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THERMO-CHEMICAL REACTIONS AND STRUCTURAL EVOLUTION OF ACRYLAMIDE-MODIFIED POLYACRYLONITRILE

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Abstract Thermal properties of acrylonitrile (AN)-acrylamide (AM) copolymers for carbon fibers were studied by DSC and *in situ* FTIR techniques in nitrogen (N_2) and air flows. The cyclization mechanism and stabilization behavior of polyacrylonitrile (PAN) were discussed. In N_2 flow, it was found that AM had the ability to initiate and accelerate cyclization process, which was confirmed by the fact that the initiation of nitriles shifted to a lower temperature. Compared to AN homopolymer, the initiation temperature of cyclization was ahead 32 K by introducing 3.59 mol% AM into the copolymer. The exothermic reaction was relaxed due to the presence of two separated exothermic peaks. Accompanied by DSC, *in situ* FTIR and calculation of activation energy, the two peaks were proved to be caused by ionic cyclization and free radical cyclization, respectively, and the corresponding cyclization mechanism was proposed. With increasing in AM content, the ionic cyclization tends to be dominant and the total heat liberated first increases and then decreases. For AN homopolymer, the activation energy of cyclization is 179 kJ/mol. For AN-AM copolymer (containing 3.59 mol% AM), the activation energy of ionic cyclization is 96 kJ/mol and that of free radical cyclization is 338 kJ/mol. In air flow, similar cyclization routes occur and the difference is the contribution of oxidation. The oxygen in environment has no remarkable effect on cyclization of AN homopolymer but retards the cyclization of AN-AM copolymers. For AN-AM copolymer with 3.59 mol% AM, the cyclization temperature is postponed 10°C in air.

Keywords: Carbon fibers; Acrylonitrile-acrylamide copolymers; Thermal properties; Activation energy; Cyclization mechanism.

INTRODUCTION

Polyacrylonitrile (PAN) based carbon fibers, as excellent reinforces for composites, have gained a wide range of applications in various areas due to high strength and modulus. In the process of carbon fiber preparation, stabilization is an important step, *i.e.* heating the PAN precursor at 200°C to 300°C in air or oxygen-containing atmosphere. This process insures the formation of infusible ladder structure and so benefits for the subsequent carbonization[1–7]. It is also a complex process, including three major reactions: cyclization, dehydrogenation and oxidation[1–7]. Among them, cyclization reaction plays an important role in controlling the quality of carbon fiber. The mechanic pathway of cyclization is either free radical or ionic, which depends on the polymer structure and stabilization environment[8–13]. In both cases, the cyclization occurs only when the carbon atoms in nitriles are attacked by hetero atoms.

The demand for high quality PAN carbon fibers has intensified the interest in the study on the thermal characterization of polyacrylonitrile. The acrylonitrile (AN) homopolymer shows a sharp exothermic behavior and thus is not capable for preparation of carbon fibers. To the date, various vinyl comonomers are incorporated

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into PAN polymer chains to relax the exothermic reaction and improve the stabilization process. Generally, three types of monomers are added, *i.e.* acid monomers such as itaconic acid[5, 6, 9, 14–17], neutral ones such as ester[13] and alkaline ones such as amine[14, 18, 19]. For example, the itaconic acid (IA) has been increasingly focused in recent years. IA is generally believed to promote the process of stabilization because the nitriles oligomerization is apparently relaxed and initiated at lower temperature[6, 9, 17]. However, little study has been concerning on the influence of alkaline monomers such as acrylamide (AM). In fact, many previous studies demonstrate that the selection of comonomer is not only based on the precursor stability but also the dope spinnability[20, 21]. The spinnability and coagulation process are greatly affected by the hydrophilic property of PAN copolymers. The hydrophilic comonomer AM has been the interest of researchers. Further, the acyl group in AM may accelerate the next stabilization process. Grassie and coworkers[13] studied the effects of some comonomers on lowering the stabilization temperature, and some comonomers could lower the exothermic peak temperature and also decrease the peak height in the following order: itaconic acid > methacrylic acid > acrylic acid > acrylamide. The cyclization in the presence of AM units was the same sharp one as that for AN homopolymer. The corresponding mechanic pathway was a free radical one and so AM was not preferable to be introduced to prepare carbon fibers. Some other researchers[3] observed the same phenomenon, namely the exothermic peak of AN-AM copolymer shifted to a higher temperature and the structure changed more rapidly than PAN homopolymer. However, Sivy *et al.*[10, 12, 19] reported that AM units acted as the initiation sites for nitriles oligomerization and the oligomerization propagation occurred through an ionic mechanic pathway, leading to a relaxed exothermic reaction. Thus, as they reported, the incorporation of AM units was benefit for preparing PAN carbon fibers.

Up to present, a range of techniques have been successfully developed to investigate the morphology and structural transformation in stabilization, such as differential scanning calorimetry (DSC)[9, 13, 15], thermal weight loss (TG) analysis[9, 14], X-ray photoelectron spectroscopy[8], H-NMR[22] and FTIR[9, 10] *etc*. In this paper, DSC and *in situ* FTIR techniques are used to investigate the thermal properties of AN-AM copolymers. For the purpose of comparison, the thermal behavior of AN homopolymer is also studied.

EXPERIMENTAL

AN with purity of 99.99% (analyzed by gas chromatogram) was obtained by distillation. AM (Aldrich Co., 99%), dimethylsulfoxide (DMSO) and azobisisobutyronitrile (AIBN) were used without any further purification.

The solution polymerization was conducted using a 500 mL four-necked round bottom flask fit with a condenser, glass stirring and nitrogen inlet tube. First, AN, AM, AIBN and DMSO were poured into the flask, and it was blown with nitrogen for 1 h to remove oxygen. Then the polymerization was carried out for 6 h at 60°C. Upon completion of polymerization, the product was precipitated in large excess of water and washed many times to eliminate the residual monomers and solvent, then vacuum-dried at 50°C for 12 h. The composition and the intrinsic viscosity along with the copolymer code used for thermal studies are given in Table 1.

Table 1. Structural parameters for AN homopolymer and AN-AM copolymers

Sample	Code	AM content in the polymer (mol%)	Intrinsic viscosity (dL/g)
PAN	P0	0.00	3.8
P(AN-AM)	PA1	3.59	4.1
	PA2	5.40	3.7

Thermal properties of samples were characterized using a NETZSCH STA 409PC. Samples (by powder) with 5–7 mg weight were heated at a heating rate of 5 K/min under N_2 and air flow, respectively. The scanning range was 50–500°C.

The activation energy of cyclization was measured through the method described elsewhere[15]. The measurement was carried out on a NETZSCH STA 409PC in N_2 flow. The heating rate was varied between 2 K/min and 20 K/min.

Chemical structural transformations during heat treatment of AN homopolymer and AN-AM copolymers were investigated by *in situ* FTIR technique (Nicolet corporation). The polymer powders were shaped as a circular slice through heating at 150°C under 150 MPa pressure. The slice was transparent to ensure a good absorbance. IR measurements were carried out on a slice sandwiched between two KBr disks[17]. Changes of spectrum from 25°C to 400°C were recorded under a heating rate of 5 K/min.

RESULTS AND DISCUSSION

DSC Studies under N_2 Flow

Figure 1 shows the exothermic behavior of AN homopolymer and AN-AM copolymers in N_2 atmosphere, the corresponding data are listed in Table 2.

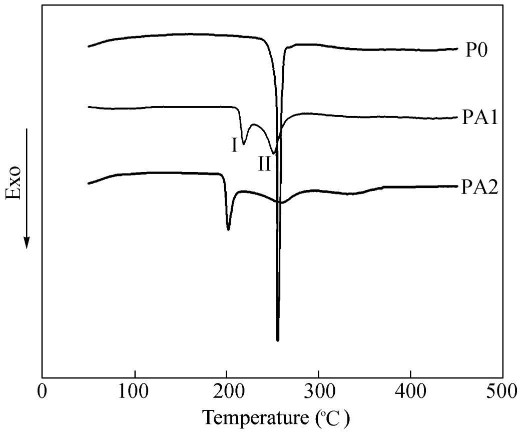


Fig. 1 DSC curves of AN homopolymer and AN-AM copolymers under N_2 flow

Table 2. Parameters for the degradation behavior of AN homopolymer and AN-AM copolymers

Code	Condition	T_i (°C)	T_f (°C)	T_{pk1} (°C)	T_{pk2} (°C)	ΔH (J/g)
P0	N_2	245	260	–	256	448
PA1	N_2	213	261	219	251	469
PA2	N_2	195	277	203	261	219
P0	Air	245	355	302	–	4302
PA1	Air	225	–	247	277	4723
PA2	Air	213	238	229	–	977

T_i: initiation temperature of the exotherm; T_f: final temperature of the exotherm;

T_{pk1}: the primary peak temperature; T_{pk2}: the secondary peak temperature; ΔH: total heat liberated

In the case of AN homopolymer (P0), only one exothermic peak was observed and the peak was very sharp, which implied that only one fast reaction occurs with a high exothermic rate. Apparently, the cyclization of homopolymer occurs through a free radical mechanism as generally believed[13]. What should be noted is the exothermic behavior of AN-AM copolymers (PA1, PA2). Upon heating from 50°C to 500°C, the exothermic reaction is considerably relaxed by the appearance of two exothermic peaks, that is peak I and peak II. The primary peak temperature (T_{pk1}) is 219°C, and the secondary peak temperature (T_{pk2}) is 251°C. This result is obviously different from that of any previous report[9, 13, 18]. In general, the exothermic peak was just broader or narrower with introducing comonomers and no two exothermic peaks were observed[9, 13]. Theoretically, the only exothermic peak determined by DSC in N_2, is a result of cyclization reaction. The appearance of two separated peaks in DSC of AN-AM copolymers implies the occurrence of two distinct reactions, namely the existence of two different cyclization pathways. Furthermore, it was observed that the peak I shifted to a lower temperature with increasing in AM content (203°C for T_{pk1} of PA2). In other word, the initiation temperature decreases, which is obviously in accordance with the characterization of ionic cyclization[9, 13, 18]. For the peak II, the peak temperature (T_{pk2}) shifts slightly and is almost the same as that of P0. Thus, it is logical to make an assumption that the peak I is resulted from an ionic propagation initiated by AM units; however, the peak II could be caused by a free radical one. The separation of peak I and II may be arising from different levels of their cyclization activation energy. On the other hand, the total exothermic reaction is apparently relaxed by two steps cyclization on introducing AM comonomer. With increasing in AM content, the area of peak I increases, suggesting that the ionic cyclization tends to be more dominant. This may be due to that the lower value of activation energy of ionic cyclization results in more nitriles to be ionic oligomerized. Further experimental evidence and more detailed explanation will be discussed below.

The heat liberation is directly proportional to the amount of nitriles oligomerized, which can be calculated from peak areas (shown in Table 2). In N_2 flow, the heat liberation is 448 J/g for P0 and 469 J/g for PA1, respectively. From such data, it can be concluded that the introduction of AM units results in more nitriles being oligomerized. However, the increase of AM content also causes the decrease of the absolute content of AN in the copolymer chain, directly reducing the amount of nitriles to be cyclized. Therefore, the total heat liberation decreases with further increase of AM content (219 J/g for PA2).

In situ IR Analysis under N_2 Flow

Figure 2 shows the structural transformation of AN homopolymers heated at different temperatures (200°C to 270°C) under N_2 flow.

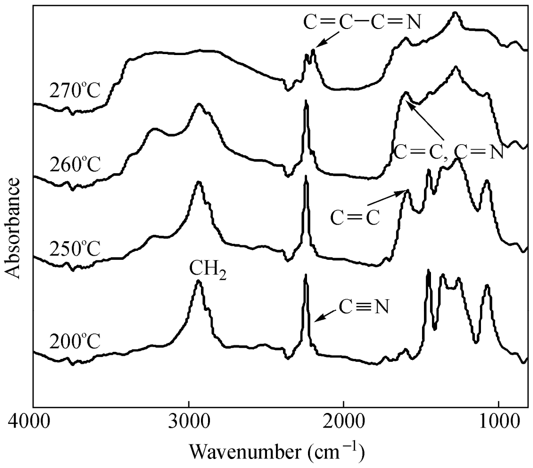
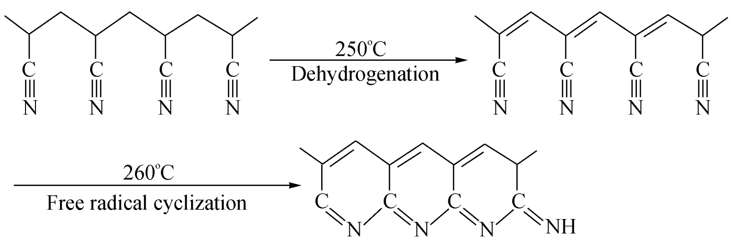


Fig. 2 IR spectra of AN homopolymer (P0) heated at different temperatures under N_2 flow

At 200°C the major absorption bands of AN homopolymer are: 2939 cm^{-1} region due to C—H stretching, 2239 cm^{-1} due to C≡N stretching, 1444 cm^{-1} due to CH_2 bending and 1253 cm^{-1} due to the twisting deformation of C—H. The shoulder peak at 2239 cm^{-1} is caused by α,β-unsaturated conjugated nitrile (C=C—C=N), such as ketonitrile defect formed in the process of polymerization[1]. It is interesting to note the observation of absorption bands at 1725 cm^{-1} due to C=O and 1598 cm^{-1} due to C=N or C=C, which may be also some structure defects[14].

Little differences were observed between 200°C to 250°C. While heated to 250°C, there is a decrease in CH_2 absorption bands at 2939, 1444, 1353, 1253, 1072 cm^{-1}. Simultaneously, a new band appears at 1582 cm^{-1} due to either C=C or C=N groups, which is the symbol of dehydrogenation or cyclization[9, 10, 12, 17]. When heating PAN in N_2, two reactions may take place, namely dehydrogenation and cyclization. Since the band at 2239 cm^{-1} ascribed to C≡N keeps unchanged, the cyclization of C≡N to C=N is not possible to occur and thus the 1582 cm^{-1} band after heating at 250°C can be ascribed to C=C groups from dehydrogenation (Scheme 1).



Scheme 1 Probable cyclization mechanism of AN homopolymer

At 260°C, the C≡N absorption band at 2239 cm^{-1} starts to diminish, accompanied by the enhance of the shoulder peak (C=C—C=N), suggesting the occurrence of nitriles cyclization. With further heating (to 270°C), the absorption bands in the range of 2500–3500 cm^{-1} level off, the C≡N absorption decreases significantly and the C=C—C=N absorption increases obviously. It indicates the nitrile cyclization is rapidly completed within 10 K (from 260°C to 270°C). These results are consistent with the above DSC studies. Accompanied by the DSC studies, the total stabilization process of AN homopolymer in N_2 can be expressed as Scheme 1.

Figure 3 depicts the chemical structure transformation of AN-AM copolymer (PA1) during heating in N_2. At 200°C, the major absorptions at 2939 and 2239 cm^{-1} are due to CH_2 and C≡N, respectively. Due to introduction of AM, the bands at 3471 and 3364 $cm^{-1}$are ascribed to the absorption of N—H and the band at 1685 cm^{-1} is ascribed to C=O.

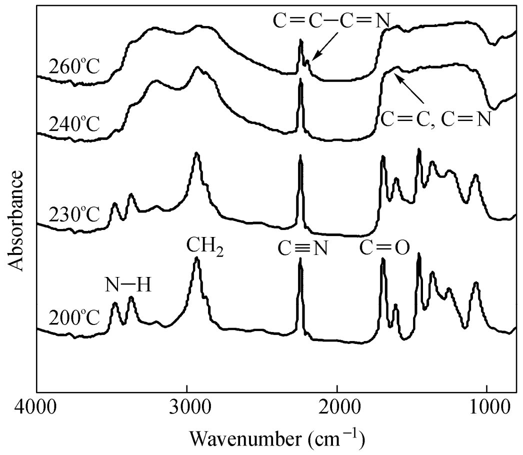
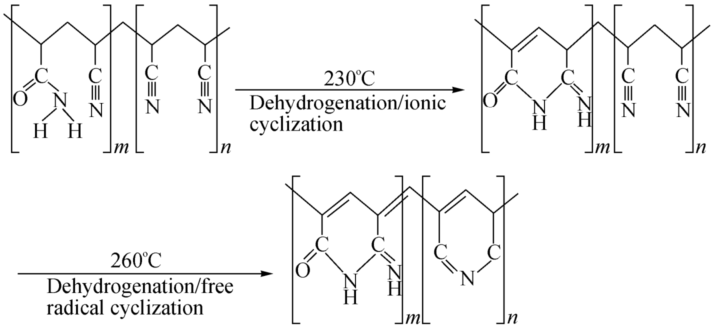


Fig. 3 IR spectra of AN-AM copolymer (PA1) heated at different temperatures under N_2 flow

Below 230°C, the absorption bands do not change. At 230°C, the CH_2 absorptions (2939, 1444, 1353, 1253 and 1072 cm^{-1}) start to diminish, indicating that the dehydrogenation occurs. While the absorption of C=C groups (1586 cm^{-1}), a symbol of dehydrogenation, was not observed at this temperature until the heat temperature was up to 240°C. The absence of 1586 cm^{-1} band at 230°C may be due to the cover of C=O absorption. During heating from 230°C to 260°C, the CH_2 absorption decreases continuously, indicating the development of dehydrogenation. Theoretically, C=C—C=O is more stable than C=C—C=N in structure. On the other hand, no change at 2191 cm^{-1} (C=C—C=N)[1] is observed in the temperature range of 230–260°C. Based on those results, the dehydrogenation process from 230°C to 260°C can be expressed by Scheme 2.

The decrease of N—H and C≡N absorptions also should be noted at 230°C. The bands at 3471, 3364 cm^{-1} (N—H) and 2239 cm^{-1} (C≡N) start to diminish. It means that a cyclization occurs simultaneously and the AM units participate in this reaction. The slight decline of N—H and C≡N absorptions in 230–260°C range suggests the cyclization is not sharp. Thus, as discussed in DSC studies, it can be concluded that the cyclization in the 230–260°C range may be an ionic pathway (shown in Scheme 2). However, the AM content is low in AN-AM copolymers (here lower than 5.4 mol%), and the long AN sequences exists[23]. Usually 5–6 atoms can be cyclized to form a ring[12]. The auto-catalyzed cyclization of part nitriles is also possible. As a result, similar spectrum changes to that of AN homopolymer are observed when heated to 260°C. The absorption of nitriles decreases markedly again and the absorption of 2191 cm^{-1} (C=C—C=N) increases rapidly, suggesting the uncyclized nitriles may be oligomerized again by a free radical propagation like AN homopolymer (P0) (shown in Scheme 2). Accompanied by DSC studies, the total stabilization process of AN-AM copolymer (PA1) in N_2 can be explained by Scheme 2.



Scheme 2 Probable cyclization mechanism of AN-AM copolymer (PA1)

Calculation of Cyclization Activation Energy

In order to further validate the rationality of two cyclization routes, the Arrhenius activation energy (*E*) is calculated from the following equation[15].

$$-E/R = \mathrm{d}\ln(\varphi/T_{\mathrm{pk}}^2)/\mathrm{d}(1/T_{\mathrm{pk}})$$

Where *R* is the gas constant, φ represents the heating rate and T_{pk} means the peak temperature of exothermic reaction. As mentioned above, the only exothermic reaction determined by DSC under N_2 is a cyclization. As a result, the calculated activation energy is just for a cyclization one. For AN-AM copolymer, two separated exothermic peaks were observed in N_2 (Figure 1). The two peaks are assigned as results from ionic and free radical cyclization, respectively, as discussed above. Thus the two types of cyclization activation energy are both calculated for AN-AM copolymers. The E_1 means an activation energy of ionic cyclization and the E_2 is that of a free radical one.

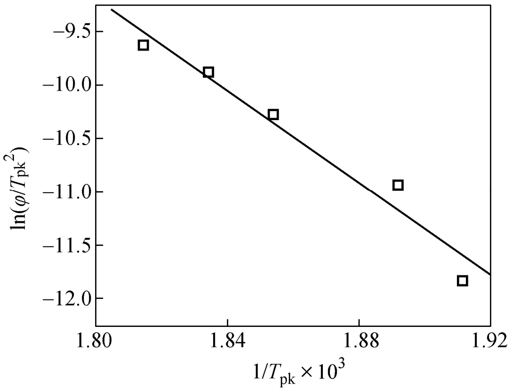


Fig. 4 Plot of $\ln(\varphi/T_{pk}^2)$ versus $1/T_{pk}$ of AN homopolymer (P0)

The activation energy is obtained from the slope of plot $\ln(\varphi/T_{pk}^2)$ versus $1/T_{pk}$ as given in Fig. 4, Fig. 5 and Fig. 6, respectively. The plots show a good linearity and the calculated results of activation energy are shown in Table 3. For P0, the E_2 value is 179 kJ/mol. For PA1, the E_1 value is 96 kJ/mol and the E_2 value is 338 kJ/mol. The lower value of E_1 for PA1 further proves that the AM comonomer has the ability to initiate the ionic cyclization of nitriles. With further increase of AM content in PAN (PA2), the E_1 value further decreases, *i.e.* 52 kJ/mol, suggesting the ionic cyclization is further accelerated.

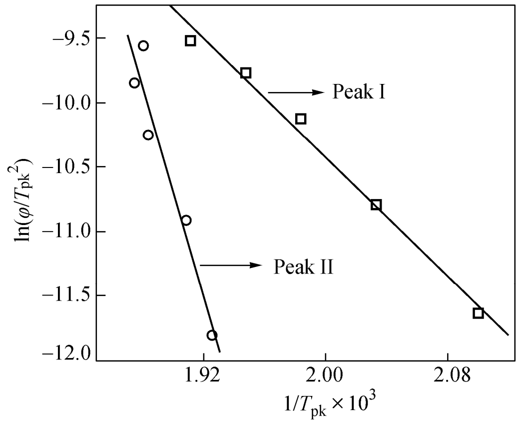


Fig. 5 Plot of $\ln(\varphi/T_{pk}^2)$ versus $1/T_{pk}$ of AN-AM copolymer (PA1)

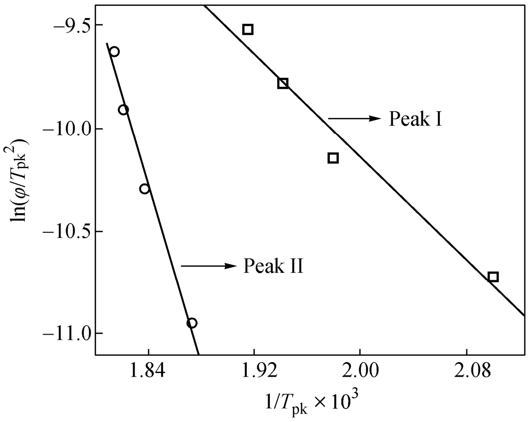


Fig. 6 Plot of $\ln(\varphi/T_{pk}^2)$ versus $1/T_{pk}$ of AN-AM copolymer (PA2)

Table 3. Cyclization activation energy of AN homopolymer and AN-AM Copolymers

Code	AM content in polymer (mol%)	E_1 (kJ/mol)	E_2 (kJ/mol)
P0	0.00	–	179
PA1	3.59	96	338
PA2	5.40	52	183

E_1: ionic cyclization activation energy; E_2: free radical cyclization activation energy

Interestingly, it should be noted that the activation energy for free radical cyclization propagation (E_2) is elevated by introducing AM into polymer chains (179 kJ/mol for P0 and 338 kJ/mol for PA1). It means that the free radical cyclization is hindered by AM units in AN-AM copolymers. Surprisingly, the E_2 value decreases with further increase of AM content (183 kJ/mol for PA2). On the one hand, as mentioned above, the AM units can initiate the ionic cyclization of nitriles and thus the ionic activation energy of cyclization remarkably decreases. On the other hand, the free radical cyclization of nitriles is inevitably affected. The value of cyclization activation energy is affected by several key factors, *i.e.* tacticity, steric structure and molecular forces[23]. On introducing 3.59% AM (PA1), the larger size of acyl groups from AM hinders the free radical propagation of oligomerized nitriles and so the E_2 value is increased (179 kJ/mol for P0 and 338 kJ/mol for PA1). While, the activation energy is also affected by tacticity which is also related with AM content. On further introducing 5.40% AM (PA2), the effect of tacticity on E_2 becomes a dominant factor. According to our previous study, the tacticity increases with the AM content[24] and thus the E_2 value decreases to 183 kJ/mol for PA2.

DSC Studies under in Air Flow

The stabilization of PAN fibers is industrially carried out in oxygen-containing environment. Figure 7 illustrates the exothermic profiles of AN homopolymer and AN-AM copolymers in air atmosphere. Due to the contribution of oxidation, the exothermic peak of P0 broadens and the heat liberated is higher than that under N_2 (Table 2). In the case of PA1, the existence of AM comonomer accelerates the separation of cyclization and oxidation, leading to a triplet character shown in DSC curve. Usually the oxidation occurs behind cyclization. So, accompanied by the above DSC discussions in N_2, here the first peak and the second one could be assigned to the ionic cyclization and free radical cyclization, respectively, the third peak could be ascribed to the secondary oxidative reaction[13, 24]. With increasing in AM content (PA2), the exothermic peak shifts to lower temperature (213°C of T_i) and exothermic reaction is relaxed. This also proves that AM units act as initiation sites of nitriles and promote the nitriles cyclization. Moreover, two kinds of cyclization mechanisms exist for AN-AM copolymers. Similarly, the ionic route tends to be more dominant with increasing in AM content (PA2) which can be proved by the fact that the first peak increases while the other two peaks almost disappear.

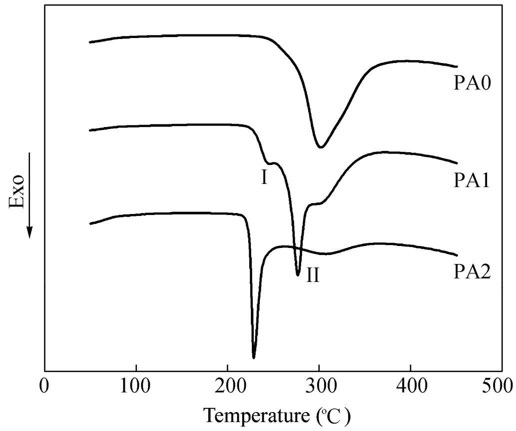


Fig. 7 DSC curves of AN homopolymer and AN-AM copolymers under air atmosphere

Also, the effect of oxygen on cyclization should be noted here. For AN homopolymer, the T_i value is 245°C whether under N_2 or air flow (Table 2). For AN-AM copolymers, the T_i values are 213°C (PA1) and 195°C (PA2) under N_2, but increase to 225°C (PA1) and 213°C (PA2) under air flow, respectively (Table 2). Apparently, the presence of oxygen does not affect the free radical cyclization, but retards the ionic cyclization. The similar conclusion has also been reported[1, 22].

In situ IR Analysis under Air Flow

Figure 8 illustrates the structural transformation of AN homopolymer during heating in air atmosphere up to 270°C. At 200°C, the spectrum is similar to that under N_2. At 250°C, the bands at 1600 cm^{-1} (C=C or C=N) and 3218 cm^{-1} increase, while the bands at 1454 and 2939 cm^{-1} (CH_2) decrease evidently. No remarkable changes were observed at other bands. At 260°C, the nitrile absorption starts to diminish remarkably. At the same time, the band absorption at 2191 cm^{-1} increases, implying the formation of C=C—C=N structure.

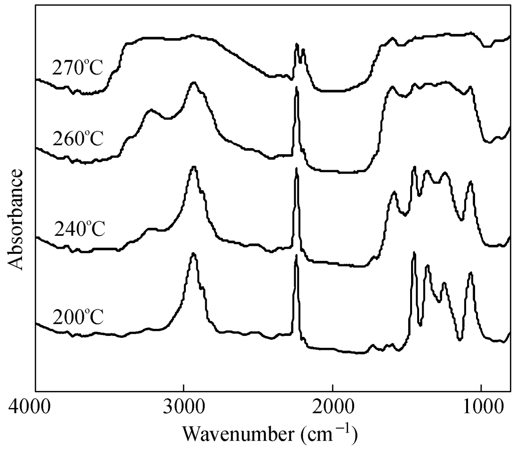


Fig. 8 IR spectra of AN homopolymer (P0) heated at different temperatures in air atmosphere

According to the above spectra change, it is apparent that some reaction occurs at 250°C. It is known that three reactions exist in stabilization of PAN, *i.e.* dehydrogenation, cyclization and oxidation. According to the results of DSC, the cyclization and oxidation take place at high temperatures (about 275°C). Also, in the heating range of 200–250°C, the absorption of nitrile groups (2239 cm^{-1}) does not change. Thus such reaction at 250°C may be due to dehydrogenation. The corresponding absorption band at 1600 cm^{-1} in spectra should be attributed to C=C groups, not C=N groups.

The spectra also show that the nitrile groups start to oligomerize at 260°C evidenced by the diminishing of the nitriles absorption and simultaneous formation of C=C—C=N (2191 cm^{-1}) structure. This is in agreement with the cyclization process of AN homopolymer in nitrogen atmosphere, indicating that the presence of oxygen seems no effect on cyclization. It is interesting to note that the absence of bands of C=O groups in the spectrum during heating was also observed by previous researchers[9, 17]. It doesn't mean that oxidation does not occur. A possible reason may be due to the saturated absorption of 1600 cm^{-1} band when heated to 260°C. On the other hand, it is difficult to differentiate C=N, C=C and C=O groups because they nearly appear at the same range (around 1600 cm^{-1}). Deconvolution method may be a good candidate choice to solve this problem which has been adopted by previous workers[10, 13].

In the case of AN-AM copolymers as shown in Fig. 9, remarkable changes of the absorption bands take place at 240°C. The absorption band at 2238 cm^{-1} (C≡N), 3484 cm^{-1} and 3373 cm^{-1} (N—H), 1685 cm^{-1} (C=O in AM) and 2939 cm^{-1} (CH_2) start to diminish, meanwhile, two new absorption bands at 3200 cm^{-1} and 1586 cm^{-1} appear. At 260°C, the remarkable changes in absorbance of the bands occur again, namely the absorbance of C≡N and CH_2 groups start to diminish remarkably again, simultaneously the shoulder peak at 2939 cm^{-1} (C=C—C=N) increases. Based on these spectrum changes, it is apparent that the AN-AM copolymer exhibits structural transformation in air atmosphere similar to that in N_2. The difference is just that the ionic cyclization temperature is postponed for 10 K (230°C under N_2 and 240°C under air flow). Then, nitrile groups are again oligomerized through a free radical mechanism at 260°C. The structural change trend is the same for AN-AM copolymers in air and in N_2, namely ionic cyclization followed by a free radical one. These results are well consistent with the DSC studies, there exists only a slight disagreement in cyclization initiation temperature due to instrument errors.

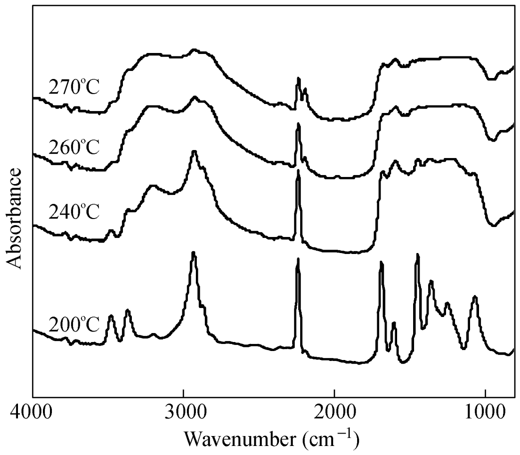


Fig. 9 IR spectra of AN-AM copolymer (PA1) during heated at different temperatures in air atmosphere

CONCLUSIONS

Based on DSC and *in situ* IR studies, it can be confirmed that the AM comonomer promotes the stabilization process with a lower initiation temperature. The exothermic reaction is relaxed by two cyclization steps, namely the free radical and ionic cyclizations. At a lower temperature, AM acts as a activate site and accelerates ionic cyclization of nitrile groups. At a higher temperature, free radical cyclization takes place. With the increase of AM content, the ionic cyclization tends to be dominant. Based on the calculated results of cyclization activation energy, the appearance of two cyclization routes gains reasonable explanation. The activation energy of cyclization of AN homopolymer is 179 kJ/mol. For PAN containing 3.59 mol% AM units, the activation energy of ionic cyclization and free radical one is 96 kJ/mol and 338 kJ/mol, respectively. It is reasonable to conclude that the precursor produced from AN-AM copolymer should be stabilized at a low temperature for obtaining high performance carbon fibers.

The dehydrogenation and oxidation reactions are also discussed. For AN homopolymer, the dehydrogenation is followed by cyclization both under N_2 and air flow. In the case of AN-AM copolymers, the dehydrogenation almost simultaneously occurs with cyclization. The presence of environmental oxygen has no remarkable influence on free radical cyclization of AN homopolymer but the cyclization of AN-AM copolymers is postponed for 10 K.

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