}{T_{pk}}\right)} \tag{3}$$

Kissinger's method uses an equation as follow:

$$-\frac{E_a}{R} = \frac{\mathrm{d}\ln\left(\frac{\phi}{T_{pk}^2}\right)}{\mathrm{d}\left(\frac{1}{T_{pk}}\right)} \tag{4}$$

where T_{pk} is the exothermal peak temperature, ϕ is the heating rate, E_a is the apparent activation energy

(kJ·mol^{-1}), and R is the molar gas constant. The values of E_a can be calculated from the slopes of the linear plots of lnϕ versus 1000/T_{pk}, and ln(ϕ/T^2_{pk}) versus 1000/T_{pk}, as shown in Figs. 13 and 14, respectively.

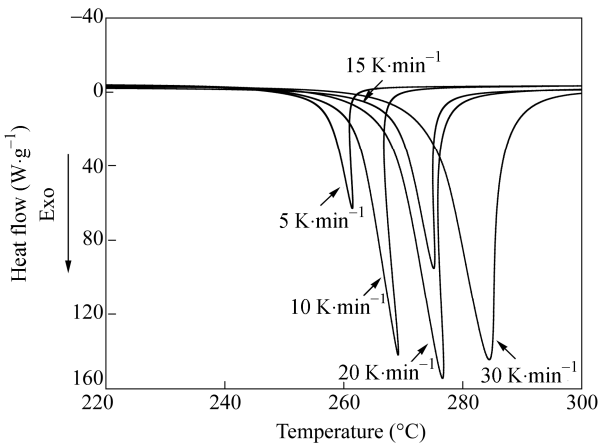


Fig. 10 DSC curves of PAN heated at different rates in N_2

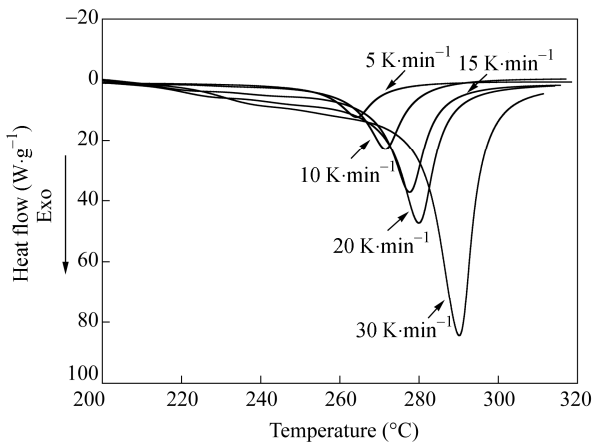


Fig. 11 DSC curves of P(AN/IA) heated at different rates in N_2

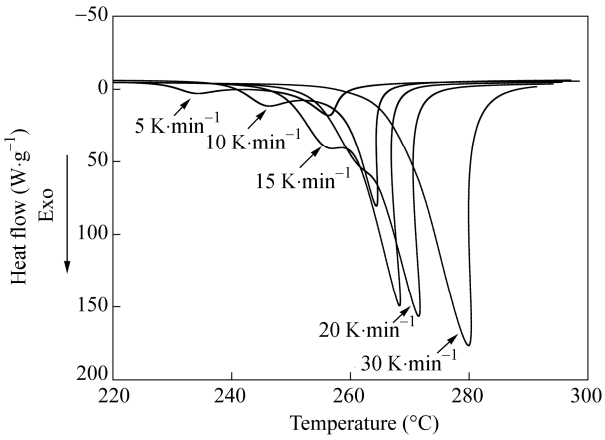


Fig. 12 DSC curves of P(AN/IA/AM) heated at different rates in N_2

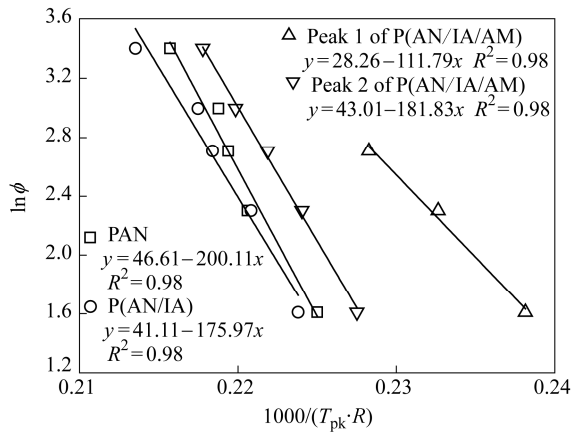


Fig. 13 Ozawa method used to quantify E_a of PAN polymers

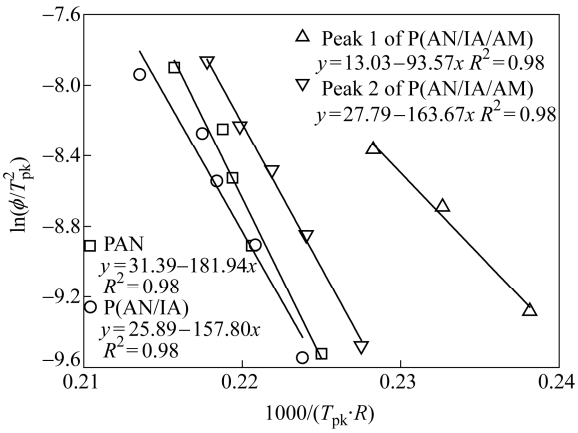


Fig. 14 Kissinger method used to quantify E_a of PAN polymers

The pre-exponential factors A in three cases can be calculated from the following Eq. (5)[17, 29, 30]:

$$A = \frac{\phi E_a}{RT_{pk}^2} e^{E_a/RT_{pk}} \tag{5}$$

As can be seen from Figs. 13 and 14, the linear dependence for each fit is as expected (R^2 = 0.98), and the calculated E_a and A are listed in Table 5. The values of E_a and A obtained from Ozawa and Kissinger methods show good agreement. For P(AN/IA/AM), E_a is split into two parts, namely E_{a1} and E_{a2}, respectively. E_{a1} calculated from the first exothermic peak is about 111.79 kJ·mol^{-1}, mainly corresponding to the cyclization initiated by an ionic mechanism, whereas E_{a2} calculated from the second exothermic peak is about 181.83 kJ·mol^{-1}, in accordance with the cyclization reaction initiated by a free radical mechanism. The lower E_{a1} from the ionic induction mechanism demonstrates that the ionic mechanism actually has a kinetic advantage for accelerating the cyclization reactions than the free radical mechanism. In addition, the value of E_{a2} of P(AN/IA/AM) is larger than that of P(AN/IA). The same result was also reported by Fu *et al.*[27] using a nonisothermal method. For P(AN/IA/AM), the value of E_{a1} is much smaller than that of PAN and P(AN/IA) (200.11 and 175.97 kJ·mol^{-1}, respectively), confirming that the cyclization of nitrile groups in P(AN/IA/AM) has been greatly promoted by AM comonomer as compared with P(AN/IA). The reason for the larger E_{a2} of P(AN/IA/AM) may be explained as follows: on one hand, it is due to the presence of AM comonomer in PAN chains, which blocks the cyclization to an extent; on the other hand, the formed annular structures by ionic mechanism increases the energy of configuration rotation of PAN macromolecules, and consequently increases the value of E_{a2}.

Table 5 Kinetic parameters determined by Ozawa and Kissinger methods

Code	Ozawa method		Kissinger method	
	E_a (kJ·mol^{-1})	A (s^{-1})	E_a (kJ·mol^{-1})	A (s^{-1})
PAN	200.11	1.41×10^{19}	181.94	1.11×10^{19}
P(AN/IA)	175.97	8.95×10^{18}	157.80	8.94×10^{18}
Peak 1 of P(AN/IA/AM)	111.79	5.45×10^{10}	93.57	3.59×10^{10}
Peak 2 of P(AN/IA/AM)	181.83	2.44×10^{17}	163.67	1.98×10^{17}

Figure 15 shows the rate constant κ at different temperatures calculated from E_a and A by Arrhenius equation, $\kappa = A\,e^{-E_a/RT}$ [27, 30]. It shows that the rate of cyclization of P(AN/IA/AM) is the fastest in three cases, although the value of E_{a2} assigned to the radical cyclization reactions is larger than that of P(AN/IA). The results further demonstrate that the presence of AM comonomer in PAN chains has promoted the cyclization significantly.

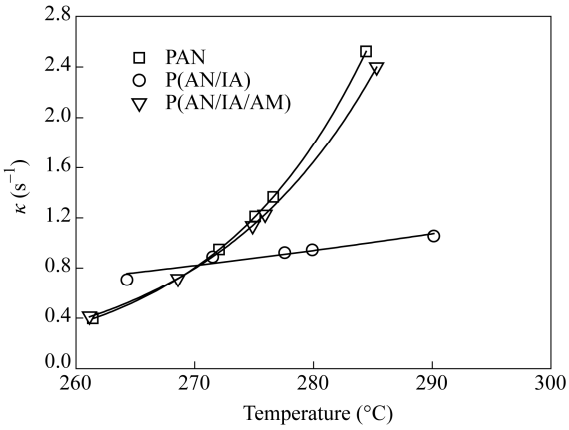


Fig. 15 Temperature dependency of rate constants for PAN polymers

DSC (Isothermal Mode)

The isothermal DSC thermograms of PAN, P(AN/IA) and P(AN/IA/AM) at different temperatures in air atmosphere are presented in Figs. 16–18, respectively. It can be found that the heat flow behavior as a function of time shows a distinct peak, which is due to the fast and instantaneous initiation and propagation of the cyclization reaction. As the temperature increases, the exothermic peak is reached sooner, which indicates that isothermal temperature has significant influence on the initiation and the propagation time of the reaction to achieve the maximum. A comparison of heat flow behavior of PAN at 200 and 240 °C shows that the cyclization starts in 25.82 min and reaches the maximum in 45.15 min at 200 °C, while in this polymer, the exotherm starts earlier at 240 °C, 12.42 min, and reaches the maximum in a shorter time, *i.e.*, 15.53 min. The total heat liberated, however, is increased from 195 $J \cdot g^{-1}$ to 327 $J \cdot g^{-1}$ at 200 °C to 240 °C, respectively (data not shown). From the DSC curves, we can see that as increasing the temperature, the rate and extent of cyclization increase significantly, which is consistent with the result of FTIR analysis. Comparing the thermal behavior of these three PAN polymers at 240 °C, in the case of P(AN/IA), the onset of cyclization begins in 7.53 min and reaches its maximum in 16.48 min with ΔH of 260 $J \cdot g^{-1}$. However, P(AN/IA/AM) showed a different behavior, *i.e.*, the onset of cyclization reaction is fastest, and takes 5.27 min. It reaches its first and second maximum in 7.35 and 16.38 min, respectively. Similar phenomenon was observed by Bahrami[13] and Collins[43]. In this work, the major difference between (IA) and (IA/AM) as comonomers is the number of cyclic reaction initiation groups, which provides more opportunities to induce the nitrile group to cyclize following the ionic mechanism.

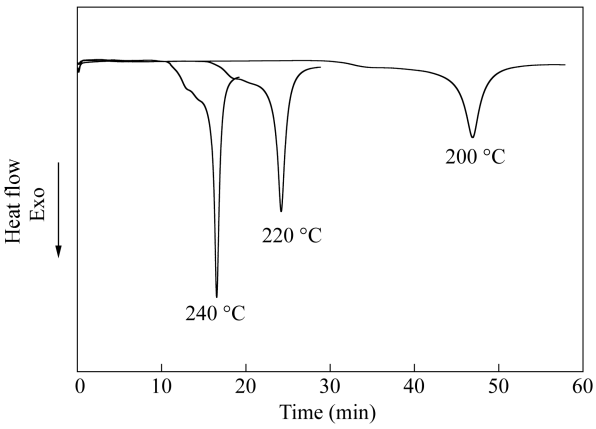


Fig. 16 DSC curves (isothermal mode) of PAN at different temperatures

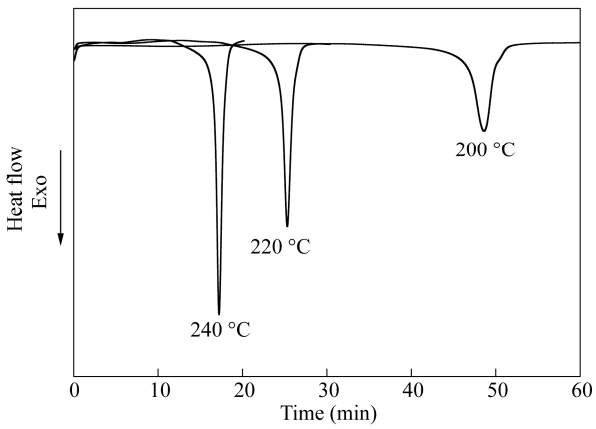


Fig. 17 DSC curves (isothermal mode) of P(AN/IA) at different temperatures

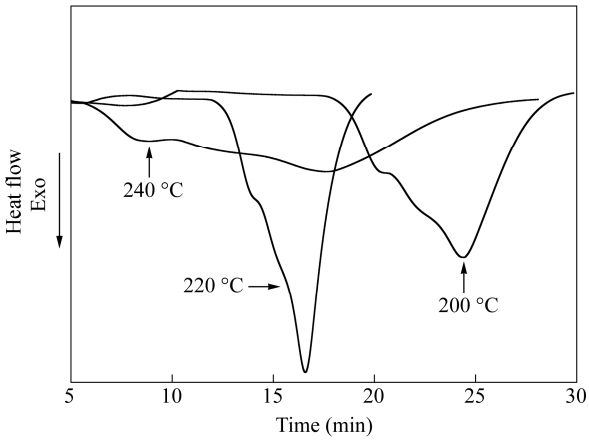


Fig. 18 DSC curves (isothermal mode) of P(AN/IA/AM) at different temperatures

Therefore, it is expected that the terpolymer containing IA and AM simultaneously experiences more cyclization than the copolymer containing only IA, promoting the extent of stabilization.

CONCLUSIONS

PAN, P(AN/IA) and P(AN/IA/AM) are successfully synthesized by aqueous suspension polymerization technique. The FTIR and DSC results show that the presence of AM comonomer in P(AN/IA/AM) promotes the cyclization reactions with lower initiation temperature and broadened exothermic peak compared with P(AN/IA) and PAN. Based on FTIR and TG studies, it is confirmed that the comonomer AM accelerates the thermal oxidative stabilization process in P(AN/IA/AM). From FTIR, XRD, DSC and TG analysis, it can be concluded that P(AN/IA/AM) has better thermal stability than P(AN/IA), *e.g.*, smaller weight loss and E_a, as well as higher rate constant κ. The results also show that the ionic mechanism has a kinetic advantage for promoting thermal stability as compared to the free radical mechanism. The synthesized P(AN/IA/AM) terpolymers possess larger room to adjust manufacture parameters for fabricating the high performance of PAN-based carbon fibers.

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