

공기분위기 하에서 열처리된 고입체 규칙성 폴리아크릴로니트릴의 XRD에 의한 환화반응 속도 연구

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(2007년 12월 13일 접수, 2008년 1월 18일 채택)

Kinetic Study of Cyclization of High-Tacticity Polyacrylonitrile Heat-Treated under Air Atmosphere via XRD

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(Received December 13, 2007; Accepted January 18, 2008)

Abstract : Two different polyacrylonitrile samples (PANs, triad tacticity fraction is 0.25 and 0.64) were synthesized and used to study the kinetics of cyclization. Polymers were treated at different temperatures between 250 to 300 °C under air atmosphere, and analyzed by X-ray diffractometer. The sharp and strong peak at $2\theta = 16.5^\circ$ corresponds to a lateral repeat distance that is the (100) diffraction in hexagonal lattice, while the peak at $2\theta = 25.5^\circ$ reflects the (101) diffraction. In comparing their areas of different heat treated samples, the cyclization of both PANs was identified as a first-order reaction. The rate constants of cyclization reaction at different temperatures and the active energy parameter were obtained. This results might provide an important effect on pre-oxidation of polyacrylonitrile fiber.

Keywords : high-tacticity polyacrylonitrile, cyclization, kinetics.

Introduction

Carbon fibers are finding an importance place in high-tech-technology areas. The quality of the final carbon fiber depends strongly on the quality of precursor materials.¹ Among the precursors available, polyacrylonitrile (PAN)-based fibers remain one of the best materials for making carbon fibers.² Microstructure of PAN alters the thermal characteristics in the desired manner to give carbon fiber with good quality.^{3–7}

One of the most important steps in the development of carbon fibers from PAN is pre-oxidation.^{8,9} Watt¹⁰ reported that, to obtain carbon fibers with the best mechanical properties, the cyclization of PAN should be carried out to such an extent about 50%. The stability in the structure of PAN during pre-oxidation is achieved through the conversion of an open chain structure into a closed chain or aromatic struc-

ture, and the aromaticity developed can be determined by X-ray diffraction (XRD).⁸ From the process of producing PAN-based carbon fiber, the key index of pre-oxidation is the cyclization degree of nitrile groups in PAN molecule. The higher the cyclization degree is, the better the quality of pre-oxidation fiber is. But the important factor is tacticity which decides the cyclization degree during the pre-oxidation. Therefore, it is necessary to study the effect of tacticity on pre-oxidation. It is regret that there is not any more people for attention. Recently, we have detailedly studied the polymerization of acrylonitrile for producing high tacticity PAN¹¹ and the effect of the tacticity by DSC, FT-IR and XRD.¹²

It can be suggested that tacticity of PAN has strong relation with formation of the cyclization structure during pre-oxidation. High tacticity PAN-based carbon fiber might have good performances in many aspects.

The cyclization rate of atactic PAN has been studied using infrared spectroscopy (IR),^{13–15} differential scanning calori-

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metry (DSC)¹⁶ and differential thermal analysis (DTA).¹⁷ Our interest here is to study the kinetics of cyclization reaction of high tacticity PAN under air atmosphere by means of changes of peak area of XRD at $2\theta=16.5^\circ$ or $2\theta=25.5^\circ$ as a function of temperatures for various time and to compare kinetic parameter with low-tacticity PAN.

Experimental

Materials. Acrylonitrile (AN, Beijing Chemical Reagents Co., A. R. grade) was vacuum distilled from CaH_2 just before polymerization. Azobisisobutyronitrile (AIBN) recrystallized from ethanol was used as an initiator. Dimethyl sulphoxide (DMSO) and deionized water were adopted as the polymerization solvent and precipitator.

Both low-tacticity PAN (atactic-PAN) and high-tacticity PAN (isotactic-PAN) were homopolymers, triad tacticity fractions (mm) of which are 0.25 and 0.64 determined by ^{13}C -nuclear magnetic resonance (^{13}C -NMR), respectively.¹⁸ Atactic-PAN was prepared by solution polymerization of AN initiated by AIBN, and isotactic-PAN was synthesized by polymerization of AN using organo compound as initiator^{19–22} made in our laboratory. And their viscosity-average molecular weight is 190000 and 220000, respectively.

In order to eliminate the effect of the metal ion in PAN samples on XRD, ion-exchange was used in order to remove metal ions from the isotactic-PAN polymer. The isotactic-PAN sample was dissolved in dimethyl sulphoxide (DMSO) and the solution was passed through an H-ion-exchange resin column. Purified isotactic-PAN was precipitated from the solution using de-ionized water as precipitant and separated by filtration and the resulting solid was dried in vacuum. The metal ion contents before and after ion-exchange were determined using an SP8000 inductively coupled plasma atomic emission spectrometer. Solid powders filtered through a 400-mesh screen were used for preparing pre-oxidation products, used for XRD, at different temperatures for different time in the oven with controllable heating rate under air atmosphere.

Characterization. ^{13}C -NMR spectra of atactic-PAN and isotactic-PAN were recorded on an Av600 NMR spectrometer using $\text{DMSO}-d_6$ as solvent.

A Rigaku D/MAX 2500 VB2+/PC X-ray diffractometer (Japan) was used to study XRD patterns at 40 kV and 200 mA with nickel-filtered $\text{Cu } K_\alpha$ radiation ($\lambda=1.54056 \text{ \AA}$). Samples in the disc form were prepared by compressing the PAN powder. Scanning speed was $10^\circ/\text{min}$ and scanning step was 0.02° .

Kinetic Study Method of the Cyclization Reaction. The scheme of formation of cyclization structures in pre-oxidation of PAN can be represented as follows²³:

Because of the interactivity between PAN molecules by cyanic ($-\text{CN}$) groups, the XRD pattern characteristic of PAN is displayed, with a prominent peak at a Bragg angle of 16.5° and another one of lesser intensity appearing at approximately 29° . As the temperature increase, cyclization reaction in PAN molecule chain, attributing to the reactions between cyanic ($-\text{CN}$) groups, takes place simultaneously, and intensity of peak at a Bragg angle of 16.5° is declined. Based on this result, XRD may be employed to quantify the conversion of $-\text{CN}$ groups to ladder-like polymer.

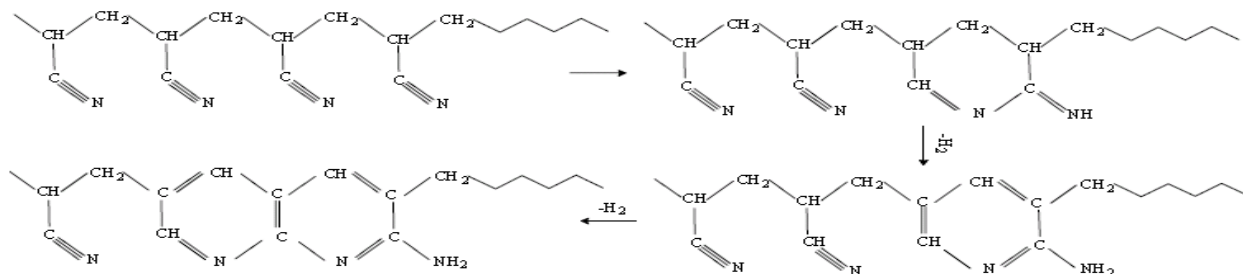
Peak-fit technique was used to analyze the XRD patterns. The peak area percents at a Bragg angle of 16.5° at different temperatures for different time can be calculated. The variations of the peak area percent reflect the reaction degree (α) of $-\text{CN}$ groups. Therefore, cyclization kinetics of PAN can be studied using the variations of peak area percent at a Bragg angle of 16.5° .

The kinetic equation of pre-oxidation is followed by:

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \quad (1)$$

$$\alpha = \frac{S_0 - S_t}{S_0 - S_{\min}}$$

Where t : time of pre-oxidation,
 S_0 : (100) peak area (percent) as $t=0$,
 S_t : (100) peak area (percent) as time is t ,
 $S_{\min}$: (100) peak area (percent) as $t \rightarrow \infty$,
 k : reaction rate constant.
 n : order of reaction



Scheme 1. The formation of cyclization structures in pre-oxidation of PAN.

It can be known from Arrhenius equation (2) that $\ln(k)$ has linear relation with $1/T$, the active energy E_a may be obtained from slope coefficient of the line. k can be obtained from slope coefficient of line.

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad (2)$$

Where E_a : activation energy (kJ/mol),
 A : constant coefficient
 R : ideal gas constant (8.31 kJ/kmol · K⁻¹)

When $n=1$, $\ln\left(\frac{1}{1-\alpha}\right) = kt$, $\ln\left(\frac{1}{1-\alpha}\right)$ is linear relation with t

When $n=2$, $\frac{1}{1-\alpha} = kt$, $\frac{1}{1-\alpha}$ is linear relation with t .

Results and Discussion

¹³C-NMR Spectrum Analysis. ¹³C-NMR spectra of atactic-PAN and isotactic-PAN prepared in our laboratory were shown

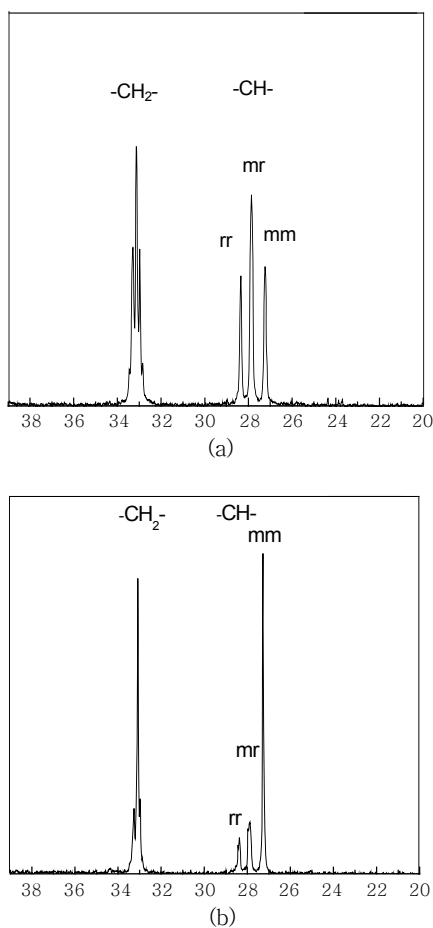


Figure 1. ¹³C-NMR spectrum of atactic-PAN (a) and isotactic-PAN (b).

in Figure 1. Their triad tacticity fractions, calculated by the Origin 7.0 software, were 0.25 and 0.64, respectively.

Variations of the XRD Patterns. The XRD patterns of the isotactic-PAN heat-treated at 250 °C for different time and at different temperatures for 10 min are shown in Figure 2. Generally, XRD spectrum of PAN shows a sharp strong diffraction at $2\theta=16.5^\circ$ and a sharp weak diffraction at $2\theta=29^\circ$, with scattering maximum situated at around $2\theta=25^\circ$. The sharp and intense diffraction corresponds to a lateral repeat distance that represented the (100) diffraction in hexagonal lattice. The reflection at $2\theta=29^\circ$ confirms a second-order structure of (100) diffraction, representing the (110) diffraction.²⁴ The broad profile between (100) and (110) peak is related to the irregular structure domain, indicating the irregular structure of isotactic-PAN macromolecule throughout the polymer sample.²⁵ With increasing temperature or prolonging heat treatment time, a new peak at $2\theta=25.5^\circ$, corresponding to the

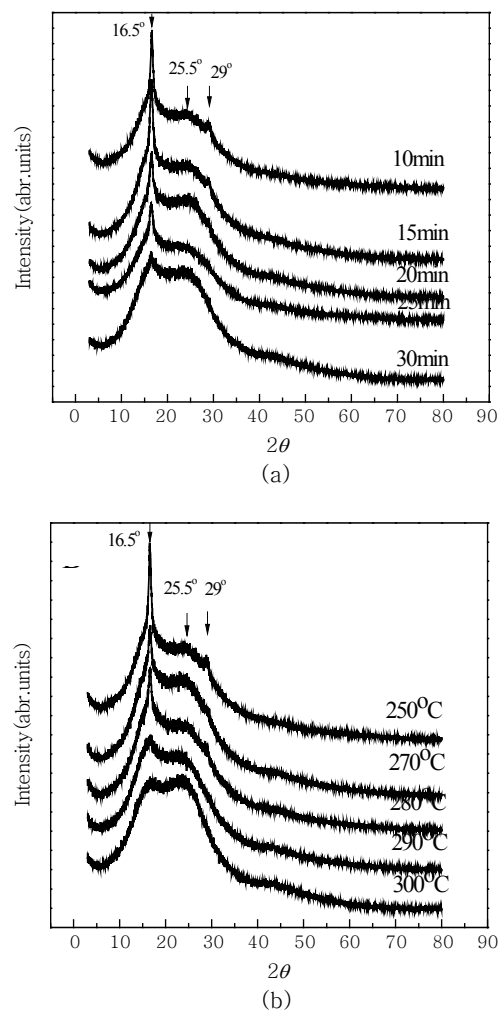


Figure 2. WAXS patterns of the isotactic-PAN heat-treated at 250 °C as a function of times (a) and as a function of temperatures for 10 min (b).

(101) diffraction, was appeared in XRD patterns, as can be observed in Figure 2. It suggested that a reaction between $-CN$ groups took place and a ladder-like structure was formed with increasing temperature or prolonging heat treatment time.

At 250 °C for 20 min (see Figure 2(a)) or at 270 °C for 10 min (see Figure 2(b)) under air atmosphere, (100) peak intensity became weak and the (110) peak almost disappeared, and however, the (101) peak intensity became strong obviously. This indicates that the regular domain in isotactic-PAN sample was destroyed gradually and the cyclization reaction occurred around the regular domain, forming ladder-like structure.

As shown in Figure 2(a), peak intensity of (100), (110) and (101) peak changed constantly with prolonging heating time at 250 °C. Diffraction intensity of both (100) peaks and (101) peaks became weaker and weaker, and the peak width at half-height did wider gradually with increasing heat treatment time, revealing that macromolecular chains of isotactic-PAN tend to be irregular with increasing heat treatment time. However, the (101) peak appeared at $2\theta=25.5^\circ$ became stronger and stronger, indicating that original regular structures were destroyed and new regular structures were formed gradually, confirming the formation of the tetrahydropyridine ladder-like structure through the cyclization of $-CN$ groups.²⁶ It is deduced that changes of (101) peak was attributed to the pileup of cyclization structure derived from isotactic-PAN during pre-oxidation.

Figure 2(b) shows the variations of peak intensity of XRD patterns of isotactic-PAN heat-treated at different temperatures for 10 min. As can be observed, a new diffraction peak appeared at $2\theta=25.5^\circ$ and its intensity increased with rising temperature. It suggests an increase of pileup of new regular structure. Meanwhile, (100) peaks became weaker and weaker and the (110) peak disappeared gradually. This means $-CN$ groups in regular domain reacted with each other to form a new structure gradually, in accordance with the report that amounts of $-CN$ groups deciding regular array reduce constantly and amounts of conjugate-nitrile groups ($-C=N-$) increase gradually.²⁷ So kinetics of cyclization reaction of $-CN$ groups can be studied quantitative by tracing the variations of (100) peaks with increasing temperature and prolonging heat treatment time. The study of the kinetics of cyclization reaction has important directive effect on pre-oxidation of PAN fiber, because PAN fiber structure is highly regular.

Cyclization Kinetic Investigation of Isotactic-PAN. In this paper, the kinetic equation of cyclization was studied from two aspects. One is from variations of (100) peak's area with varying the temperature and heat treatment time. And another is from

variations of (101) peak's area. Under the same temperature and heat treatment time, the bigger the (100) peak's area is, the less the reaction degree of $-CN$ groups and the volume cyclization structure are, and the greater the unreacted $-CN$ groups are. However, the bigger the (101) peak's area is, the bigger the reaction degree of $-CN$ groups and the volume cyclization structure are, and the less the unreacted $-CN$ groups are. The reaction degree at different temperatures and heat treatment time can be obtained from calculation of peak-fit of XRD patterns using Origin 7.0 software.

Figure 3 displays the changes of XRD peak area of isotactic-PAN heat-treated at different temperatures for different time under air atmosphere at $2\theta=16.5^\circ$. It can be found that curves in Figure 3 can be divided into two parts. Before 30 min, area of (100) peaks declined greatly with increasing heat treatment time, indicating a high reaction rate of $-CN$ groups, but after 30 min, the reaction rate of the $-CN$ groups is rather low and almost remains a constant. This case might be attributed to the previous cyclization of macromolecular chains, being very acute, and residual $-CN$ groups are less. Not all the $-CN$ groups would participate the cyclization reaction. Therefore, area of the (100) peak would level off at the

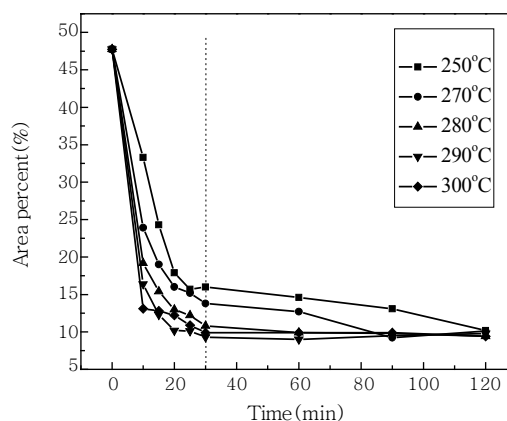


Figure 3. Changes of XRD peak area percent of the isotactic-PAN heat-treated at different temperatures for different times under air atmosphere at $2\theta=16.5^\circ$.

Table 1. Reaction Degree of $-CN$ Groups in Isotactic-PAN Macromolecule Heat-Treated at Different Temperatures and Different Heat Treatment Times under Air Atmosphere, Calculated by XRD Peak at $2\theta=16.5^\circ$

Time (min)	Temperature (°C)				
	250	270	280	290	300
0	0.000	0.000	0.000	0.000	0.000
10	0.378	0.624	0.745	0.820	0.906
15	0.613	0.752	0.846	0.923	0.914
20	0.780	0.830	0.908	0.982	0.929
25	0.838	0.851	0.929	0.984	0.963
30	0.830	0.888	0.982	1.000	0.999

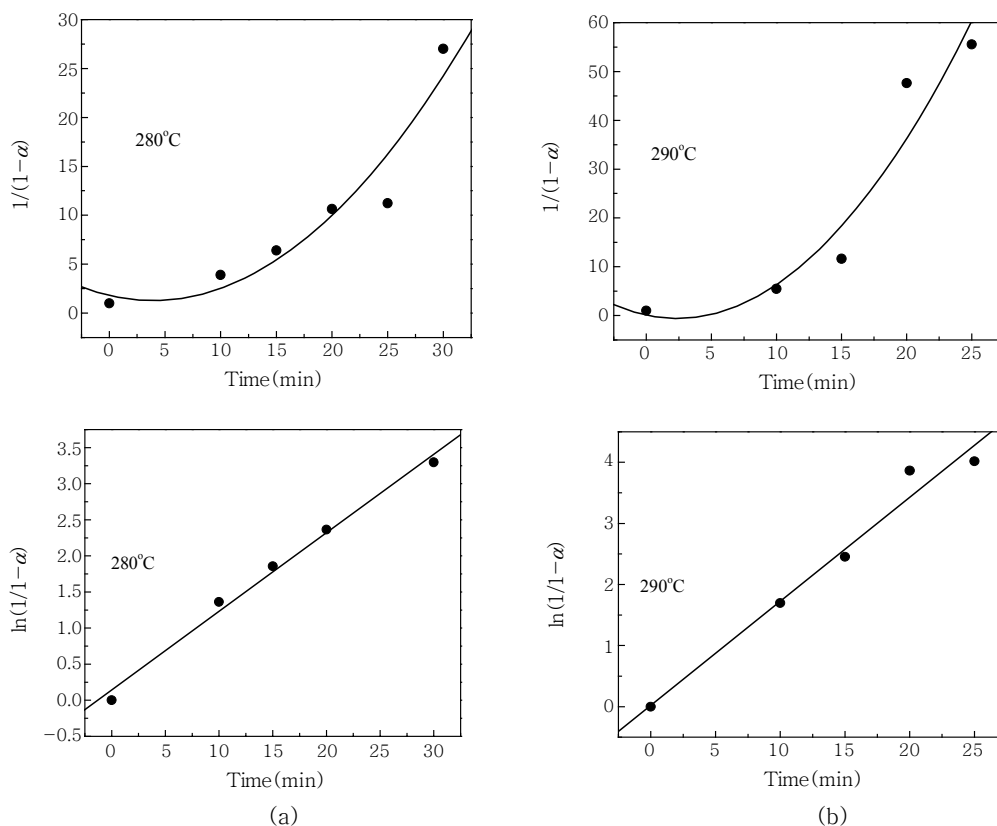


Figure 4. Partial plots of $1/(1-\alpha)$ vs. time and $\ln(1/(1-\alpha))$ vs. time of isotactic-PAN heat-treated at different temperatures from 0 to 30 min under air atmosphere, calculated by XRD peak at $2\theta=16.5^\circ$; 280 °C (a) and 290 °C (b).

Table 2. Reaction Rate Constants of Cyanic Groups in Atactic-PAN and Isotactic-PAN Heat-Treated at Different Temperatures under Air Atmosphere

		Temperature (°C)			
		270	280	290	300
k_p	isotactic-PAN	0.0722	0.1224	0.1765	0.2480
(min^{-1})	atactic-PAN	0.0253	0.0467	0.0600	0.1029

point of about 10% free $-\text{CN}$ groups being remained. So we studied cyclization kinetics of isotactic-PAN from 0 to 30 min.

According to the definition of reaction degree (α) the results are shown in Table 1. Figure 4 shows partial plots of $1/(1-\alpha)$ vs. time and $\ln(1/(1-\alpha))$ vs. time of isotactic-PAN heat-treated calculated by (100) peak at different temperatures from 0 to 30 min under air atmosphere. It can be clearly observed that $1/(1-\alpha)$ is not linear relation with time, revealing cyclization reaction is not second-order reaction. However, $\ln(1/(1-\alpha))$ is linear relation with time, indicating that cyclization reaction of isotactic-PAN belongs to first-order reaction. The rate constants are shown in Table 2.

The activation energy (E_a), achieved from the slope coefficient of the plot of $\ln k$ vs. $1/T$ according to Arrhenius

Table 3. Reaction Degree of $-\text{CN}$ Groups in the Isotactic-PAN Heat-Treated at Different Temperatures and Different Times under Air Atmosphere, Calculated by XRD Peak at $2\theta=25.5^\circ$

Time (min)	Temperature (°C)				
	250	270	280	290	300
0	0.000	0.000	0.000	0.000	0.000
10	0.377	0.518	0.744	0.817	0.904
15	0.606	0.750	0.844	0.914	0.911
20	0.778	0.828	0.906	0.979	0.927
25	0.836	0.849	0.911	0.982	0.961
30	0.828	0.885	0.963	1.000	0.987

equation, was 106.92 kJ/mol.

With the same method, variations of the (100) peak of atactic-PAN and reaction degrees of $-\text{CN}$ groups at different temperatures for different time were obtained. It is proved that cyclization reaction of atactic-PAN also belongs to first-order reaction. The reaction rate constants are listed in Table 2. The activation energy is 114.89 kJ/mol, which is slightly more than that of isotactic-PAN (106.92 kJ/mol). It might be that atactic-PAN macromolecules have good flexibility forming more regular array than isotactic-PAN macromolecule. This result might contribute to activation energy.

In order to validate further kinetics order and parameter

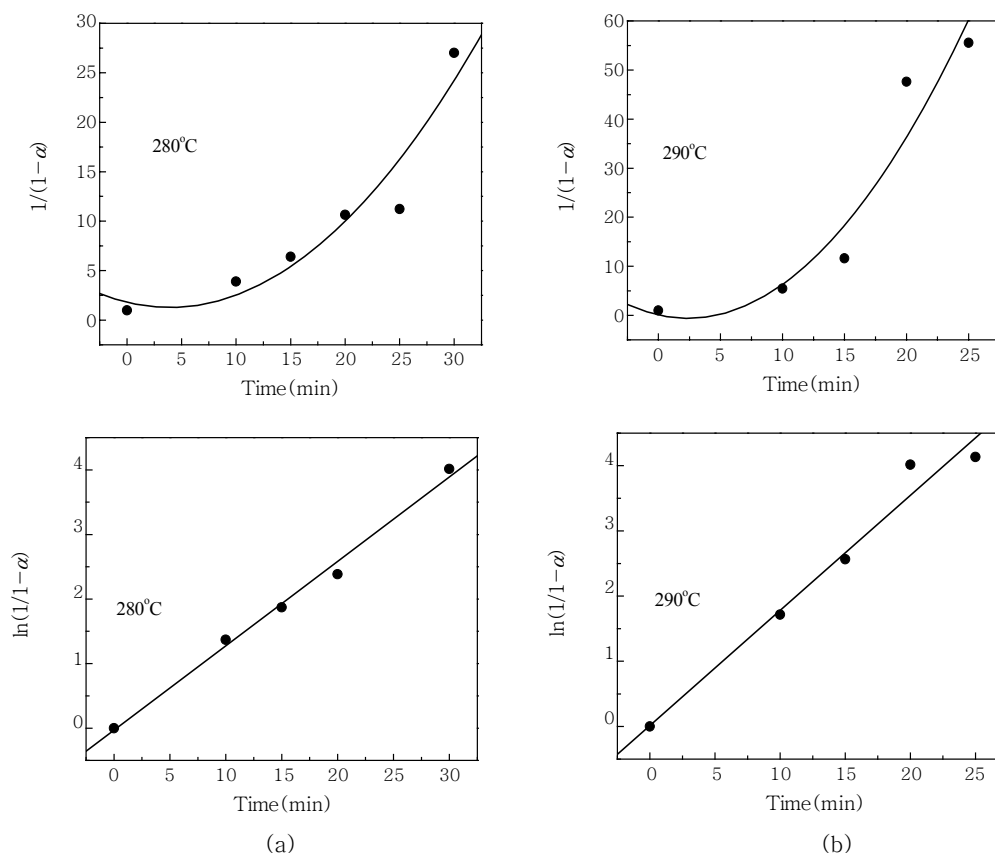


Figure 5. Partial plots of $1/(1-\alpha)$ vs. time and $\ln(1/(1-\alpha))$ vs. time of the isotactic-PAN heat-treated at different temperature from 0 to 30 min under air atmosphere, calculated by XRD peak at $2\theta=25.5^\circ$; at 280 °C (a) and at 290 °C (b).

of cyclization of $-\text{CN}$ groups in isotactic-PAN macromolecule under air atmosphere, kinetics was studied from variations of the (101) peak, which reflects the pileup of structure units of polyimide formed. The reaction degree of $-\text{CN}$ groups is defined as :

$$\alpha = \frac{S_t - S_0}{S_{\max} - S_0} \quad (3)$$

Where S_0 : (101) peak area as $t=0$,
 S_t : (101) peak area as time is t ,
 $S_{\max}$: (101) peak area as $t \rightarrow \infty$.

The values of reaction degree are listed in Table 3. $\ln(1/(1-\alpha))$ has linear relation with time (see Figure 5), revealing the reaction is first-order reaction. The reaction rate constants were obtained from slope coefficient of the line. According to Arrhenius equation $k=A \exp(-E_a/RT)$, the activation energy calculated is 112.05 kJ/mol, which is slightly higher than that (106.92 kJ/mol) calculated from variations of the (100) peak. The reason might be that cyclization reaction of $-\text{CN}$ groups in irregular domain contributes to the variations

of the (101) peak.

Conclusions

Structure characteristics and peak changes in XRD pattern of isotactic-PAN heat-treated at different temperatures for different time were investigated. The kinetics of cyclization of both isotactic-PAN and atactic-PAN was studied using XRD, and is confirmed that it belongs to first-order. Activation energy of isotactic-PAN is calculated 106.92 kJ/mol, slightly less than that of atactic-PAN (114.89 kJ/mol). This offers an important scientific basis for controlling the pre-oxidation process for producing PAN-based carbon fibers with high performance.

Acknowledgements. This work was supported by the State Key Laboratory of Chemical Resource Engineering of China in Beijing University of Chemical Technology and State Nature Science Fund of China (NSFC 50333060) during the conduct of this research.

References

1. O. P. Bahl, R. B. Mathur, and K. D. Kundra, *Fibre Sci.*

- Technol.*, **15**, 147 (1981).
2. D. D. Edie, *Carbon*, **36**, 345 (1998).
3. V. A. Bhanu, P. Rangarajan, K. Wiles, M. Bortner, M. Sankarpandian, and D. Godshall, *Polymer*, **43**, 4841 (2002).
4. T. S. Tsai and C. H. Lin, *J. Appl. Polym. Sci.*, **42**, 3045 (1991).
5. W. M. Thomas and J. J. Pelon, *J. Polym. Sci.*, **13**, 329 (1954).
6. E. Maslowski and A. Urbanska, *Am. Text Intern.*, **5**, FW 6-8 (1989).
7. P. Rangarajan, V. A. Bhanu, D. Godshall, G. L. Wilkes, J. E. Mcgrath, and D. G. Baird, *Polymer*, **43**, 2699 (2002).
8. J. S. Tsai, *J. Mater. Sci. Lett.*, **12**, 1911 (1993).
9. O. P. Bahl and L. M. Manocha, *Carbon*, **12**, 417 (1974).
10. W. Watt, *Carbon*, **10**, 121 (1972).
11. X. Zhixian and J. Riguang, *Journal of Beijing University of Chemical Technology*, **34**, 608 (2007).
12. X. Zhixian and J. Riguang, *J. Appl. Polym. Sci.*, (waiting publish).
13. M. G. Dunham and D. D. Edie, *Carbon*, **30**, 435 (1992).
14. I. Noh and H. Yu, *J. Polym. Sci.; Part B: Polym. Lett.*, **4**, 721 (1966).
15. K. Morita, H. Miyachi, and T. Hiramatsu, *Carbon*, **19**, 11 (1981).
16. J. N. Hay, *J. Polym. Sci., A-1*, **6**, 2127 (1968).
17. E. Fitzer and D. J. Müller, *Carbon*, **13**, 63 (1975).
18. K. Kamide, H. Ono, and K. Hisatani, *Polym. J.*, **24**, 917 (1992).
19. Y. Nakano and K. Hisatani, *Polym. Inter.*, **35**, 207 (1994).
20. Y. Nakano, K. Hisatani, and K. Kamide, *Polym. Inter.*, **35**, 249 (1994).
21. Y. Nakano, K. Hisatani, and K. Kamide, *Polym. Inter.*, **35**, 397 (1994).
22. Y. Nakano, K. Hisatani, and K. Kamide, *Polym. Inter.*, **36**, 87 (1995).
23. K. E. Perepelkin, *Fibre Chem.*, **35**, 409 (2003).
24. H. Hu, *X-ray diffraction technology*, Textile Industrial Company, China, p 43 (1988).
25. C. R. Bohn, J. R. Schaefgen, and W. O. Slatton, *J. Polym. Sci.*, **55**, 531 (1961).
26. D. Renjith, C. P. R. Nair, P. Sivadasan, and K. N. Ninan, *Polym. Int.*, **54**, 1110 (2005).
27. G. Zhao and B. Chen, *J. Appl. Sci.*, **6**, 278 (1988).