Structural Changes and Molecular Motion of Polyacrylonitrile Fibers During Pyrolysis

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Synopsis

The stabilization process of polyacrylonitrile (PAN) fiber is necessary to develop high-performance carbon fiber. This work is concerned with studies of the activation energy of PAN fibers during the stabilization process. A wide-angle X-ray diffractometer combined with a fiber specimen holder for heating was used to measure the activation energy of crystal transition E_c. E_c is almost the same as the activation energy of the cyclization reaction E which is measured by a differential thermal analysis (DTA). The variation of crystal size in PAN fiber and a model of the ladder polymer in stabilized fiber transformed from acrylontrile (AN) units of PAN fiber are discussed also. The crystal size of PAN fiber increases when the thermal treatment temperature is raised. When exposed to temperatures above the crystal degradation temperature T_d, the molecular rods of PAN fiber are destroyed completely, and ladder polymer is formed in the ordered phase of the original PAN fiber. The transformation of ladder polymer is initiated in the disordered phase, and then at the boundaries of the ordered phase.

INTRODUCTION

Polyacrylonitrile (PAN) fibers have been found to be the most suitable precursor for making high-performance carbon fiber. The stabilization process of PAN fiber for transformation of the ladder polymer is best achieved in air between 200 and 300°C to obtain high-performance carbon fiber.[1-3] The transformation of ladder polymer from PAN fiber is an exothermic reaction, which is related to the cyclization of PAN fiber.[4-7] This exothermic reaction can be observed in a vacuum and in other atmospheres.[5,8-10] Fitzer and Müller[11] have used a differential thermal analysis (DTA) measurement to study the kinetics of the cyclization and oxidation of PAN during thermal treatment in nitrogen and air. They have found that the cyclization is a first-order reaction with an activation energy [the amount of energy required to raise the molecules to the activated state, here after referred to as E] of about 30 kcal/mol in nitrogen, about 34 kcal/mol in air, and a lower E for copolymer PAN (5% methylacrylate). A lower value of E suggests that the cyclization reaction of PAN fiber should be initiated at a lower temperature.[12]

The present report is concerned with studies of the activation energy of PAN fibers during the stabilization process. An wide-angle X-ray diffractometer combined with a fiber specimen holder for heating was used in this experiment. The result of this new method is compared with DTA and differential scanning calorimeter (DSC) measuring methods from previous

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experiments.[11,12] The molecular motion of PAN fiber during thermal treatment and a model of stabilized fiber transforming from PAN fiber are also discussed.

EXPERIMENTAL

A special grade acrylic fiber, Courtelle fiber (Courtaulds Ltd., UK) sample A, containing 6% methyl acrylate and 1% (itaconic) acid copolymer, and a PAN fiber, sample C supplied by the Catalyst Research Center (CRC) of China Technical Consultants, containing 96% AN were used in this work. A single tow of Courtelle fiber and one of sample C contain 6000 and 1500 strands of 1.1 denier monofilament, respectively. Courtelle fibers were modified with potassium permanganate solution at 85°C for 2 min, and designated sample B.

A Rigaku wide-angle X-ray diffractometer, D/max-III with Ni-filtered Cu K_α radiation, was used to measure the crystalline-related properties of the sample. The step-scan method was used to determine the lattice spacing and crystal size $L(hkl)$; the step-interval was set at 0.1 degree. The variations of crystal size in thermal treatment were measured by a wide-angle X-ray diffractometer combined with a fiber specimen for heating, and the heating rate was 2°C/min and $L(hkl)$ was calculated by the Scherrer formula:

$$L(hkl)(\text{in Å unit}) = K\lambda/B\cos\Theta \tag{1}$$

in which B is the line breadth (radians in 2Θ), K is the apparatus constant ($= 1.0$), λ is the wavelength of the Cu K_α X-ray used, and $\cos\Theta$ is determined from the position of the observed line.

The activation energy of crystal transition E_c was determined by the difractometer combined with a fiber specimen holder for heating. The precursors were located at around 17 degrees (2Θ) [the (100) plane of PAN fiber which is thought to have a hexagonal structure]. The heating rate was varied between 1 and 10°C/min.

The DTA measurement was carried out in air using a Rigaku Thermal Analyzer. The heating rate was varied between 2 and 20°C/min. The powder sample weight was around 3.5 mg. The peak maximum of three precursors is strongly affected by the heating rate. Thus the Kissinger method[13] can be used for evaluation. The activation energy E is calculated from the temperature dependence of the peak maximum T_m (°K) on the heating rates ϕ(°K/min) according to Eq. (2):

$$\frac{E}{R} = \frac{dln(\phi/T_m^2)}{d(l/T_m)} \tag{2}$$

where

R is the universal gas constant.

A Mettler TA 3000 thermal analyser with a DSC 20 module was used to study the reaction kinetics of the samples. Each sample weight was 3.5 mg and the heating rate was 10°C/min, heated to 450°C in air atmosphere. The

DSC unit was connected to a TC-10 microprocessor which printed out the E values on the attached printer-plotter.

Densities were measured at 23°C according to the density gradient column method. The density column was prepared with a mixture of n-heptane and carbon tetrachloride so that a density gradient of about 1.2 to 1.5 g/cm^3 extended from top to bottom.

RESULTS AND DISCUSSION

Evaluation of Activation Energy from DTA

Typical DTA-curves are presented in Figure 1. A strong exothermic reaction begins at about 200°C and reaches a maximum T_m at 284, 279, and 275°C as recorded for samples A, B, and C, respectively. Fitzer and Müller[11] used DTA measurements to study the kinetics of cyclization and oxidation of PAN being heat-treated in air and nitrogen, and observed the cyclization to be a first-order reaction. These polymerization reactions may result from the stabilization of PAN fiber in an inert or oxidizing atmosphere, and give rise to a thermally

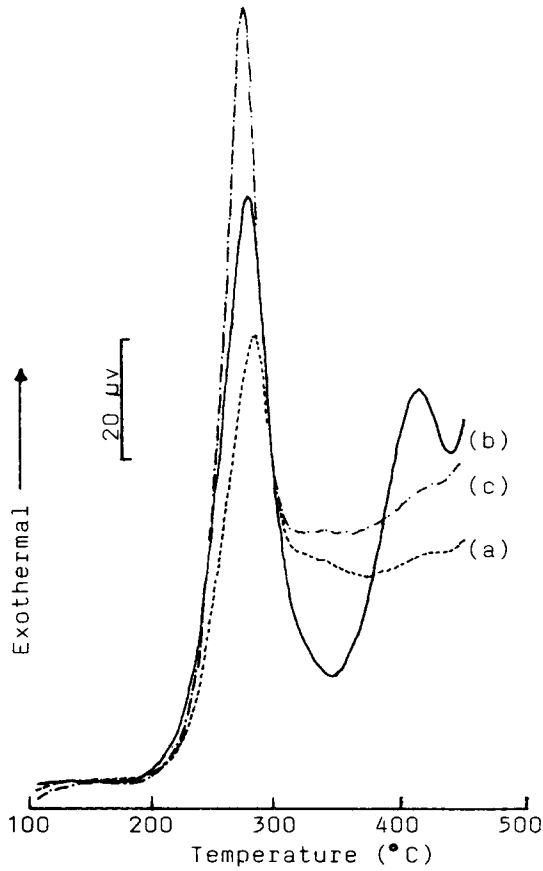
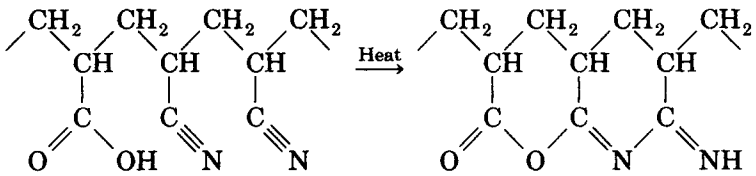


Fig. 1. DTA curves of PAN fibers (heating rate: 10°C/min, in air): (a) sample A, (b) sample B, (c) sample C.

TABLE I
Experimental Results for the Shift of the Cyclization Exotherm of PAN Fibers During a Series of Heating Rates

Heating rate ϕ (°C/min)	Sample A T_m (°C)	Sample B T_m (°C)	Sample C T_m (°C)
2	254	252	252
5	271	268	267
10	284	279	275
15	298	299	288
20	300	301	295

stable cyclized structure which is often referred to as a ladder polymer. The acid constituent of PAN fibers acts as an initiator for ladder polymer by the following mechanism as shown by Grassie and Hay:[14]



The kinetic data were evaluated by the varied heating rates of DTA measurement. The experimental results are shown in Table I. The activation energy E is calculated by the Kissinger method[13] according to Eq. (2).

The resulting data of the cyclization reaction are shown in Table II. Sample C has higher activation energy (E) than samples A and B. The activation energy depends on such conditions as steric factors, the positions of nitrile groups, and the amount of atacticity of PAN fiber,[15] and the formation of activated centers for cyclization reaction, etc. There is a lamellar-like texture of the fibrils which aligned parallel to the fiber axis for samples A and B, which was reported by Warner et al.[16] The morphological structure of sample C is not similar to that reported by Warner et al. That is why sample C needs more hours of time to oxidize at 230°C than samples A and B during the stabilization process. The activation energy of sample B is lower than that of sample A, indicating that potassium permanganate acts as a catalyst in the formation of ladder structure and initiates the cyclization reaction at a lower temperature.[17] That is why PAN fiber modified with potassium permanganate

TABLE II
Experimental Results of E_c Which Was Measured with an X-ray Diffractometer and E Which Was Measured with a DSC and DTA

Sample	X-ray diffractometer (kcal/mol)	DSC (kcal/mol)	DTA (kcal/mol)
Sample A	29 ± 2	30 ± 3	27 ± 2
Sample B	23 ± 2	24 ± 1	24 ± 3
Sample C	32 ± 3	—	30 ± 3

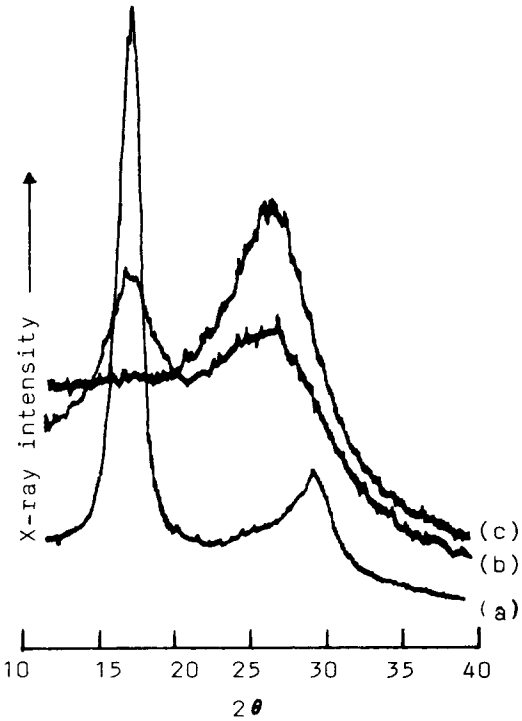


Fig. 2. Wide-angle X-ray diffractograms of PAN fiber and stabilized fibers (scan speed: 1°C/min): (a) PAN fiber, (b) PAN fiber treated at 230°C for 1 h, (c) PAN fiber treated at 230°C for 6 h.

solution needs less stabilization time to develop high-performance carbon fibers.

Evaluation of the Activation Energy of Crystal Transition

PAN fibers studied by X-ray diffraction give two peaks at the Bragg angle 2Θ at 17° and 29°, respectively. The diffraction maximum at around $2\Theta = 17°$ has been interpreted as the (100) plane of a hexagonal unit.[18] When PAN fibers are heated at 230°C in air, a new peak appears at about 25° which corresponds to the sheetlike structure of the ladder polymer. During the stabilization process, the intensity of the new peak increases, but the intensities of the original two peaks decrease as shown in Figure 2.

In this work, the Kissinger method is tried and the X-ray intensity variation at $2\Theta = 17°$ is recorded during the thermal treatment process. In Figure 3 the X-ray intensity of PAN fiber at $2\Theta = 17°$ increases until it reaches the crystal transition temperature (T_c), and then decreases rapidly during heat treatment. When the intensity of $2\Theta = 17°$ decreases at transition temperature T_c, and then the intensity at $2\Theta = 25°$ (the ladder polymer structure) starts increasing (Fig. 4), signifying that the ladder polymer structure has been transferred from the PAN structure.

It is proposed that the amount of the extra energy required for the PAN molecules to separate from the AN cells (PAN fiber) and then enter the ladder

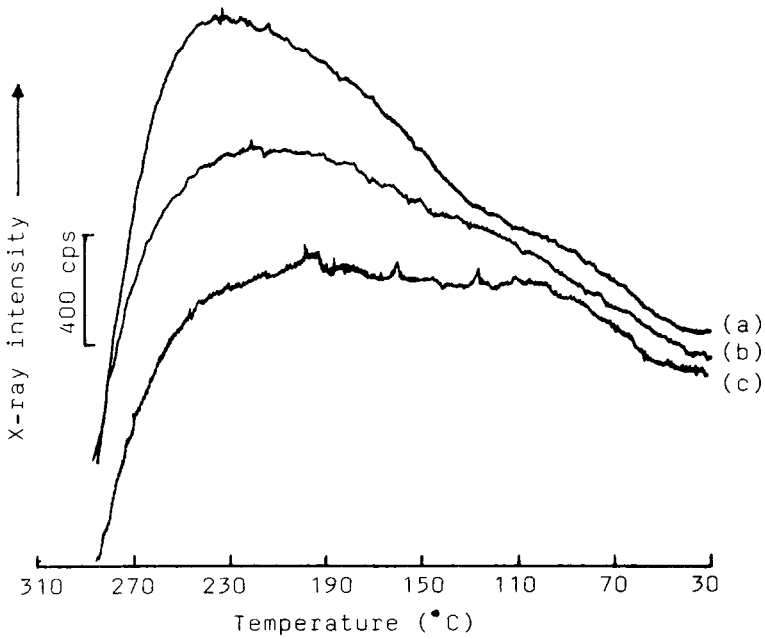


Fig. 3. Variation of X-ray intensity of PAN fibers at $2\Theta = 17°$ as a function of thermal treatment (the heating rate is 5°C/min): (a) sample A, (b) sample B, (c) sample C.

polymer cells (stabilized fiber) be defined as the activation energy of crystal transition E_c. Figure 5 shows the value of $\ln(\phi/T_c^2)$ vs. $1/T_c$ calculated from an X-ray diffractometer experimental data. The five points for each sample can be joined to form a straight line as expected in the theory. The greatest deviation is less than 10%, as reported in the Kissinger method.[13] Table II shows the E_c data combined with E data which are calculated by DTA and

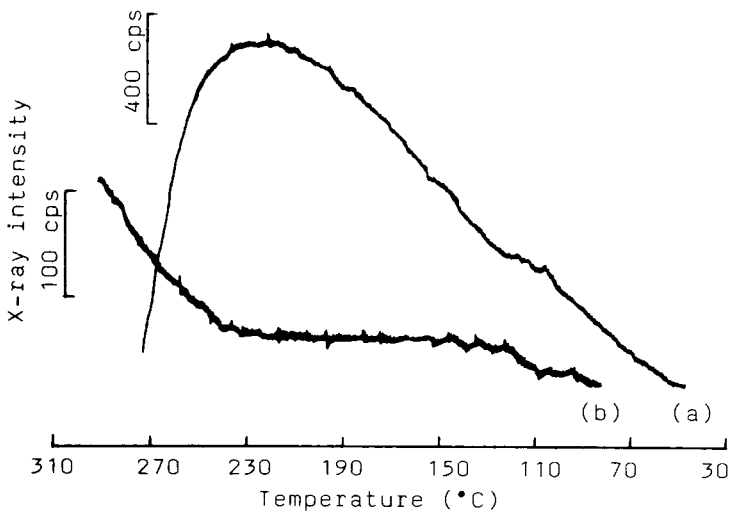


Fig. 4. Variation of X-ray intensity of sample A as a function of thermal treatment (the heating rate is 2°C/min): (a) $2\Theta = 17°$, (b) $2\Theta = 25°$

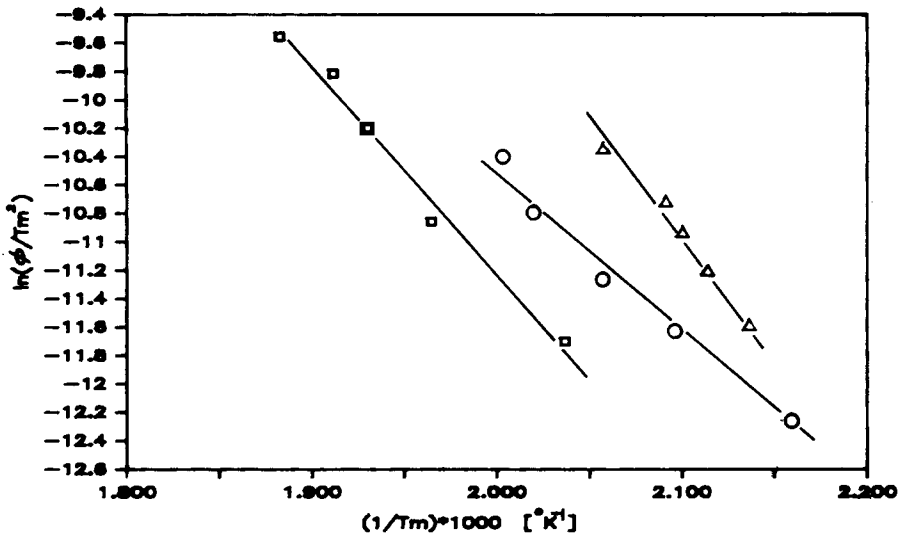


Fig. 5. Evaluation of activation energy from an X-ray diffractometer: (□) sample A, (○) sample B, (△) sample C.

DSC; both of them are calculated from the slopes of Arrhenius plots. It is found that the E_c values are almost equal to the E values. It indicates that the E_c and the E value are the same. We discuss the cyclization reaction from the physical viewpoint, while Fitzer and Müller[11] discussed it from the chemical viewpoint.

Molecular Motion of Stabilized Fiber Transferred from PAN fiber

The typical wide-angle X-ray diffraction pattern of PAN fiber is shown in Figure 2(a), which shows a remarkably intense peak at about $2\Theta = 17°$ and a less intense peak at about $2\Theta = 29°$.[18-22] Structural differences in PAN developed from different preparation methods have been discussed.[18,22-24] It is generally thought that the molecular chains of PAN fiber are of an irregular helical conformation owing to the intramolecular dipole–dipole interactions between the nitrile group pairs.[18,25,26] The bound nitrile group pairs were formed between the neighboring rods, due to the intermolecular dipole–dipole interactions.

The irregular helical conformation fits into a cylinder-like molecular rod, whose diameter is about 6 Å.[16,18] Our value is 5.0 Å for sample Å; and 5.4 Å for sample B, which is modified with potassium permanganate solution.[17] It was assumed that the amorphous phase was composed of the irregular helical conformation of PAN molecules which is due to the intramolecular dipolar interactions between the nitrile groups.[27] The intermolecular nitrile group pairings are assumed to be less formed in the amorphous regions, owing to the random alignment of molecular chains. However, there are more intermolecular and more intramolecular dipolar interactions between the nitrile groups in the molecular rods (ordered phase) of PAN fiber.

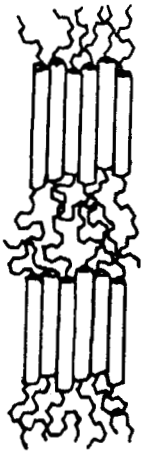


Fig. 6. Schemata of amorphous phase in two-phase structure of PAN, jumbled molecular chain structure, used with permission from ref. 16.

Warner et al.[16] supposed that the amorphous (disordered) phase of PAN fiber was a jumbled molecular chain structure (as shown in Fig. 6), but Gupta and Singhal[27] considered it to be some kind of random alignment of molecular rods (as shown in Fig. 7). This article does not attempt to debate these two views of the structure of the amorphous phase of PAN fiber, but both structure models can be used to discuss the molecular motion of stabilized fiber transferred from PAN fiber during thermal treatment.

In order to understand the molecular motion of the molecular chain in PAN fiber during thermal treatment, we looked at the structural differences of a molecular rod which was heated during thermal treatment as indicated in Figure 8.

When a fiber is heated at a low temperature, both phases (amorphous and ordered) are rigid and the molecular chain is completely stable [Fig. 8(a)]. At a

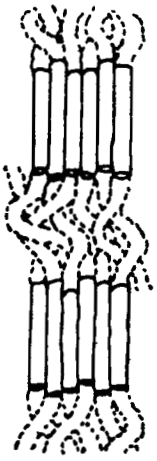


Fig. 7. Schemata of amorphous phase in two-phase structure of PAN, disordered arrangement of molecular rods, used with permission from ref. 27.

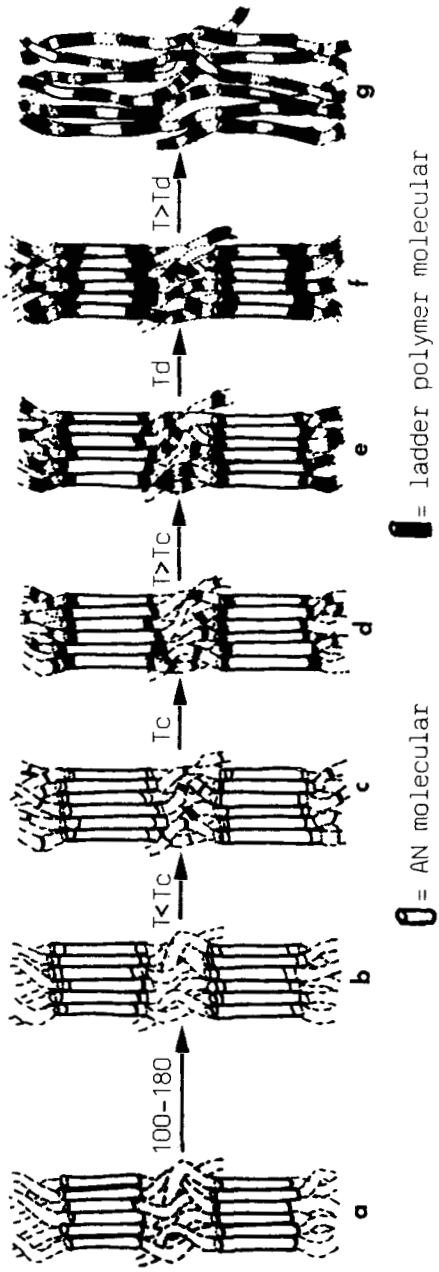


Fig. 8. The history of molecular motion models for AN molecular chain during thermal treatment: (a) the molecular chain structure of PAN fiber; (b) a small amount of AN units packing into the molecular rods from the disordered phase; (c) at about 180°C, the cyclization reaction beginning in unordered phase; (d) at T_c, AN molecules beginning to transform into the ladder polymer at the boundary of molecular rods; (e) the amount of ladder polymer increasing; (f) at T_d, the amount of ladder polymers reached saturation; (g) above T_d, the AN units of molecular rods rapidly transferred into ladder polymer.

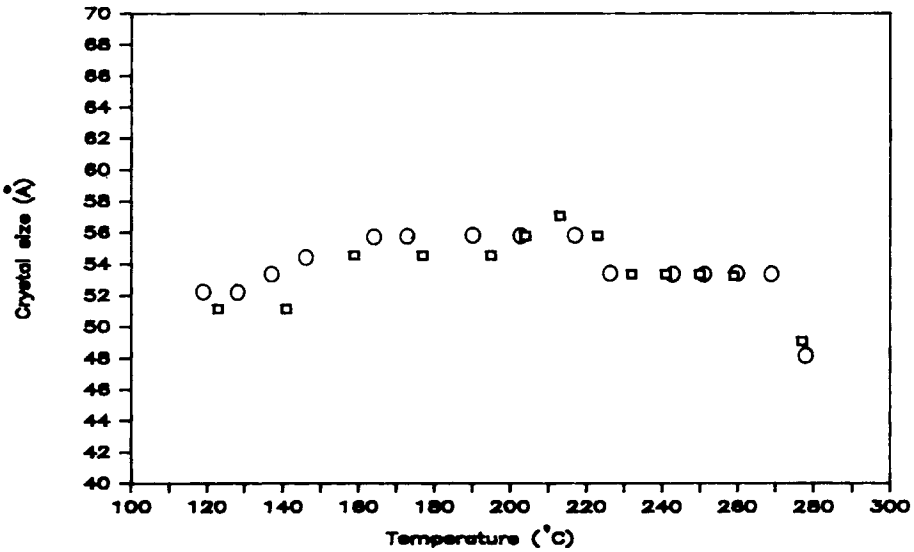


Fig. 9. Crystal size of PAN fiber as a function of thermal treatment: (□) original PAN fiber, (+) modified PAN fiber.

somewhat higher temperature [from 100°C to the ladder polymer formative temperature (about 180°C)], owing to the ordered phase containing a greater number of intermolecularly bound nitrile groups, the lesser number of free nitrile groups, and greater restrictions on the segmental mobility than the amorphous phase, the molecular chain of the amorphous phase becomes flexible, and starts vibrating and rotating. Thus the segmental mobility helps to gradually readjust the mutual alignment of nitrile group pairs to form a stronger dipolar interaction during thermal treatment. In the same way, the dipole interactional formation of the —C≡N groups increases gradually with the rising temperature [Fig. 8(b)]. At this stage, a small amount of molecular chains pack into a molecular rod from the amorphous phase; this leads to an increase in crystal size L(100) (Fig. 9). At around 160°C, the molecular chains start slipping. A light yellow color can be observed at this temperature. At a higher temperature (above 180°C to T_c), the intermolecularly bound nitrile group pairs break,[21,28] and the AN units start transferring to ladder polymer structure in unordered phase of PAN fiber. A deep yellow color can be observed at about 190°C. The crystal size grows continuously, but at a very slow rate [Figs. 8(c) and 9]. When the thermal treatment temperature rises to the crystal transition temperature T_c, the X-ray scatter intensity at $2\Theta = 17°$ reaches the highest point, the AN units at the boundary of molecular rods (ordered phase) of PAN fiber start forming to ladder polymer structures [Fig. 8(d)], and the X-ray diffractograph at $2\Theta = 25°$ shows a new peak.

The crystal transition temperature T_c is 218°C in sample A, and 204°C in sample B. As shown in Table II, the values of E and E_c are lower for sample B which was modified with potassium permanganate. Lower E, E_c, and T_c values in sample B are due to the potassium permanganate acting as a catalyst to initiate the cyclization reaction at a lower temperature.[17]

When the thermal treatment temperature is over T_c, the X-ray intensity at $2\Theta = 17°$ decreases slowly, and at $2\Theta = 25°$ it increases slowly (as shown in Fig. 4). However, the crystal size also decreases gradually which is due to the formation of ladder polymer (Fig. 9). In this stage, the amount of ladder polymer increases in the unordered phase and at the boundary of molecular rods [Fig. (8)]. At an even higher temperature (the crystal degradation temperature T_d), the thermal fluctuations become large enough to rupture the molecular chains of the AN structure, which transfer to the ladder polymer structure rapidly [Fig. 8(f)]. Moreover, as shown in Figures 8 and 9, the crystal size of L(100) plane in PAN fiber decreases sharply. After T_d, the energy absorbed by the sample is capable of breaking the dipole interactions between molecular rods, and a large amount of ladder polymer in an ordered phase is formed during the thermal treatment [Fig. 8(g)].

The AN unit transferring to a ladder polymer is not only a physical reaction but also a chemical reaction. The mechanism of stabilization of PAN fibers has been the subject of numerous investigations, and consequently several different structures have been proposed for stabilized fiber.[29-35] The formation of ladder polymer initiates at about 200°C, and develops rapidly at 230°C.[35] However, we are interested in knowing at which point PAN fiber initiates the formation of ladder polymer—in the amorphous phase or in the ordered phase. "A.I." values must be defined first before it can be discussed.

Uchida et al.[36] defined an aromatization index A.I. as

$$\text{A.I.} = I_a/(I_p + I_a) \tag{3}$$

in which I_a is the diffraction pattern given by the aromatic structure (ladder polymer) at $2\Theta = 25°$, and I_p is the diffraction by the PAN crystal at $2\Theta = 17°$. It was found that the A.I. value increases with heat treatment time

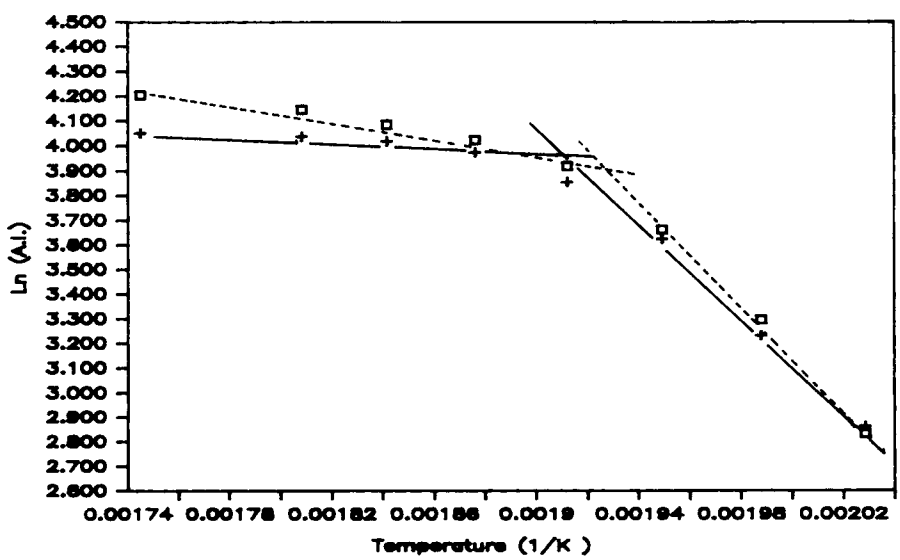


Fig. 10. Aromatization index A.I. as a function of thermal treatment: (□) original PAN fiber, (+) modified PAN fiber.

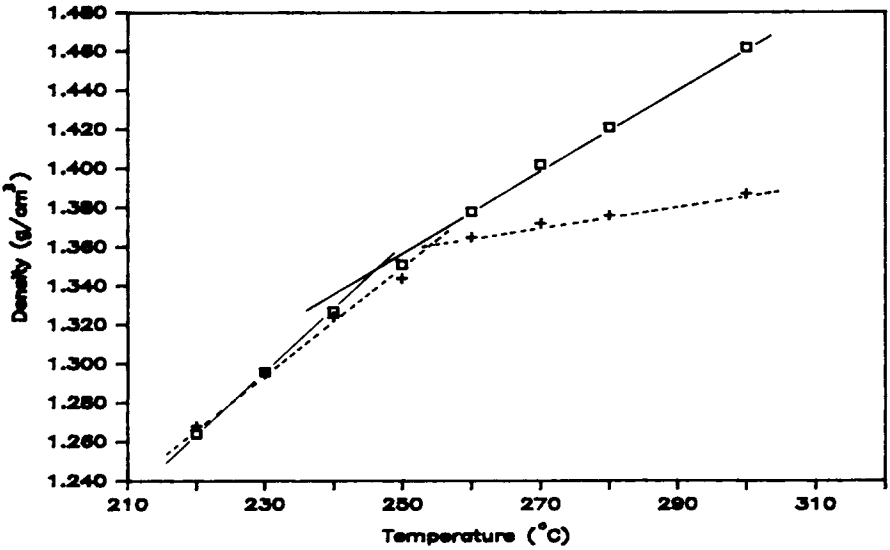


Fig. 11. Variation of PAN fiber density during heat treatment; (□) original PAN fiber, (+) modified PAN fiber.

and/or a temperature increase during the stabilization process.[15,29,36] Ko et al.[17] have modified the testing method and recommended that the A.I. value be a criterion in checking the stabilization process and a method to estimate the amount of ladder polymer.

As shown in Figure 10, which presents the plots of the aromatization index versus the thermal treatment temperature for the fibers, the temperature increasing rate is 2°C/min. The A.I. value of the stabilized fiber increases when the thermal treatment temperature is raised. In the early stage of thermal treatment, the amount of ladder polymer increases rapidly, and after the transition temperature it increases less rapidly with rising thermal temperature. Figure 11 shows the variation of density with heated treatment time. The density of stabilized fiber increases as the thermal treatment temperature is raised, and the A.I. values increase at the same rate. Both the density and the A.I. values have a transition point of about 245°C for sample A and about 255°C for sample B.

With the crystal size of (100) plane in PAN fiber decreasing very slowly between T_c and T_d (Fig. 9), and the A.I. value (the amount of ladder polymer) increasing very rapidly until about 250°C (Fig. 10), the number of nitrile groups in the ordered phase is considered almost unchanged. Therefore, the ladder polymer was converted from the nitrile group in the amorphous phase or from the crystalline boundaries. That the ladder polymer is formed by heating PAN fiber (containing acid copolymer) in air at temperature of 180–200°C is well established. In the ordered phase, the AN units begin to transform into the ladder polymer structure at temperatures slightly over T_c because the X-ray intensity at $2\Theta = 17°$ reaches the highest point at T_c. It seems that the greater part of the ladder polymer is converted from the amorphous phase after the reaction temperature of cyclization (about 180°C), and then the smaller part of the ladder polymer is converted from the crystalline boundaries after T_c [Fig. 8(c)–(e)].

At T_d, the intermolecular and intramolecular dipolar interactions among the nitrile groups in the molecular rods may be destroyed completely and thus the ordered phase of PAN fiber collapses. Above T_d, the AN units in the ordered phase are rapidly transferred to ladder polymer [Fig. 8(f)].

In fact, in our recent work, using transmission electron microscopy and scanning electron microscopy to study the microstructure of stabilized fiber, we found that stabilized fiber has two chemical structures, original AN units and ladder polymer.[37] Each structure can be composed also of two phases, an amorphous and an ordered phase. In this work, a simple model for the ladder polymer formation (as shown in Fig. 8) lets us understand the molecular motion history of the PAN molecular chain during thermal treatment.

CONCLUSIONS

First, the activation energy E of the cyclization reaction is almost equal to that of crystal transition E_c. However, the variation of PAN fiber crystals can be studied and understood by measuring E_c with an X-ray diffractometer.

Second, the E, E_c, and T_c of the modified PAN fiber are lower than those of the original PAN fiber.

Third, the transformation of ladder polymer from AN units is initiated in the disordered phase, and then forms the boundaries of the ordered phase.

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