Uniplanar Orientation of Poly(*p*-phenylene Terephthalamide) Crystal in Thin Film and Its Effect on Mechanical Properties

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Synopsis

The uniplanar orientation of poly(*p*-phenylene terephthalamide) (PPTA) crystal was investigated by x-ray and infrared measurements. Thin PPTA films 3–15 μm thick were prepared by coagulating a sulfuric acid solution of PPTA with various coagulants. Two types of uniplanar orientation were observed, depending on the coagulant used. Thin film coagulated with water exhibits ($0k0$) uniplanar orientation and film coagulated with other coagulants such as methanol, ethanol, and acetone exhibits ($h00$) uniplanar orientation. These ($h00$) and ($0k0$) uniplanar orientations are formed with crystal modifications I and II, respectively. The ($0k0$) uniplanar orientation transforms to ($h00$) upon annealing, accompanying crystal transformation from modification II to modifications I. These uniplanar orientations may result from anisotropic crystal growth due to polymer–coagulant interaction along the hydrogen bond direction. The effect of these uniplanar orientations on the mechanical properties was also examined. The thin film having the ($0k0$) uniplanar orientation shows ductile fracture, whereas the one having the ($h00$) uniplanar orientation shows brittle fracture upon tensile deformation. These results are explained on the basis of the direction of the uniplanar orientation of the hydrogen-bonded sheet.

INTRODUCTION

The poly(*p*-phenylene terephthalamide) (PPTA) molecule, which is wholly *para*-aromatic polyamide, is known to be typically rigid. Its fiber, available under the registered trademark Kevlar (E. I. du Pont de Nemours and Co.) has good thermal stability and ultrahigh modulus and strength.[1] In recent years several investigations in the field of structure and properties were made on the crystal structure of PPTA fibers,[2–5] the morphology of PPTA crystal aggregates formed during polymerization,[6] the molecular orientation and the fine structure of PPTA fibers,[7–10] and the conformation of PPTA in sulfuric acid solution.[11,12] However, no detailed structural study of the regenerated PPTA films has been reported.

In a previous paper[13] we reported two kinds of crystal modifications, modifications I and II, for regenerated PPTA films. Figure 1 shows the crystal structures of modifications I and II, being projected on the paper surface along the *c*-axis. The crystal of modification II is formed in film coagulated with water, and that of modification I is formed in films coagulated with organic liquids such as methanol, ethanol, and acetone. Modification II irreversibly transforms to modification I upon annealing, and the facility of the transformation depends on polymer concentration in the sulfuric acid solution used. In the case of film prepared from a solution of low polymer concentration (below 8 wt-%), modification II completely transforms to modification I. On the other hand, in the case
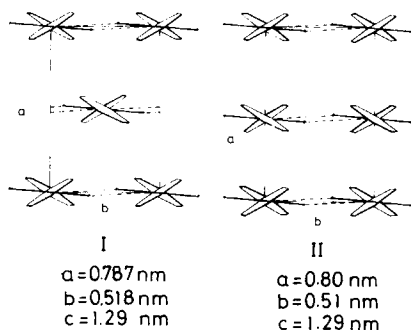
0021/8995/79/0023-0903$01.00

Fig. 1. *c*-Axis projections of crystal structures of modifications I and II.

of film prepared from a solution of high polymer concentration (above 8 wt-%), modification II is thermally stable and transforms to modification I very little. Furthermore, we discussed the mechanisms of formation of modification II and proposed a liquid crystal-like, swollen structure in film swollen with water during the course of coagulation.

In the present paper the formation of the uniplanar orentation was studied based on x-ray and infrared measurements for PPTA thin films prepared from sulfuric acid solutions by coagulation. Also, the effect of the uniplanar orientation on the mechanical properties of PPTA thin film was investigated from the viewpoint of orientation of the hydrogen-bonded sheet.

EXPERIMENTAL

Sample Preparation

Commercial poly(*p*-phenylene terephthalamide) (PPTA) fiber (Kevlar, du Pont Co., Ltd.) with a density of 1.44 g/cm^3 and an intrinsic viscosity of 6.5 dl/g (97.5% H_2SO_4, 303 K) was dried at 473 K in vacuo for 2 hr and dissolved in sulfuric acid (97.5% H_2SO_4). The polymer concentration in sulfuric acid solution was 3 wt-%. Thin films of PPTA were prepared by coagulating this sulfuric acid solution with various coagulants. The solution was thinly smeared on a glass plate with uniform thickness and soaked in a coagulant. Water, methanol, ethanol, and acetone were used as coagulants. After sulfuric acid was thoroughly removed from the regenerated film with a coagulant, the films were dried in vacuo at room temperature. For convenience, these dried films were designated as the original thin films. The thickness of a thin film was 3–15 μm. The original thin films were annealed in vacuo for 30 min at various temperatures from 373 K to 773 K.

Measurements

Wide-angle x-ray photographs were taken with Ni-filtered CuKα radiation using a Rigaku Denki rotating-anode unit (Rotaunit Ru-3). The x-ray diffraction photographs were taken on a multilayered thin film of about 15 films, with the x-ray beam normal (through view: TV) and parallel (edge view: EV) to the film surface, as indicated in Figure 2.

The infrared absorption spectra of the PPTA thin films were obtained by a grating infrared spectrophotometer (Perkin-Elmer 567).

Fig. 2. Direction of incident x-ray beam. Directions normal and parallel to the film surface are designated through view (TV) and edge view (EV), respectively.

The specimen for tensile testing measurement was 25 mm long and 2 mm wide. The stress–strain relationship for uniaxial stretching was recorded by a tensile tester (Tensilon UTM-III-500, Toyo Baldein Co., Ltd.) with a testing speed of 10 mm/min and at a testing temperature of 300 K.

RESULTS AND DISCUSSION

Uniplanar Orientation in PPTA Thin Film Coagulated with Water

Figure 3 shows x-ray diffraction photographs taken along the TV and EV directions for the original thin films prepared by coagulating with water. All reflections of the TV and EV photographs can be indexed by the crystallographic lattice constants of modification II reported in the previous paper.[13] The film surface for the EV photograph is positioned along the vertical direction. The schematic diagrams of these reflections are shown in Figure 4. A very diffuse reflection, which is rather intensified on the equator in the EV photograph, is observed between 0.4 and 0.5 nm, but we exclude this reflection from the discussions that follow because the reflection almost disappears upon annealing at temperatures below 430 K. In the TV photograph, the (200), (004), and (006) reflections are observed as Debye rings, but the (010) reflection is not observed. On the other hand, in the EV photograph, the intensity of the (010) reflection

Fig. 3. Wide-angle x-ray TV and EV photographs of PPTA original thin films prepared by coagulating with water.
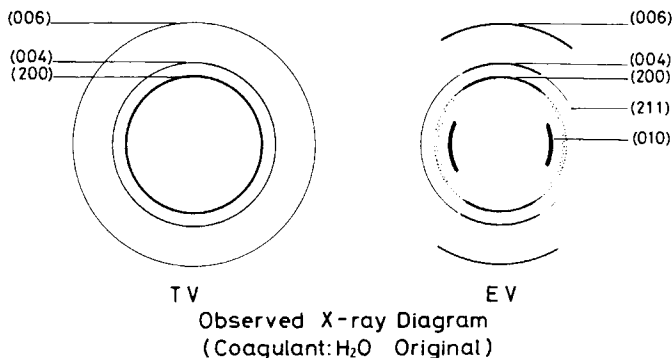
Fig. 4. Schematic diagram of observed x-ray photograph shown in Figure 3.

is increased on the equator, and the intensities of the (200), (004), and (006) reflections are increased on the meridian.

The intensity variations and the directions of the (hkl) reflections are helpful to investigate the oriented state of the PPTA crystal. The absence of the (010) reflection in the TV photograph and the reflection directions of the (010), (200), (004), and (006) planes in the EV photograph undoubtedly indicate that the (0k0) plane of the PPTA crystal is oriented parallel to the film surface. Furthermore, the observed apparent Debye rings in the TV photograph indicate that PPTA crystal is oriented statistically at random with respect to the axis perpendicular to the film surface (TV direction). This orientation can be termed the (0k0) uniplanar orientation according to Heffelfinger and Burton.[14] The schematic representation for this uniplanar orientation is illustrated in Figure 5(a), in which the ac-plane of the crystal is randomly rotated about the b-axis within the plane parallel to the film surface. It should be noted that the hydrogen bond direction is perpendicular to the film surface in the (0k0) uniplanar orientation, and it means that the hydrogen-bonded sheet is perpendicular to the film surface.

As reported in the previous paper,[13] modification II transforms to modification I only through annealing for film prepared from a sulfuric acid solution of low polymer concentration. Therefore, the relationship between transformation of crystal structure and uniplanar orientation was examined.

Figure 6 shows the x-ray photographs of TV and EV for thin film prepared by coagulating with water and annealing at 683 K. All reflections in Figure 6 can be indexed by the crystal structure of modification I reported by Northolt[2] and Tadokoro et al.,[3] although few reflections are associated with the remaining crystals of modification II. The reflection indices for these diagrams are illustrated schematically in Figure 7. The sample surface is positioned along the vertical direction for the EV photographs in Figures 6 and 7. The x-ray diffraction patterns in Figures 3 and 4 change to those in Figures 6 and 7, respectively, only upon annealing. In the TV photograph, the (110), (111), (004), and (006) reflections of modification I are observed as Debye rings, but the (200) reflection of modification I is not observed. On the other hand, in the EV photograph the (200) (I) reflection is intensified on the equator, and the (004) (I) and (006) (I) reflections are intensified on the meridian. The (110) (I) reflection splits into four spots, as shown in Figure 7. These observations indicate that the crystal orientation in the annealed thin film greatly differs from that in the original one. The observed Debye rings in the TV photograph indicate that the PPTA crystal aggregates with random orientation about the axis perpendicular
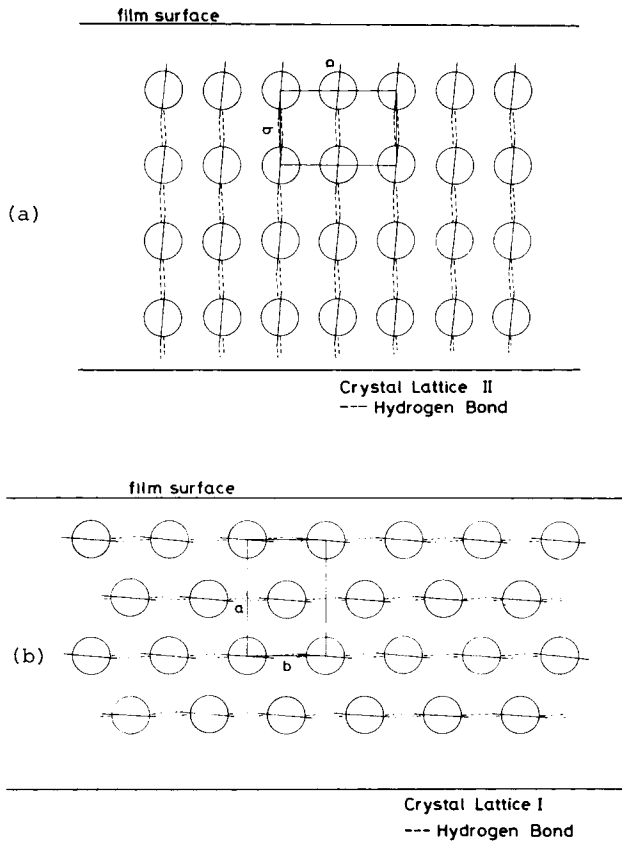
Fig. 5. Schematic representation of uniplanar orientation in PPTA thin film: (a) (0k0) uniplanar orientation; (b) (h00) uniplanar orientation.
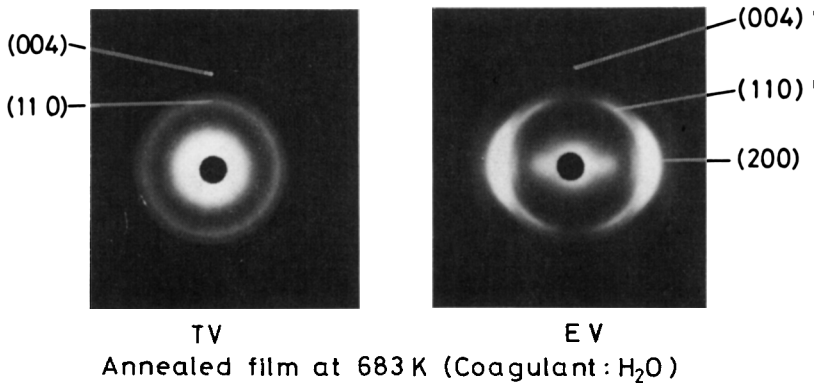

Annealed film at 683 K (Coagulant : H_2O)

Fig. 6. Wide-angle x-ray TV and EV photographs of PPTA thin film coagulated with water and annealed at 683 K for 30 min.

to the film surface in a similar manner as in the original film. Also, the x-ray intensity variations and diffraction directions of the (hkl) planes in the TV and EV photographs strongly indicate that PPTA crystal aggregates with the (h00) plane parallel to the film surface, which is called the (h00) uniplanar orientation. The schematic representation for this uniplanar orientation is illustrated in Figure 5(b), in which the bc-plane of the crystal is randomly rotated about the

Observed X-ray Diagram
(Coagulant: H_2O, Annealed at 683 K)
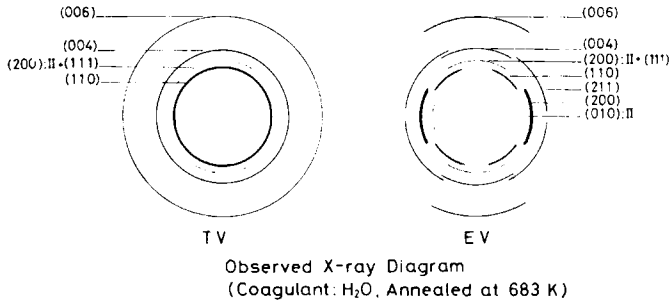
Fig. 7. Schematic diagrams of the observed x-ray photographs shown in Figure 6.

a-axis. In this case, the hydrogen bond direction is parallel to the film surface, contrary to the case of the ($0k0$) uniplanar orientation.

Thus, it is apparent that the original thin film coagulated with water exhibits a ($0k0$) uniplanar orientation and also that this uniplanar orientation transforms to the ($h00$) uniplanar orientation upon annealing, accompanying crystal transformation from modification II to modification I.

Uniplanar Orientation in Thin Film Coagulated with Other Coagulants

Figure 8 shows the TV and EV diffraction photographs for the original thin films prepared by coagulating with methanol. All reflections can be indexed by the lattice constants of modification I. The x-ray diffraction patterns in Figure 8 are essentially equal to those in Figure 6, except for the weak diffractions

T V   E V
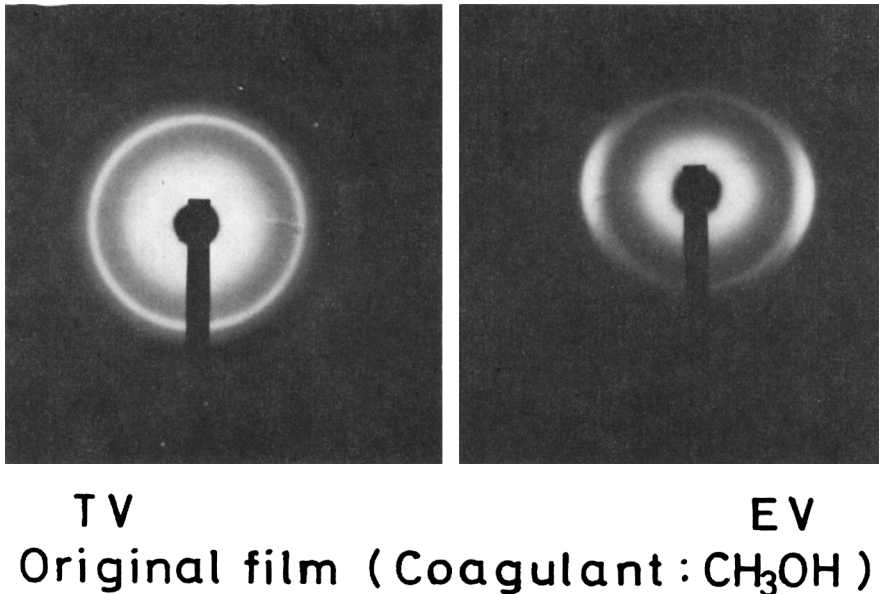Original film (Coagulant : CH_3OH)

Fig. 8. Wide-angle x-ray TV and EV photographs of PPTA original thin film prepared by coagulating with methanol.

from modification II. Therefore, Figure 8 indicates that the (h00) uniplanar orientation is formed in the original thin film coagulated with methanol. As shown in the EV photograph of Figure 8, the (110) reflection is not observed as the distinct four-point diffraction; also, the other diffraction arcs are broader around the azimuthal angle than those for the thin film coagulated with water and annealed at 683 K, shown in Figure 6(b). These observations indicate that the degree of the (h00) uniplanar orientation for the original thin film coagulated with methanol is lower than that for the annealed film coagulated with water.

The thin films coagulated with ethanol and acetone exhibit the same uniplanar orientation as the thin film coagulated with methanol. Therefore, the coagulants studied here are classified into two groups—water and other coagulants—on the basis of the type of the uniplanar orientation as well as the crystal modification as described in the previous paper.[13] Also, since the x-ray diffraction patterns for the thin films coagulated with the other coagulants except water hardly change upon annealing, these annealed films exhibit the (h00) uniplanar orientation.

Infrared Absorption Spectra of Film Coagulated with Water and Other Coagulants

Figure 9 shows the infrared absorption spectra in the range of amide A, amide I, and amide II bands for the original thin films prepared by coagulating with water (modification II) and the same film annealed at 719 K (modification I). The band at 3325 cm^{-1} is assigned to the amide A band, which corresponds to the N—H stretching mode. The bands at 1650 and 1545 cm^{-1} are assigned to the amide I and amide II bands, which mainly involve the C=O stretching mode and the coupled N-H in-plane deformation and C-N stretching modes, respectively. These assignments are confirmed by the infrared absorption spectra of the deuterated thin films; that is, the bands at 3325, 1650, and 1545 cm^{-1} shift to 2980, 1644, and 1300 cm^{-1}, respectively, by deuteration. As shown in Figure 9, the intensities of these amide-characteristic bands for the annealed thin film are stronger than those for the original one. Taking into account the directions
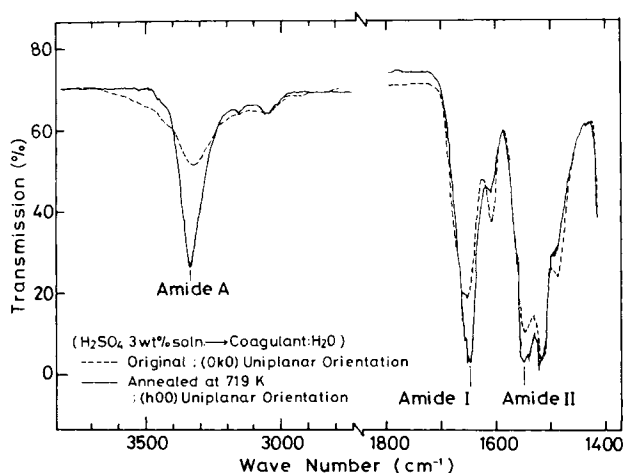

Fig. 9. Infrared absorption spectra in the range of amide A, amide I, and amide II bands for the original and annealed thin films coagulated with water.

of transition moments of these amide-characteristic bands, these observations support the tendency that the hydrogen bond direction in the original thin film is perpendicular to the film surface, and that the direction of the same specimen annealed at 719 K is parallel to the film surface. These results reconfirm the $(0k0)$ and $(h00)$ uniplanar orientations revealed by the x-ray diffraction studies, as shown in Figures 5(a) and (b).

The infrared absorption spectra for the thin films regenerated from sulfuric acid solution with coagulants such as methanol, ethanol, and acetone are found to be very similar to that for the annealed thin film coagulated with water. This again indicates that the $(h00)$ uniplanar orientation is formed in the thin films coagulated with the other coagulants except water, which agrees with the result of the x-ray diffraction measurement.

Mechanisms of Formation of Two Types of Uniplanar Orientation During Coagulation

It has been shown that two different types of uniplanar orientation are induced spontaneously in the regenerated PPTA thin films depending on the coagulant. The dependences of the uniplanar orientation on the coagulant and the crystal structure for the original and annealed thin films are summarized in Table I. The $(0k0)$ uniplanar orientation of modification II and the $(h00)$ uniplanar orientation of modification I are formed in the original thin films coagulated with water and methanol, respectively. The $(0k0)$ uniplanar orientation transforms to the (h00) one upon annealing, accompanying crystal transformation from modification II to modification I. Then, the relationship between the type of uniplanar orientation and crystal structure for the original thin film still holds in the annealed films.

Next, we discuss the mechanism for the formation of uniplanar orientations during coagulation from sulfuric acid solution. In the previous paper[13] we discussed the mechanism for the formation of modification II and concluded that PPTA molecules form a liquid crystal-like swollen structure at the beginning of coagulation with water. Figure 10(a) is a schematic model of liquid crystal-like swollen structure. In this structure, PPTA molecules are ordered along the a-axis with a fairly regular intermolecular spacing, along which PPTA molecules are aligned by van der Waals forces, whereas the arrangements of PPTA molecules along the hydrogen bond direction are hindered by the water molecules bound in amide linkages through hydrogen bonds. It may be reasonable to consider that these crystals, having a geometric anisotropy, as represented by the broken lines in Figure 10(a), tend to array themselves so that their ac-planes are parallel to the film surface in the process of the formation of solid film due to geometric requirements. Hence, the $(0k0)$ uniplanar orientation is accom-

TABLE I
Relationship Between Crystal Structure and Uniplanar Orientation for PPTA Thin Films

| | Coagulant | | | |
| | Water | | Methanol | |
	Original	Annealed	Original	Annealed
Crystal modification	II	I	I	I
Uniplanar orientation	$(0k0)$ plane	$(h00)$ plane	$(h00)$ plane	$(h00)$ plane

(a) Liquid Crystal-like Swollen
Structure

ϕ: PPTA , $\bullet$: Water Molecule

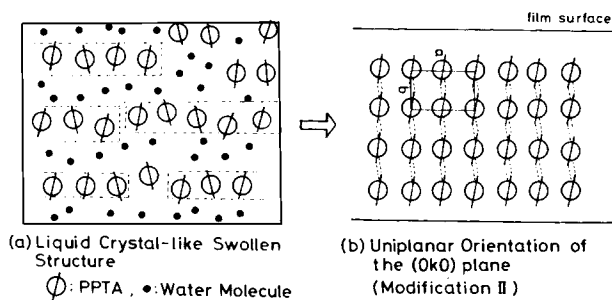(b) Uniplanar Orientation of
the (0k0) plane
(Modification II)

Fig. 10. Schematic representation aggregation states of PPTA (ϕ) and water molecules ($\bullet$) in the swollen and solid states: (a) swollen state; liquid crystal-like swollen structure; (b) solid state; crystal structure of modification II and (0k0) uniplanar orientation.

plished by accompanying the appearance of modification II after removal of water molecules. Figure 10(b) shows the final crystal structure and orientation. Consequently, the direction of the hydrogen bond of the PPTA crystal is perpendicular to the film surface.

A similar effect of water as a coagulant on uniplanar orientation has been reported for the regeneration of poly(vinyl alcohol)[15] and cellulose II.[16,17] Uniplanar orientation is formed in these films in which the hydrogen bond direction is perpendicular to the film surface.

On the other hand, the coagulant molecules such as methanol and acetone do not form strong hydrogen bond with amide groups, and the crystallization of PPTA molecules along the hydrogen bond direction is not interfered with as in the case of water coagulation. Therefore, in the initial step of coagulation, PPTA molecules aggregate with stronger correlation along the hydrogen bond direction than the van der Walls direction. This trend may induce the formation of crystal having a geometric anisotropy which is extended along the bc-plane. These crystals may array themselves so that their bc-planes are parallel to the film surface in the process of the solid film formation. In this case, the direction of the hydrogen bond becomes parallel to the film surface as shown in Figure 5(b). Thus, we have been able to explain the mechanisms of formation of the (h00) and (0k0) uniplanar orientations on the basis of anisotropic crystal growth depending on the relative magnitudes of the polymer–coagulant and polymer–polymer interactions.

Effect of (h00) and (0k0) Uniplanar Orientations on Mechanical Properties

In the previous section we discussed the (h00) and (0k0) uniplanar orientation having a hydrogen-bonded sheet parallel and perpendicular to the surface of PPTA thin films. The uniplanar orientation determined by the characteristic hydrogen bond direction must affect the deformation behavior of the thin film. In this section, the stress–strain behavior of these PPTA thin films is discussed by taking into account the effect of the uniplanar orientation.

Figure 11 illustrates the relationship between the drawing direction and the orientation of the hydrogen-bonded sheet (the (h00) plane) in the thin film. Figures 11(a) and (b) show the (h00) and (0k0) uniplanar orientations for which the hydrogen-bonded sheets exist parallel and perpendicular to the film surface, respectively. A notch is given at the edge of the thin film with a razor blade, as
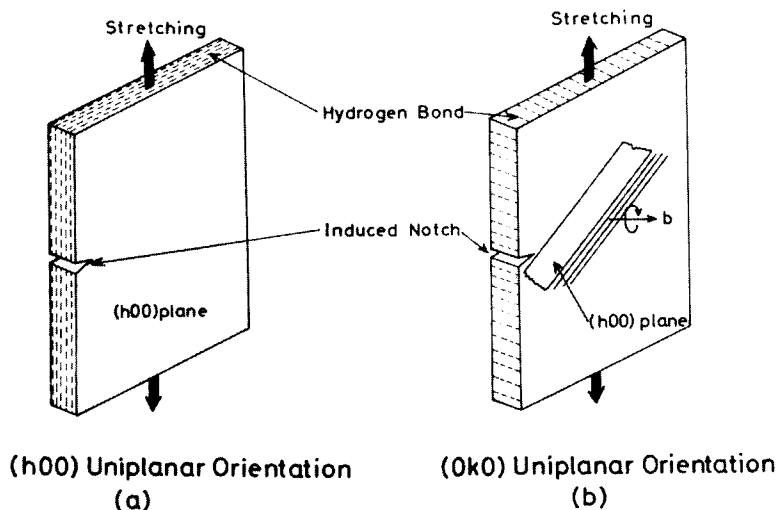
(h00) Uniplanar Orientation
(a)

(0k0) Uniplanar Orientation
(b)

Fig. 11. Illustration showing direction of induced notch of PPTA thin films and also hydrogen-bonded sheet, (h00) plane.

shown in Figure 11, prior to uniaxial stretching. The fracture surface propagates almost perpendicular to the stretching direction from the induced notch.

Figure 12 shows the stress–strain relationship for the PPTA thin films with the (h00) and ($0k$0) uniplanar orientations. The values of ultimate strain, ultimate stress, and initial modulus are summarized in Table II. The stress–strain behavior is quite different for the two cases. Figures 12(a) and 12(b) show the characteristic curves of the brittle and ductile deformations, respectively. The difference in stress–strain behavior can be explained based on the slip of the hydrogen-bonded sheets depending on the (h00) and ($0k$0) uniplanar orientations. Although the notch is produced at the edge of the specimen in the
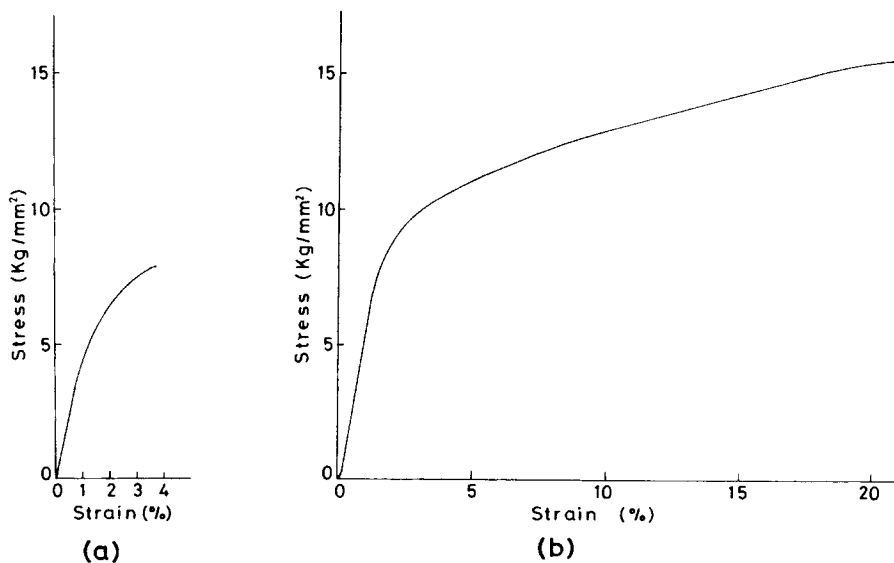

(a)   **(b)**

Fig. 12. Stress–strain curves for the PPTA thin films of (h00) and ($0k$0) uniplanar orientations.

TABLE II
Mechanical Properties of PPTA Original Thin Films

Uniplanar orientation	Ultimate strain, %	Ultimate stress, GN/m^2	Young's modulus, GN/m^2
$(h00)$ Plane	3.8	0.077	4.1
$(0k0)$ plane	20.9	0.153	6.3

same direction with respect to the stretching direction in both cases, the induced notch front is set normal and parallel to the hydrogen-bonded sheet, as illustrated in Figures 11(a) and (b), respectively. In the former case, the notch front almost instantaneously travels across the thin film when the sample is stretched to a certain elongation. No remarkable yielding can be observed because the propagation of the crack tears the hydrogen-bonded sheets. On the other hand, in the latter case, Figure 11(b), the specimen shows remarkable ductile deformation. Such a deformation is easily conceivable if a great deal of shear deformation parallel to the hydrogen-bonded sheets takes place. Thus, the stress–strain curves are well explained by assuming that the hydrogen-bonded sheet plays a primary role as a slip plane during tensile deformation. Zaukelies[18] has investigated the fracture behavior using biaxially oriented sheets of nylon 6 and 6,10. Uniaxial stress was applied along the molecular axis while the notch was indented beforehand in two ways, in parallel and perpendicular to the hydrogen-bonded planes. He concluded that the resulting fracture is of the ductile type when the induced notch front is parallel to the slip plane (hydrogen-bonded sheet), whereas the resulting fracture is of the brittle type when it is perpendicular to the slip plane. His results agree well with our results.

Conclusions

1. Two types of uniplanar orientation occur in the PPTA thin films, depending on the coagulant. PPTA thin film coagulated with water exhibits $(0k0)$ uniplanar orientation in which the hydrogen bond direction of PPTA crystal is perpendicular to the film surface. PPTA thin films coagulated with organic liquids such as methanol, ethanol, and acetone exhibit $(h00)$ uniplanar orientation in which the hydrogen bond direction is parallel to the film surface. The $(h00)$ and $(0k0)$ uniplanar orientations occur in accordance with the crystal structures of modifications I and II, respectively.

2. The mechanisms of formation of the two types of uniplanar orientation are explained by the anisotropic aggregation character of PPTA molecules due to the difference of the relative magnitude between polymer–polymer and polymer–coagulant interactions in the course of coagulation.

3. The transformation from the $(0k0)$ uniplanar orientation to the $(h00)$ orientation takes place upon annealing, accompanying the crystal transformation from modification II to I. The $(h00)$ uniplanar orientation does not change upon annealing.

4. The stress–strain behavior of the original thin film having the $(h00)$ and $(0k0)$ uniplanar orientations reveal the character of brittle fracture and ductile deformation, respectively. These tensile deformation behaviors can be explained by the magnitude of shear deformation parallel to the hydrogeon-bonded sheet in both specimens.

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