

Thermal Properties of Acrylonitrile/Itaconic Acid Polymers in Oxidative and Nonoxidative Atmospheres

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ABSTRACT: Thermal stabilization of polyacrylonitrile (PAN) fibers is an indispensable process in the manufacture of carbon fibers. The effects of acidic comonomers on the thermal properties of PAN have attracted much attention because of their importance in the fibers spinning and heat treatment process. In this study, oxidative and nonoxidative atmospheres are adopted in differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) test to disclose the key effects of oxygen on the thermal properties of PAN/itaconic acid (IA) polymers. The DSC results under oxidative atmosphere are consistent to the reports by previous researchers: the exothermic curves of copolymers containing 0.6 wt % and 1.0 wt % IA exhibit lower initiation temperature and more broaden shapes than that of PAN homopolymer, indicating that IA facili-

tates both cyclization and oxidation reactions. However, copolymers containing the same content of IA shows no apparent improving effect on the thermal properties under inert atmosphere, which has not been mentioned in the published literature. TGA indicates that oxygen remarkably increases the thermal stability of AN/IA copolymers structure, and will bring high carbon yield in the eventual carbon fibers. The influential mechanisms of oxidative and nonoxidative atmospheres on thermal stabilization reactions of PAN were discussed. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 1207–1212, 2010

Key words: differential scanning calorimetry (DSC); thermogravimetric analysis (TGA); thermal properties; polyacrylonitrile; carbon fibers

INTRODUCTION

Polyacrylonitrile (PAN) fibers are the most widely used precursor for high-property carbon fibers, the important reinforced materials for advanced composites in many fields, such as aerospace, sports, transportation, and petrochemical industry. Thermal stabilization, during which ladder structure is formed to enable PAN fibers infusible and nonflammable, is an indispensable process in the manufacture of carbon fibers. For industrial production, thermal stabilization of PAN fibers is usually performed in a temperature range of 200–300°C under certain stretching force in air. Besides temperature and stretching ratio, the medium atmosphere and the comonomer used in PAN precursor are the other two main important factors for the quality of carbon fiber.

There are many studies focused on the effect of various acidic comonomers, such as itaconic acid (IA), acrylic acid (AA), methacrylic acid (MAA) on the thermal properties of PAN copolymers, aiming at improving the productivity and moderating the heat release during thermal stabilization of PAN.^{1–4} The acidic comonomers will promote cyclization of nitrile groups and lower the initiation temperature of exothermic reactions, of which IA has the most remarkable effect.^{5–9} It is known that cyclization of nitrile groups may proceed not only in an oxidative atmosphere, but in an inert atmosphere. However, if the atmosphere is oxidative like air, the reactions are more complicated. Viewpoints from different researchers have not been consistency on the role of oxygen in thermal stabilization reactions and on the bond form of oxygen to PAN molecular chains. The study by Fitzer^{10,11} has revealed that a greater stability will be obtained when PAN is stabilized in air. On the other hand, the limited oxygen diffusion results in skin-core structure, which is deemed responsible for low quality of carbon fibers.¹²

Until now, it is not very clear as for which is the key factor that facilitates cyclization reactions, air or IA, or the both? In this study, the independent and the combined effects of oxidative atmosphere and IA

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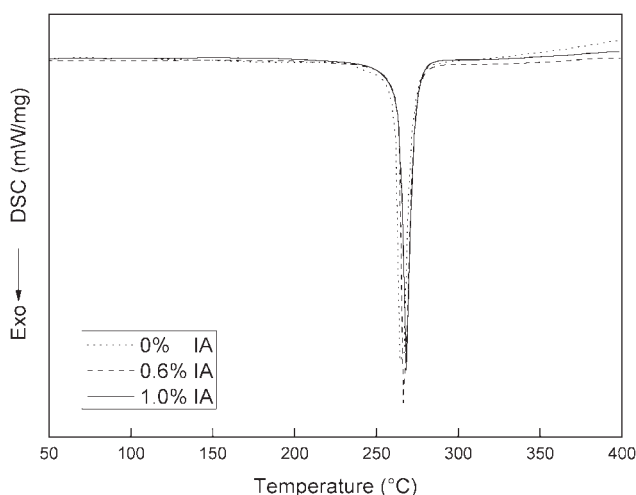


Figure 1 DSC exothermic curves of PAN homopolymer and copolymers with different contents of IA in argon atmosphere.

comonomer on the thermal properties of PAN copolymers were investigated by differential scanning calorimetry (DSC) in oxidative and nonoxidative atmospheres by comparing AN homopolymer and AN/IA copolymers containing different content of IA. The mechanism of oxygen influence on the stability of molecular chains was disclosed by weight loss analysis in thermogravimetric analysis (TGA). The aim of present work is to give a better and deeper understanding on thermal stabilization in oxidative atmosphere, and supply guidance for actual manufacturing of high performance carbon fibers.

EXPERIMENTAL

Materials

Acrylonitrile was purified by alkali washing, followed by distillation between 76 and 78°C. IA was recrystallized twice from water. Pure AN and IA of different weight fractions (0.6 wt % and 1 wt %) was copolymerized using α,α -azobisisobutyronitrile as initiator in dimethylsulphoxide (DMSO) at 58–60°C under nitrogen atmosphere to obtain AN/IA polymers.

Thermal analysis

The exothermic reactions and the weight loss of poly (AN-co-IA) during thermal stabilization and low temperature carbonization stage were measured by DSC and TGA using NETZSCH DSC 404C Thermal Analyzer. To detect the possible effects of atmosphere and IA comonomer on thermal stabilization reactions, DSC scans were carried out at a heating rate of 5°C/min in air and argon, the flow rate is 30 mL/min. TGA scans were carried out at a heating rate of 30°C/min from room temperature to 200°C,

10°C/min from 200 to 300°C, and 30°C/min from 300 to 900°C in air and nitrogen.

RESULTS AND DISCUSSION

Independent effect of comonomer or atmosphere on the thermal properties of PAN polymers

To investigate the independent effect of comonomer on thermal stabilization without consideration of oxygen, DSC analysis is carried out in inert atmosphere. The exothermic curves of PAN homopolymer and copolymers with 0.6% IA and 1.0% IA in argon are compared in Figure 1. It can be seen that the three curves superpose each other with little difference. They all have only one sharp exothermic peak at $\sim 266^\circ\text{C}$ with initiation temperature at $\sim 240^\circ\text{C}$ and final temperature at $\sim 290^\circ\text{C}$. The peak is attributed to cyclization reaction as no oxidation reaction takes place under inert atmosphere. The results indicate that IA comonomer plays neither evident facilitating nor inhabiting role on cyclization reaction in nonoxidative atmosphere. That is to say, oxidative atmosphere is a necessary condition for IA comonomer to promote cyclization of nitrile groups during thermal stabilization of PAN.

Figure 2 shows the independent effect of atmosphere on thermal stabilization of PAN homopolymer. The DSC exothermic curve of PAN homopolymer have only one peak at $\sim 268^\circ\text{C}$ in argon, but it exhibits two maximums at $\sim 270^\circ\text{C}$ and $\sim 305^\circ\text{C}$ in air. According to studies by Gupta et al.,⁸ different kinds of reactions are responsible for the multiple peaks, such as cyclization, primary and secondary oxidation. In the present work, Gaussian curve-fitting method is used to resolve the whole exotherm into three peaks: Peak1, Peak2, and Peak3 with peak temperatures at $\sim 270^\circ\text{C}$, $\sim 305^\circ\text{C}$, and 324°C ,

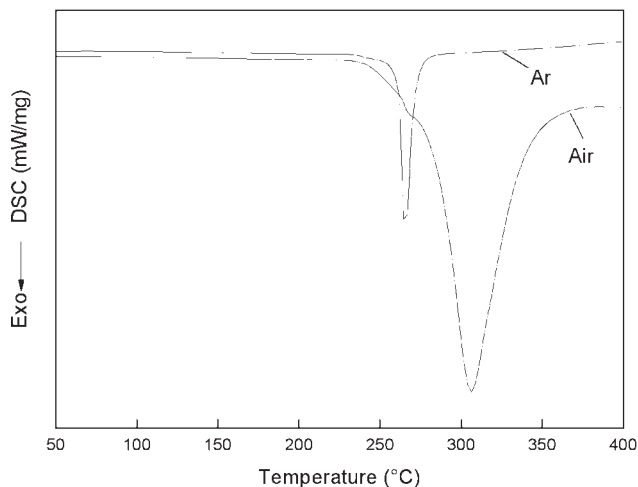


Figure 2 DSC exothermic curves of PAN homopolymer in argon and air atmosphere.

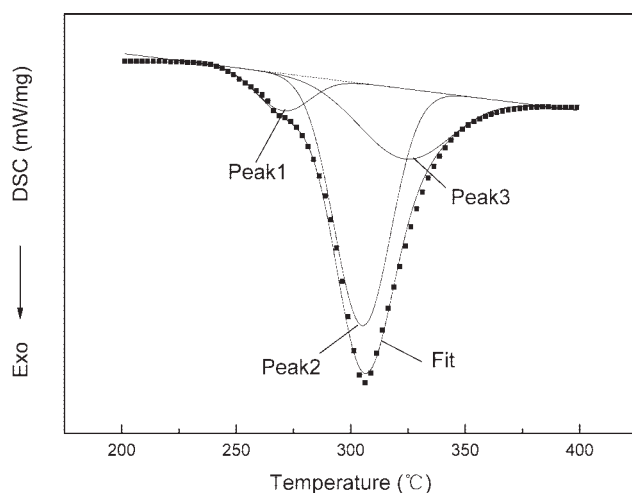


Figure 3 Curve fits to DSC exotherm of PAN homopolymer in air atmosphere.

respectively, shown in Figure 3. On the basis of our previous FTIR study which indicates the cyclization of nitrile groups propagates intensively between 235 and 275°C,¹³ Peak1 can be attributed to cyclization reaction, while Peak2 and Peak3 to primary and secondary oxidation reactions.

Therefore, it indicates from Figures 2 and 3 that the cyclization reaction of PAN homopolymer starts at a little lower temperature but finishes at higher temperature in air than in argon, while the reaction gets its climax at almost the same temperature ($\sim 270^\circ\text{C}$) in the two atmospheres. Besides, there is no obvious difference in the amount of heat released by cyclization reaction in different atmosphere, but large amount of heat is released by oxidation reaction in the case of air atmosphere. The result indicates that if no acidic comonomer is involved in PAN, the oxidative atmosphere has no apparent

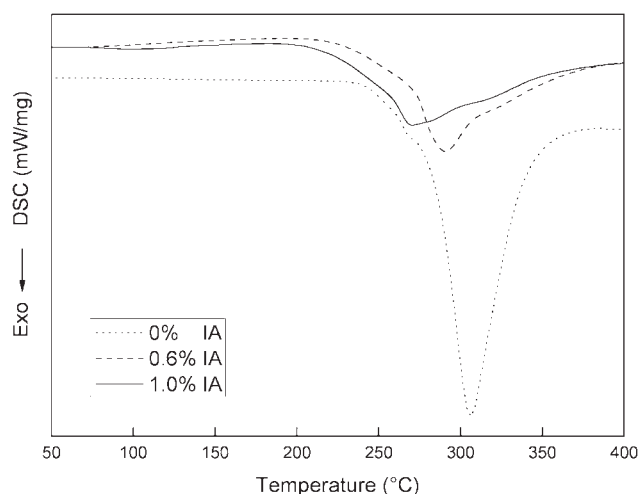


Figure 4 DSC exothermic curves of PAN homopolymer and copolymers with different contents of IA in air atmosphere.

TABLE I
Relevant Parameters of DSC Exothermic Curves of PAN Homopolymer and Copolymers with Different Contents of IA in Air Atmosphere

Samples	T_i ($^\circ\text{C}$)	T_p ($^\circ\text{C}$)	T_f ($^\circ\text{C}$)	ΔH (J/g)
AN/0%IA	238	305	369	4505
AN/0.6%IA	202	290	388	2538
AN/1.0%IA	190	270	400	2245

effect on the cyclization reaction during thermal stabilization process.

Combined effect of comonomer and atmosphere on the thermal properties of PAN polymers

Since IA comonomer has little effect on thermal stabilization reactions if inert atmosphere is applied, we use air in the next DSC examination to find out the combined effect of IA comonomer and oxidative atmosphere on thermal stabilization of PAN copolymers. As shown in Figure 4, the exothermic curve is much broader for copolymers than that for homopolymer. With the increasing content of IA, exothermic reactions starts at rather lower temperature and ends at higher temperature along with much less drastic heat release. The relevant parameters of the exothermic curves including initiation temperature T_i , peak temperature T_p , final temperature T_f , and the amount of heat released ΔH are listed in Table I. It can be seen that IA comonomer facilitates the thermal stabilization reactions by lowering the initiation temperature and alleviating heat release in oxidative atmosphere.

The exothermic curves of AN/IA copolymers can also be resolved into three peaks by Gaussian curve-fitting, as shown in Figures 5 and 6. The corresponding peak temperatures and the fractions of peak area

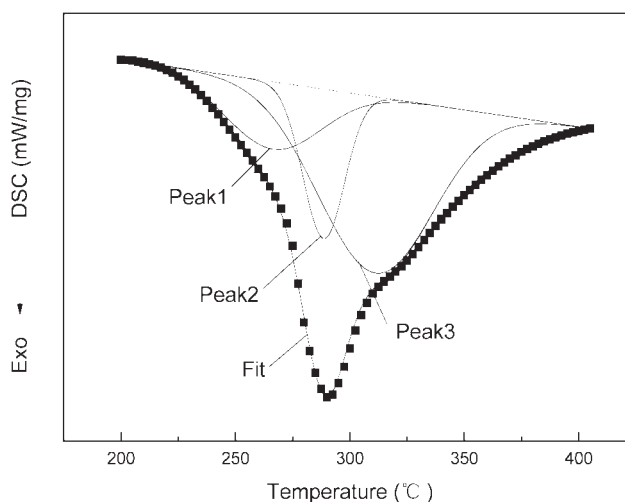


Figure 5 Curve fits to DSC exotherm of AN/0.6%IA copolymer in air atmosphere.

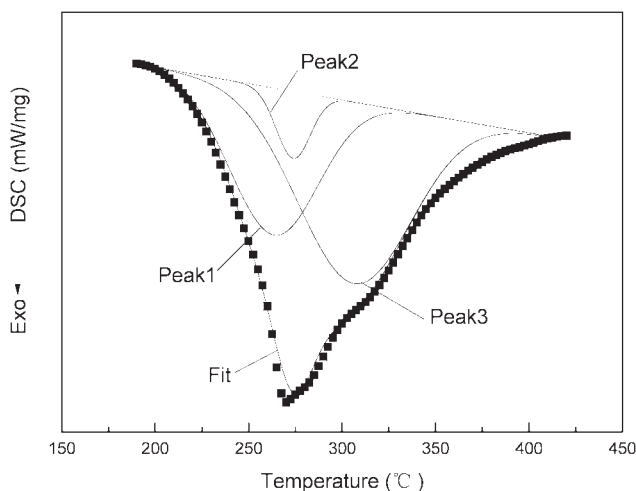


Figure 6 Curve fits to DSC exotherm of AN/1.0%IA copolymer in air atmosphere.

are listed in Table II. It is apparent from the data given in Table II that with IA content increasing, each peak of copolymers shifts to lower temperature compared with the corresponding peaks of PAN homopolymer. The shapes of exotherms are different between PAN homopolymer and copolymers, because the amount of heat release of various reactions changes with different IA contents. Among the three figures (Figures 3, 5, and 6), Peak1 is related to cyclization reaction, while Peak2 and Peak3 to primary and secondary oxidation reactions. It is known that the fraction of the area under different resolved peaks with respect to the total area of the exotherm is proportional to the relative amount of heat release of corresponding reactions. So comparing the area fractions of different peaks, PAN homopolymer has the least area fraction of Peak1 and Peak3, but the largest area fraction of Peak2. It indicates that in air atmosphere, IA comonomer enhances the cyclization reaction and the secondary oxidation reaction, but it remarkably inhabits the primary oxidation reaction meanwhile.

In summary, if no oxidative atmosphere is applied, the acidic comonomer itself hardly has any effect on cyclization reaction; if no acidic comonomer is applied, oxidative atmosphere itself has a little facilitating effect on cyclization reaction. Only

TABLE II
 T_p of Resolved Peaks of the Exotherm for Different Samples Corresponding to Figures 3, 5, and 6

Samples	T_p of Peak1 (°C)	T_p of Peak2 (°C)	T_p of Peak3 (°C)	Area fraction of Peak1	Area fraction of Peak2	Area fraction of Peak3
AN/0%IA	270	305	324	0.09	0.62	0.29
AN/0.6%IA	256	288	311	0.2	0.19	0.61
AN/1.0%IA	263	274	306	0.35	0.04	0.61

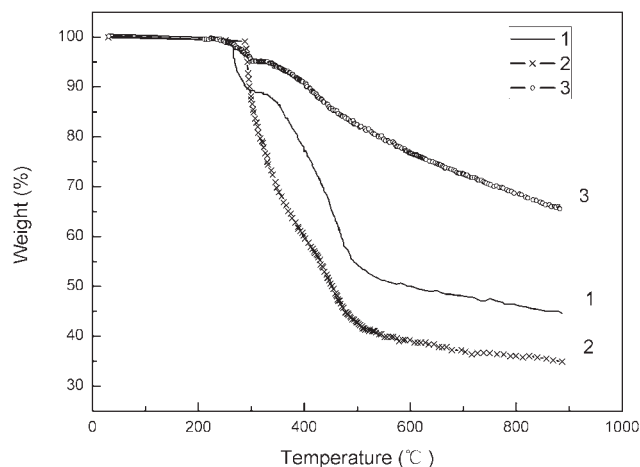


Figure 7 TGA curves under different conditions: curve 1 – in nitrogen atmosphere at heating rate of 30°C/min; curve 2 – in nitrogen atmosphere at heating rate of 30°C/min below 200°C, 3°C/min between 200 and 300°C, 30°C/min above 300°C; curve 3 – first in air atmosphere at heating rate of 30°C/min below 200°C, 3°C/min between 200 and 300°C, then in nitrogen atmosphere at heating rate of 30°C/min above 300°C.

when thermal stabilization of AN/IA copolymer is performed in oxidative atmosphere, both cyclization and oxidation reactions starts at very low temperature and ends at high temperature along with less amount of heat release.

Effect of oxidative atmosphere on the thermal stability of PAN polymers

TGA of AN/1.0%IA copolymer was measured in nitrogen and air to investigate the effect of oxygen on the stability of PAN at high temperature, as shown in Figure 7. Some relevant data based on Figure 7 is listed in Table III. The curves 1 and 2 compare the influence of time on weight loss between 200 and 900°C in nitrogen by two heating schemes: (1) at heating rate of 30°C/min in the whole temperature range; (2) at heating rate of 30°C/min below 200°C, 3°C/min between 200°C and 300°C, 30°C/min above 300°C. Namely, it spends about 3 min to undergo thermal stabilization process (200–300°C) for the former but about 30 min for the latter. The total weight loss is 55.55 and 65.42% correspondingly. Therefore, longer thermal stabilization time in inert atmosphere can not improve but reduce the stability of PAN.

Similar TGA test is carried out in air under the same heating rate as the second scheme in nitrogen. Comparing between curves 2 and 3 in Figure 7, the TGA curve is steeper in nitrogen than in air, and the total weight loss is much more for the former than for the latter. The whole temperature range can be divided into three intervals: 200–300°C, 300–500°C, and 500–900°C. The first interval is equivalent to the

TABLE III
Relevant Data of Thermal Stability Based on TGA Curves in Figure 7

TGA curves	Initial decomposition temperature (°C)	Weight loss at 300°C (%)	Weight loss at 500°C (%)	Total weight loss (%)
Curve 1	263	11.03	35.45	55.55
Curve 2	281	12.52	44.73	65.42
Curve 3	225	4.89	12.71	34.65

often used temperature range for thermal stabilization, the second and the third intervals correspond to low temperature carbonization. It can be seen that the weight loss from 200 to 300°C in air is about 4.89%, much less than that in nitrogen, 12.52%. After heated in air, the sample is successively heated in nitrogen from 300 to 900°C. The weight loss of this period is ~ 30%, which is much lower than the corresponding weight loss in nitrogen ~ 53%.

From the results of TGA, conclusions can be drawn that oxygen can greatly improve the stability of AN/1.0%IA copolymer not only in thermal stabilization process but in the successive carbonization process at higher temperature.

Influential mechanism of oxidative and nonoxidative atmospheres

Cyclization and oxidation are the two main reactions of thermal stabilization of PAN in oxidative atmosphere. The cyclization reaction is reported to be initiated through a radical mechanism in the case of PAN homopolymer but an ionic mechanism in the presence of acidic comonomers.^{1,14}

For copolymer, the —OH bond of carboxylic group breaks in cyclization reaction, producing carboxylate ion with negative charge on the oxygen. The pair of electrons transfers from oxygen to nitrogen of adjacent nitrile group as a result of the formation of C—O bond. This process continues as the pair of electrons transfers from nitrogen to adjacent nitrogen with the formation of C—N bond. Therefore, if thermal stabilization of PAN copolymer proceeds in air, more ionic active sites, namely the pair of electrons, will be generated by oxidative dehydrogenation. If it proceeds in inert atmosphere like argon, higher temperature is necessary for the generation of ionic active sites. This mechanism accounts for why cyclization reaction of AN/IA copolymers initiates at much lower temperature in air than in argon. It also gives a reasonable explanation for why inert atmosphere has little influence on the cyclization reaction of copolymers with different IA contents.

For PAN homopolymer, the free radicals are generated by homolysis bond fission at a higher temperature producing an odd electron on the nitrogen of the nitrile group. This odd electron helps in forming a bond between this nitrogen and the carbon of the

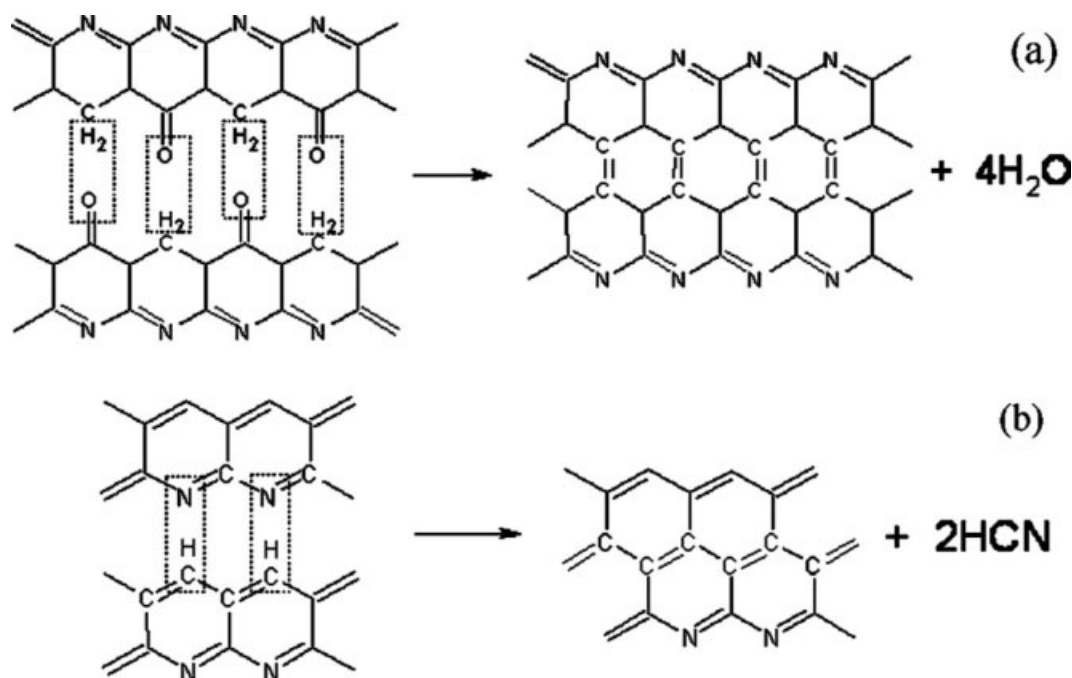


Figure 8 Dehydrogenation reaction mechanisms during carbonization process (a) in form of H₂O; (b) in form of HCN.

adjacent nitrile group by using one of the electrons of the nitrile group. This results in the production of an odd electron on the nitrogen of the latter nitrile group, which helps continue the reaction. Thus, high temperature but not oxidative atmosphere is the main factor for the cyclization reactions of PAN homopolymer.

Our experimental results are consistent with the study by Beltz and Gustafson.¹⁵ Their work concludes that cyclization in oxidizing environments exhibits no induction period for the IA copolymers, but homopolymer PAN still exhibits an induction period. This confirms that oxygen can enhance the cyclization reaction of ionic mechanism.

Of the thermal stabilization reactions of PAN, oxidation is the least understood reaction. From Figures 3, 5, and 6, it can be seen that in air atmosphere the exothermic curves derived from oxidation and cyclization reactions overlap each other by different degree dependent on different contents of IA comonomer. Oxygen containing groups may form at rather lower temperature for AN/IA copolymer with higher IA content than for PAN homopolymer.

A lot of documents show that oxygen is bonded in the molecular chain by complex reactions. In this work, we mean not to discuss the exact bonding form of oxygen, but to prove that the introduction of oxygen has great importance for the stability of the chain structure by the experiment results. Once the ladder structure bonded with oxygen groups has formed during thermal stabilization in oxidative atmosphere, the oxygen groups favor for oxidative dehydrogenation. A large part of hydrogen atoms are removed in form of H₂O [see Fig. 8(a)] and some others are removed in form of HCN [see Fig. 8(b)], which facilitates the formation of carbon networks and insures high carbon yield during carbonization process. If thermal stabilization takes place in inert atmosphere, most of hydrogen atoms are removed by HCN during carbonization process and inevitably leads to low carbon yield. Therefore, the total weight loss in the case of thermal stabilization being performed in air (see the curve 3 in Fig. 7) is far less than that in the case of in nitrogen (see the curve 2 in Fig. 7).

CONCLUSIONS

The independent and combined effects of IA comonomer and atmosphere on thermal stabilization reactions of PAN homopolymer and AN/IA copolymers have been studied in detail. IA comonomer itself hardly has any effect on the initiation temperature, peak temperature or the amount of heat release of cyclization reaction in inert atmosphere; oxidative atmosphere itself has a little facilitating effect on cyclization reaction if no IA comonomer is applied. Only when the thermal stabilization of AN/IA copolymer is performed in oxidative atmosphere, both cyclization and oxidation reactions starts at very low temperature and ends at high temperature along with much less amount of heat release than that of PAN homopolymer. The introduction of oxygen into the molecular chains has great importance for the stability of the chain structure, which facilitates the formation of carbon networks and insures high carbon yield during carbonization process.

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