

## Mechanism and Kinetics of Oxidation During the Thermal Stabilization of Polyacrylonitrile Fibers

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**ABSTRACT:** The thermal behavior and structural evolution during the thermal stabilization of polyacrylonitrile (PAN) fibers in N<sub>2</sub> and air were investigated using differential scanning calorimetry and solid-state <sup>13</sup>C nuclear magnetic resonance. It was found that an oxidation reaction, that generated carbonyl (C=O) groups could occur at 160°C which has not been reported in the literature. It is proposed that the cyclized structures in the PAN macromolecule chains are a prerequisite for the oxidation. Further investigations indicate that with more cyclized structures in the PAN macromolecule chains, the oxidation proceeds more readily, which is consistent with the proposed mechanism. The kinetic parameters for the oxidation and cyclization reactions were estimated using the Kissinger method. The activation energies for the reactions of oxidation and cyclization for PAN fibers are about 96.4 kJ/mol and 190.0 kJ/mol, respectively, which implies that the cyclization is the rate determining step during the thermal stabilization of PAN fibers. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** polyacrylonitrile; stabilization; oxidation; cyclization; kinetics

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### INTRODUCTION

The thermal stabilization of polyacrylonitrile (PAN) fibers is an important process in the fabrication of high performance carbon fibers. Throughout the stabilization, PAN fibers are converted to infusible, non-flammable fibers by heating at 180–300°C for approximately 1 h. During this process, complex chemical reactions occur, which accompanied with significant enthalpy changes. The main reactions are cyclization, oxidation, and dehydrogenation. Since the 1950s, various types of reaction mechanism have been proposed to interpret the phenomena that occur throughout stabilization.<sup>1–14</sup> In inert atmosphere, cyclization and the liberation of molecular gases takes place. In air, the situation becomes much more complicated, owing to the presence of oxygen.

Oxygen plays a critical role in the stabilization. Many studies have focused on the mechanism and kinetics of oxidation, and a range of views have been proposed.<sup>7,11,15–21</sup> Fitzer and Müller<sup>7</sup> studied the cyclization and oxidation of PAN fibers in N<sub>2</sub> and air using differential thermal analysis (DTA), and concluded that oxidation preceded cyclization, but was slower during the thermal treatment of PAN in air. It proceeded, even after cyclization was completed. However, Collins et al.<sup>15</sup> investigated the

kinetics for the reactions during the stabilization of PAN, and proposed a dual consecutive first-order kinetic model to describe the mechanistic relationships among nitrile consumption, heat generation, and oxygen uptake. They argued that the oxidation took place after cyclization. Watt and Johnson<sup>11</sup> investigated the stabilization of PAN at 230°C and proposed that the formation of a cyclized polymer was a prerequisite to oxidation. Sivy et al.<sup>19</sup> conducted degradation studies on acrylamide containing PAN copolymers in air at 200°C and concluded that oxidation and cyclization were two competing reactions in the primary stages of the thermal stabilization. Owing to the complex chemical reactions and the limited applicable characterization methods, the mechanism for the oxidation during the stabilization of PAN was not completely understood.

Therefore, it is necessary to further explore the mechanism of these knotted reactions (oxidation specifically) throughout the stabilization of PAN fibers. In this study, the thermal behaviors and structural evolutions for PAN fibers pretreated under different conditions have been employed to probe the mechanism of oxidation using differential scanning calorimetry (DSC), solid-state <sup>13</sup>C nuclear magnetic resonance (NMR), Fourier transform infrared spectroscopy (FTIR), and elemental analysis (EA). The

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**Table I.** PAN Fiber Samples

Samples	Step 1 (in N <sub>2</sub> )		Step 2 (in air)		Samples	Step 1 (in N <sub>2</sub> )		Step 2 (in air)	
	T (°C)	t (min)	T (°C)	t (min)		T (°C)	t (min)	T (°C)	t (min)
Precursor					S6	240	600	/	/
S0	/	/	/	/	S7	240	120	160	120
Pre-treated PAN samples					S8	/	/	200	120
S1	240	10	/	/	S9	240	10	240	10
S2	240	30	/	/	S10	240	30	240	10
S3	240	60	/	/	S11	240	60	240	10
S4	240	90	/	/	S12	240	90	240	10
S5	240	120	/	/	S13	240	120	240	10

kinetic parameters, such as the activation energies and pre-exponential factors for the oxidation and cyclization steps have also been determined using the Kissinger method.

## EXPERIMENTAL

### Materials and Sample Preparation

A commercial PAN fiber sample, containing low levels of itaconic acid (IA) and methacrylate (MA) co-monomer, was obtained to prepare the precursor fibers. These were thermally pretreated in N<sub>2</sub> or air under different conditions. These prepared fiber samples are summarized in Table I, together with the heat treatment conditions. The PAN precursor (S0) was pretreated at 240°C for 10, 30, 60, 90, 120, and 600 min under N<sub>2</sub> to obtain fibers (S1–S6) with different contents of cyclized structures. S9–S13 were prepared from S1 to S5, which subsequently treated at 240°C for 10 min in air, to investigate the influence of cyclized structures on the oxidation. In addition, based on the DSC analysis, S7 and S8 were prepared to study the cyclized and oxidation structures in depth. S7 was obtained as follows. The precursor was pretreated at 240°C for 120 min in N<sub>2</sub> followed by the treatment at 160°C for 120 min in air. S8 is the fiber that the precursor was pretreated at 200°C for 120 min in air directly. The precursor fiber sample was also used as the reference material.

### Measurements

**Differential Scanning Calorimetry.** The enthalpy changes for the prepared fiber samples throughout the heating process were investigated using a TA instrument DSC Q100 from 40 to 400°C either in air or N<sub>2</sub> atmosphere. The heating rates varied from 2 to 10 °C/min. The sample size for the measurements was approximately 3 mg. The gas flow rate was 50 mL/min.

**Fourier Transform Infrared Spectroscopy.** Infrared spectral measurements were performed using a Nicolet 5700 instrument. KBr disks were prepared by homogeneously mixing KBr and the sample powder.

**Solid-State <sup>13</sup>C Nuclear Magnetic Resonance.** The cross-polarization/magic angle spinning (CP/MAS) solid-state <sup>13</sup>C-NMR spectra for the fiber samples were measured on a Bruker AV-300 NMR spectrometer. A resonance frequency of 73.5 MHz, a CP contact time of 3 ms, and a delay time of 5 s were set as the operating parameters. The probe size for the CP/MAS was 4 mm and a rotation speed of 12 kHz was employed. For a good

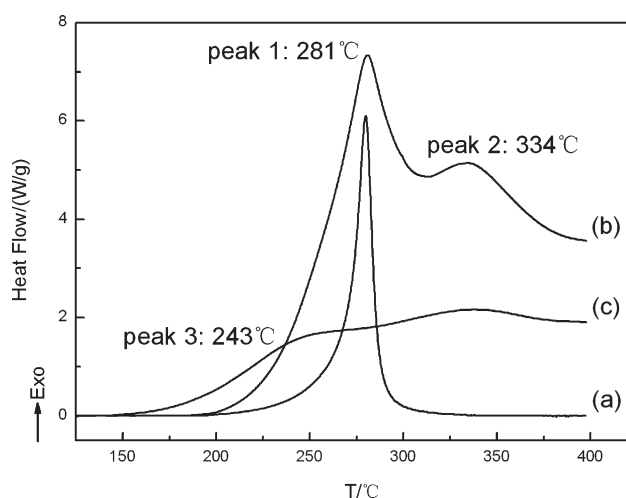
signal-to-noise ratio, 300–3175 scans were required. Tetramethylsilane (TMS) was used as the internal reference to determine the correct chemical shifts.

**Elemental Analysis.** The oxygen contents for the PAN fiber samples were determined via an Elmentar Analysensysteme Gob (Italy) VAEIO EL 3 elemental analysis using the CHN model. The oxygen content was calculated by subtracting the contents of C, H, and N.

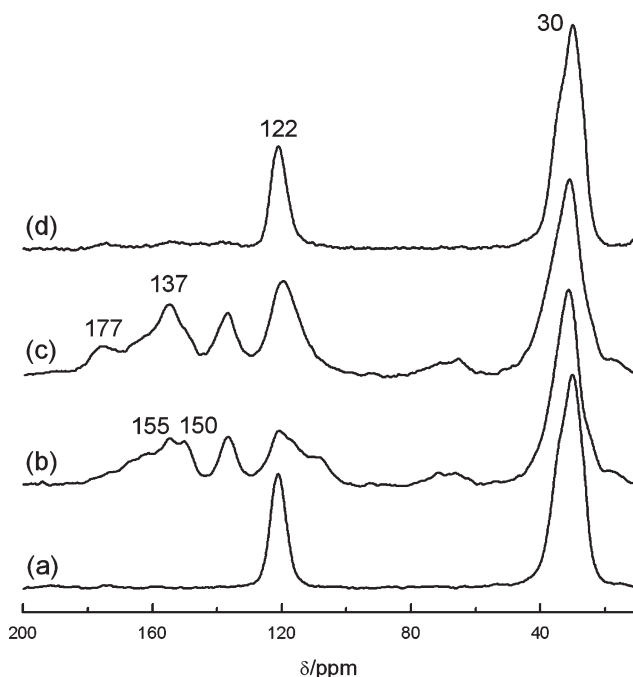
## RESULTS AND DISCUSSION

### Mechanism of Oxidation During the Thermal Stabilization of PAN Fibers

**Analysis of Oxidation.** Figure 1 shows the DSC curves for the PAN precursor (S0) in N<sub>2</sub> and air. For comparison, the DSC curve in air for the fiber (S5) pretreated in N<sub>2</sub> at 240°C for 120 min was added in the figure. Under N<sub>2</sub> (curve (a)), the PAN precursor exhibits a sharp single exothermic peak at 281°C. This can be attributed to the cyclization reaction. Under air (curve (b)), this peak becomes broader and a second peak appears at 334°C, which results from the complex range of crosslinking and oxidative destruction reactions. To gain a clearer understanding of these reactions, the DSC testing was



**Figure 1.** DSC curves for the PAN fibers: (a) precursor in N<sub>2</sub>; (b) precursor in air; (c) the fiber with cyclized structures (pretreated in N<sub>2</sub> at 240°C for 120 min) in air. ( $\beta = 10$  °C/min)



**Figure 2.** NMR spectra for the PAN fibers heat-treated under different conditions: (a) precursor; (b) the fiber pretreated at 240°C for 120 min in N<sub>2</sub>; (c) the fiber pretreated at 240°C for 120 min in N<sub>2</sub> followed by the treatment that at 160°C for 120 min in air; (d) the fiber pretreated at 200°C for 120 min in air directly.

conducted for the fiber (S5) pretreated in N<sub>2</sub> at 240°C for 120 min and the DSC curve is also shown in Figure 1 for comparison. As there is no oxygen in the atmosphere, it can be assumed that the predominant reaction taking place during the pretreatment was cyclization. The prepared sample (S5) was then analyzed by DSC in air. The result is shown as curve (c) in Figure 1. It can be seen that an obvious decrease in intensity for the peaks at 281 and 334°C. It is noteworthy that a new broad peak, initiating at 160°C and centering at around 243°C, is observed. It implies the existence of a new reaction at lower temperature. We proposed that the cyclization of the PAN macromolecule is a prerequisite for this newly identified reaction.

The solid-state <sup>13</sup>C-NMR was used to investigate the mechanism of this interesting reaction. Figure 2 shows the NMR spectra for the PAN precursor and the samples pretreated under N<sub>2</sub> and air. For PAN precursor [Figure 2(a)], two resonance peaks, which appeared at 122 and 30 ppm, can be attributed to the nitrile groups and the alkyl (sp<sup>3</sup>) groups such as methylene, respectively. For the fiber pretreated in N<sub>2</sub> at 240°C for 120 min [Figure 2(b)], three new resonance peaks, which at 137, 150, and 155 ppm, can be assigned to the unsaturated C=C in the

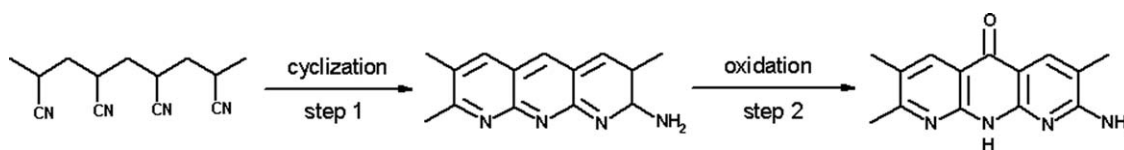
polymer backbone, the unsaturated C=N species and the conjugated C=N species, respectively. This indicates that, as the stabilization proceeds at 240°C in N<sub>2</sub>, cyclization reactions take place which result in generating unsaturated carbon structures (sp<sup>2</sup>). Compared to Figure 2(b), there is a new resonance peak centered at 177 ppm in the NMR spectrum of the fiber pretreated at 240°C for 120 min in N<sub>2</sub> followed by the treatment at 160°C for 120 min in air [Figure 2(c)], which can be attributed to carbonyl C=O group. The existence of C=O group confirms that the oxidation occurs. However, for the fiber pretreated at 200°C for 120 min in air directly [Figure 2(d)], the NMR spectrum is almost the same as the precursor, which suggests that negligible oxidation has taken place. Therefore, a mechanism for the oxidation reaction throughout the stabilization is proposed, as shown in Figure 3. During the stabilization of the PAN fibers, the cyclization and oxidation reactions occur sequentially. This is hard to confirm using conventional thermal analysis methods, since the energy barrier for the oxidation is lower than that for the cyclization. Oxidation takes place immediately if the cyclized structures are present in the PAN macromolecule chains. Therefore, in DSC curve of PAN precursor in air, the exothermic peak of the oxidation cannot be separated from the exothermic peak of cyclization.

**Influence of Cyclized Structures on the Oxidation.** To verify the mechanism proposed above and further investigate the influence of cyclized structures on the oxidation, a series of PAN samples with varying levels of cyclized structure content were obtained. The PAN precursor was prepared at 240°C for 10, 30, 60, 90, and 120 min under N<sub>2</sub> to obtain fibers with different contents of cyclized structures. These obtained fibers were then heat treated under the same conditions (at 240°C for 10 min) in air to compare the difference of the levels of oxidation.

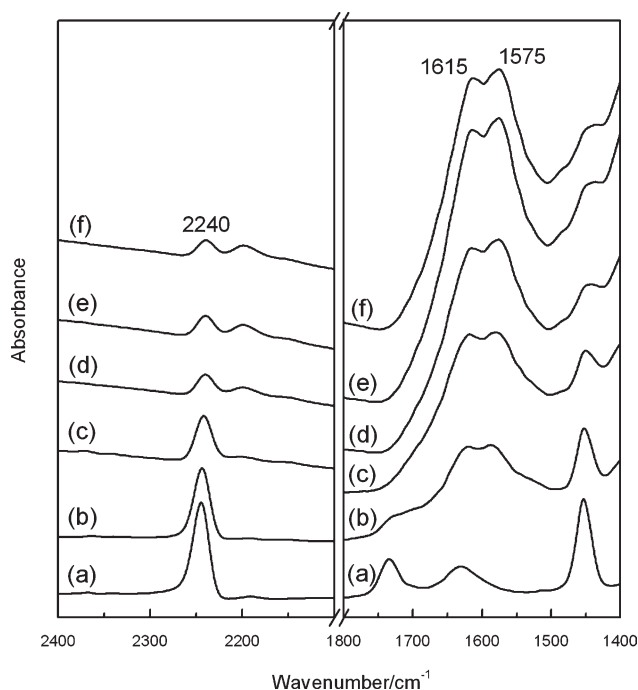
Figure 4 shows the FTIR spectra for PAN fibers heated for different times at 240°C under N<sub>2</sub>. There is a strong absorption band at 2240 cm<sup>-1</sup> assigned to the ν<sub>C≡N</sub> band (nitrile group stretching mode). Two bands at 1615 and 1575 cm<sup>-1</sup> can also be observed, which are assigned to ν<sub>C=N</sub> and ν<sub>C=C</sub>, respectively. The fraction of the C=N groups can be calculated to evaluate the level of cyclization, according to the equation presented by Collins et al.<sup>15</sup>:

$$f_c = \frac{0.29I_{C=N}}{(I_{C=N} + 0.29I_{C=N})} \quad (1)$$

where  $f_c$  denotes the fraction of cyclized structures and  $I$  is the measured absorption intensity. Figure 5 shows the dependent cyclized structures on the heat treatment time. The increase of  $f_c$  with increasing of time indicates that more cyclized structures are formed in the PAN macromolecule chains at longer time in N<sub>2</sub>.



**Figure 3.** Scheme for the oxidation of PAN fibers throughout the stabilization.

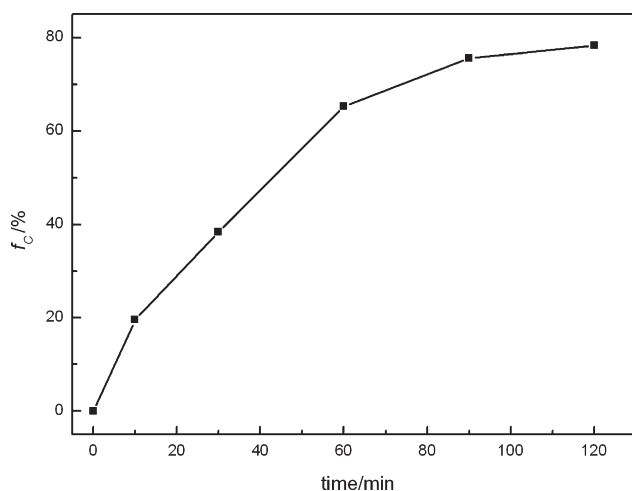


**Figure 4.** FTIR spectra for the PAN fibers heated under different times at 240°C under N<sub>2</sub>: (a) 0 min; (b) 10 min; (c) 30 min; (d) 60 min; (e) 90 min; (f) 120 min.

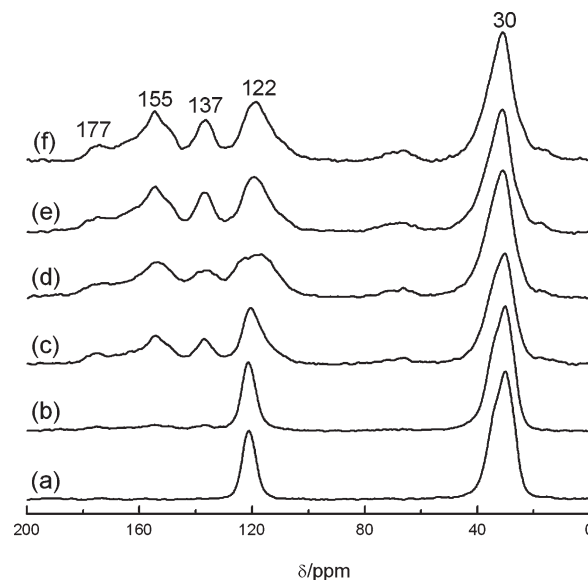
The <sup>13</sup>C-NMR was applied for characterizing the oxidation structures for the fibers with different proportion of cyclized structures after heat treated at 240°C for 10 min in air (Figure 6). The resonance centered at 177 ppm, which is C=O, becomes more obvious for the fibers with more cyclized structures. To evaluate the extent of oxidation, a parameter is defined as follows:

$$OI = \frac{A_{C=O}}{A_{C=O} + A_{Alkyl\ groups}} \quad (2)$$

where OI represents the fraction of the oxidation structures,  $A_{C=O}$  is the measured area of the resonance peak at 177ppm,



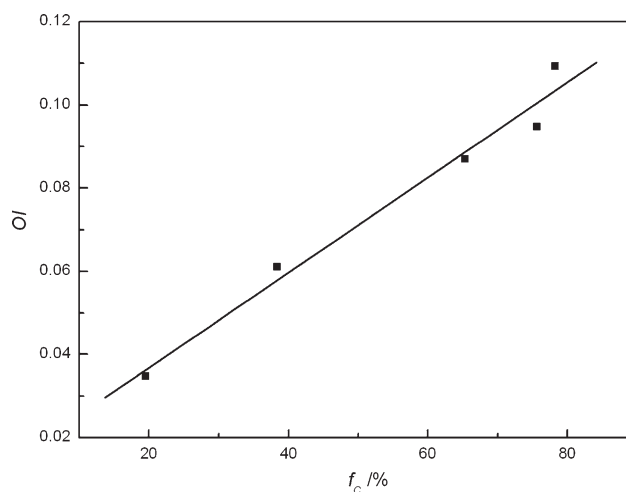
**Figure 5.** Relationship between cyclized structure level and heat treatment time at 240°C under N<sub>2</sub>.



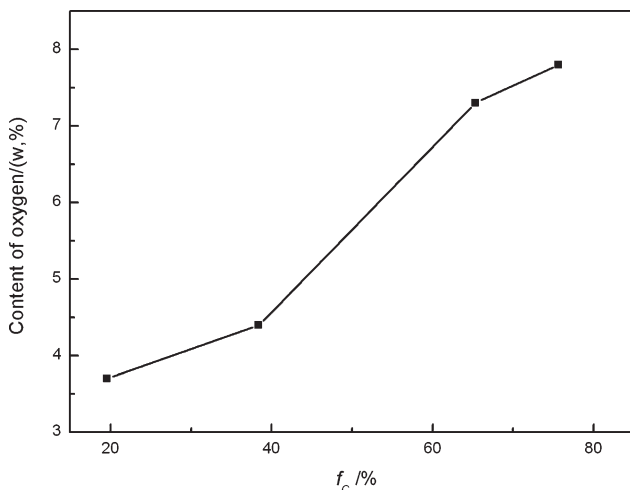
**Figure 6.** NMR spectra for the PAN fibers pretreated under conditions as follows: the fiber pretreated at 240°C for (a) 0 min; (b) 10 min; (c) 30 min; (d) 60 min; (e) 90 min; (f) 120 min in N<sub>2</sub> followed by the treatment that at 240°C for 10 min in air.

and  $A_{Alkyl\ groups}$  is the measured area of the resonance peak at 30 ppm. These were separated and calculated using peak deconvolution software. Figure 7 shows the fitted plot for OI versus  $f_c$  for the PAN fibers throughout the stabilization. With increasing values of  $f_c$ , the value of OI increases proportionally. This suggests that more oxidation structures generated for the fibers with more cyclized structures. Due to the fact that these fibers were exposed to the same oxygen-containing atmosphere, it can be concluded that cyclized structures within the PAN are a prerequisite for oxidation.

EA analysis of these fibers shows that the oxygen content increases with increasing of  $f_c$  (Figure 8). It indicates that after heat treatment in air, more oxidation structures generate in



**Figure 7.** Fitted plots for OI versus  $f_c$  for the PAN fibers throughout stabilization.



**Figure 8.** Relationship between oxygen content and  $f_c$  for the PAN fibers.

PAN fibers with more cyclized structures. This is in good accordance with the results of NMR analysis and support the proposed mechanism.

### Kinetics for the Oxidation

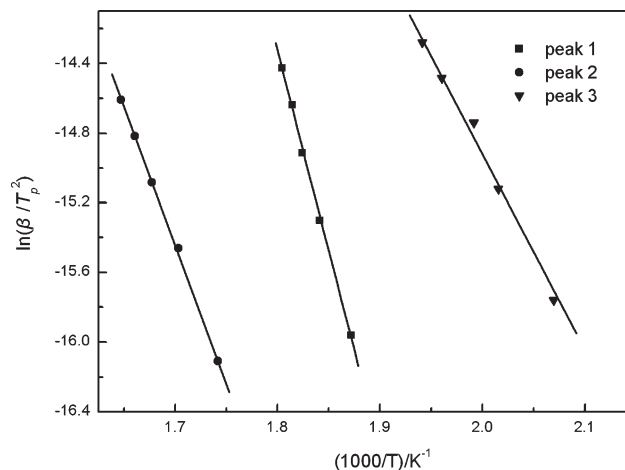
From the results above, we interpreted the experimental data by the investigation of the oxidation. In this part, the thermal stabilization kinetics for PAN fibers in air were investigated based on the obtained DSC data.

The Kissinger<sup>22</sup> method was applied to determine the kinetic parameters for the thermal stabilization reactions. This method is frequently encountered in the literature as they only require simple measurement of a series of thermal behavior curves at different heating rates. Table II shows the peak temperatures ( $T_p$ ) obtained from the DSC curves for the PAN fibers at various heating rates under air. Peaks 1–3 (Figure 1) represent the cyclization reaction, the apparent oxidation, and the oxidation without influences of the cyclized structures, respectively. Peak 2 is usually used to calculate the kinetic parameters for the oxidation. However, based on the results above, we know that the cyclization reaction influences the oxidation and these two types of reactions overlap with one another for fibers treated in air directly. Therefore, the kinetic parameters obtained via Peak 2 may be some deviation from the true values. It is assumed that after pretreatment in  $N_2$  at 240°C for 600 min, the cyclized structures are generated to their maximum degree. When this

**Table II.** Peak Temperatures for the PAN Fibers Determined by the DSC Curves in Air

Heating rate (°C/min)	$T_{p1}^a$ (°C)	$T_{p2}^b$ (°C)	$T_{p3}^c$ (°C)
2	261	301	210
4	270	314	223
6	275	323	229
8	278	329	237
10	281	334	242

<sup>a,b</sup> $T_{p1}$  and  $T_{p2}$  are the first and second peak temperatures for PAN precursor (S0), respectively., <sup>c</sup> $T_{p3}$  is the first peak temperature for the PAN fibers pre-treated in  $N_2$  at 240°C for 600 min (S6).



**Figure 9.** Linear fitted plots from the kinetics for different reactions during the stabilization of PAN fibers by the Kissinger method.

fiber with maximum cyclized structures is subsequently heated in air, the oxidation proceeds in the absence of any cyclization reaction influence. Therefore, the kinetic parameters can be calculated from Peak 3 more precisely than that from Peak 2. As shown in Table II, with increasing heating rate ( $\beta$ ),  $T_p$  undergoes a regular increase due to the lagging effect.

The mathematical expression for the Kissinger method is as follows [22]:

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{R} \frac{1}{T_p} \quad (3)$$

where  $T_p$  is the peak temperature;  $\beta$  is the heating rate;  $E_a$  is the apparent activation energy;  $A$  is the pre-exponential factor, and  $R$  is the molecular gas constant. According to this equation,  $E_a$  and  $A$  can be calculated from a linear fitted plot of  $\ln(\beta/T_p^2)$  against  $1/T_p$  (slope and intercept, respectively).

Figure 9 shows the fitted plots for Peaks 1–3 according to the DSC curves, using the Kissinger method. The linear dependence for each fit is as expected, and the determined values for  $E_a$  and  $A$  are summarized in Table III. The value for  $E_a(R1)$  is 190.0 kJ/mol, which is higher than those for  $E_a(R2)$  and  $E_a(R3)$ . This indicates that the energy barrier for cyclization is higher than that for oxidation. The activation energy for oxidation, as calculated from Peak 2, is 35 kJ/mol higher than that calculated from Peak 3.  $E_a(R2)$  is only an apparent value, since the rate of formation of the cyclized structures has significant influences on the oxidation.  $E_a(R3)$  measured in the absence of any cyclization influences is 96.4 kJ/mol, which is closer to the true value. The comparison of the rate constants for cyclization and oxidation reactions during stabilization of PAN fibers determined by Kissinger method is shown in Figure 10. The rate constant was calculated by Arrhenius equation:

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad (4)$$

where  $k$  is the rate constant;  $E_a$  is the apparent activation energy;  $A$  is the pre-exponential factor;  $R$  is the molecular gas constant; and  $T$  is the temperature. It shows that the value of  $k$

**Table III.** Kinetic Parameters for the Different Reactions During the Stabilization of PAN Fibers

Reaction	$E_a$ (kJ/mol)	$A$ ( $s^{-1}$ )
R1(peak 1) <sup>a</sup>	190.0	$1.004 \times 10^{16}$
R2(peak 2) <sup>b</sup>	131.0	$1.343 \times 10^9$
R3(peak 3) <sup>c</sup>	96.4	$4.481 \times 10^7$

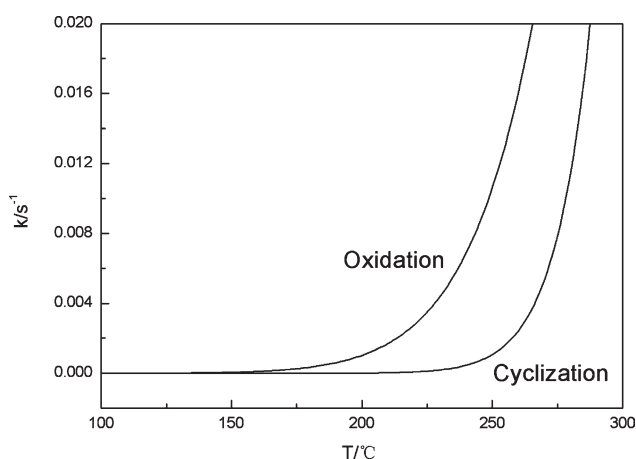
<sup>a</sup>R1 is the cyclization reaction., <sup>b</sup>R2 is the apparent oxidation., <sup>c</sup>R3 is the oxidation in the absence of any cyclization influences.

for oxidation is higher than that for cyclization at the same temperature. It is verified again that the energy barrier for the oxidation is lower than that for the cyclization. The derived kinetic results are consistent with the proposed mechanism in section "Mechanism of Oxidation During the Thermal Stabilization of PAN Fibers." Throughout the stabilization of PAN fibers, the cyclization and oxidation occur sequentially (shown in Figure 3), and the former is the rate determining step. That is to say, the cyclized intermediates can react rapidly with oxygen once they have been generated during the stabilization.

## CONCLUSIONS

By separating the complicated reactions that occur during the thermal stabilization of PAN fibers in air, an oxidation that generates carbonyl (C=O) groups has been observed to occur at 160°C, based on both DSC and solid-state <sup>13</sup>C-NMR analysis. It is proposed that the cyclized structures within the PAN macromolecule chains are a prerequisite to oxidation, which would explain why the oxidation reaction is difficult at 160°C, using conventional methods without any pretreatment under N<sub>2</sub>. With higher degrees of cyclization in PAN, increased levels of oxidation are observed. Thus, more cyclized structures in PAN macromolecule chains allow a more facile oxidation, which is consistent with the proposed mechanism.

The kinetic results developed using the Kissinger method show that, by eliminating the influence of the cyclized structures, the activation energy for the oxidation is 96.4 kJ/mol. This is much lower than that for the cyclization reaction (190.0 kJ/mol). In



**Figure 10.** The rate constants determined by Kissinger method for oxidation and cyclization of PAN fibers.

addition, the value of the rate constant for oxidation is higher than that for cyclization at the same temperature. The mechanism proposed above is reasonable from a kinetics viewpoint. Throughout the stabilization of the PAN fibers, the cyclization and oxidation reactions occur sequentially, and the former is the rate determining step.

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