The Microstructure of Stabilized Fibers

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Synopsis

The morphology and microstructure of a stabilized fiber, nonburning fiber, has been investigated under optical and electron microscopes, and a model for the structure of the stabilized fiber is presented. Skin-core morphology was found in the cross section of the stabilized fiber. The proposed model is consistent with the lamellar-plate-like structure, measuring about 400–700 Å in thickness, 500–4000 Å in breadth and 0.1–0.5 μm in length along the fiber axis, which is composed of microfibrils. The structure has some circumferential distribution in the outer zone, while the inner zone has a radical distribution. Evidence for the lamellar-plate structure, including two chemical structures and having two different crystalline phases, which are the original AN units and the ladder polymer, were obtained from electron microscopy, wide-angle X-ray, and electron diffraction analyses.

INTRODUCTION

For many years, in the pyrolysis of polyacrylonitrile (PAN) fibers, the stabilization process was found to be necessary to obtain high quality carbon fibers, while stabilized acrylic fiber materials were used directly in applications where a nonburning fiber was required. The stabilization process of acrylonitrile homopolymers or copolymer fibers in an oxygen-containing atmosphere at temperatures in the range of 200–300°C which involves (a) an oxidative crosslinking reaction of adjoining molecules and (b) a cyclization reaction of nitrile groups. It is generally recognized that the rate at which the stabilization reaction takes place increases with the stabilization temperature and the stabilization time of the oxygen-containing atmosphere.[1,2] Layden[3] and Warner et al.[4] have examined the cross section of stabilized fibers. The fibers displayed a two-zone morphology, the dark-colored exterior zone and the cream-colored interior zone. The cream-colored zone was changed to the dark-colored zone when the fibers were attacked by oxygen during stabilization process. The dimension of the dark-colored zone increased with both oxidation time and temperature. In this case, the antiburning reaction of the stabilized fiber was increased and the strain of stabilized fiber was decreased. Hence, to use the stabilized fiber as raw material for flame-retarding fibers, it should have the basic characteristics of higher strain, and thus more suitable for mixing, spinning, weaving, and other textile processing.
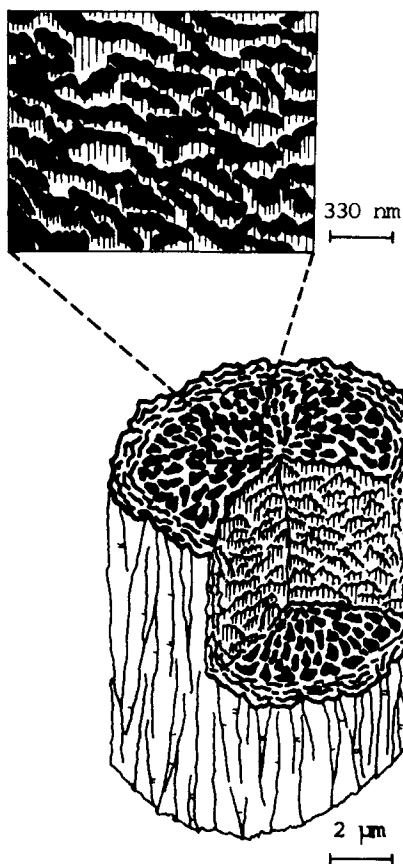
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Fig. 1.   Structure model for a stabilized fiber (nonburning fiber).

The mechanical properties, physical properties, chemical reaction, and chemical structures of stabilized fibers have been discussed by many scientists. Bahl and Manocha[5,6] showed that the strength of stabilized fiber decreased rapidly in the beginning and slowly in the following hours of the stabilization process. Warner and his co-workers[4] reported that two different limiting conditions of stabilization, designated diffusion-limited and reaction-limited, have been noted to occur in the heat treatment of acrylic fibers. DTA measurements were used to study of the kinetics of the cyclization and oxidation of PAN during the thermal treatment in air and nitrogen.[7] Several types of chemical reactions during stabilization process of PAN fiber are cyclization, crosslinking, dehydrogenation and degradation and have been discussed by several authors.[8-12]

Most chemists and textile scientists have focused their interests on how chemical reactions occur and physical properties change during the PAN fiber stabilization. In this paper we wish to report additional aspects of the morphology of stabilized fiber and to establish a microstructure model (Fig. 1). We believe this model is helpful for the understanding of the microstructure and physical properties of stabilized fiber, nonburning fiber, and carbon fiber.

EXPERIMENTAL

A special grade polyacrylonitrile fiber tows (Courtelle) containing 6000 monofilaments of 1.1 denier each, was used in the present study. Stabilization of PAN fiber was carried out in a constant temperature zone furnace with fixed length method at 230°C for 2 h, in purified air atmosphere. The flow rate of air about 0.3 nL/min was maintained in all the experiments reported here. The oven temperature was controlled with a digital PID programmed controller with a built-in microprocessor.

Scanning electron microscopes (SEM), Hitachi Model S-520 and Cambridge Model S600, were used to examine the fracture surfaces and the longitudinal surface of the stabilized fibers at 25 kV accelerating potential. The specimens were coated with Au to get a better image.

A tow of the stabilized fiber was cut and embedded in resin for sectioning and the prepared samples were then subjected to subsequent examinations in a transmission electron microscope (TEM), Hitachi Model H-600, at 100 kV. The cross-sectional, longitudinal, and inclined sections of fibers were cut on an LKB ultramicrotome using a glass knife and collected on a 200 mesh copper grids coated with thin Formvar film. Many samples were cut this way and examined under TEM, and the bright-field images, dark-field images, and electron diffraction patterns were recorded.

RESULTS AND DISCUSSION

Presently PAN fiber is recognized as the most important and promising precursor in the manufacture of carbon fibers. PAN fibers during a thermal process of about at 200–300°C, it was modified into a stabilized fiber with nonburning character, and it is not significantly disrupted during the carbonization treatment at higher temperatures, converted to a carbon fiber with good mechanical properties. In order to understand the mechanical and physical properties of the PAN, stabilized, and carbon fibers, it is important to look into the morphological rearrangements taking place in those fibers. Polyacrylonitrile fibers are known to be highly atactic, having ordered crystalline regions interspersed with disordered or amorphous phase. Recently, Warner et al.[1] have proposed a model for the morphological structure of PAN fibers wherein the lamellarlike texture is a result of the rods being ordered into a liquid crystal-like texture. X-ray and electron diffraction studies of the microstructure of PAN-based carbon fibers, first reported by Watt and Johnson,[14] showed that these carbon fibers were found to be fibrous with small turbostratic crystals arranged in the form of fibrils with preferential orientation of basal planes parallel to the fiber axis. However, more than 10 kinds of the structure model for carbon fibers were established during last 15 years.[15] To our knowledge the morphology of stabilized fibers has been observed by a small number of researchers with SEM or optical microscopes.[3,4,6] In our work, the longitudinal and cross sections of stabilized fiber, 500 Å–1 μm, were cut with ultramicrotome and examined in an Olympus BHT microscope with a closed-circuit television camera. A transmission optical micrographs of stabilized fibers [Figs. 2(a) and (b)] showed the existence of "skin–core" morphology, the dark outer ring and the cream-colored core. The outer ring
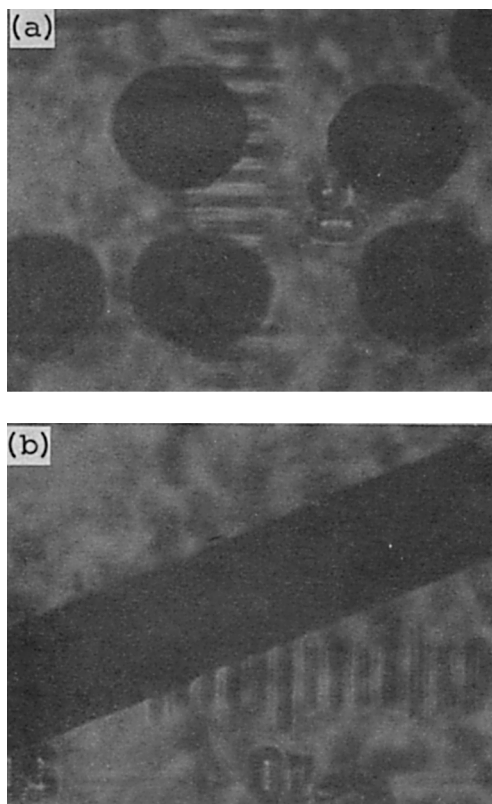
Fig. 2. Transmission optical micrograph of Courtelle fiber heated in air at 275°C for 60 min: (a) cross section; (b) longitudinal section.

has been identified as an oxygen-rich zone, with the cream-colored core containing less oxygen. The chemical reaction and mechanism have been discussed by Grassie and Hay[12] and Watt and Johnson.[1] A series of color changes of the PAN fibers during thermal treatment process have been observed. A light yellow color can be observed at about 160°C; as the temperature increased to 230°C, Courtelle fibers change to dark color. The color change occurred rapidly from 220 to 230°C, and the skin–core morphology was found in the cross section of the stabilized fibers which were heat-treated after 230°C. The thickness of the outer rings, measured with an optical microscope, increased linearly with the square root of the stabilization time at constant temperature (e.g., at 230°C for several hours).[6] The oxygen uptake of Courtelle fiber also has a similar behavior.[4,6] The core area continued to decrease with the stabilization time and finally disappeared, in that no sheath–core structure was visible in the cross section of the stabilized fibers, that is, the fully stabilized PAN fibers.[16] The type I and II carbon fibers developed from the fully stabilized PAN fibers have higher mechanical properties than those developed from the partially stabilized PAN fibers.[17] However, the strain of the fully stabilized PAN fiber is very small, about 1–2%. It is not suited for mixing, spinning, weaving, and other textile processes. In another word, the nonburning fibers, having higher strain, is more flexible and has two-zone morphology.
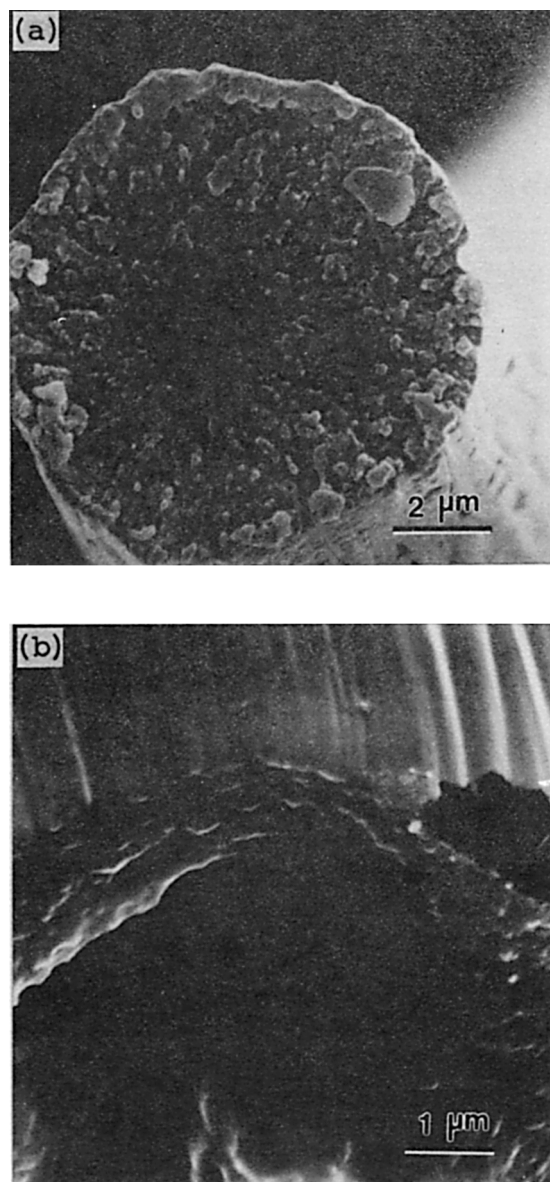
Fig. 3.   SEM images of fracture surface of stabilized fibers.

The fractured ends of stabilized fibers have been examined on a stereoscan. A typical fractured end of stabilized fiber, nonburning fiber was shown in Figure 3, the microstructure is similar to that of the partially stabilized Courtelle carbon fiber.[18] As shown in Figures 3(a) and 3(b), the stabilized fiber has the wraparound basal plane structure in the outer zone, and has a radial structure in the core. This microstructure is developed from the air-thermal treatment of the Courtelle, which is controlled by the diffusion-limited reaction condition.[4] In Figure 3(c), the fibrillarlike fractured surface is clearly seen, the strip-layer-like fibrils are parallel to the fiber axis, and these fibrils
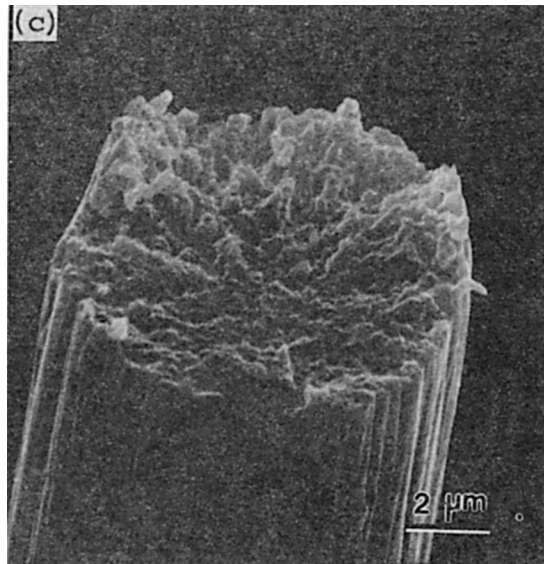
Fig. 3. (*Continued from the previous page.*)

were considered to be made up of lamellar-plate-like structures by a TEM analyses.

In our past work, we found that when PAN fiber was heated in oxygen-free Ar atmosphere at 265°C for 2 h, the color of a thermal-treated fiber is sorrel and the cross section has single zone. The color of this fiber will change to fuscous from sorrel if left at room temperature in air for a long time (2 or 3 months) and is degraded rapidly in a 50 wt % sulfuric acid solution. The analysis indicated that the chemical structure of the fiber was unstable. Warner and his co-workers[4] have studied the morphology of stabilized fiber by etching it in a sulfuric acid solution. The inner zone of the stabilized fiber was dissolved to form a hollow tube. The skin zone is sulfuric-acid-resistant, indicating that it is composed of a stable chemical structure with a rich oxygen content and thus more flame-resistant.

The surfaces of stabilized fibers are shown in Figure 4, it has a system of rough ridges or grooves parallel to the fiber axis. It is now well established that these features on the PAN fiber surface were developed during the fiber spinning stage. The surface morphologies are similar between the PAN fiber and the stabilized fiber.

A transmission electron micrograph of an inclined section of a representative stabilized fiber, having lamellar-plate-like structure, about 400–700 Å in thickness, 500–4000 Å in breadth, and 0.1–0.5 μm in length, is shown in Figure 5. The enlarged section of the microstructure model shown in Figure 1 is a copy from a part of Figure 5(a). The spacing is from 100 Å to several hundred Å between two lamellar-plate structures. Lamellar plates are packed together in the fiber which is oriented parallel to the fiber axis. In Figure 6, the TEM micrograph shows different lamellar-plate structure packing in the outer zone and the inner zone. Similarly it has an interface line between the two zones; the densities are about 1.3–1.4 g/cm^3 in the outer zone and about 1.1–1.2
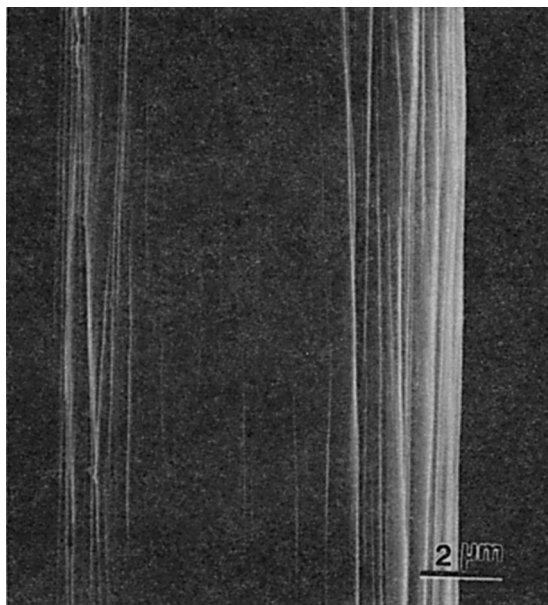
Fig. 4.   The longitudinal surface of stabilized fiber.

g/cm^3 in the inner zone. And in Figures 5 and 7, by micrograph analysis, there is likely no bonding between two lamellar-plate structures, the structures may be joined by van der Waals forces. The packing of the lamellar-plate structure for the outer zone is more compact and orderly than that of the inner zone. The direct consequence is that when tensile strength is applied to the fiber, the outer zone is more capable of impeding the propagation of microcracks than the inner zone, and the microcracks developed could propagate freely between two neighboring lamellar-plate structures in the inner zone. This may be able to explain why the structure of inner zone has radical distribution and that of outer zone has circumferential distribution from fracture surface analyses. Consequently, the dimension of the outer zone of the stabilized fiber grew both with increasing stabilization time or temperature, and the packing became more compact which led to higher density in the outer zone.

Figures 5 and 7 are shown with the lamellar-plate structure of a stabilized fiber, which seems to be composed of microfibrils. Microfibrillar bundles pack side by side to form lamellar-plate-like structure, which is the basic unit of stabilized fiber. These microfibrils are observed in their natural matrix consisting of other microfibril and are seen to run along the axis of the lamellar-plate structure. The voids existing in all kinds of irregular shapes are randomly distributed between two microfibrils also observed in Figure 7. While we cannot rule out the presence of either the original PAN structure which did not take part in cyclization reaction or the ladder polymer which were converted from the AN units from the bright-field image analysis, it is possible to use the dark-field image analysis to get a better answer. Figures 8(a), 8(b), and 8(c) are TEM images to study the same area of the stabilized fiber. Figure 8(a) shows the bright-field image of an inclined section of the lamellar-plate structure, Figure 8(b) shows the 001 dark-field image (2θ $\cong$
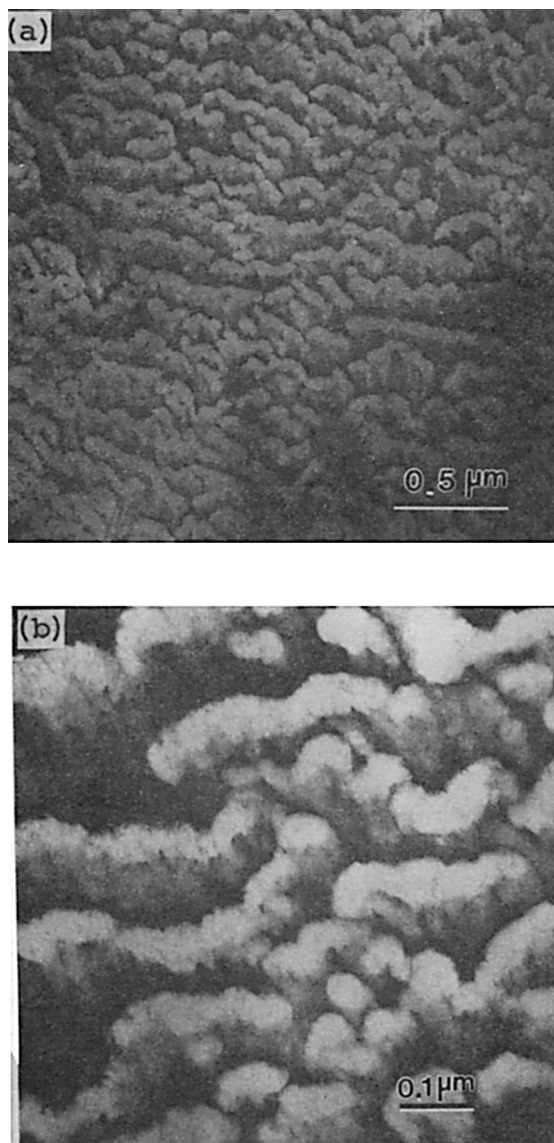
Fig. 5.   Bright-field image of a stabilized fiber: (a) inclined section of showing the lamellar-plate structure; (b) enlargement picture.

17°) of the original AN structure which remains in the stabilized fiber, and Figure 8(c) shows the 002 dark-field image ($2\theta \cong 25°$) of the ladder polymers that correspond to the bright domains found in the dark-field images; each domain represents the ordered phase and the crystalline zone, respectively. The lamellar-plate-like structure is composed of microfibrils. Each microfibrils is made up from the original AN structure and the ladder polymer, and the distribution of these structures in the microfibrils is unorderly. Due to the random distribution of the domains, it is difficult to measure the size of each domain. And the calculated crystalline size of the stabilized fiber is very rough

Fig. 6. A skin/core morphology of stabilized fiber, the outer zone (on the right) and the inner zone (on the left).
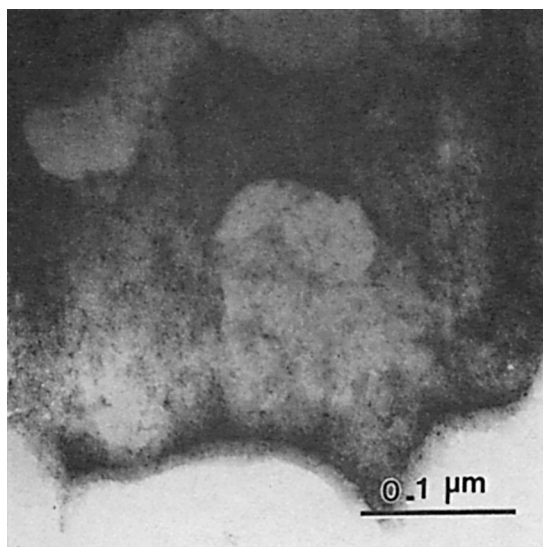

Fig. 7. Bright-field image of lamellar-plate structure composed of microfibrils, and voids distribution between microfibrils.

by the wide-angle X-ray diffractometer method because the stabilized fiber has two different chemical structures, original AN structure and ladder polymer, and four physical phases, both disordered and ordered phase for each chemical structures. In that case, separation of X-ray scattering curve to calculate the crystalline size of stabilized fiber is very difficult. The X-ray diffraction pattern of the stabilized fiber is shown in Figure 9; the external arcs are from the ladder polymer, and the inner arcs are from the original
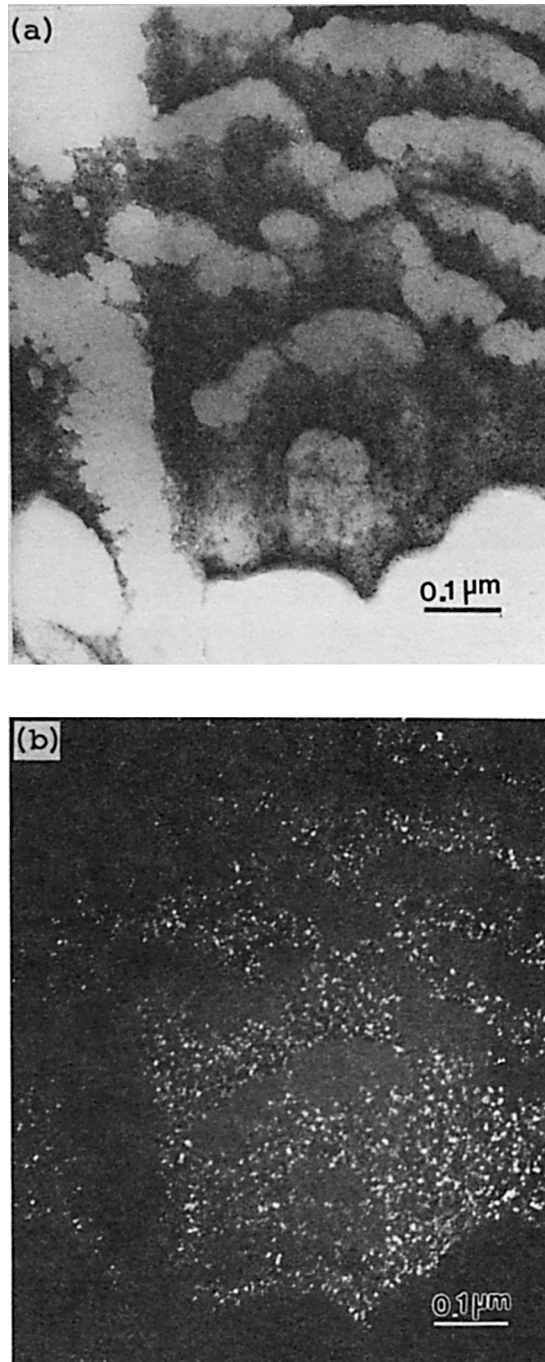
Fig. 8. Inclined section of stabilized fiber: (a) bright-field image; (b) 100 dark-field image (original AN structure which did not take part in the cyclization reaction); (c) 002 dark-field image (ladder polymer structure converted from AN structure).
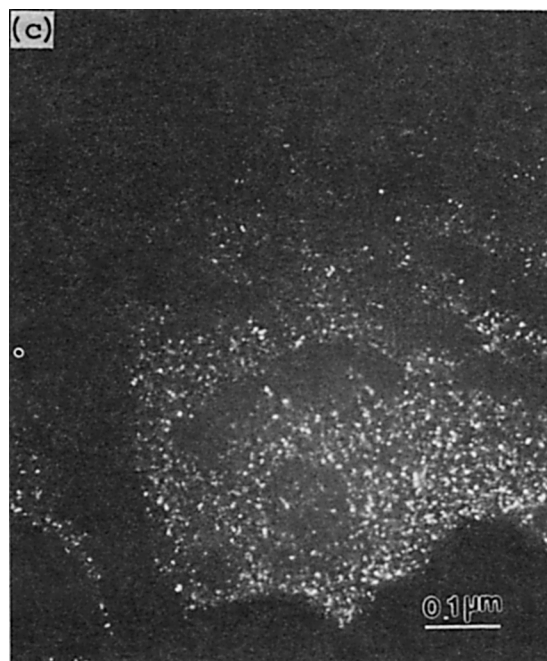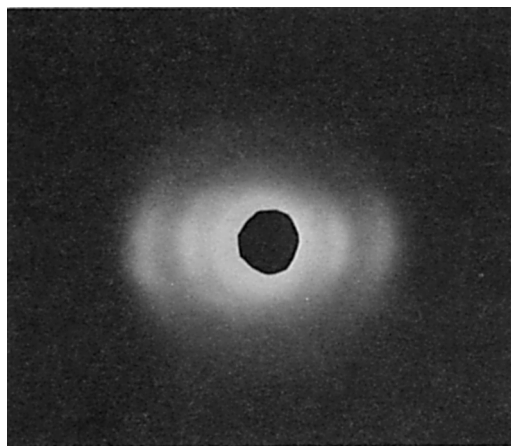
Fig. 8.   (*Continued from the previous page.*)

Fig. 9.   Wide-angle X-ray diffraction patterns of stabilized fiber.

PAN. Further studies are in progress; we hope to solve the problem in the near future. In this report, the structure model for stabilized fiber, the nonburning fiber, was established by optical and electron microscopes analyses. This model could help us to understand the microstructure and morphology of stabilized fiber (nonburning fiber) and the relationship between its microstructure and physical properties.

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