

## Influence of Oxygen on the Stabilization Reaction of Polyacrylonitrile Fibers

Shijie Xiao,<sup>1,2</sup> Bin Wang,<sup>1</sup> Chun Zhao,<sup>1</sup> Lianghua Xu,<sup>1</sup> Biaohua Chen<sup>2</sup>

<sup>1</sup>National Carbon Fiber Engineering Research Center, College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China

<sup>2</sup>State Key Laboratory of Chemical Resource Engineering, College of Chemical Engineering, Beijing University of Chemical Technology, Beijing 100029, China

Correspondence to: L. Xu (E-mail: xulh@mail.buct.edu.cn)

**ABSTRACT:** Stabilized polyacrylonitrile (PAN) fibers pretreated under N<sub>2</sub> and air atmospheres were prepared and their thermal behaviors were compared by differential scanning calorimetry and thermogravimetry methods. The results indicated that the subsequent stabilization reaction of PAN pretreated in air was more obvious than that in N<sub>2</sub>. In addition, the thermal stability of PAN pretreated in air is better than that in N<sub>2</sub>. The structural analysis by Fourier transform infrared spectroscopy and solid state <sup>13</sup>C nuclear magnetic resonance implied that oxygen promoted dehydrogenation and a compact conjugated structure was formed in PAN. In addition, the C=O structures were generated in air and increased gradually with temperature. The contents of oxygen in PAN fibers studied by elemental analysis corresponded with the structural evolution. Further investigation indicated that the C=O structures helped dehydration and also promoted formation of the cross-linked structures. A mechanism for structural evolution in PAN during stabilization in air was proposed. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** polyacrylonitrile; stabilization; thermal behavior; oxygen-bearing structure

Received 31 May 2011; accepted 19 April 2012; published online

DOI: 10.1002/app.37930

### INTRODUCTION

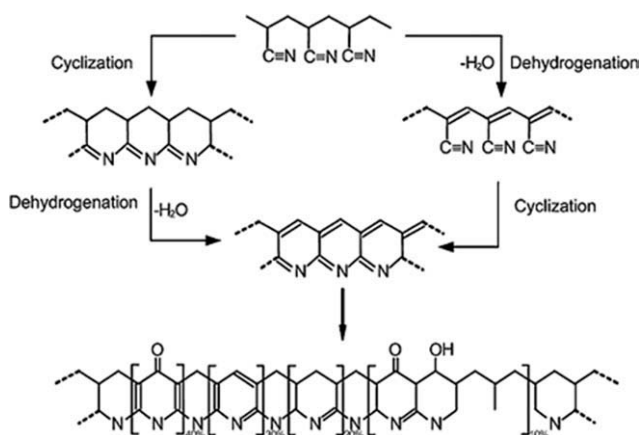
Polyacrylonitrile (PAN) fibers are used widely as precursors for fabricating high performance carbon fibers. The thermal stabilization is one of the key processes in carbon fiber production, during which PAN fibers are converted to infusible, nonflammable fibers by heating to 180–280°C for about 1 h. During this process, complex chemical reactions occur, accompanied by significant enthalpy changes, with the main reactions being cyclization, oxidation, and fragmentation. The chemical reaction mechanism during the thermal stabilization of PAN has been investigated by many researchers.<sup>1–15</sup> In an inert atmosphere, cyclization of the PAN molecular chains and the liberation of micromolecular gases take place. In air, the situation becomes much more complicated owing to the presence of oxygen. Figure 1 shows the chemical reaction mechanism for the thermal stabilization of PAN<sup>13</sup> that is accepted by most of the investigators.

Stabilization of PAN is conducted in air because better mechanical properties and higher carbon yields are obtained than when stabilized in an inert atmosphere. An important topic, the influence of oxygen on the chemical reactions during the thermal stabilization of PAN has been focused on throughout the time

from the 1950s until now.<sup>16–26</sup> By studying the kinetics of the cyclization and oxidation of PAN in air and nitrogen, Fitzer and Müller<sup>16</sup> reported that oxygen promotes the initiation of cyclization as an initiator for the formation of activated centers but does not catalyze the cyclization itself. Beltz and Gustafson<sup>18</sup> examined the cyclization kinetics of PAN in nitrogen, 10.5 and 21% oxygen atmospheres and proposed that oxygen-retarded cyclization. Watt and Johnson<sup>11</sup> studied the stabilization of two PAN copolymers and concluded that the formation of the cyclized polymer was a prerequisite for oxidation. Sivy et al.<sup>24</sup> conducted degradation studies on acrylamide containing PAN copolymers in air at 200°C and concluded that there were two competing reactions, one of which was the generation of a 1,1,2 tri-substituted olefin structure through a reaction with oxygen during the primary stage of the thermal stabilization.

Although the influence of oxygen on the stabilization reaction of PAN fibers has been studied throughout the history of carbon fiber fabrication, the influence mechanism of oxygen is not completely clear due to the complex reaction during the stabilization. In this work, it was found that the influence of oxygen on the stabilization reaction mainly contains two aspects:

© 2012 Wiley Periodicals, Inc.



**Figure 1.** Proposed chemical reaction mechanism for PAN stabilization.

(a) Oxygen promotes the dehydrogenation and compact conjugate structures are formed in PAN macromolecules; (b) The oxygen-bearing structures are generated in PAN macromolecules and impel the subsequent stabilization reaction. The latter has been seldom reported in the literature.

In this study, the thermal behaviors and structures of partly stabilized PAN fibers pretreated under  $N_2$  and air atmospheres were investigated by differential scanning calorimetry (DSC), thermogravimetry (TG), Fourier transform infrared spectroscopy (FTIR), solid state  $^{13}C$  nuclear magnetic resonance (NMR), and elemental analysis (EA). The influence of medium oxygen on the thermal stabilization reaction of PAN and the influence of the oxygen-bearing structures on the subsequent stabilization reaction was investigated in depth.

## EXPERIMENTAL

### Materials

A commercial PAN fiber sample containing 1% itaconic acid (IA) and 1% methacrylate (MA) comonomers was obtained to prepare the precursor fiber, which was thermally stabilized in air or nitrogen under different conditions. These prepared fiber samples are listed in Table I together with the stabilization conditions. The precursor fiber sample was also used as the reference material. These samples were subjected to characterization by DSC, TG, FTIR, NMR, and EA.

### Measurements

#### Differential Scanning Calorimetry

The enthalpy change of the prepared fiber samples during the heating process was investigated using a TA instrument DSC Q100 from 40 to 400°C under an  $N_2$  atmosphere at heating rate of 5°C/min. The sample size for the measurements was about 3 mg. The gas flow rate was 50 mL/min.

**Thermogravimetry.** The mass loss of PAN short fibers was investigated using a Netzsch TG 209F3 instrument. About 2 mg of samples were evenly dispersed in an  $Al_2O_3$  pan and scanned at various heating rate of 5°C/min under  $N_2$  atmosphere between 40 and 400°C.

**Fourier Transform Infrared Spectroscopy.** Infrared spectral measurements were performed using a Nicolet 5700 instrument

**Table I.** PAN Fiber Samples

Sample numbers	Atmosphere	Treating temperature (°C)	Treating time (min)
Precursor			
S0	/	/	/
stabilized fibers			
S1	$N_2$	220	120
S2	Air	180	120
S3	Air	200	120
S4	Air	220	120
S5	Air	240	120

over 4000–400  $cm^{-1}$  at 16  $cm^{-1}$  resolution. KBr disks were prepared by homogeneously mixing KBr and sample powder.

**Solid state  $^{13}C$  Nuclear Magnetic Resonance.** The cross-polarization/magic angle spinning (CP/MAS) solid state  $^{13}C$ -NMR spectra of the fiber samples were measured by a Bruker AV-300 NMR spectrometer. A resonance frequency of 73.5 MHz, CP contact time of 3 ms and delay time of 5 s were employed. The probe size of CP/MAS was 4 mm and the rotation speed of the rotor was 8 KHz. 300–3175 scans were required to obtain a good signal-to-noise ratio. Tetramethylsilane (TMS) was used as the reference to determine the chemical shifts of structures in samples.

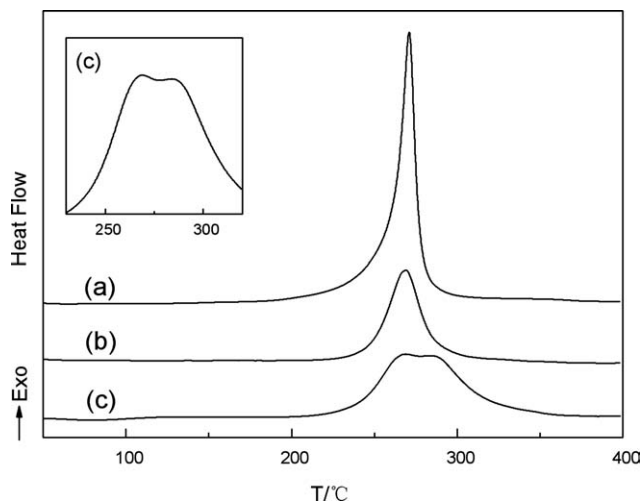
**Elemental Analysis.** The oxygen contents of PAN fiber samples were determined by a ThermoQuest (Italy) EA1112 elemental analysis with full automation. An oxygen model was employed to obtain accurate oxygen content.

## RESULTS AND DISCUSSION

### Thermal Behaviors of PAN Stabilized Fibers After Heat

#### Treatment in Different Atmospheres

Figure 2 shows the DSC curves of PAN precursor (S0) and the stabilized PAN fibers after heat-treatment in  $N_2$  (S1) and air



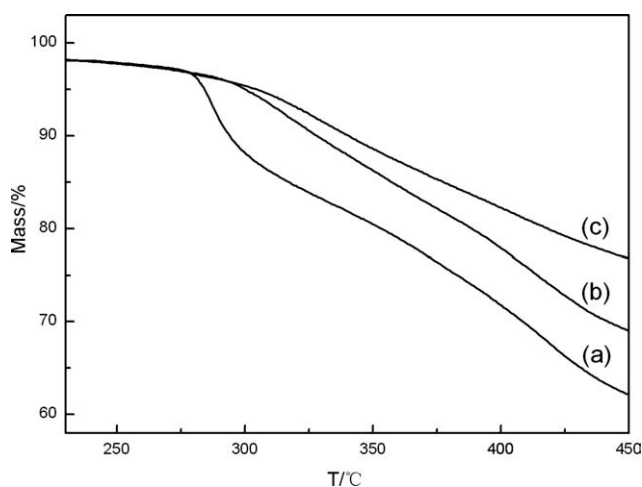
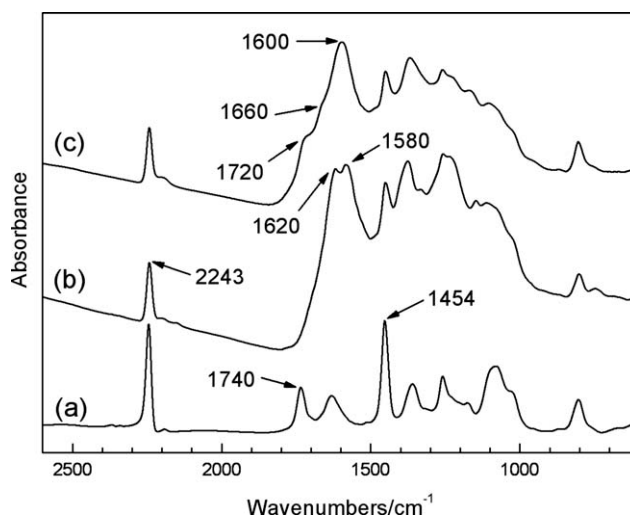
**Figure 2.** DSC curves of stabilized PAN fibers heat-treated under different atmospheres: (a) S0; (b) S1; (c) S4.

**Table II.** Characteristic Parameters in Figure 2

Sample numbers	$T_i$ (°C)	$T_p$ (°C)	$T_f$ (°C)	$\Delta H$ (J/g)
S0	204	271	306	577.3
S1	209	269	312	306.9
S4	208	269, 285	367	504.0

(S4), respectively. These curves were obtained under the DSC operating conditions described in Section Differential scanning calorimetry. Significant differences can be found in the DSC curves between S1 and S4. S1 exhibits the same exothermic peak shape as S0, whereas S4 shows a clearly different DSC curve, with two obvious exothermic peaks. The doublet exothermic peaks indicate that at least two types of reactions took place. That is to say, different structures were formed in S1 and S4 after the heat treatment. By analyzing the difference in detail, the characteristic parameters of these three DSC curves are shown in Table II, where  $T_i$  is the initial temperature,  $T_p$  is the peak temperature,  $T_f$  is the final temperature, and  $\Delta H$  is the change of enthalpy. S1 and S0 have similar  $T_i$ ,  $T_p$ , and  $T_f$  values, whereas  $T_f$ (S4) is much higher than  $T_f$ (S1). This indicates that the range of heat release for S4 is wider than that for S1. In addition, the order of the value for  $\Delta H$  is  $\Delta H(S1) < \Delta H(S4) < \Delta H(S0)$ .  $\Delta H$  reflects the subsequent stabilization reaction of PAN stabilized fibers. Cyclization of PAN precursor occurs during the heat-treatment process in either  $N_2$  or air, so the values of  $\Delta H(S1)$  and  $\Delta H(S4)$  are lower than that of  $\Delta H(S0)$ . It is worth noting that the value of  $\Delta H(S4)$  is much higher than that of  $\Delta H(S1)$ , which implies that the extent of the subsequent stabilization reaction of S4 is much higher than that of S1.

Figure 3 shows the TG curves of PAN precursor (S0) and the stabilized PAN fibers after heat-treatment in  $N_2$  (S1) and air (S4), respectively. The mass loss of PAN precursor is higher than that of stabilized PAN fibers. This is because cyclized structures make stabilized fibers have better thermal stability. It can be found that the mass loss of S4 is less than that of S1, which indicates that S4 has better thermal stability than S1.

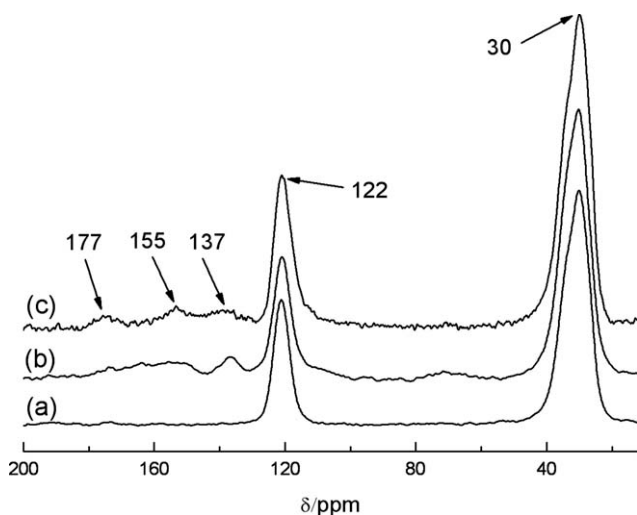
**Figure 3.** TG curves of stabilized PAN fibers heat-treated under different atmospheres: (a) S0; (b) S1; (c) S4.**Figure 4.** FT-IR spectra of stabilized PAN fibers heat-treated under different atmospheres: (a) S0; (b) S1; (c) S4.

Apart from their atmosphere, S1 and S4 were heat-treated under identical conditions. In air, the oxidation reaction of the PAN precursor occurs in addition to the cyclization reaction. Oxygen plays a significant role during the stabilization of PAN fibers. Based on the analysis of the thermal behaviors above, a hypothesis can be proposed as follows. In air, oxygen improves the thermal stability of PAN fibers during the stabilization. In addition, the oxygen-bearing structures are generated in PAN fibers and promote the subsequent stabilization reaction. Therefore, the two exothermic peaks in DSC curve and less mass loss in TG curve of PAN fibers are observed in air.

#### Structural Analysis of PAN Stabilized Fibers After Heat Treatment in Different Atmospheres

In order to identify the structures formed in PAN fibers after the heat treatment, FTIR and solid state  $^{13}C$ -NMR were employed to analyze the structural changes in PAN macromolecular chains. The FTIR and NMR spectra of S0, S1, and S4 are shown in Figures 4 and 5, respectively.

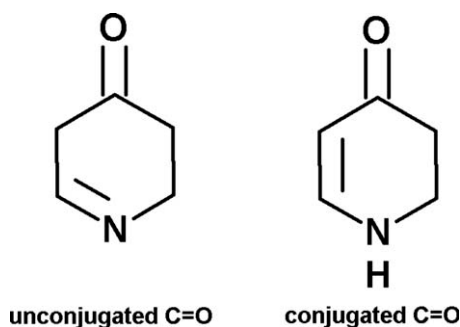
Figure 4(a) shows the spectrum for the PAN precursor (S0). There is a strong absorption band at  $2243\text{ cm}^{-1}$  assigned to the  $\nu_{C\equiv N}$  band (the stretching mode of the nitrile group). The band at  $1454\text{ cm}^{-1}$  is assigned to the  $\delta_{C-H}$  band (the bending vibration of C-H) of methylene, and the band at  $1740\text{ cm}^{-1}$  is assigned to the  $\nu_{C=O}$  band of carboxy for IA copolymer. As shown in Figure 4(b,c), after the heat treatment, all these characteristic bands of the PAN precursor decreased. In Figure 4(b), two new bands at  $1620$  and  $1580\text{ cm}^{-1}$  can be observed, which are assigned to  $\nu_{C-N}$  and  $\nu_{C-C}$ , respectively. Kakida and Tashiro<sup>10</sup> suggested that under an  $N_2$  atmosphere, the stabilized structure does not completely conjugate. The imine-enamine tautomerism results in the splitting of the  $1620\text{ cm}^{-1}$  ( $\nu_{C-N}$ ) and  $1580\text{ cm}^{-1}$  ( $\nu_{C-C}$ ) bands. However, in air, a singlet band at  $1600\text{ cm}^{-1}$  appeared [Figure 4(c)], which may have come from the formation of a fully conjugated structure due to dehydrogenation. It indicates that oxygen promotes dehydrogenation of PAN macromolecules during stabilization. It is worth noting that the bands at  $1660$  and  $1720\text{ cm}^{-1}$  appeared after air



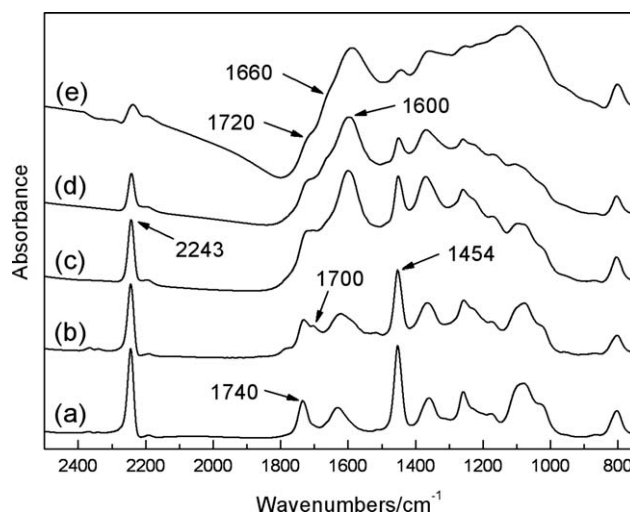
**Figure 5.** Solid state  $^{13}\text{C}$ -NMR spectra of stabilized PAN fibers heat-treated under different atmospheres: (a) S0; (b) S1; (c) S4.

stabilization but could not be observed after  $\text{N}_2$  stabilization. As suggested by Shimada<sup>27</sup> and Ouyang,<sup>1</sup> the band at  $1720\text{ cm}^{-1}$  is due to the unconjugated  $\text{C}=\text{O}$  groups and the  $1660\text{ cm}^{-1}$  band is assigned to the conjugated  $\text{C}=\text{O}$  groups, which are shown in Figure 6. These groups are generated by oxygen uptake reactions.

The NMR spectrum of PAN precursor is shown in Figure 5(a). The resonance at 30 ppm can be attributed to alkyl ( $\text{sp}^3$ ) carbons such as methylene and methane groups and the resonance centered at 122 ppm arises from unsaturated nitrile groups. As shown in Figure 5(b,c), resonances at 137 and 155 ppm can be observed in both spectra. The former is assigned to unsaturated  $\text{C}=\text{C}$  in the polymer backbone and the latter is a contribution from conjugated  $\text{C}=\text{N}$  species. This indicates that regardless of whether stabilization is carried out in  $\text{N}_2$  or air, as the stabilization proceeds, cyclization reactions take place and result in unsaturated carbon structures ( $\text{sp}^2$ ). However, in Figure 5(c), when PAN fibers were heat-treated in air, there was a significant resonance centered at 177 ppm, which could be assigned to carbonyl  $\text{C}=\text{O}$ .<sup>3–5</sup> It is argued that, during the subsequent stabilization, these  $\text{C}=\text{O}$  structures help dehydration and also impel formation of the cross-linked structures. These are exothermic



**Figure 6.** Scheme of oxygen-bearing structures generated in stabilized PAN fibers heat-treated in air.



**Figure 7.** FTIR spectra of stabilized PAN fibers heat-treated under different temperatures in air: (a) S0; (b) S2; (c) S3; (d) S4; (e) S5.

reactions resulting in heat release. In addition, these reactions cause better thermal stability of PAN fibers.

#### Structural Evolution of PAN During Stabilization in Air

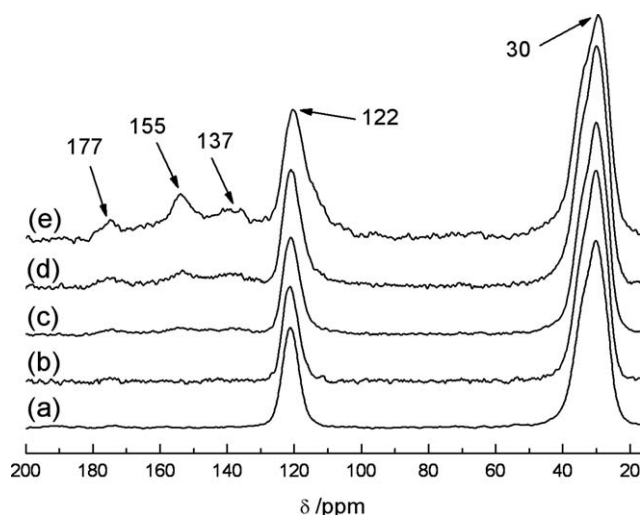
A series of PAN stabilized fibers after heat treatment at different temperatures in air were obtained to investigate the evolution of the oxygen-bearing structures. Figure 7 shows the FTIR spectra of PAN precursor and stabilized fibers after heat treatment at different temperatures. When the temperature increased from 180 to  $240^\circ\text{C}$ , it was found that the bands at 2243 and  $1454\text{ cm}^{-1}$  decreased and the band at  $1600\text{ cm}^{-1}$  increased. This means that cyclization and dehydrogenation reactions occurred. As shown in Figure 7(b), the  $1700\text{ cm}^{-1}$   $\nu_{\text{C}=\text{O}}$  band of the reacted IA appeared and bands at 1620 and  $1580\text{ cm}^{-1}$  could be observed at  $180^\circ\text{C}$ . This indicates that the cyclization reaction is initiated by IA and a tautomeric structure is formed at low temperatures. It is worth noting that the bands at 1720 and  $1660\text{ cm}^{-1}$  could not be observed until PAN was heat-treated at  $200^\circ\text{C}$  and became more obvious with increasing temperature, which implies that oxygen uptake reactions take place, resulting in the formation of the  $\text{C}=\text{O}$  structures at no less than  $200^\circ\text{C}$ .

The NMR spectra of PAN precursor and stabilized fibers after heat treatment at different temperatures are shown in Figure 8. Resonance at 177 ppm appeared in Figure 8(c–e) and the intensity increased with increasing temperature, which corresponds with the FTIR spectra. This implies that the  $\text{C}=\text{O}$  structures were not generated until the heat treatment temperature reached  $200^\circ\text{C}$  and their content increased when PAN fibers were heated at higher temperatures below  $240^\circ\text{C}$ .

Figure 9 shows the oxygen content of PAN stabilized fibers heat-treated at different temperatures in air. With an increasing heat treatment temperature, the oxygen content of PAN macromolecular chains increased. This indicates that more oxygen-bearing structures were generated at higher temperature, again corresponding with the FTIR and NMR results.

According to the above analysis, the mechanism for structural evolution for PAN during stabilization in air is proposed in



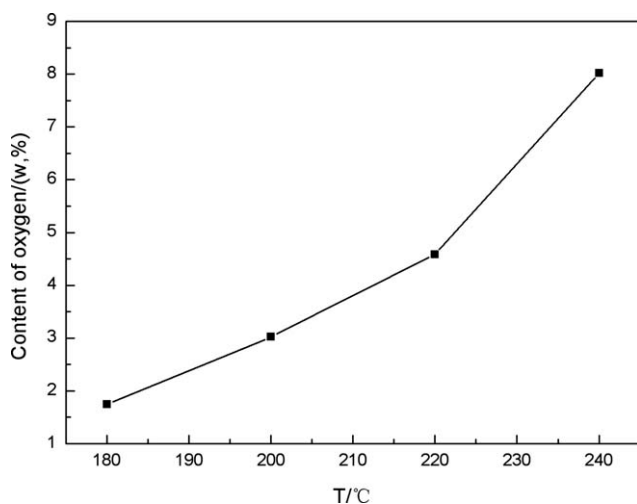


**Figure 8.** Solid state  $^{13}\text{C}$ -NMR spectra of stabilized PAN fibers heat-treated under different temperatures in air: (a) S0; (b) S2; (c) S3; (d) S4; (e) S5.

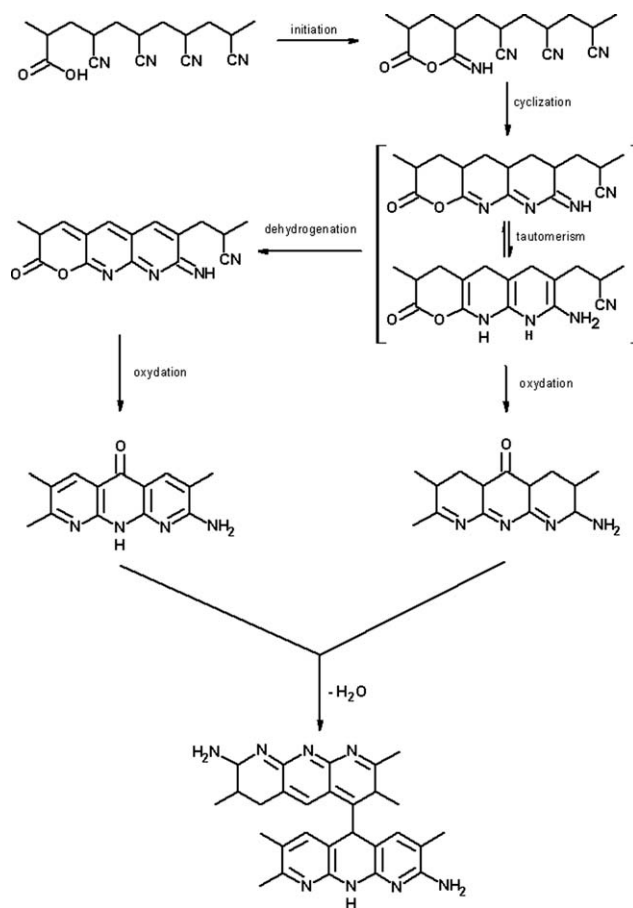
Figure 10. At first, the carboxy groups in IA copolymer induce the cyclization reaction by reacting with the adjacent nitrile groups. The cyclization reaction then occurs and results in forming imine-enamine tautomer structures at  $180^\circ\text{C}$ . When PAN is heated at  $200^\circ\text{C}$ , because of the influence of oxygen, dehydrogenation takes place causing the generation of the conjugated structure. In addition, the  $\text{C}=\text{O}$  structures are generated via oxidation in the cyclic structures. With increasing temperature, the  $\text{C}=\text{O}$  structures react with adjacent hydrogen and dehydration reaction occurs resulting in formation of the cross-linked structures.

### Influence of the Oxygen-Bearing Structures on the Subsequent Stabilization Reaction

PAN stabilized fibers containing different contents of oxygen were obtained under different temperatures. Figure 11 shows the DSC curves of these samples to investigate the influence of

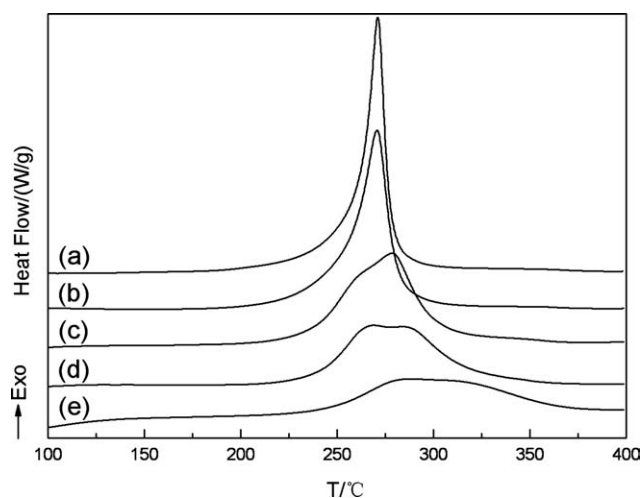


**Figure 9.** Oxygen contents in stabilized PAN fibers heat-treated under different temperatures in air: (a) S0; (b) S2; (c) S3; (d) S4; (e) S5.

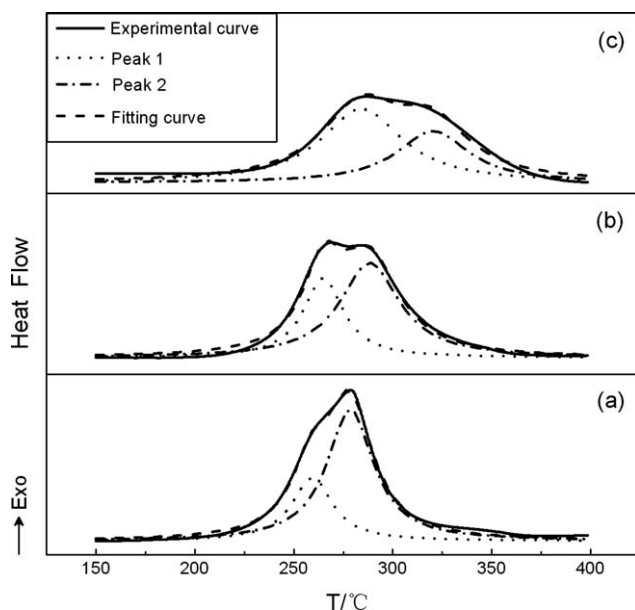


**Figure 10.** Structural evolution during stabilization of PAN in air.

the oxygen-bearing structures on the subsequent stabilization reaction. It can be seen that the doublet exothermic peak appeared at no less than  $200^\circ\text{C}$  and became more obvious with an increase of oxygen in PAN, which is consistent with the evolution of the  $\text{C}=\text{O}$  structures. This indicates that the  $\text{C}=\text{O}$  structures indeed promote the subsequent stabilization reaction.



**Figure 11.** DSC curves of stabilized PAN fibers containing different contents of oxygen: (a) 0%; (b) 1.7%; (c) 3.0%; (d) 4.6%; (e) 8.0%.



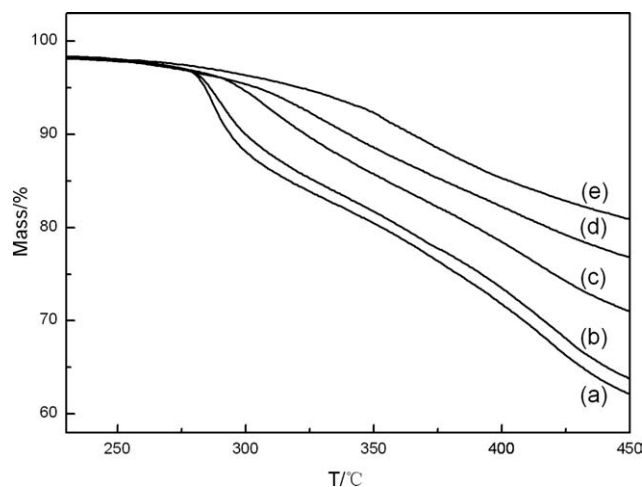
**Figure 12.** DSC peak deconvolution of stabilized PAN fibers containing different contents of oxygen: (a) 3.0%; (b) 4.6%; (c) 8.0%.

To study the subsequent stabilization reaction in more depth, the overlapping peaks in the DSC curves were separated, as shown in Figure 12. In addition, Table III shows further details of the two peaks. With increased contents of oxygen, PAN exhibits a significant tendency for the intensity of peak 1 to increase, while the intensity of peak 2 decreases. It is argued that peak 1 can be assigned to the subsequent stabilization reaction based on the C=O structures and peak 2 should be attributed to the conventional cyclization reaction. On the one hand, more C=O structures were generated in PAN at higher temperature and provided more active sites for the stabilization reaction, resulting in a corresponding increase in the enthalpy of peak 1. On the other hand, when PAN was heated at a higher temperature during the sample preparation process, more nitrile groups were consumed. Therefore, the intensity of peak 2 decreased. In addition, the total enthalpy change of PAN ( $\Delta H_T$ ) also decreased, as shown in Figure 12 and Table III.

Figure 13 shows the TG curves of stabilized PAN fibers containing different contents of oxygen. With increased contents of oxygen, the mass loss of PAN fibers decreases. It indicates that, during the stabilization in air, the C=O structures have obvious action on improving the thermal stability of PAN fibers. This can be explained by the proposed mechanism as follows. The C=O structures promote dehydration and the cross-linked

**Table III.** Characteristic Parameters in Figure 12

Sample	$T_{p1}$ (peak 1) (°C)	$\Delta H_1$ (peak 1) (J/g)	$T_{p2}$ (peak 2) (°C)	$\Delta H_2$ (peak 2) (J/g)	$\Delta H_T$ (J/g)
S3	263	164.4	278	397.4	561.8
S4	269	181.0	285	323.0	504.0
S5	287	233.1	308	143.4	376.5



**Figure 13.** TG curves of stabilized PAN fibers containing different contents of oxygen: (a) 0%; (b) 1.7%; (c) 3.0%; (d) 4.6%; (e) 8.0%.

structures are generated in PAN macromolecules. Therefore, the C=O structures are beneficial to enhance the thermal stability of PAN fibers.

## CONCLUSIONS

Thermal behaviors of partly stabilized PAN fibers pretreated under  $N_2$  and air atmospheres were compared. The DSC curve of PAN pretreated in air shows two obvious exothermic peaks, which are very different from that of PAN pretreated in  $N_2$ , with only a single exothermic peak. In addition, the thermal stability of PAN pretreated in air is better than that in  $N_2$ . The structural analysis by FTIR and solid state  $^{13}C$ -NMR methods indicated that oxygen promoted the dehydrogenation and the conjugated structure was formed in PAN. The C=O structures were generated when PAN fibers were heat-treated at 220°C in air. It was proposed that the C=O structures could react with adjacent hydrogen and dehydration reaction occurs resulting in formation of the cross-linked structures. Further investigation implied that the C=O structures were not generated until the heat-treated temperature reached 200°C and their contents increased gradually with temperature. The contents of oxygen in PAN fibers corresponded with the structural evolution. The influence of oxygen on the subsequent stabilization reaction was studied. The results indicated that the C=O structures were beneficial to promote the subsequent stabilization reaction and improve the thermal stability of PAN, which is consistent with the proposal.

## ACKNOWLEDGMENTS

Financial support from the National Basic Research Program of China (2011CB605602) is gratefully acknowledged.

## REFERENCES

- OuYang, Q.; Lu, C.; Wang, H. J.; Li, K.X. *Polym. Degrad. Stab.* **2008**, *93*, 1415.
- Bajaj, P.; Sreekumar, T. V.; Sen, K. *Polymer* **2001**, *42*, 1707.

3. Fochler, H. S.; Mooney, J. R.; Ball, L. E.; Boyer, R. D.; Grasselli, J. G. *Spectrochim Acta A* **1985**, *41*, 271.
4. Martin, S. C.; Liggat, J. J.; Snape, C. E. *Polym. Degrad. Stab.* **2001**, *74*, 407.
5. Usami, T.; Itoh, T.; Ohtani, H.; Tsuge, S. *Macromolecules* **1990**, *23*, 2460.
6. Xiao, S. J.; Lv, H. H.; Tong, Y. J.; Xu, L. H.; Chen, B. H. *J. Appl. Polym. Sci.* **2011**, *122*, 480.
7. Xue, T. J.; Mckinney, M. A.; Wilkie, C. A. *Polym. Degrad. Stab.* **1997**, *58*, 193.
8. Ouyang, Q.; Cheng, L.; Wang, H. J.; Li, K. X. *J. Therm. Anal. Calorim.* **2008**, *94*, 85.
9. He, D. X.; Wang, C. G.; Bai, Y. J.; Lun, N.; Zhu, B.; Wang, Y. X. *J. Mater. Sci.* **2007**, *42*, 7402.
10. Kakida, H.; Tashiro, K. *Polym. J.* **1998**, *30*, 463.
11. Watt, W.; Johnson, W. *Nature* **1975**, *257*, 210.
12. Coleman, M. M.; Sivy, G. T.; Painter, P. C.; Snyder, R. W.; Gordon, B. *Carbon* **1983**, *21*, 255.
13. Rahaman M. S. A.; Ismail, A. F.; Mustafa, A. *Polym. Degrad. Stab.* **2007**, *92*, 1421.
14. Hou, Y. P.; Sun, T. Q.; Wang, H. J.; Wu, D. *J. Appl. Polym. Sci.* **2009**, *114*, 3668.
15. Cui, C. S.; Yu, L. N.; Wang, C. G. *J. Appl. Polym. Sci.* **2010**, *117*, 1596.
16. Fitzer, E.; Müller, D. J. *Carbon* **1975**, *13*, 63.
17. Collins, G. L.; Thomas, N. W.; Williams, G. E. *Carbon* **1988**, *26*, 671.
18. Beltz, L. A.; Gustafson, R. R. *Cabon* **1996**, *34*, 561.
19. Bashir, Z. *Cabon* **1991**, *29*, 1081.
20. Fitzer, E.; Frohs, W.; Heine, M. *Carbon* **1986**, *24*, 387.
21. Yu, M. J.; Wang, C. G.; Bai, Y. J.; Xu, Y.; Zhu, B. *J. Appl. Polym. Sci.* **2008**, *107*, 1939.
22. Yu, M. J.; Wang, C. G.; Bai, Y. J.; Wang, Y. X.; Xu, Y. *Polym. Bull.* **2006**, *57*, 757.
23. Morita, K.; Miyachi, H.; Hiramatsu, T. *Carbon* **1981**, *19*, 1.
24. Sivy, G. T.; Gordon, B.; Coleman, M. M. *Carbon* **1983**, *21*, 573.
25. Takahagi, T.; Shimada, I.; Fukuhara, M.; Morita, K.; Ishitani, A. *J. Polym. Sci. Polym. Chem.* **1986**, *24*, 3101.
26. Sugimoto, T.; Sawai, D.; Kanamoto, T. *Tanso* **2007**, *226*, 13.
27. Shimada, I.; Takahagi, T.; Morita, K.; Ishitani, A. *J. Polym. Sci. Polym. Chem.* **1986**, *24*, 1989.