

Evolution of the crystalline structure and cyclization with changing tension during the stabilization of polyacrylonitrile fibers

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ABSTRACT: The effects of tension on the crystalline structure and cyclization of polyacrylonitrile fibers during stabilization were investigated. The degree of cyclization was measured by Fourier transform infrared spectroscopy and differential scanning calorimetry. The crystalline structure was characterized by wide-angle X-ray diffraction. When the fibers were heat-treated at temperatures between 175 and 218°C, the tension mainly affected the cyclization in the amorphous regions through changes in the spatial distance of the chain segments; this led to a relatively higher cyclization degree under moderate tension. When the temperatures ranged from 226 to 232°C, the reactions extended to the crystalline regions. The chemical bonds became greater in the cross section of the fibers, and this was caused by cyclization structures formed in the former stage. Therefore, the optimum tension was higher than in the prior temperature range. At higher temperatures ranging from 238 to 270°C, a crosslinked structure formed, so the optimum tension increased continually. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42182.

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INTRODUCTION

The properties of carbon fibers depend mostly on the qualities of their precursor fibers and the heat-treatment steps, including stabilization and carbonization. Among those processes, stabilization is considered to be an indispensable step because high-performance carbon fibers are generally obtained only when a modest degree of stabilization is achieved.¹

However, during oxidative stabilization, the preferred orientation of fibers usually decreases; this is attributed to physical shrinkage of the molecular chains and chemical reactions.^{2–4} Therefore, tension must be applied during the stabilization to resist the shrinkage and improve the orientation of the fibers. Tension can prevent the physical shrinkage of polyacrylonitrile (PAN) chains and improve their orientation degree.⁵ Nonetheless, it can affect the chemical shrinkage simultaneously; this leads to the formation of ladder structures and affects the carbon yields. Such a situation raises a critical demand for researchers in the field to find a proper tension that is capable of improving the orientation of the PAN chains without compromising their cyclization degree.^{5–13} Bahl and Mathur¹⁴ found that the oxidation shrinkage continued to decrease with increasing load at 240°C. However, Lian *et al.*¹⁵ reported that at 180°C, when the stretching ratio was smaller than 1.04, the cyclization degree was hardly influenced. However, when the stretching ratio exceeded 1.06, the

cyclization degree decreased. On the basis of the Arrhenius equation, the cyclization reaction rate will be higher when the temperature is higher. Wu *et al.*¹⁶ indicated that from 190 to 210°C, stretching had a favorable effect on cyclization during heat treatment. From 210 to 230°C, when the chains were treated at temperatures high enough to vibrate and rotate themselves, stretching imposed a depressing effect on the initiation of cyclization. In addition, Wang *et al.*¹⁷ found that cyclization was affected by the aggregation structure, and the degree of cyclization in this primary stage increased relatively slowly. When the temperature became high enough, molecular chains in the crystalline regions started to participate in cyclization, and the original crystalline structures were destroyed.

These results show that various tensions should be applied at different stabilization stages. In the previous studies, the effect of tension on the cyclization degree of polyacrylonitrile molecules was mainly focused on temperatures below 230°C,^{10,13,15–17} in which the reactions mostly took place in the amorphous region, and the comparison between different temperature ranges was not sufficient. Because there are two aggregated structures of PAN chains in fibers in the form of crystalline and amorphous regions, the cyclization reactions in the crystalline and amorphous regions are different; this reveals that research on crystalline evolution with tension is necessary.

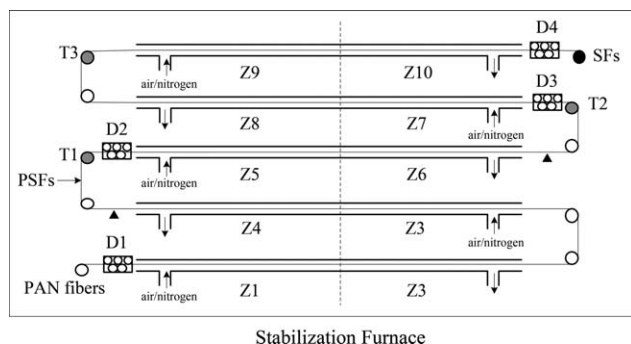


Figure 1. Scheme of the continuous stabilization line: (Z1–Z10) temperature zones, (D1–D4) stretching rollers, and (T1–T3) tension sensors. The fibers going through Z1 to Z4 were named PSFs, and those going through Z1 to Z10 were named SFs.

In addition, most stabilization treatments in the literature were carried out in air, where the oxidation reaction would make it complex to individually study the cyclization reaction. To overcome such a problem, it is possible to separate reactions by alteration of environment in air or nitrogen. Furthermore, the effect of the crosslinked structure formed by oxygen on the shrinkage of the fibers cannot be ignored when the temperature is up to 242°C.

In this study, to clarify the effect of tension on the evolution of the crystalline structure and cyclization during stabilization, various tensions were applied on PAN precursor fibers at different stages of stabilization in either air or nitrogen.

EXPERIMENTAL

Materials

The precursor fibers used in this research (the precursors of carbon fibers, TR 30S 3L, Mitsubishi Co., Japan) were made of copolymers of acrylonitrile/acrylamide/methacrylic acid [as determined by the results of Fourier transform infrared (FTIR) spectroscopy and differential scanning calorimetry (DSC) of these precursor fibers and comparison with the results of the precursor fibers with known chemical compositions and the comonomers] and had 3000 filaments in a bundle. The average diameter was 11.3 μm (as measured by a CYG-055C optical microscope with a closed-circuit television camera). The sonic velocity and sonic modulus of the PAN fibers were 6.25 km/s and 46.3 GPa. The average crystal size was 14.05 nm. The orientation degree of the PAN crystallite was 86.5%, and the crystallinity was 43.9%.

Stabilization

The whole stabilization was carried out in a self-designed continuous production line composed of a 10-zone tube furnace (each tube had two zones), as illustrated in Figure 1. The precursor PAN fibers were oxidized continuously by being passed through each tube 500 mm in length and 32.5 mm in diameter for 13.6 min. In this study, the 10 temperature zones were classified into three stages, and in different stages, the tensions were adjusted by self-correction of the rotating speed of the rollers separately through the sending of the feedback from the tension sensor to the stretching rollers. Before the experiment, the ten-

sion sensors (TSH-5000-A3-R1, Schmidt, Germany, with $\pm 1\%$ precision) were calibrated by analytical weights of 50, 100, 200, and 500 g. The oxidation temperatures from Z1 to Z10 were 175, 190, 208, 218, 226, 232, 238, 248, 258, and 270°C, respectively; these were determined by DSC of raw PAN to ensure the reaction heat was gradual and stable in the process of oxidation. To investigate the effect of tension on cyclization, the experiments were carried out in air and nitrogen, respectively, with the other parameters kept the same. Samples were obtained at the ends of zones 4, 6, and 10; these samples were named A4 and N4, A6 and N6, and A10 and N10, respectively, where A indicates experiments performed in air and N indicates experiments performed in nitrogen. Also, tensions applied on the fibers from 300 to 700 cN were labeled as 3 to 7 after the hyphen, as shown in Table I.

The detailed parameters are listed in Table I

Characterization

FTIR Analysis. FTIR spectroscopy was conducted on a Nicolet-8700 FTIR spectrometer in the 4000–400 cm^{-1} range with a 2- cm^{-1} resolution with an attenuated total reflectance accessory. The samples were obtained from the production line after they were treated in different zones. The ring closure index (RCI) of the heat-treated PAN fibers was introduced and is defined as follows:^{18,19}

$$\text{RCI} = \frac{\frac{I_{\text{C}=\text{N}}}{(I_{\text{C}=\text{N}})_{\infty}}}{\frac{I_{\text{C}=\text{N}}}{(I_{\text{C}=\text{N}})_{\infty}} + \frac{I_{\text{C}\equiv\text{N}}}{(I_{\text{C}\equiv\text{N}})_0}} \times 100\% = \frac{\frac{(I_{\text{C}\equiv\text{N}})_0}{(I_{\text{C}\equiv\text{N}})_{\infty}} I_{\text{C}=\text{N}}}{\frac{(I_{\text{C}\equiv\text{N}})_0}{(I_{\text{C}\equiv\text{N}})_{\infty}} I_{\text{C}=\text{N}} + I_{\text{C}\equiv\text{N}}} \times 100\% \times \frac{f \cdot I}{f \cdot I_{\text{C}=\text{N}} + I_{\text{C}\equiv\text{N}}} \times 100\% \quad (1)$$

where $I_{\text{C}=\text{N}}$ and $I_{\text{C}\equiv\text{N}}$ are the C=N absorbance centered at 1600 cm^{-1} and the C \equiv N absorbance centered at 2243 cm^{-1} ,

Table I. Processing Parameters of Continuous Stabilization

Sample		Tension (cN)		
In air	In nitrogen	Z1–Z4	Z5–Z6	Z7–Z10
A4-3	N4-3	300	—	—
A4-4	N4-4	400	—	—
A4-5	N4-5	500	—	—
A4-6	N4-6	600	—	—
A4-7	N4-7	700	—	—
A6-3	N6-3	500	300	—
A6-4	N6-4	500	400	—
A6-5	N6-5	500	500	—
A6-6	N6-6	500	600	—
A6-7	N6-7	500	700	—
A10-3	N10-3	500	500	300
A10-4	N10-4	500	500	400
A10-5	N10-5	500	500	500
A10-6	N10-6	500	500	600
A10-7	N10-7	500	500	700

A and N in the sample names indicate experiments that were performed in air and nitrogen, respectively.

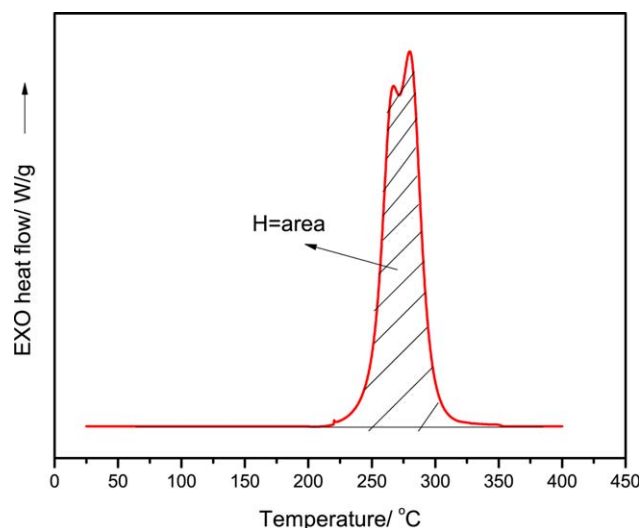


Figure 2. Scheme for the calculation of H . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

respectively. The constant parameter f represents the ratio of the respective absorptivity constants (as) centered at 2243 and 1600 cm^{-1} . Because the nitrile concentration (I_0) was equal to $I_0 = I_{(2243)}/a_{(2243)}$ at reaction time $t = 0$ and $I_0 = I_{(1600)}/a_{(1600)}$ at $t = \infty$, where $I_{(2243)}$ and $I_{(1600)}$ are the respective measured absorptions at 2243 and 1600 cm^{-1} , an estimate of f could be obtained by the ratio of $I_{(2243)}$ at $t = 0$ to $I_{(1600)}$ at $t = \infty$. The subscripts 0 and ∞ indicate that the times were 0 and a sufficiently long time (in this study, the time was 1000 min, and the sample was heated from 170 to 270 °C with a heating rate of 0.1 °C/min) during the thermal oxidative stabilization, and the value of f was 0.29.

Wide-Angle X-ray Diffraction (WAXD) Analysis. The wide-angle diffraction pattern were measured at Shanghai Synchrotron Radiation Facility BL14B1 beam line station. The average size of the laterally order domains (L_c) referred to as the crystal size, was estimated with the Scherrer equation:

$$L_c = K\lambda / (B \cos \theta) \quad (2)$$

where λ is the wavelength of the X-ray (1.24 Å); B is the full width at half the maximum intensity, which was estimated from the (100) peak at $2\theta = 13.5^\circ$; θ is the angle of incidence; and K is a constant, assigned as 0.89. Because the position of the peak was related to λ , the peak of (100) was different than in some other works.^{16,20}

The crystallinity was determined by the fitting of the WAXD curves and with the ratio of the area of the crystalline peaks to the total area.

The orientation degree of the crystalline PAN (f_c) was determined by the following equation, where w is the full width at half of the Azimuthal angle:²¹

$$f_c = \left(1 - \frac{w}{180}\right) \times 100\% \quad (3)$$

Thermal Analysis. DSC was carried out in a Mettler Toledo DSC-822 machine (Mettler Toledo, Switzerland) under nitrogen. The scanning range was from 25 to 450 °C, and the heating rate was 10 °C/min. The degree of cyclization (DC) was determined by the following equation:²²

$$DC = \left(1 - \frac{H}{H_0}\right) \times 100\% \quad (4)$$

where H_0 and H are the enthalpies of the PAN precursor fibers and oxidative stabilized fibers in a nitrogen atmosphere. H_0 and H were calculated by the integration of the total area under the exothermic peaks related to the stabilization reactions in the DSC plots, as shown in Figure 2.

Sound Velocimeter Analysis. The sonic velocity along the fiber axis to indicate the overall orientation of molecules was measured by an SCY-III D sound velocimeter (Donghua Kaili Co., China). The sonic modulus was determined by the following equation:²³

$$E = \rho V^2 \quad (5)$$

where E is the modulus in units of force per unit cross-sectional area; ρ is the volume density, which was measured by the sink–float method; and V is the sound velocity.

RESULTS AND DISCUSSION

Effect of Tension on the Orientation Degree and Crystallinity

The densities together with the sonic velocity of all of samples are show in Table II. The sonic modulus of the partially stabilized fibers, as shown in Figure 3, indicated the relationship between the overall orientation (including both crystalline and amorphous regions) and the applied tension. It was clear that the sonic moduli of both the A4 and N4 series increased with increasing tension, and the sonic modulus of the fibers treated in nitrogen was higher than those treated in air under the same tension. Obviously, as shown in Figure 3(c,d), the sonic modulus of both A6 and N6 increased more slowly than that of A4 and N4, and the sonic modulus got lower than it had been in

Table II. Densities and Sonic Velocities of Partially Stabilized Fibers in Air and Nitrogen Under Different Tensions

Tension (cN)	Density (g/cm ³)					Sonic velocity (km/s)				
	A4	N4	A6	N6	A10	A4	N4	A6	N6	A10
300	1.1903	1.212	1.206	1.3199	1.3672	3.6	4.3	3.5	3.7	2.2
400	1.1887	1.2005	1.1975	1.3236	1.3704	3.8	4.7	3.9	3.8	2.2
500	1.1852	1.2063	1.1964	1.3228	1.3737	4.9	5.5	4.0	5.0	2.2
600	1.1834	1.2053	1.1987	1.3241	1.3748	5.2	5.7	3.9	4.4	2.4
700	1.1816	1.2028	1.1996	1.3257	1.393	5.5	5.9	4.4	4.5	2.5

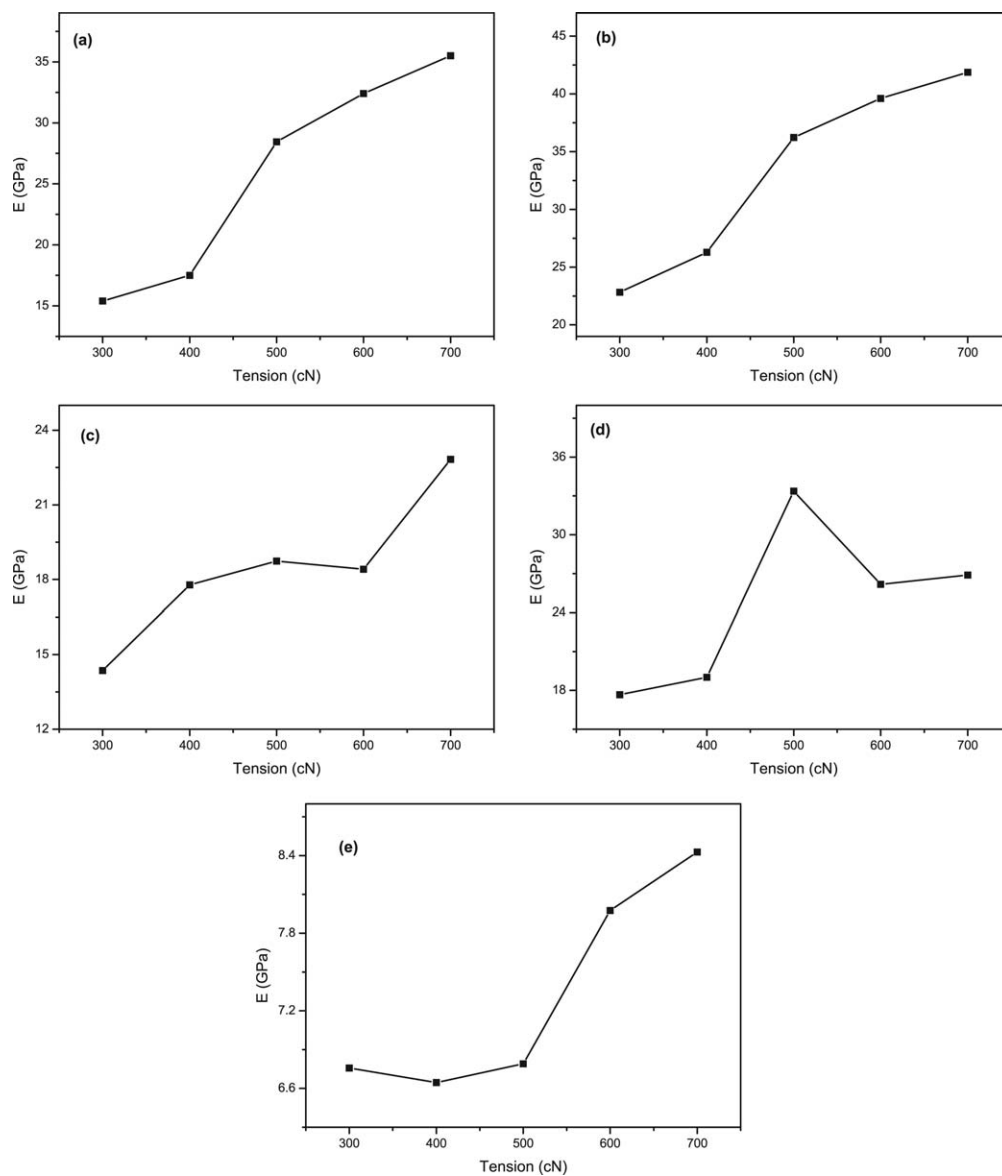


Figure 3. Sonic moduli of the partially stabilized fibers in air and nitrogen atmospheres under different tensions: (a) A4, (b) N4, (c) A6, (d) N6, and (e) A10.

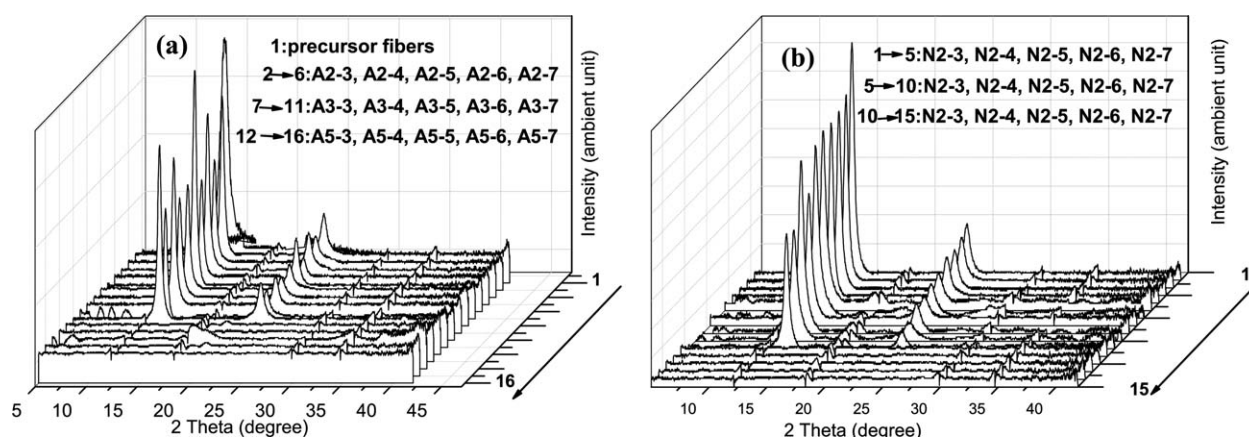


Figure 4. WAXD patterns of the partially stabilized fibers and stabilized fibers under different tensions: (a) air atmosphere and (b) nitrogen atmosphere.

Table III. Crystallite Parameters of the Partially Stabilized Fibers in Air and Nitrogen Under Different Tensions

Sample	f_c (%)	L_c (nm)	Crystallinity (%)	Sample	f_c (%)	L_c (nm)	Crystallinity (%)
A4-3	85.4	13.7	43.5	N4-3	84.3	13.3	38.6
A4-4	85.8	14.0	44.3	N4-4	85.4	13.5	39.6
A4-5	86.3	14.0	45.3	N4-5	85.9	13.8	40.6
A4-6	87.7	14.1	46.2	N4-6	86.6	13.9	42.7
A4-7	87.3	14.7	46.4	N4-7	86.9	14.1	42.8
A6-3	77.9	13.2	38.7	N6-3	83.4	13.3	34.4
A6-4	83.2	13.4	39.9	N6-4	82.8	13.2	31.5
A6-5	83.6	13.6	40.8	N6-5	81.3	13.1	31.6
A6-6	86.6	13.8	40.8	N6-6	80.8	12.9	32.0
A6-7	87.3	13.9	40.9	N6-7	82.1	12.9	30.3
PAN	86.5	14.1	43.9	—	—	—	—

f_c represents the orientation degree of crystalline PAN.

the former stage. This means that the thermal reactions in air or in nitrogen decreased the molecular orientation, and the applied tensions along the fibers restrained the disorientation efficiently.

By the way, the samples obtained from the temperatures ranging from 238 to 270°C in nitrogen were very brittle because of a few intermolecular crosslinks produced by oxygen. That was why they could not be measured by the sound velocimeter. The sonic moduli of the fully stabilized fibers in air showed little increase with tension, as depicted in Figure 3(e). On the basis of the Arrhenius equation, the cyclization reaction rate increased quickly with increasing temperature, accompanied with increased shrinkage; Hence, the applied tensions along the fibers restrained the shrinkage.

The WAXD patterns of the partially stabilized fibers are shown in Figure 4. The values in Table III are calculated from the information shown in Figure 4; this indicates that the crystalline parameters of the fibers had a relationship with the tension. At temperatures from 175 to 218°C, the crystalline parameters of the fibers treated in nitrogen were smaller than those of the fibers treated in air, although their crystallinities all increased with increasing tension. In the next temperature range, from 226 to 232°C, the crystallite parameters still increased with increasing tension in air.

When the fibers were treated in a lower temperature range, from 175 to 218°C, in air or in nitrogen, not only did both the overall orientation and the orientation of crystalline regions increase with increasing tension, but the crystallinity and L_c also increased. We considered that most of the chemical reactions did not largely happen in this temperature range; therefore, the crystalline regions were mostly preserved during this period. Without the applied tension, in this heat treatment, the molecular chains shrank because of entropic shrinkage of the oriented molecular chains in the amorphous regions, and the crystalline regions acted as crosslinks and held the structures together.⁵ Thus, the overall orientation and the orientation of the crystalline regions varied with applied tension. The tension detected was attributed to two reasons: one stemmed from the restrain-

ing of the entropic shrinkage of the molecular chains, and the other came from the applied stretching at different ratios. Thereby, the tension reduced the side effects of entropy induced by the disorientation of the PAN chains in amorphous regions and improved the orientation of the crystalline regions. The tension was likely to make some PAN chains near the crystallite boundary adjust and align in an orderly manner; this led to the growth of crystallinity and also caused an increase in L_c .

At a higher temperature ranges from 226 to 232°C, the crystallinity and L_c became lower in comparison with the previous stage, whereas the crystallinity of the fibers treated in air increased gradually from 38.68 to 40.90% with increasing tension from 300 to 700 cN. The results suggest that in this stage, the reactions possibly extended to crystalline regions at the rising and turned the PAN linear macromolecule into a ladder structure.¹⁶ As shown by the data in Table III, the tension also promoted both the crystallinity and orientation degree of the crystalline regions; this indicated a similar but slower adjusting process happened in this stage.

DSC measurements of both A4 and N4 were placed in nitrogen, as shown in Figure 5, in which only a cyclization reaction occurred. The onset temperature of N4-5 was 194°C, which was lower than that of A4-5 (215°C); this indicated further cyclization of the partially stabilized fibers depended on its heating history in nitrogen or in air. The main reason for the difference was caused by the existence of oxygen. According to Fitzer and Müller,²⁴ the consecutive cyclization of activated centers is inhibited by oxygen because of the increase in the activation energy.

When the cyclization reaction extended into the crystalline regions in nitrogen, the original rigid crystalline structures were destroyed, as evidenced by the decrease in the crystalline orientation, which was accompanied a decrease in the crystallinity with increasing tension. The orientation of the crystalline regions decreased; this may have been due to the increasing mobility of the molecular chains in the crystalline regions and the shrinkage caused by cyclization in these regions. The overall orientation of the PAN fibers still had a tendency to increase;

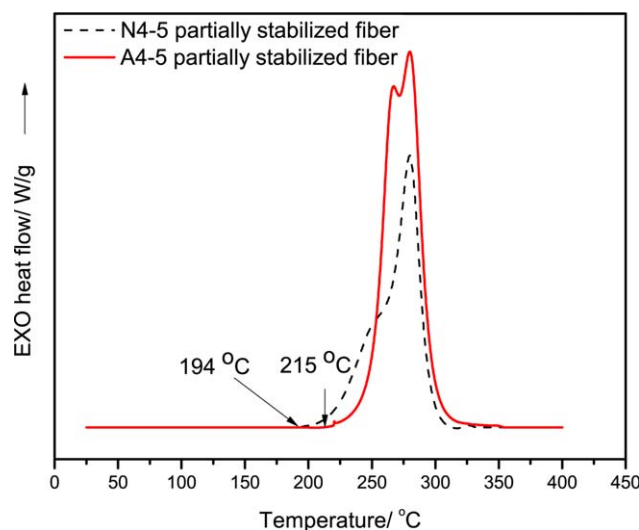


Figure 5. DSC curves of the partially stabilized fibers of N4–5 and A4–5 at a heating rate of 10°C/min in nitrogen. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

this implied that the tension mostly improved the orientation of amorphous regions in this stage.

Effect of Tension on the Cyclization

The cyclization index (CI) values of the partially stabilized fibers and fully stabilized fibers were evaluated by DSC and FTIR analysis. As shown in Figure 6, although the values of CI were not the same, the variation tendencies were similar.

For the fibers treated at the temperatures from 175 to 218°C, the CI evaluated by both DSC and FTIR spectroscopy showed a slight increase from 300 to 400 cN and then decreased when the tension increased from 400 to 700 cN. In this temperature range, most of the cyclization reactions occurred in the amorphous regions, and the initiation of cyclization probably depended on stereochemical features of the PAN chains. Appropriate relative positions of the adjacent nitrile groups were beneficial to the formation of a conjugated ladder structure.^{17,25}

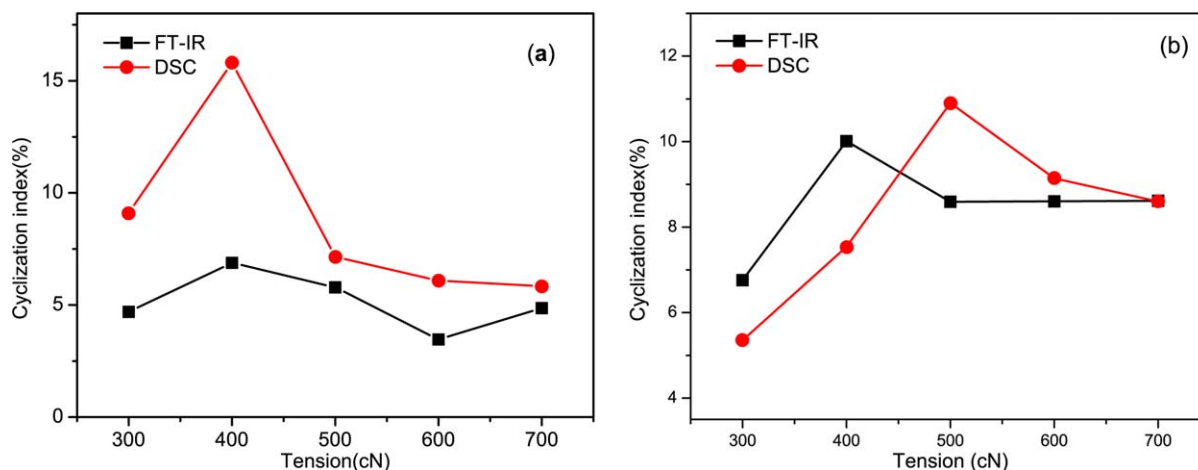


Figure 6. Degree of cyclization of partially stabilized fibers under various tensions: (a) A4 and (b) N4. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Within this temperature range, where the PAN chains were in a high elastic state and the number and mobility of the chain segments participating in cyclization were limited, the applied tension had an effect on molecular chains through chemical bond rotation or chain segment movement to adjust their spatial conformation. It is possible that an appropriate tension was able to prevent the PAN chains from entangling and made a portion of the chain segments overcome the dipole repulsion between nitrile groups; this then led the chain segments or chains in the amorphous regions having enough energy to overcome the hindrance and adjust themselves to a position suitable for cyclization.

When the tension became higher, the draw ratio changed from -0.2% at 300 cN to 0.9% at 400 cN and kept increasing with increasing tension. A higher extension of the PAN fibers could have been the induced deformation of PAN chains, especially in amorphous regions. Adjacent nitrile groups were drawn away from each other, and the spatial distance between the nitrile groups along the helix molecule chains increased. This made the cyclization reaction more difficult.

Another probable reason for the decrease in CI was that the tension induced some PAN chains near the crystalline regions to adjust and align in an orderly manner. This led to the growth of crystallinity. The growth in crystallinity meant that fewer nitrile groups in the amorphous regions reacted during cyclization.

The CI of partially stabilized fibers treated from 226 to 232°C is shown in Figure 7. In this temperature range, the mobility of the chain segments became higher; this made more chain segments in the amorphous regions have enough energy to vibrate and rotate for cyclization.

CI of the fibers treated in air increased when the tension changed from 300 to 500 cN and then gradually decreased with increasing tension from 500 to 700 cN. The crystallinity of the partially stabilized fibers in air still increased with increasing tension, the same as the orientation of the ordered regions changed. However, the extent of the increase was slower than in the previous stage; this implied that more chain segments participated in cyclization,

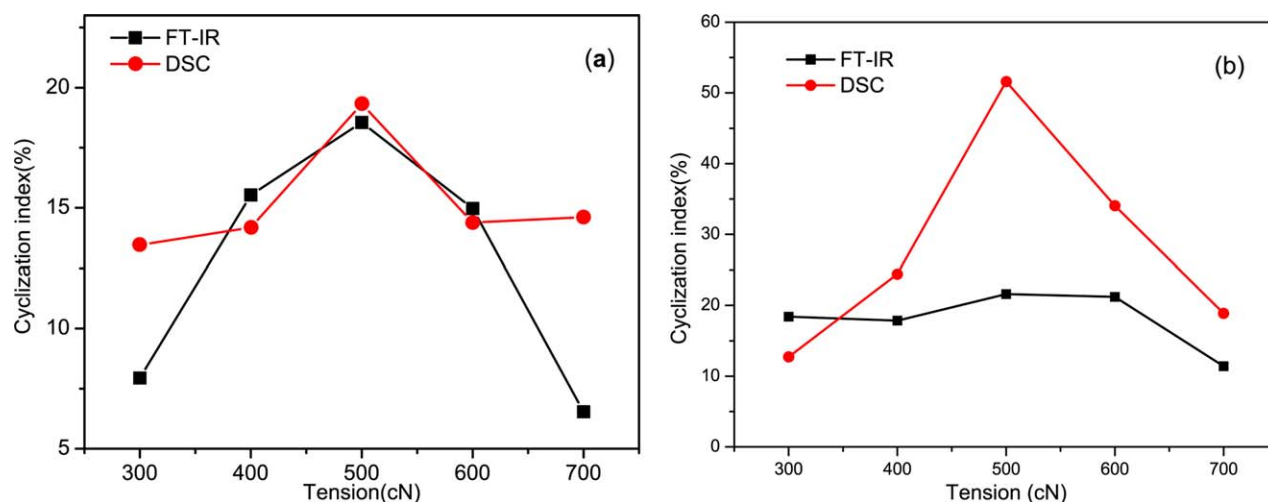


Figure 7. Degree of cyclization of the partially stabilized fibers under various tensions: (a) A6 and (b) N6. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

perhaps in the newly formed ordered regions, which were more or less flexible, and the growth of crystallinity became slower with the induction of tension. Both the orientation of the PAN chains and the orientation of the ordered regions increased with increasing tension. It could be speculated that the effects of the tension were similar to those in the previous stage. The tension facilitated cyclization when it was increased to a moderate amount, and excessive tension had negative effects on cyclization; this was consistent with previous work.¹⁶

Figure 7(b) shows that the values of CI of the fiber treated in nitrogen were higher than those of the fibers treated in air. For fibers stabilized in nitrogen, only a cyclization reaction occurred, and the cyclization reacted faster and sharper without the inhibition of oxygen. Both the crystallinity and orientation of the crystalline regions were lower than those of the partially stabilized fibers in air at the same temperature. The values of the crystallinity and orientation of ordered regions decreased gradually with increasing tension. We considered that the cyclization reaction extended into the crystalline regions in nitrogen.

When the cyclization reaction occurred in these regions, the original crystalline structure was destroyed because of the decreasing crystallinity.

There were many oriented chains in the crystalline regions. When the crystalline structure was destroyed, the mobility of the chain became better at high temperatures; this caused a decrease in the orientation. Perhaps the original ordered PAN chains became disordered and had no time to rearrange before cyclization occurred.

Figure 7(b) shows although CI of the fibers treated in nitrogen changed similarly to that of the fibers treated in air, the structural and chemical changes were different. At relatively smaller tensions from 300 to 500 cN, the CI increased obviously with increasing tension. With a slight increase in the overall orientation of PAN chains, the orientation of ordered regions decreased. The tension improved the orientation of the amorphous regions. Perhaps the appropriate tensions applied positive effects, namely, the restraint of the disorientation of molecular chains and the induction of PAN chains to rearrange for

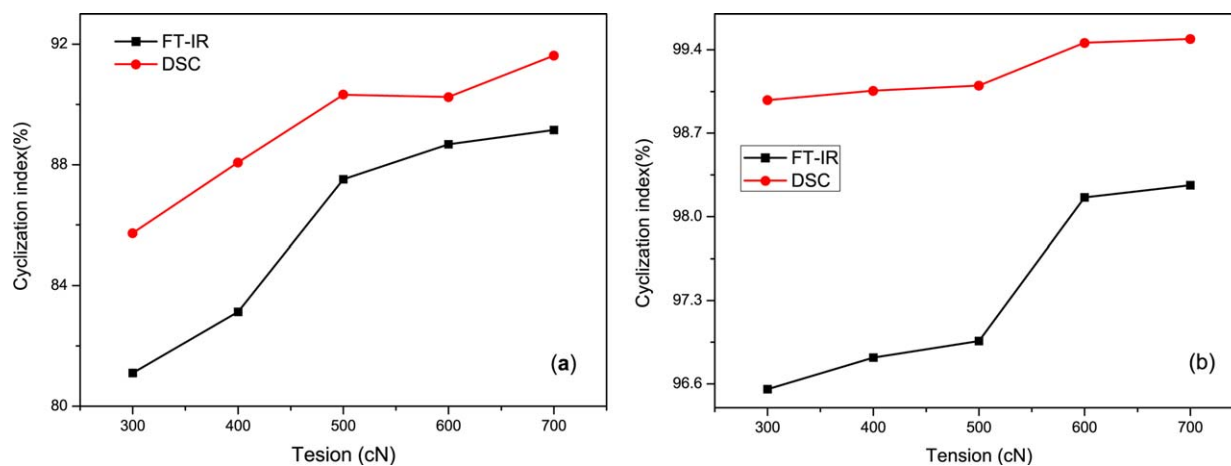


Figure 8. Degree of cyclization of the stabilized fibers under various tensions: (a) A10 and (b) N10. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

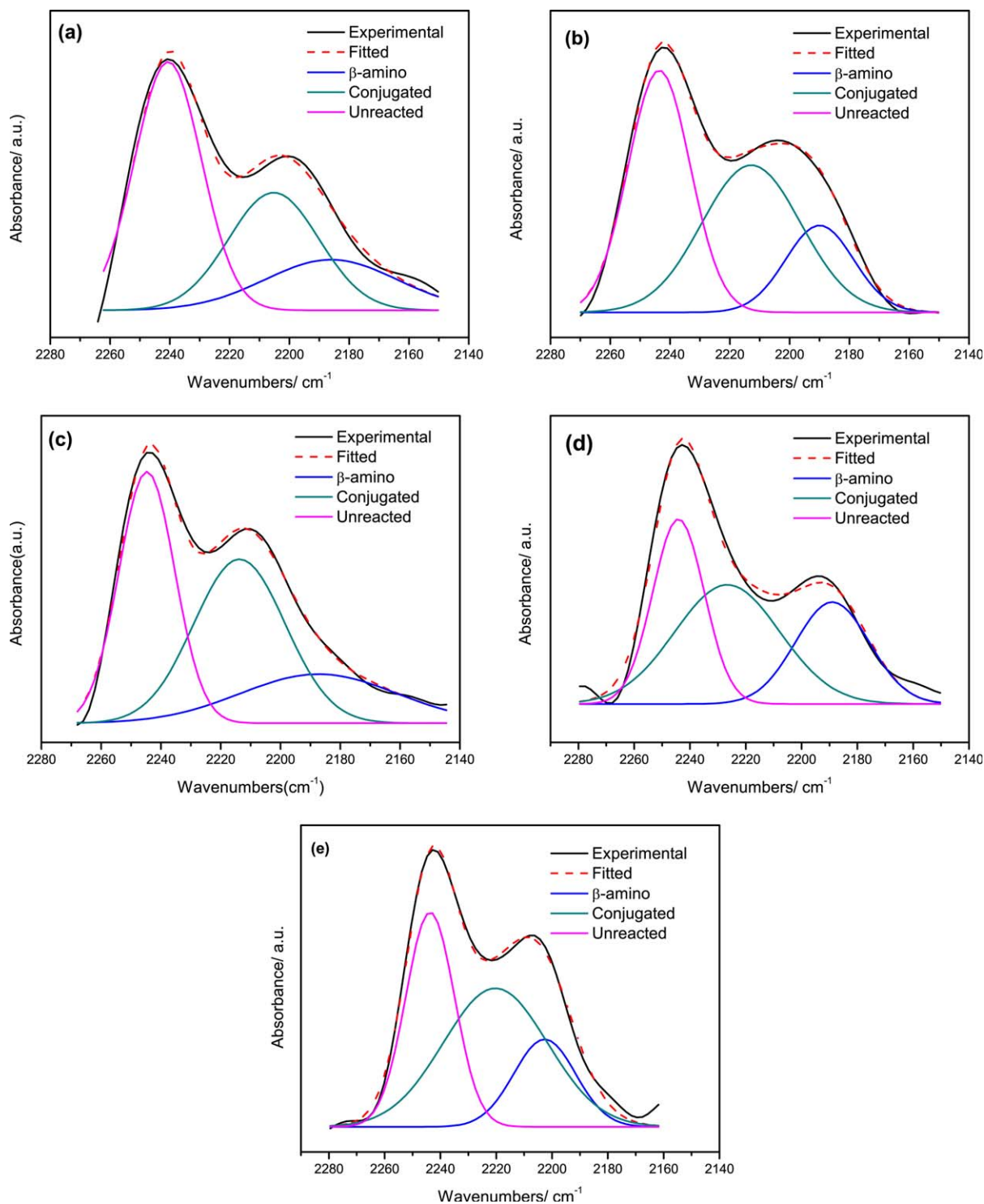


Figure 9. Nitrile-band peak-fitting results for the stabilized fibers: (a) N10-3, (b) N10-4, (c) N10-5, (d) N10-6, and (e) N10-7. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

cyclization. The tensions also accelerated the corruption of rigid crystalline structures in the higher temperature range. Another reason why the optimum became higher than the prior temperature range was that the cyclization structures formed by the former stage led to more chemical bonds in the cross section of the fibers.

When the tension increased from 500 to 700 cN, the CI values decreased. The overall orientation of the PAN chains and the orientation of the ordered regions both decreased when the tension increased; this implied that the tension on the crystalline regions became weaker, probably because the molecule chains could hardly be stretched under tension because they lacked

Table IV. Peak-Fitting Results from the FTIR Spectra for the Stabilized Fibers in Nitrogen

Sample	Area fraction by peak deconvolution			
	Unreacted nitrile: S_1 (%)	Conjugated nitrile: S_2 (%)	β -Amino nitrile: S_3 (%)	S_2/S_3
N10-3	49.0	31.3	19.7	1.6
N10-4	38.3	40.7	20.9	1.9
N10-5	34.2	44.9	20.9	2.1
N10-6	41.5	41.6	16.9	2.5
N10-7	34.5	47.6	17.9	2.7

intercrosslinking, which is usually produced in the presence of oxygen. The same reason could be used to explain the decrease in orientation.

The ability to form a system of conjugated bonds ($-\text{C}=\text{N}-$), during heat treatment depends on the isotacticity of the polymer; this means that appropriate conformations are conducive to the interaction of nitrile groups. A quantum chemical method was used to calculate the conformational energy of models for isotactic and syndiotactic PAN macromolecules; the total conformational energy changed with changing angles between adjacent $\text{C}\equiv\text{N}$ groups and $\text{C}-\text{C}-\text{C}$. The minimum at minimum conformation was separated from the others by a considerable energy gap. A short-range straightening of the helical conformation of individual macromolecules increased the internal energy and forced the molecules into a zig-zag conformation against the repulsion of adjacent $\text{C}\equiv\text{N}$ groups.^{26,27} This movement lifted $\text{C}\equiv\text{N}$ groups out of lowest energy position. After the shifting, the tension helped the $\text{C}\equiv\text{N}$ groups overcome the rotational barrier, and this made more new interactions become possible.

When tensions were applied to the PAN chains, the chain segments were stretched and rearranged, and their end-to-end distances were in an extended state. The conformational change in the chains was possible as a consequence of chemical transformations and thermal motion. Conformational analysis also indicated that the stereoregular and stereoirregular model chains of PAN had several minimum energy conformations; this indicated that when the chains were stretched under different tensions, the PAN chains could be in different energy states. The external stretching made the $\text{C}\equiv\text{N}$ groups rotate around the backbone chain; this resulted in an internal energy that was higher than the lowest energy state. The energy difference between conformations may have been relative to the energy barrier, and a relatively higher internal energy conformation decreased the energy barrier with reactions to overcome. Therefore, at the same temperature and other experimental conditions except tension, the higher cyclization could be attributed to activating energy changes induced by tension.²⁸

For the fibers treated from 238 to 270°C, with increasing temperature, the (100) diffraction peak tended to be lower and broader and could be hardly distinguished from the WAXD pattern; this implied that the crystalline regions collapsed, and plenty of molecular chains in the crystalline regions underwent cyclization.

Figure 8 shows the variation in CI with increasing tension in this temperature range. Compared to the CI in the previous period, the CI values were larger; this indicated that the cyclization reacted rapidly in this temperature range. The continuous increase of the optimum tension might have been due to the following effects:

On the one hand, the chemical bonds became greater in the cross section of the fibers; this was caused by the cyclization structures formed in the former stages. Therefore, the optimum tension was higher than in the prior temperature range. On the other hand, the crosslinked structure quickly formed when the temperature was up to 242°C in air.²⁹ Both of the two factors restricted the movement of a single molecular chain, and to the best of our knowledge, these factors were ignored in previous works.

The crystalline regions barely existed at this time, so the tension mainly had effects on the amorphous regions. In this stage, most nitrile groups had participated in cyclization, and the uncyclized nitrile groups could be divided into three categories, the unreacted (2240 cm^{-1}), conjugated (2210 cm^{-1}), and β -amino (2190 cm^{-1}) nitrile groups. Conjugated nitrile groups were produced by the dehydrogenation of β -carbon atoms, which were easy to cyclize, and β -amino nitrile groups were produced by a cyclization termination reaction, which was hard to cyclize. The peak fit was used to quantitatively analyze the three kinds of groups by the fixing of the peak position and the variation of the peak width and intensity.² The optimum peak fitting of various nitrile groups for stabilized fibers are shown in Figure 9, and the corresponding data are listed in Table IV, S_1 , S_2 , and S_3 are the area fractions of the unreacted, conjugated, and β -amino nitriles, respectively. The area fractions of the different nitrile groups reflected the quantities of different nitrile groups. The area fraction of conjugated nitrile groups increased with increasing tension, whereas the area fraction of the β -amino nitrile groups decreased with increasing tension. Therefore, the ratio of the area fraction of conjugated nitrile groups to the area fraction of β -amino nitrile groups increased with increasing tension; this indicated that more conjugated nitrile groups and fewer β -amino nitrile groups were produced with increasing tension.

In this stage, most nitrile groups participated in cyclization and then formed the ladder structures. The remaining nitrile groups required more energy and higher tension to adjust to a favorable position where they could form conjugated nitrile groups. Conjugated nitrile groups transformed the chain conformation from helical form to planar form; this facilitated the

intramolecular cyclization reaction. In this way, a higher tension helped the formation of conjugated nitrile groups and easily formed a longer ladder polymer with more aromatic repeated structures and also reduced cyclization terminations. Therefore, the degree of cyclization increased with increasing tension.

CONCLUSIONS

The tension affected the cyclization of the PAN fibers during stabilization, mostly in two-phase structural changes and the transformation of conformations. At temperatures from 175 to 218°C, where most crystalline regions were preserved, the effect of the tension applied to amorphous regions made the degree of cyclization increase at first and then decrease because the nitrile groups had enough energy to overcome the hindrance and adjust themselves to a position suitable for cyclization at first. Then, the increasing spatial distance made it difficult for adjacent groups to participate in the cyclization reaction. At the temperatures from 226 to 232°C, where the reactions extended to the crystalline regions, there were more PAN chains becoming flexible. When the PAN chains were arranged to suitable conformations, the relatively higher internal energy conformation decreased the energy barrier that had to be overcome, and the degree of cyclization could reach a relatively higher value. When temperature rose from 238 to 270°C, crystalline regions barely existed with increasing temperature. Compared with the former stage, the optimum tension continuously increased because the crosslinked structure was formed in this temperature range in addition to the reasons mentioned previously.

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