

# Mass DSC/TG and IR Ascertained Structure and Color Change of Polyacrylonitrile Fibers in Air/Nitrogen During Thermal Stabilization

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**ABSTRACT:** The structure evolution was studied by mass spectrum (MS), differential scanning calorimetry (DSC) and thermogravimetry (TG), Fourier transform infrared (FTIR) spectroscopy. The results indicated that the C=N and C=C groups appeared gradually with the increase of the temperature in air and nitrogen. The C=O groups appeared because of oxidative reaction in air. The C=N, C=C and C=O groups were all chromophores. The effect of conjugated C=N and C=C on the absorption of the visible light was shifted to longer wavelengths and indicated  $\pi$ - $\pi^*$  transition. There was a strong bathochromic effect as the number of C=C bonds were increased. The effect of C=O and -NH<sub>2</sub> on the absorption of the visible light was shifted to longer wavelengths and indicated  $n$ - $\pi^*$

transition. Oxygen could facilitate chemical reactions in air. Hence, the color of PAN in air was deeper than in nitrogen at the same temperature. The structural change of PAN in air was faster and more complex than in nitrogen. PAN fibers treated in air turned black after 230°C. However, PAN fibers turned black at 350°C in nitrogen. The MS and FTIR indicated that cyclization occurred before dehydrogenation during stabilization in air and nitrogen. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 462–468, 2010

**Key words:** polyacrylonitrile (PAN) fiber; differential scanning calorimetry (DSC); FTIR; mass spectrometry; structure change; color change; thermal stabilization

## INTRODUCTION

Thermal degradation of PAN fibers has been the subject of intensive research activity over the years. It is the precursor material for carbon fiber, an outstanding engineering material. It has been reported<sup>1,2</sup> to undergo chemical reactions in stages on thermal treatment. The following chemical reactions are believed to take place: (1) cyclization of nitrile groups leading to hydronaphthiridine rings (cyclization)<sup>3–5</sup>; (2) oxidation of hydrogenation leading to a certain degree of aromatization (dehydrogenation)<sup>6</sup>; and (3) oxidation of hydronaphthiridine rings leading mainly to acridone and some other structure (oxidative reaction).<sup>7</sup> During stabilization, the bulk of the chemical changes are accompanied by release of exothermic energy and are able to thermochemical analysis.<sup>8,9</sup> Among these chemical reactions, dehydrogenation, cyclization are the main two processes occurring during early stabilization of PAN fibers. Fitzer and Muller<sup>10</sup> have proposed that

dehydrogenation occurs prior to cyclization while according to previous literature,<sup>3,11–14</sup> the two processes are occurring simultaneously. Therefore, the problem which reaction occurs earlier is uncertain. During stabilization, the color of PAN fibers changes interestingly with the increase of temperature. The higher the temperature is, the deeper the color is. The color of PAN fibers treated in the presence of air is deeper than in the presence of nitrogen at the same temperature. Because of these phenomena, we conclude that the color changes may have the relation with the structure changes. The relation between the color changes and structure changes has been rarely reported.

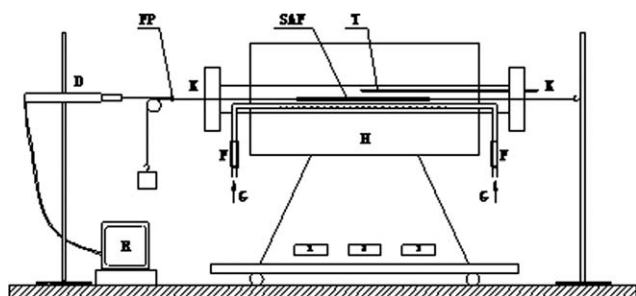
In this article, MS, FTIR, DSC/TG, etc., have been employed to discuss the relation between the color changes and structure changes. Studies were carried out to confirm the order of cyclization and dehydrogenation.

## EXPERIMENTAL

### Precursor

The selected PAN precursor was supplied by Huitong. (Yangzhou, China) in tows of 3000 fibers with an average density of 1.18 g/cc and a mean

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**Figure 1** Apparatus used for thermal strain measurements: SAF-PAN Fiber T-Thermocouple K-Kevlar FP-Fixed Point F-Flowmeter G-Purge Gas D-Displacement Pickup H-Zone Furnace R-paperless recorder.

diameter of 12.4  $\mu\text{m}$ . This precursor fiber was most probably a copolymer of acrylonitrile, methylacrylate, and itaconic acid. The designation P is given to the precursor fiber.

### Stabilization

Stabilization was carried out in batch scale furnace (Fig. 1). Furnace temperature was measured by thermocouple placed in the furnace tube. For constant tension modes experiments, the precursor fiber was free to shrink and stabilization was carried out in continuously flowing air and nitrogen (3.3 L/min). The heat treatment temperature was designated 150, 180, 200, 210, 220, 230, 240, 250, 260, 270, 285, and 350°C. The heating rate is 2°C/min. The designations P<sub>1</sub>-P<sub>12</sub> are given to the samples in the presence of air. The designations p<sub>1</sub>-p<sub>12</sub> are given to the samples in the presence of nitrogen.

### MS

MS measurements were made on Omnistar 200 mass spectroscopy (Blazers Ltd., Blazers, Switzerland). The heating rate is programmed at 2°C/min from 30 to 400°C. The sample size was 4–10 mg. The air and nitrogen atmosphere were maintained over the sample. The gas flow is 40 mL/min.

### FTIR

Infrared spectroscopy was performed to observe the structure changes of PAN fibers. FT-IR measurements were made on a Nicolet (Madison, WI) Magna 550 Fourier transform infrared spectrometer using a resolution of 2  $\text{cm}^{-1}$  and 64 scans per sample.

### DSC/TG

DSC/TG of PAN fibers was carried out on a NETZSCH STA 409 instrument (NETZSCH-Gerätebau GmbH, Germany). The heating rate was 2°C/

min and the sample size was 4–10 mg. The air and nitrogen atmospheres were maintained over the samples.

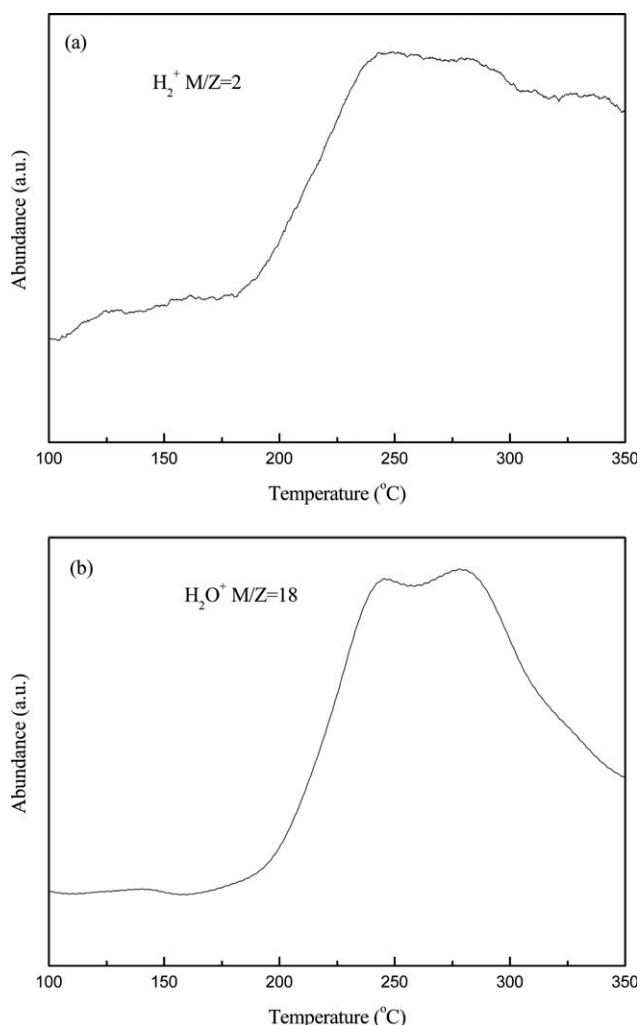
### Density

The density of various fibers was obtained at 25°C with the gradient column. The column consisted of a mixture of toluene ( $d = 0.866 \text{ g/cc}$ ) and carbon tetrachloride ( $d = 1.585 \text{ g/cc}$ ) with a gradient of 1.00–1.60 g/cc.

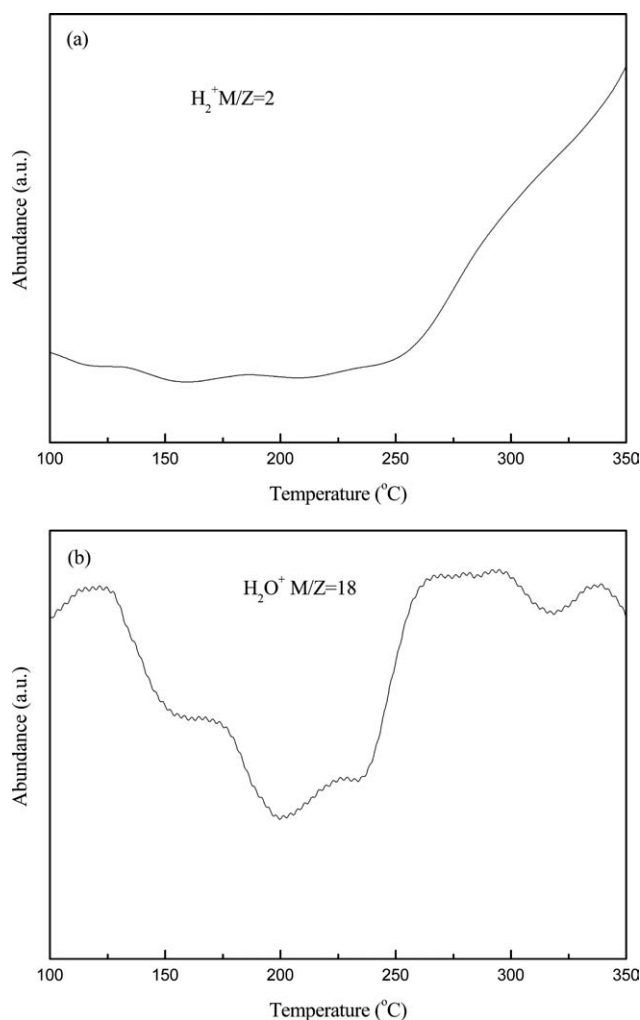
## RESULTS AND DISCUSSION

### MS analysis

During stabilization, PAN undergoes some chemical reactions. Dehydrogenation reaction is one of these chemical reactions.<sup>15</sup> In our experiment, the mass measurements were used to confirm the initial temperature of dehydrogenation reaction. Figure 2



**Figure 2** Abundance of ion current for PAN fibers heated in air at the heating rate of 2°C/min: (a)  $\text{H}_2^+$   $M/Z = 2$ , (b)  $\text{H}_2\text{O}^+$   $M/Z = 18$ .



**Figure 3** Abundance of ion current for PAN fibers heated in nitrogen at the heating rate of 2°C/min: (a)  $H_2^+$   $M/Z = 2$ , (b)  $H_2O^+$   $M/Z = 18$ .

shows the abundance of some ion currents for PAN fibers heated in air at the heating rate of 2°C/min. The curves indicate that the elimination of hydrogen in the form  $H_2$ ,  $H_2O$  begins at about 180°C, 160°C, separately.

Figure 3 shows the abundance of some ion currents for stabilized PAN fibers in nitrogen at the heating rate of 2°C/min. From Figure 3, it is recognized that the elimination of hydrogen in the form  $H_2$ ,  $H_2O$  begins at about 260, 240°C, separately. As aforementioned, the initial temperature of dehydrogenation in air is lower than in nitrogen. This is because that there is oxygen in air. Oxygen can facilitate the dehydrogenation reaction.<sup>10</sup> Therefore, the initial temperature of dehydrogenation in air is lower than in nitrogen.

### Coloration analysis

When PAN fibers are heat treated, the surface color will change from white to yellow, brown and even-

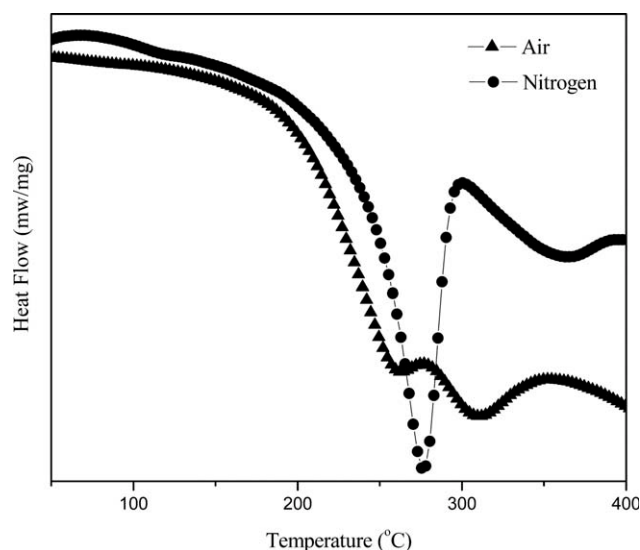
**TABLE I**  
The Color Changes of PAN Fibers Treated in Air and Nitrogen with the Rising of the Temperature

Temperature (°C)	Air	Nitrogen
PAN fiber	White	White
150	Light yellow	Light yellow
180	Golden yellow	Light yellow
200	Dark yellow	Golden yellow
210	Dark brown	Golden yellow
220	Dark brown	Yellow
230	Black	Yellow
240	Black	Dark yellow
260	Black	Light brown
270	Black	Brown
285	Black	Dark brown
350	Black	Black

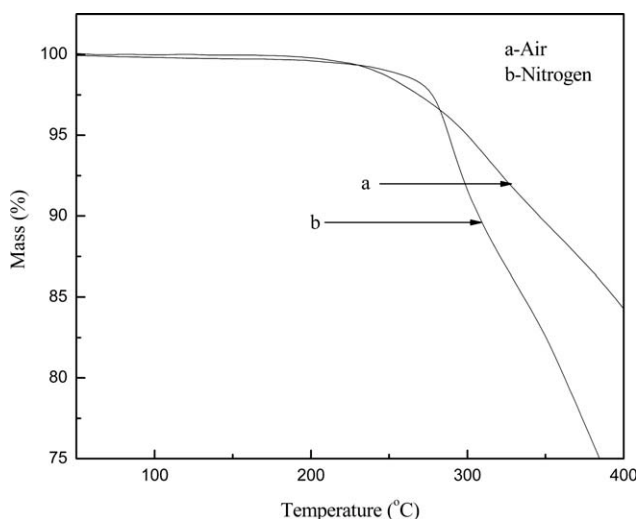
tually black with the rising of temperature. Table I shows the color changes of PAN fibers treated in air and nitrogen with the rising of temperature. From Table I, it can be seen that the color of PAN fibers treated in air is deeper than in nitrogen at the same temperature above 150°C. PAN fibers turn black in air after 230°C. However, PAN fibers turn black at 350°C in nitrogen.

### DSC/TG analysis

Figure 4 shows the DSC patterns of precursor fibers treated in air and nitrogen. From this figure, there are two exothermic peaks in air. These two peaks in air start at about 198°C, end at about 348°C and center at around 264 and 309°C. There is an exothermic peak which starts at about 240°C, ends at about 299°C and centers at around 275°C in nitrogen. Peak I in air is because of the cyclization/thermal stabilization reactions.<sup>16</sup> Peak II in air has been reported



**Figure 4** DSC patterns of precursor fibers treated in air and nitrogen.



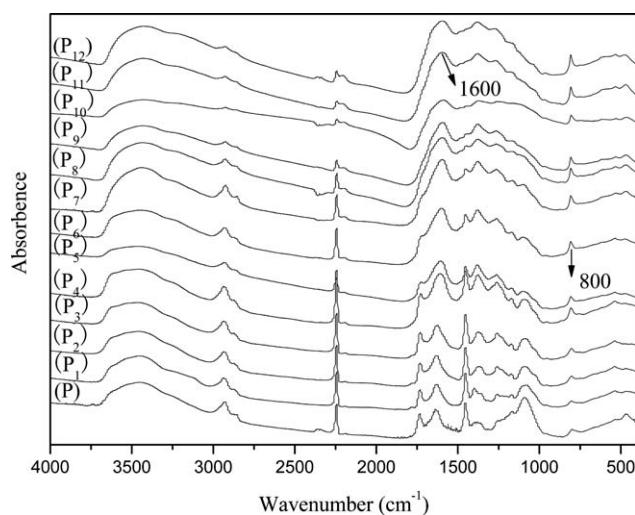
**Figure 5** TG patterns of Precursor fibers treated in nitrogen and air.

before and has been attributed to additional cross-linking reactions.<sup>17</sup> The peak in nitrogen is because of cyclization and dehydrogenation.<sup>16,17</sup>

The corresponding TG curves, synchronously recorded with the DSC curves, of the polymers are presented in Figure 5. As it can be seen from Figure 5, weight loss is very small in air and nitrogen below 230°C. When the temperature is up to 300°C, weight loss becomes quite rapid. After about 282°C, weight loss of PAN fibers in nitrogen becomes larger than in air. During this temperature range in air, on the one hand fragmentation of polymer chains occurs producing volatile particles leading to weight loss, on the other hand the oxygen uptake reactions taking place cause a certain amount of weight gain through the generation of oxygen-containing groups. Thus, the net weight loss is the total of weight loss and weight gain. However, there is only fragmentation of polymer chains. The volatile particles lead to weight loss. This is the reason that weight loss of PAN fibers in nitrogen becomes larger than in air after about 282°C. In combination with the DSC and TG results, we can conclude that the reaction mechanism of PAN stabilized in air is much different from in nitrogen.

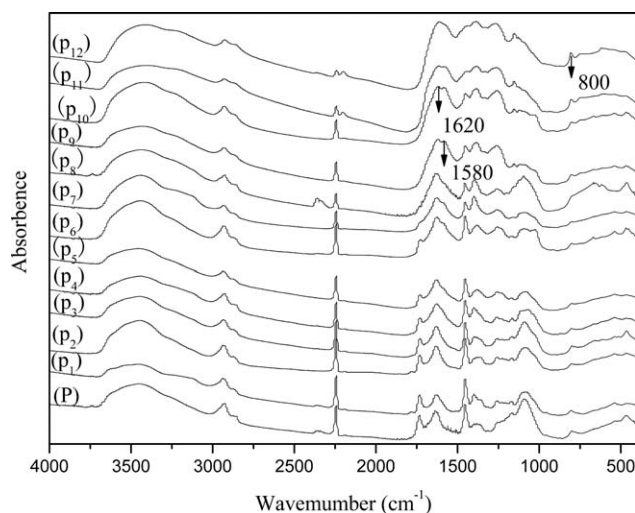
### FTIR analysis

Figures 6 and 7 are the FTIR spectra of the samples treated in air and nitrogen. The principal vibrations, some of which can be assigned according to the literature,<sup>18,19</sup> are at 2940  $\text{cm}^{-1}$  ( $\nu_{\text{as}} \text{CH}_2$ ), 2873  $\text{cm}^{-1}$  ( $\nu_{\text{s}} \text{CH}_2$ ), 2240  $\text{cm}^{-1}$  ( $\nu \text{CN}$ ), 1455  $\text{cm}^{-1}$  ( $\delta \text{CH}_2$ ), 1073  $\text{cm}^{-1}$  ( $\nu_{\text{s}} \text{C-C}$ ), where  $\nu$  and  $\delta$  denote stretching and bending modes, respectively. When PAN fibers are heated up to 150°C in air and nitrogen, peak at 2240  $\text{cm}^{-1}$  starts decreasing. This presents that the

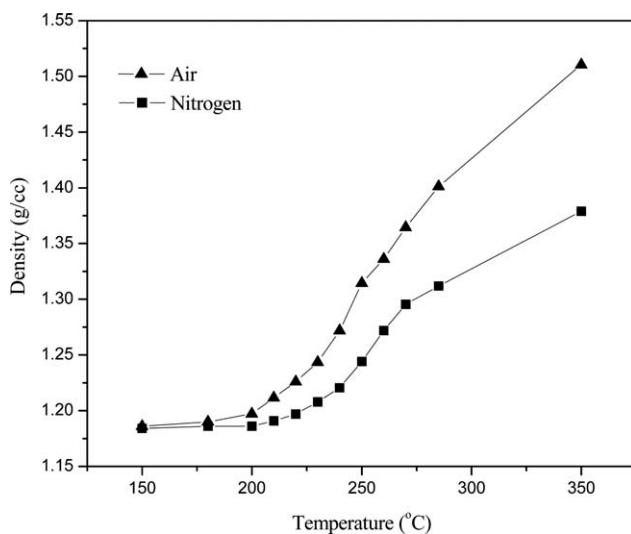


**Figure 6** FTIR spectra of the samples treated in air: (P) precursor fibers, (P<sub>1</sub>) 150°C, (P<sub>2</sub>) 180°C, (P<sub>3</sub>) 200°C, (P<sub>4</sub>) 210°C, (P<sub>5</sub>) 220°C, (P<sub>6</sub>) 230°C, (P<sub>7</sub>) 240°C, (P<sub>8</sub>) 250°C, (P<sub>9</sub>) 260°C, (P<sub>10</sub>) 270°C, (P<sub>11</sub>) 285°C, (P<sub>12</sub>) 350°C.

cyclized structure has already been created.<sup>20</sup> When the temperature is above 180°C in air, peaks at 2940  $\text{cm}^{-1}$ , 2873  $\text{cm}^{-1}$ , 1455  $\text{cm}^{-1}$ , and 1073  $\text{cm}^{-1}$  start decreasing. The decrease in the intensity of these peaks clearly indicates the formation of C=C in the cyclized structure. Therefore, new peaks around 1620–1580  $\text{cm}^{-1}$  and 800  $\text{cm}^{-1}$  start to appear in air and nitrogen. With the increase of the temperature in air, the peak around 1620  $\text{cm}^{-1}$  becomes wide. Then new peak around 1600  $\text{cm}^{-1}$  appears. This is because that the appearance of C=C bands replaces the C=N bands with the increase of the temperature in air. These are difficult to observe, since they are at more or less the same frequency. Simultaneously,



**Figure 7** FTIR spectra of the samples treated in nitrogen: (P) precursor fibers, (p<sub>1</sub>) 150°C, (p<sub>2</sub>) 180°C, (p<sub>3</sub>) 200°C, (p<sub>4</sub>) 210°C, (p<sub>5</sub>) 220°C, (p<sub>6</sub>) 230°C, (p<sub>7</sub>) 240°C, (p<sub>8</sub>) 250°C, (p<sub>9</sub>) 260°C, (p<sub>10</sub>) 270°C, (p<sub>11</sub>) 285°C, (p<sub>12</sub>) 350°C.



**Figure 8** The changes of density with the increase of the temperature in air and nitrogen.

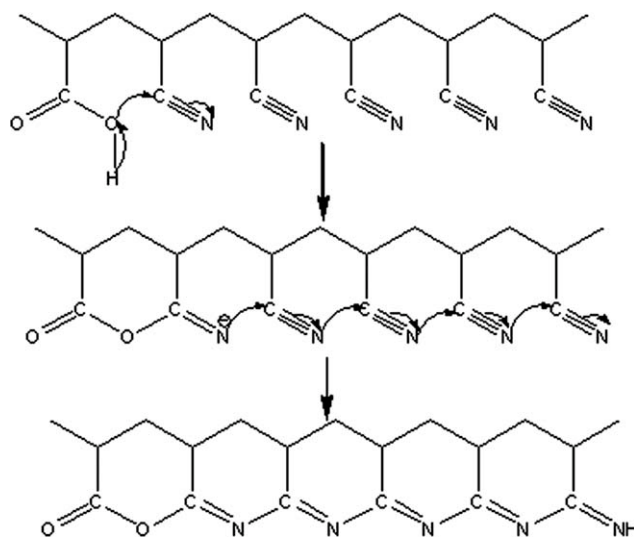
it is also difficult to resolve the C=O peak from C=N after longer oxidation times as it merges in the form of a broad band.<sup>19</sup> Therefore,  $1600\text{ cm}^{-1}$  is due to C=C, C=N, and C=O groups in air.<sup>20–23</sup> In nitrogen, on the one hand new peak at  $1620\text{ cm}^{-1}$  appears at the lower temperature, on the other hand new peak at  $1580\text{ cm}^{-1}$  appears at the higher temperature. The corresponding peak at  $1620$  and  $1580\text{ cm}^{-1}$  is due to C=N and C=C in nitrogen.<sup>22,23</sup> The band at  $800\text{ cm}^{-1}$  is due to =C–H group.<sup>20</sup> However, the increase of this peak is not obvious in nitrogen. This indicates that the amount of C=C is less. In a word, the structure evolution of PAN fibers in air is much different from in nitrogen.

### Density analysis

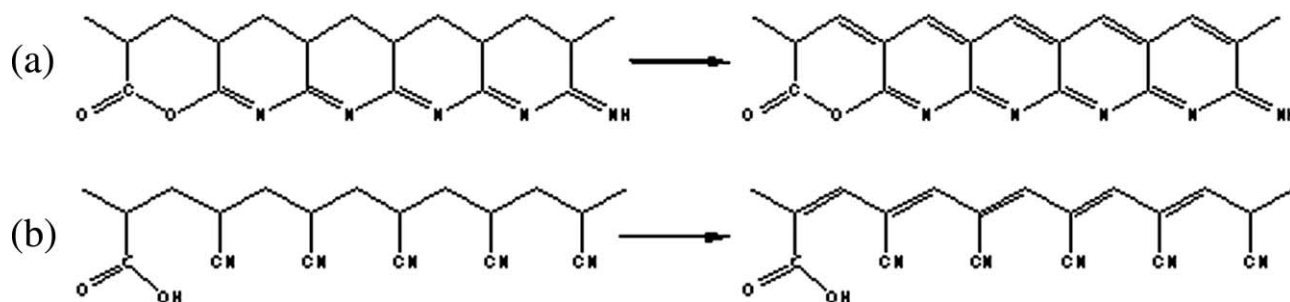
Density is believed to be a good indicator of the extent of stabilization.<sup>24,25</sup> Figure 8 shows the changes of density with the increase of the temperature in air and nitrogen. The curves indicate that densities of the stabilized fibers increase with the increase of the temperature in air and nitrogen.

As aforementioned, when PAN fibers are heated up to  $150^\circ\text{C}$  in air and nitrogen, peak at  $2240\text{ cm}^{-1}$  starts decreasing. And the color changed from white for the precursor to light yellow in air and nitrogen. It is very clear that a chemical change has taken place. It may be that cyclization reaction has taken place as Scheme 127. Scheme 1 is cyclization initiated by hydroxyl of comonomer at the beginning in air and nitrogen for PAN fibers. From Scheme 1, the electrons of oxygen in hydroxyl of comonomer are rich.<sup>26</sup> At the beginning, oxygen in hydroxyl attacks the C in C≡N. Therefore, cyclization can be initiated. This may explain the reason of cyclization at the beginning in air and nitrogen. This indicates that

there is the conversion of some C≡N groups to C=N groups leading to the rings. The conjugated C=N group is a chromophore. Thus, the coloration of PAN fibers is generally ascribed to the formation of sequences of the conjugated C=N bonds<sup>26,27</sup> at the beginning. It has been assumed that conjugation of 5 or 6 double bonds in such a way would give absorption in the visible part of the spectrum, i.e., appear colored.<sup>28</sup> It has also been assumed that lengthening the conjugation would deepen the color, i.e., shifts the absorption to the longer wavelengths. The reason which this group deepens the color is that compounds which contain hetero atoms, such as C or N have  $\pi$  electrons. When two p orbitals of C and N overlap to form a bond, two molecular orbitals [bonding ( $\pi$ ) and antibonding ( $\pi^*$ )] are formed with energies approximately equally above and below the energy of the electrons in the atoms.<sup>28</sup> When PAN fibers absorbs the visible light, the  $\pi$ - $\pi^*$  transition<sup>29</sup> will take place. During this process, one color of the visible light is absorbed. The complementary color will be seen. As seen above, cyclization is an exothermic reaction during stabilization. The initial exothermic temperatures of the fibers treated in air and nitrogen are at about  $190$  and  $240^\circ\text{C}$ . So, the amount of cyclization is less in air below  $190^\circ\text{C}$ . And the amount of cyclization is also less in nitrogen below  $240^\circ\text{C}$ . Therefore, the color of PAN fibers in air and nitrogen is almost the same at  $150^\circ\text{C}$ . However, the color of PAN fibers in air is deeper than in nitrogen above about  $180^\circ\text{C}$ . Why is the color of PAN fibers in air deeper than in nitrogen with the increase of the temperature? We conclude that there are three reasons. The first one is that the elimination of  $\text{H}_2$ ,  $\text{H}_2\text{O}$  takes place as the temperature is up to  $160^\circ\text{C}$ ,  $180^\circ\text{C}$  in air (Figs. 2 and



**Scheme 1** Cyclization initiated by hydroxyl of comonomer at the beginning in air and nitrogen for PAN fibers.



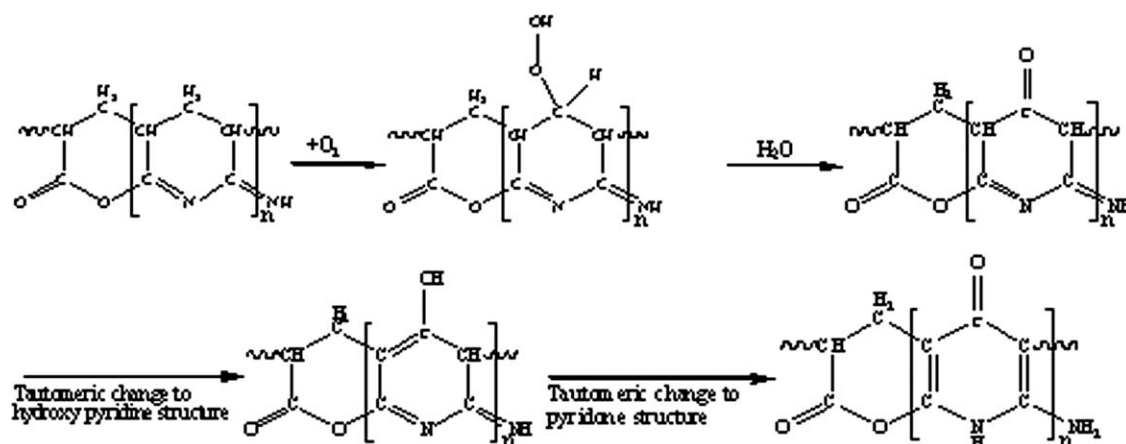
**Scheme 2** (a) The elimination of H reactions of PAN fibers during stabilization in air and nitrogen. (b) The elimination of H reactions of PAN fibers during stabilization in air and nitrogen.

6). This reaction is shown as Scheme 2(a) and Scheme 2(b).<sup>30</sup> Scheme 2(a,b) are the elimination of H reactions of PAN fibers during stabilization in air and nitrogen. As shown in Scheme 2(a,b), dehydrogenation begins to take place. This indicates that new structures have been created. Therefore, the formation of cyclic conjugation leads to a dehydropyridine type. Also, dehydrogenation leads to a conjugated polyene structure (Figs. 6 and 7).

In these new structures, the conjugated C=C group is also a chromophore.<sup>25,26</sup> The effect on the absorption of the visible light is shifted to longer wavelengths and indicates  $\pi$ - $\pi^*$  transition. So, there is a strong bathochromic effect as the number of C=C bonds are increased. In combination with mass spectra and FTIR spectra, it is very clear that there are no C=C bonds below 240°C in nitrogen. Therefore, the color of the fibers treated in air is deeper than in nitrogen below 240°C. When the temperature is up to 240°C, the elimination of H<sub>2</sub>O begins to take place in nitrogen (Fig. 3, Fig. 7). This also indicates that dehydrogenation begins to take place. It is well known that oxygen can propagate dehydrogenation in air.<sup>16</sup> Therefore, the elimination of H<sub>2</sub>O, H<sub>2</sub> in air is easier than in nitrogen. The amount of C=C bonds in air is more than in nitrogen. This is one of the reasons that the color of PAN fibers is deeper

than in nitrogen above 240°C. This is because that the C=C bond appears above 240°C. And the exotherm of the fibers treated in nitrogen starts increasing at 240°C (Fig. 4). The amount of C=C bonds also increases. So, the color change above 240°C is faster than below 240°C in nitrogen (Table I).

The second reason is that there is another reaction taking place in air. As aforementioned, peak around 1620 cm<sup>-1</sup> becomes wide at 230°C. The new structure has been created as shown in Scheme 3.<sup>22,23,31</sup> Scheme 3 is oxidation reactions of PAN fibers during stabilization in air. In this new structure, the ketonic group is also a chromophore. The reason is that this structure which contains hetero atoms such as O or N have n (non bonding) electrons as well as  $\sigma$  and  $\pi$  electron. This effect is also shifted to longer wavelengths and indicates n- $\pi^*$  transition.<sup>27,29</sup> With the increase of the temperature, densities of the fibers in air increase quickly (Fig. 8). The incorporation of oxygen contributes to the density increase of the stabilized fibers. Therefore, oxygen contents of the stabilized fibers increase. The amount of C=O groups may also increase quickly on the surface of the fibers. Thus, the absorption in the visible region increases quickly. Then the color of the fibers is deeper and deeper. On the other hand, -NH<sub>2</sub> group is the auxochrome. The effect is also shifted to



**Scheme 3** Oxidation reactions of PAN fibers during stabilization in air.

longer wavelengths and indicate  $n-\pi^*$  transition. Therefore, the  $-\text{NH}_2$  group will also deepen the color shifting the absorption to the longer wavelengths. The reason is that the  $n$  electrons do not form bonds and are therefore essentially unchanged by the formation of the bond. They are about half way between the  $\pi$  and  $\pi^*$  orbitals in terms of their energy level.<sup>4,5,30</sup> For this reason the transition energy of  $n$  electrons to the  $\pi^*$  orbital is about half that of the  $\pi-\pi^*$  transition. For this reason the transition energy of  $n$  electrons to the  $\pi^*$  orbital is about half that of the  $\pi-\pi^*$  transition. The effects of  $-\text{C}=\text{O}$  and  $-\text{NH}_2$  on the color of the fibers are not greater than the effects of  $\text{C}=\text{N}$ ,  $\text{C}=\text{C}$ . However, the new structure which is caused by oxidative reaction can also contribute to the coloration of PAN fibers.

The third reason is that there is a crosslinking reaction<sup>17</sup> taking place when the fiber is oxidized to higher temperature in air (300–350°C). The structure of the stabilized fibers in air is more complex because of the crosslinking reaction. This maybe deepens the color of the fibers. However, the final color of PAN fibers is also black at 350°C in nitrogen. Therefore, we conclude that oxidative reaction is not the ultimate reason which turns the fiber into black. This is only one of all these effects. Why is the color of the fiber turned into black? A possible reason is that the fiber absorbs all the visible light with the structure change. Oxygen facilitates the chemical reaction in air. The structural change in air is faster than in nitrogen. Hence, PAN fiber turned into black in air is prior to in nitrogen.

As aforementioned, cyclization has taken place at 150°C in air and nitrogen. In combination with the mass spectrum and FTIR spectra, the elimination of  $\text{H}_2$ ,  $\text{H}_2\text{O}$  in air begins at about 180, 160°C, separately. The elimination of  $\text{H}_2$ ,  $\text{H}_2\text{O}$  in nitrogen begins at about 260, 240°C, separately. Therefore, this is a fact that cyclization occurs prior to dehydrogenation during stabilization in air and nitrogen.

## CONCLUSIONS

During stabilization, the  $\text{C}-\text{N}$  and  $\text{C}=\text{C}$  groups appear gradually with the increase of the temperature in air and nitrogen. On the other hand, the  $\text{C}=\text{O}$  and  $-\text{NH}_2$  groups appear at the proper temperature in air. The  $\text{C}=\text{N}$ ,  $\text{C}=\text{C}$ , and  $\text{C}=\text{O}$  groups are chromophores. The  $-\text{NH}_2$  group is the auxochrome. When the stabilized PAN absorbs the visible light, the effect of conjugated  $\text{C}=\text{N}$  and  $\text{C}=\text{C}$  on the absorption of the visible light is shifted to longer wavelengths and indicates  $\pi-\pi^*$  transition. There is a strong bathochromic effect as the number of  $\text{C}=\text{C}$  bonds are increased. The effect of  $\text{C}=\text{O}$  and  $-\text{NH}_2$  on the absorption of the visible light is shifted to longer wavelengths and indicates  $n-\pi^*$  transition. All

these effects on the absorption of the visible light can account for the color changes of PAN with the increase of the temperature in air and nitrogen. Oxygen can facilitate chemical reactions in air. Hence, the color of PAN in air is deeper than in nitrogen at the same temperature. And the structural change of PAN in air is faster and more complex than in nitrogen. PAN fibers treated in air turned black after 230°C. However PAN fibers turned black at 350°C in nitrogen.

During stabilization, cyclization occurs prior to dehydrogenation in air and nitrogen.

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