

Evolution of Aggregation Structure of Polyacrylonitrile Fibers in the Cyclization Reaction

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Received 13 April 2011; accepted 26 July 2011

DOI 10.1002/app.35361

Published online 21 November 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The aggregation structure of polyacrylonitrile precursor evolves gradually with progress of cyclization. In this work, the variety of cyclization degrees were determined by Fourier transform infrared spectroscopy and the evolution of aggregation structure of PAN fibers were characterized by wide-angle X-ray diffraction. Experimental results showed that the cyclization occurred first in the amorphous parts when the heating temperature was below 200°C. After heated at 200°C for 30 min, molecular chains in the pseudo-crystalline regions started to pack into crystalline regions due to the increasing stress which was produced by cyclization occurred in the amorphous phase, and the crystallinity and crystallite size increased slowly. When the temperature reached to 220°C, pseudo-crystalline regions rearranged obviously under stress,

while molecular chains in the crystalline region started to participate in cyclization, and the original crystalline structures were destructed. The two competitive processes induced that the crystallinity and crystallite size grew to the maximum values at 30 min. When the temperature up to 240°C, the cyclization occurred in the crystalline region became more intensely, while the crystallinity and crystallite size decreased out of synchronize. A scheme of evolution of aggregation structure in cyclization was modified based on the above results. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 3413–3418, 2012

Key words: polyacrylonitrile fiber; cyclization reaction; aggregation structure; amorphous region; crystalline region

INTRODUCTION

The stabilization of polyacrylonitrile (PAN) fiber is one crucial step for making high performance carbon fibers. In this process, PAN fibers were usually heat treated in air between 200 and 300°C,^{1–3} and linear molecular chains gradually changed into ladder structures through a variety of chemical reactions including cyclization, oxidation, and some other reactions.^{4–6} The variety of chemical composition and aggregation structure of original PAN fiber have important effect on the properties of the final carbon fibers.^{7,8}

The aggregation structure of PAN fiber is complicated compared with other polymers. The molecular chains were confined to rotate free and form the irregular helical conformation due to the coexistence of dipole repulsion and hydrogen bonds come from the nitrile side group.^{9–12} So the regularity of crystalline region is not very high, while the amorphous regions are also divided to disorder and relative order region (pseudo-crystalline region).

Results from the variety of molecular motion, the thermal behaviors of chains in the amorphous and

crystalline regions are different, which leads to the difference between these structures in the process of physical and chemical changes. Ko and Lin¹³ studied the process of pyrolysis for PAN fibers and found that the transformation of ladder polymer from AN units is initiated in the disordered phase, and then at the boundaries of the ordered phase. Finally the ordered phase disappeared gradually when the temperature was sufficiently high. To reveal the mechanism of the stabilization process, the investigation of the evolution of aggregation structure from the viewpoint of molecular mobility is very important.

In this study, the cyclization reaction of copolymeric PAN fiber was performed under different heating temperatures in nitrogen atmosphere. The associated changes in aggregation structure during this process were monitored by wide-angle X-ray diffraction (WAXD), based on which the effect of time and temperature on the growth and destruction of the crystalline structure were focused on, especially. The models of the evolution of aggregation structure were described for this process.

EXPERIMENTAL

Materials

PAN fiber samples containing itaconic acid and methacrylate comonomers ($\leq 2\%$) were produced by wet spinning. Ubbelohde viscometer was used to

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Contract grant sponsor: National Basic Research Program of China; contract grant number: 2006CB605302.

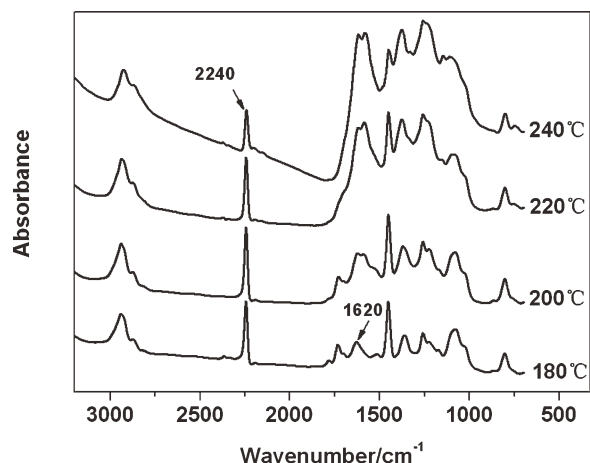


Figure 1 FT-IR spectra of PAN fiber heated at various temperatures for 30 min.

determine the viscosity of the PAN copolymer, and the weight-average molecular weight was calculated about 100,000.

Stabilization

The stabilization process was carried out in a tube furnace, which was about 60 cm in length and 8 cm in diameter. The both sides of the tube were connected to the device for nitrogen circulation. PAN fibers were fixed in a metal frame to keep a constant length and heated in the tube furnace under specific temperatures for various time.

FT-IR spectroscopy

Fourier transform infrared (FTIR) spectroscopy was performed using a Nicolet 5700 spectrometer. The infrared spectra were obtained with resolution 16 cm^{-1} in the range $4000\text{--}400\text{ cm}^{-1}$ of wavelength. Each KBr disk was prepared by 1 mg short fibers after heat treated and 100 mg KBr powder.

WAXD measurements

WAXD was performed with a D/max-2550 PC XRD (Cu $K\alpha$, wavelength $\lambda = 1.5406\text{ \AA}$) diffractometer. The X-ray generator operated at 40 kV and 250 mA.

RESULTS AND DISCUSSION

Aggregation structure changes in the cyclization reaction

When PAN fiber is heat treated in the nitrogen, there are two main chemical reactions: significant cyclization and a little dehydrogenation. Figure 1 shows the temperature dependence of the FT-IR spectrum for PAN fiber heated for 30 min, which

characterized changes of characteristics functional groups of PAN during chemical reaction. It was found that, by increasing heat treatment temperature, the intensity of the $\nu_{\text{C}\equiv\text{N}}$ band (the band at 2240 cm^{-1}) decreased rapidly, while that of the $\nu_{\text{C}=\text{N}}$ band (the band at 1620 cm^{-1}) which is generally due to the resultant unites in the stabilization PAN chains increased. It implied that the cyclization reaction progressed with the higher temperatures. A special parameter (RCI), which defined by eq. (1), was used to evaluate the relative degree of cyclization reaction.¹⁴ The result which was shown in Figure 2 indicated that during the stabilization process, the RCI was affected by temperature obviously.

$$\text{RCI} = \frac{I_{1620}}{I_{2240} + I_{1620}} \times 100\%$$

In eq. (1) RCI represents the relative degree of cyclization. I_{1620} and I_{2240} are the intensities of the absorption bands at 1620 and 2240 cm^{-1} , respectively.

Figure 3 shows the changes of WAXD profile for PAN fiber heated at temperatures in the range $180\text{--}240^\circ\text{C}$ for 30 min. In the case of as-received PAN fiber, three equatorial peaks at $2\theta = 16.9^\circ$, 25.5° , and 29.5° (θ : Bragg angle) were observed [Fig. 3(b)]. The peaks at 16.9° and 29.5° were very sharp, corresponding to the diffraction of (100) and (110) Miller planes of the crystalline part of the polymer, while the broad peak at 25.5° corresponds to the amorphous phase. It was found that when the heat treatment temperature was below 200°C , the WAXD profile of stabilized PAN fibers hardly changed. When the heat treatment temperature was increased to 220°C , the peaks at 16.9° and 29.5° became slightly

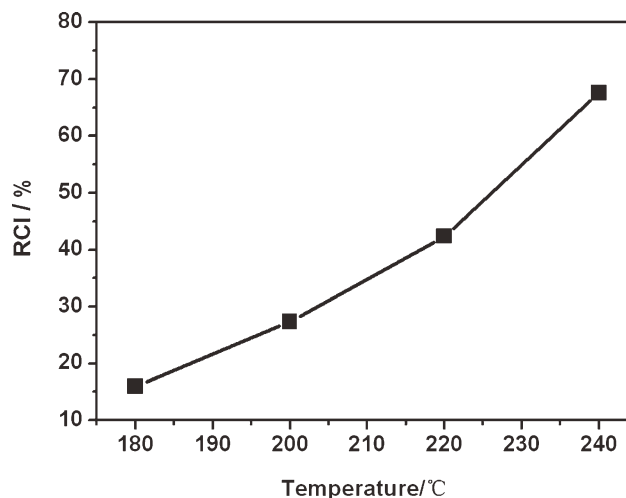


Figure 2 The temperature dependence of RCI of PAN fiber on heat treatment for 30 min.

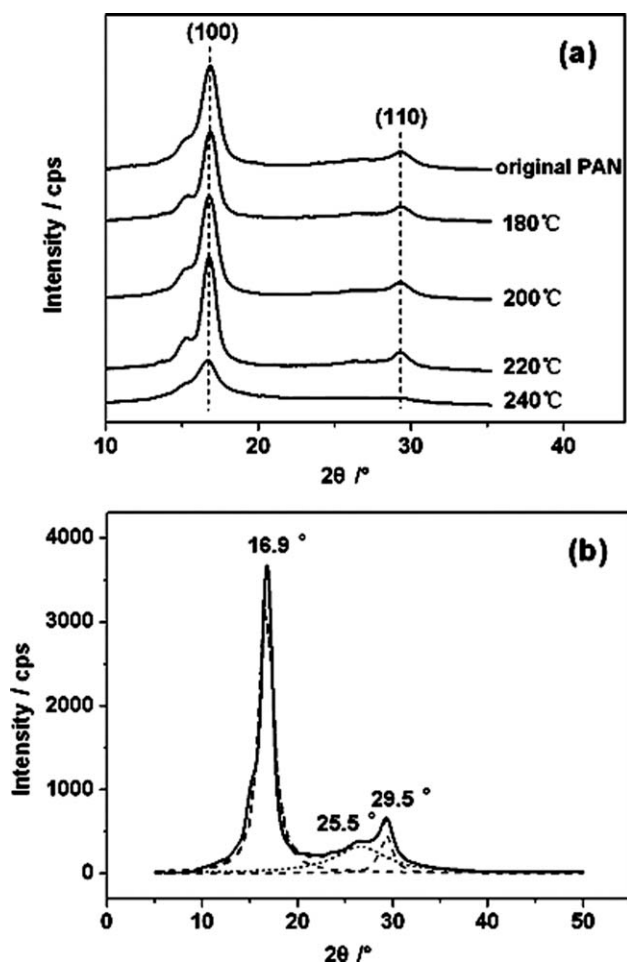


Figure 3 WAXD profiles of PAN fiber heated at various temperatures for 30 min. (a) stabilized PAN fibers; (b) the original PAN fiber, with three equatorial peaks.

sharper, which indicated that the crystal structure of PAN fiber had changed. When heating at 240°C the intensity of these two peaks decreased significantly. These changes showed that the crystal structure of the original PAN fibers gradually disappeared.

The crystallinity and crystallite size of PAN fiber before and after stabilization process were calculated by eqs. (2) and (3),^{15,16} and the results were showed in Figure 4.

$$X_c = \frac{S_c}{S_a + S_c} \times 100\%$$

where X_c represents the crystallinity of PAN fiber. S_c and S_a are the integrated intensities of the peaks for the crystalline component and amorphous phase, respectively.

$$L(a) = \frac{K\lambda}{\beta \cos\theta}$$

where $L(a)$ represents the crystallite size along the a axis. β is the half-width of the (100) diffraction peak,

K is a constant ($=0.89$), λ is the wavelength of the Cu $K\alpha$ radiation, and θ is the Bragg angle of the (100) diffraction.

When the heat treatment temperature was below 200°C, from the experimental results in Figure 2, the relative degree of cyclization had reached 27% after heated for 30 min (at 200°C). It means that the cyclization already occurred. But at this stage, the crystallinity and crystallite size did not change. Then we could conclude that the cyclization occurred only in the amorphous phase. The reason was that at this point, the thermal mobility of the molecular chains in the amorphous phase increased (above the glass transition temperature), which provided the possibility of chemical reaction of nitrile unites in PAN chains; also the comonomers which existed in the amorphous region initiated cyclization at a lower temperature through an ionic mechanism,^{17,18} thus the molecular chains in the amorphous region were converted first to ladder structure.

After the heat temperature increasing to 220°C, the crystalline size and crystallinity increased. As the crystalline structure had not been destructed, it is believed that the cyclization reaction still occurred in the amorphous phase continuously. At the same time, the mobility of the molecular chains at the boundaries of the ordered regions (pseudo-crystalline regions) enhanced, they were self-assembled into crystalline regions under the increasing stress generated by the shrinking of the molecular chains in the amorphous phase which participated in the cyclization reaction. Apparently, the crystallite size and crystallinity increased.

At 240°C, the mobility of the molecular chains in the crystalline region increased, and began to undergo cyclization and converted to the ladder structure (RCI = 69%), which resulted in the original crystal structure destructed, and the crystallite size and crystallinity decreased. By the effect of the

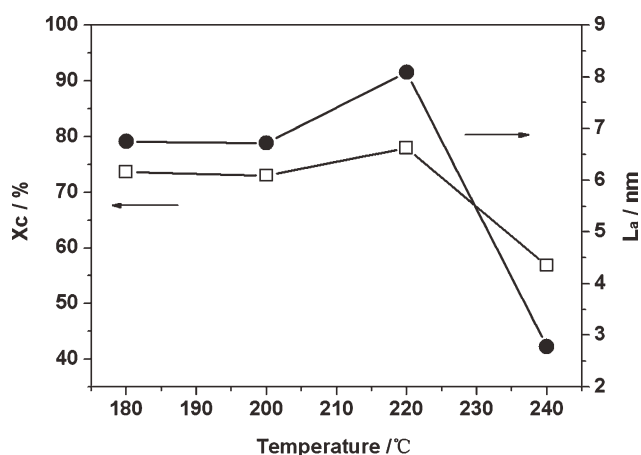


Figure 4 Crystallinity and crystallite size of PAN fiber heated at various temperatures for 30 min.

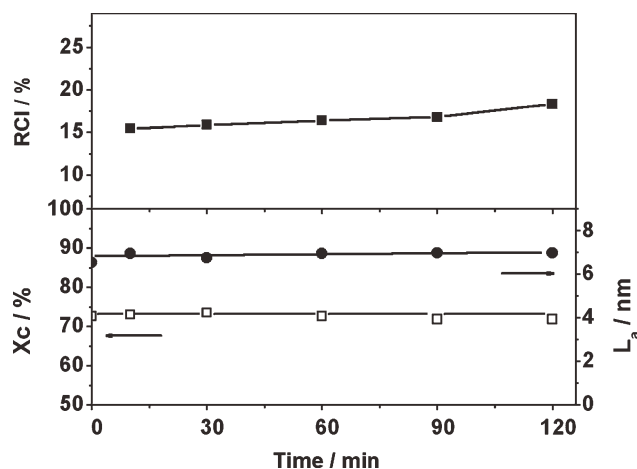


Figure 5 RCI, crystallinity and crystallite size of PAN fiber heat treated at 180°C for various times.

macromolecular structure of PAN, there are many incomplete crystalline regions in the crystal structure. It was speculated that the original crystallite split into smaller crystallite from the incomplete part as a defect of crystalline structure, and resulted in the crystallite size and crystallinity dropped out of synchronously obviously.

The effect of time and temperature on the evolution of the amorphous structure

According to the kinetics of cyclization^{19,20} the degree of cyclization is significantly dependent on the time scale. To study the time factor, PAN fiber was treated at certain temperatures for various times. Figure 5 shows the changes of RCI and crystalline structure parameters for PAN fiber heated at 180°C, as a function of time. At this treatment temperature RCI of stabilized PAN fiber increased at a very slow rate due to the relatively low content of high mobility molecular chains in the amorphous region. The crystallinity and crystallite size did not change with treatment time, indicating that cyclization occurred only in the amorphous phase at 180°C.

The RCI of stabilized PAN fiber heat treated at 200°C varied with time was showed in Figure 6. More molecular chains participated in the cyclization at 200 °C, leading to the rapid increase of RCI with the heating time over. Because the crystallinity and crystallite size did not change up to 30 min as shown in the figure, it can be concluded that cyclization reaction did not extend to the crystalline region. After 30 min, the crystallite size and crystallinity increased slowly. The aggregation structure changed at this point mainly due to the rearrangement of the pseudo-crystalline phase under the increasing stress. The schematics of the amorphous phase structure changes for PAN fiber were showed in Figure 7.

Figure 7 shows schematically the amorphous structure changes for PAN fiber with progress of the

cyclization reaction. Compared with the ordered phase, molecular chains in the amorphous phase have random alignment. At the lower treatment temperature, cyclization is assumed to be formed slowly due to suitable rotating of the molecular chains in the amorphous regions to close the nitrile group pairings (step 1 in Fig. 7). With the heat treatment temperature increasing, the reactivity of PAN molecules in amorphous regions was increased, and brought on increasing of the stress. Because the molecular chains in the pseudo-crystalline phase became more flexible and rearranged to form into crystalline regions under stress, the crystallite size and crystallinity increased (step 2 in Fig. 7).

The effect of time and temperature on the evolution of the crystalline structure

When the heat treatment temperature was increased to 220°C (Fig. 8), complex physical and chemical reactions occurred in the PAN fibers. On the one hand, with the treatment temperature further increased, molecular chains in the amorphous region involved in the cyclization reaction increased at short treatment time, which resulted the RCI of stabilized PAN fiber increased rapidly, while the molecular chains in the pseudo-crystalline phase became more flexible, and the crystallite size and crystallinity increased obviously because of the stress-induced rearrangement; on the other hand, the mobility of molecular chains in the crystal structure increased and began to participate in the cyclization at this temperature, which made the crystallite size and crystallinity decrease. These results cooperatively affected that the RCI of stabilized PAN fiber increased with time, and the crystallinity and crystallite size increased to maximum values at about 30 min (Fig. 8).

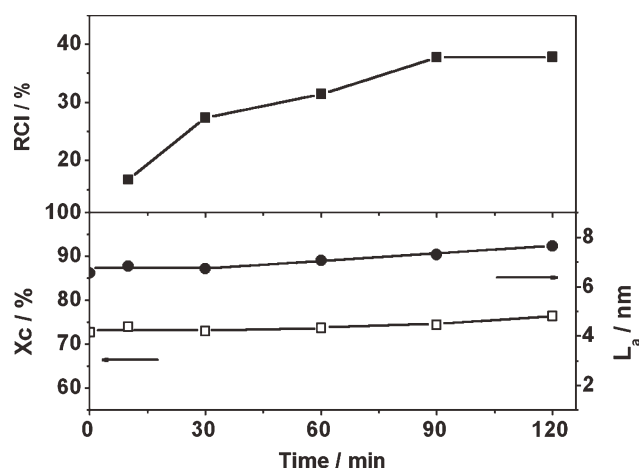


Figure 6 RCI, crystallinity and crystallite size of PAN fiber heat treated at 200°C for various times.

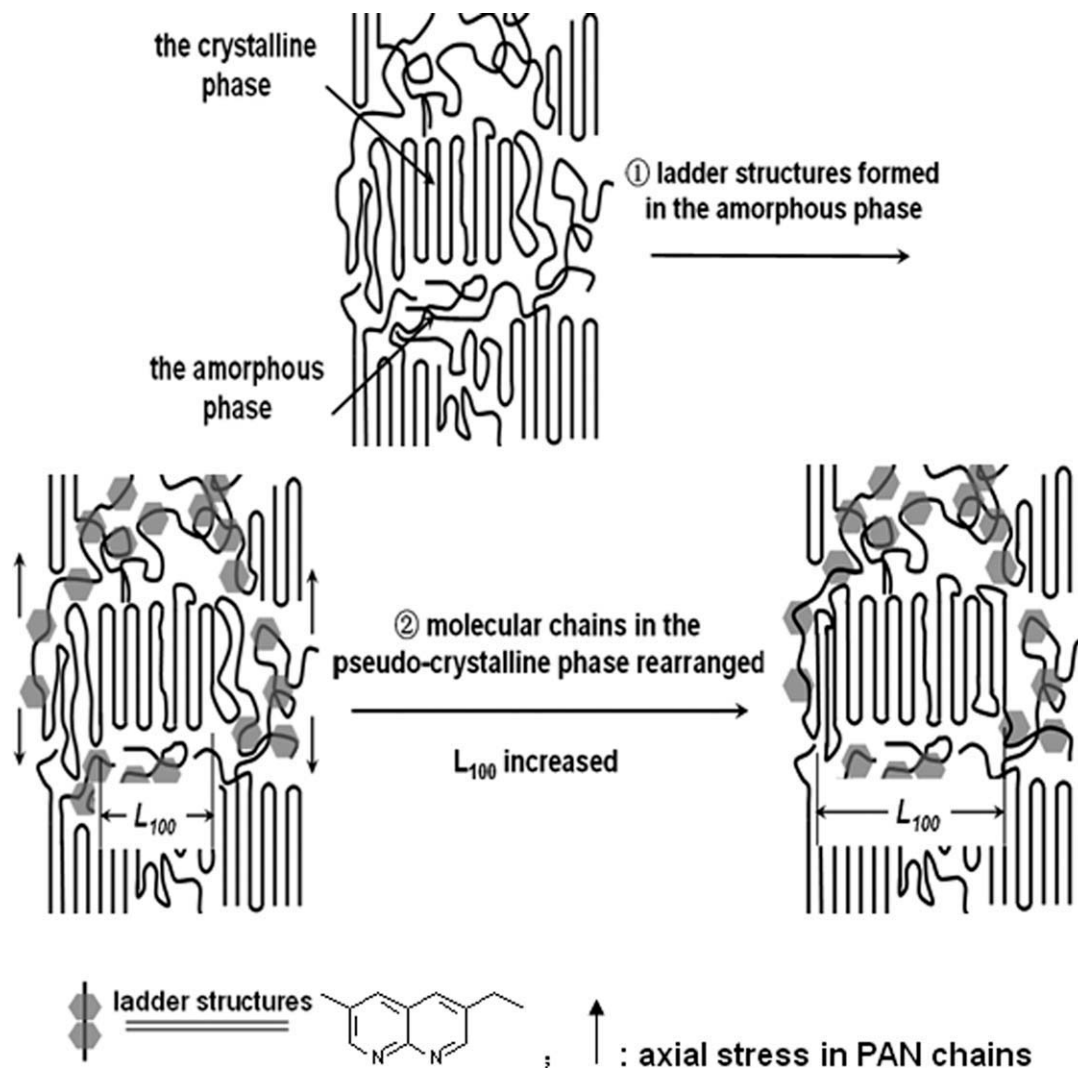


Figure 7 Depiction of evolution of amorphous structure for PAN fiber in the cyclization reaction.

When PAN fiber was heat treated at 240°C, RCI of stabilized PAN fiber increased rapidly at first (Fig. 9). After 30 min, it was significantly larger than that

of fiber heat treated at 220°C for 120 min. The crystallinity and crystallite size decreased rapidly in the first 30 min. This result implied that in the early

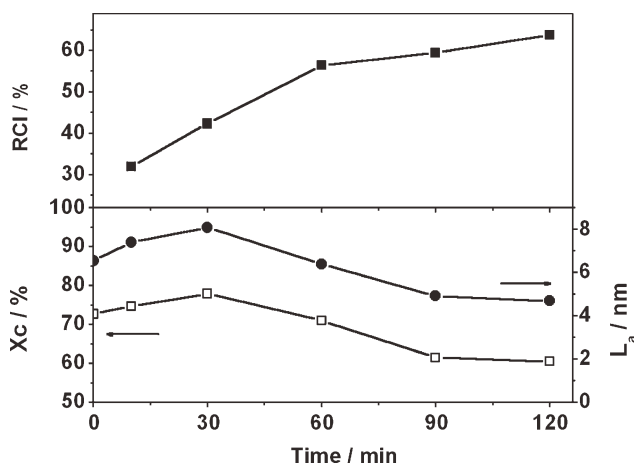


Figure 8 RCI, crystallinity and crystallite size of PAN fiber heat treated at 220°C for various times.

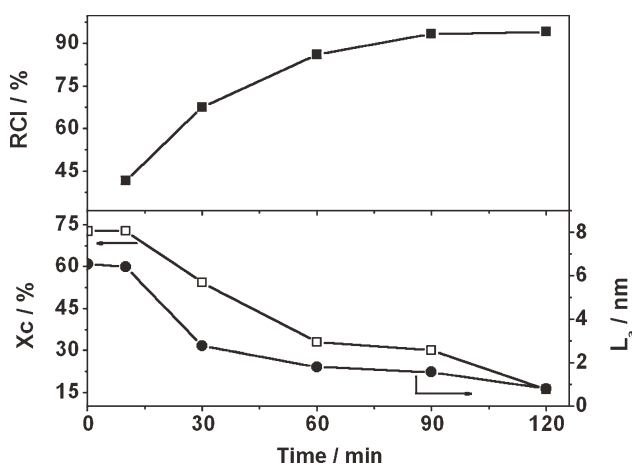


Figure 9 RCI, crystallinity and crystallite size of PAN fiber heat treated at 240°C for various times.

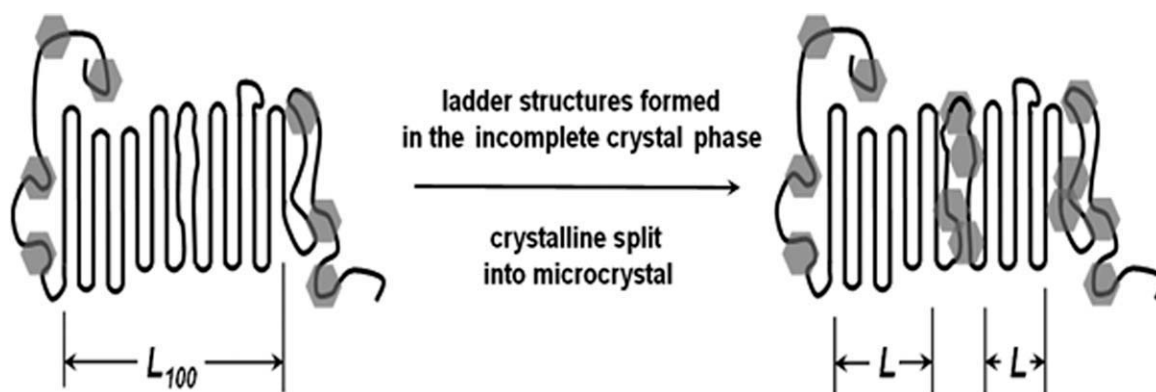


Figure 10 Depiction of cyclization occurring in the crystalline phase.

stages of heat treatment at this temperature, molecular chains in both the disordered and ordered phases participated in the cyclization, and the ladder polymer structure expanded rapidly.

The crystallite size declined significantly in the first 30 min of heat treatment time then became slowly with heat treatment for a further 30 min; while the crystallinity decreased steadily in the first 60 min of heat treatment. After 90 min the crystallinity and crystal size gradually decreased simultaneously. The interpretation of the phenomenon is that when PAN fiber was heat treated at 240°C, the molecular chains in the incomplete crystalline region participated in the cyclization rapidly, and the original crystalline structure split into smaller crystallites, then cyclization propagated in these crystallites.

As shown in Figure 10, when PAN fiber was heat treated at higher temperature, molecular chains in the incomplete crystalline region were rapidly converted to the ladder structures, and the original crystalline region split into smaller crystallites, which resulted the crystallite size declined sharply. When the cyclization propagated in these micro-crystallites, the crystallite size and crystallinity then decreased gradually and simultaneously.

CONCLUSIONS

The reactivity of the nitrile group of PAN molecules, which is important for the cyclization, was affected by the aggregation structure. Cyclization started from the amorphous phase because of the random state of molecular chains in these regions. The degree of cyclization at this primary stage increased relatively slowly due to the crystalline domains. After PAN fiber was heated at 200°C for 30 min, molecular chains in the pseudo-crystalline phase began to be activated and rearranged under stress, result-

ing in the growth of crystalline structure. Increases of both crystallinity and crystallite size could be observed. When PAN fiber was heat treated above 220°C, molecular chains in the crystalline phase were involved in the cyclization reaction. When heat treatment temperatures up to 240°C, molecular chains in the incomplete crystalline phase rapidly formed the ladder structure, and the original crystalline region split into smaller crystallites. Cyclization then extended to the whole crystalline region.

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