

Effect of Coagulation Conditions on Crystal Modification of Poly(*p*-phenylene Terephthalamide)

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Synopsis

Poly(*p*-phenylene terephthalamide)(PTTA) films were prepared from sulfuric acid solution with various coagulants. X-ray diffraction and infrared absorption measurements revealed that the crystal structure of the film coagulated with water showed a new crystal modification II, which was different from the one previously reported by Northolt and Tadokoro et al. The latter structure is called here modification I. Modification II coagulated with water from a solution of lower polymer concentration irreversibly transformed to modification I upon annealing, whereas modification II prepared from highly concentrated solution was thermally stable and scarcely transformed to modification I upon annealing. A liquid crystal-like swollen structure was found in the intermediate stage of the formation of modification II. In this swollen state, x-ray diffraction revealed that water molecules are included in hydrogen-bonded planes and the intermolecular spacing along the van der Waals force direction was unaffected by the existence of the water and remained constant throughout the process of regeneration. Both modifications I and II were found to be stable on treatment with boiling solvents. The transformation of the swollen structure to modification I took place in boiling methanol and acetone.

INTRODUCTION

In recent years, aromatic polyamides, polyimides, and polyamidehydrazides have become of major interest as superhigh tenacious, rigid, and thermally stable fibers or films. Poly(*p*-phenylene terephthalamide)(PPTA) shows various interesting properties. This polymer cannot form a fold structure because of the chain rigidity caused by the steric hindrance.¹ The solution of this polymer forms an anisotropic phase depending on the concentration and temperature.² Filaments spun from an anisotropic dope have ultrahigh modulus and strength.² The crystal structure of PPTA fiber has been reported by Northolt³ and Tadokoro et al.⁴ However, the structural study of the film prepared under various coagulating conditions has not been reported.

In this paper, the crystal modification of PPTA is surveyed on films prepared from solution in sulfuric acid by using various coagulants such as water, methanol, and so on. The thermal stability of the crystal modification is studied based on x-ray and infrared measurements. The crystallization process during the coagulation is also discussed.

EXPERIMENTAL

Sample Preparation

The commercial PPTA fiber Kevlar (du Pont., Ltd.), density of 1.44 g/cm^3 and $[\eta]$ (H_2SO_4 , 303 K) of 6.5 dl/g , was dried at 473 K in vacuo for 2 hr and dissolved in sulfuric acid (97.5% H_2SO_4). With increasing concentration of PPTA in the solution from 1 to 20 wt-%, a transition from an isotropic solution (liquid) to an anisotropic one (liquid crystal) was observed. The critical concentration for this transition was dependent on the temperature and the molecular weight (polymer axial ratio) as predicted by the theoretical calculation⁵ for the rod-like molecules in solution. The critical concentration in the sulfuric acid solution was observed at about 8 wt-% at room temperature in this investigation. Figure 1 shows the optical micrographs of typical (a) isotropic and (b) anisotropic phases observed under crossed nicols.

Films of PPTA were prepared by coagulating these solutions with various coagulants. The solution was smeared on a slide glass and soaked in a coagulant. We used 13 coagulants of water, methanol, ethanol, acetone, pyridine, N,N-dimethylformamide, acetic anhydride, ethyl ether, ethylene chlorohydrine, ethylene glycol, dichloroethane, tetrahydrofuran, and propionic acid. After sulfuric acid was thoroughly removed by exchanging the remaining liquid with a coagulant, the films were dried in vacuo at room temperature. For convenience this dried film is designated as the original film. Sulfuric acid remaining in the PPTA solid film was checked by infrared spectroscopy. The original film was annealed in vacuo at various temperatures from 373 to 773 K. For infrared absorption measurements, a thin film about $3\text{--}15 \mu\text{m}$ thick was prepared by the same method as mentioned above. In order to obtain fibers, the isotropic and anisotropic solutions were spun into a coagulant at a pressure of ca. 2.5 kg/cm^2 and then dried in vacuo at room temperature.

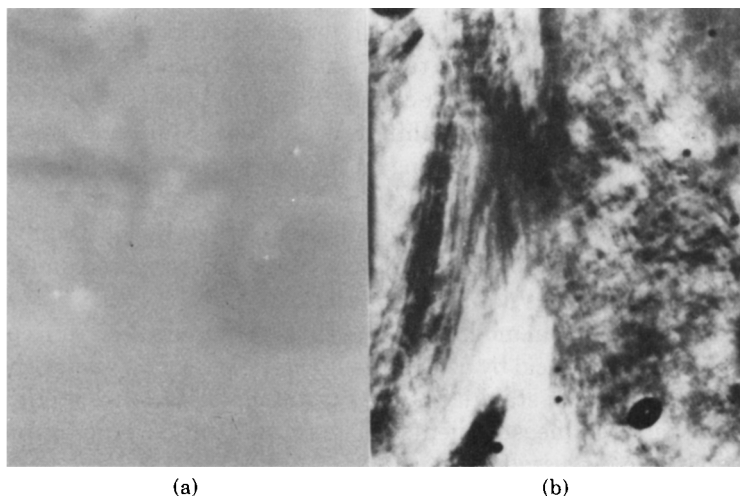


Fig. 1. Photomicrographs under crossed nicols for PPTA solutions in sulfuric acid: (a) isotropic phase; (b) anisotropic phase.

Measurements

Wide-angle x-ray photographs were taken with Ni-filtered $\text{CuK}\alpha$ radiation using a Rigaku Denki rotating anode unit (Rotaunit RU-3). The infrared absorption spectra were taken by using a grating infrared spectrophotometer (Perkin-Elmer 567). The density was measured by the floating method in carbon tetrachloride-ethanol mixture at 303 K.

RESULTS AND DISCUSSION

Effect of Coagulant on Crystal Structure of Regenerated PPTA Film

The x-ray photographs in Figures 2 (a-1) and (b-1) show typical patterns of the PPTA films prepared by coagulating a sulfuric acid solution with water and methanol, respectively. Films coagulated with all coagulants except water exhibit the same x-ray photographs as shown in Figure 2(b-1). The x-ray diffraction pattern of Figure 2(b-1) agrees with the pattern of the crystal structure reported by Northolt³ and Tadokoro et al.,⁴ whereas the one of Figure 2(a-1) is different from that of Figure 2(b-1) in the following points: (1) The very strong (110) reflection is absent. (2) A new reflection with strong intensity is observed at a Bragg spacing of about 0.51 nm, which is designated hereafter as the "inner" reflection. (3) The Bragg spacing of the (200) reflection is larger by 0.01 nm than that of Figure 2(b-1), which exceeds the experimental error. (4) Reflections with a spacing between 0.20 to 0.32 nm are not observed.

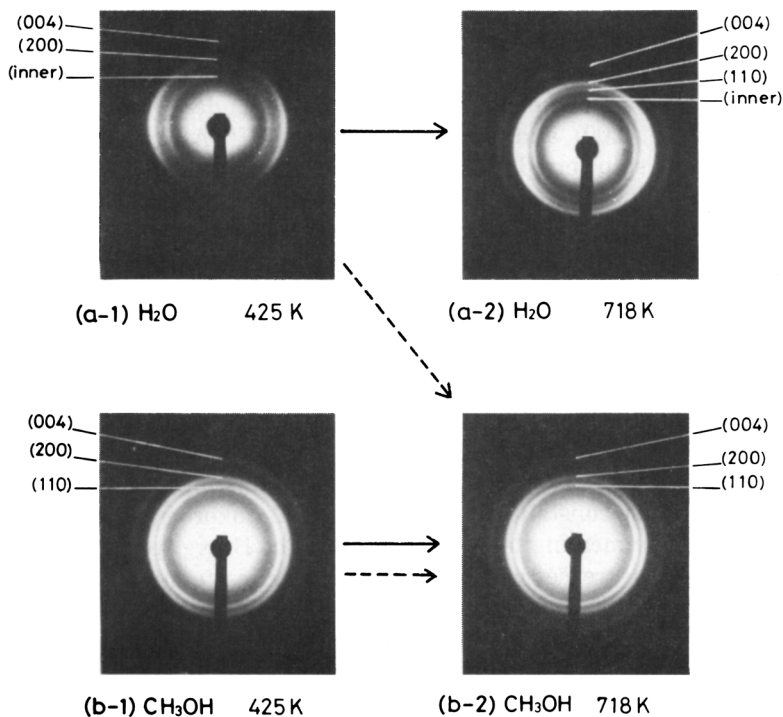


Fig. 2. X-ray diffraction photographs for PPTA films prepared by coagulating with water [(a-1) and (a-2)] and methanol [(b-1) and (b-2)] and annealing at 425 and 718 K in vacuo. Arrows in solid and broken lines indicate the change by annealing for films prepared from the PPTA solutions of 15 and 3 wt-%, respectively.

These results indicate that the PPTA film coagulated with water shows a crystal structure different from that reported in the literature. We designate the crystal structure reported by Northolt³ and Tadokoro et al.⁴ as modification I, and the one newly found here in the case of water coagulant as modification II. Thus, the water molecules are considered to play an important role as coagulant on the crystallization of PPTA from sulfuric acid solution.

In order to clarify the conditions of appearance of modification II, the effects of temperature and of the mixing ratio with other coagulants were investigated. No effect of coagulation temperature could be detected. When mixed coagulants were used, it was found that the crystal structure depended on the ratio of the coagulant. Modification II was found for films prepared when the ratio of the coagulants was larger than 55/45 (water/methanol) or 60/40 (water/acetone) in volume, whereas below this ratio modification I was found.

In order to obtain information on thermal stability of the crystal modification II, we examined the variation of x-ray diffraction patterns after annealing. In Figure 2, the arrows in the solid and broken lines indicate the variation of the crystal structure upon annealing for the original films prepared from the concentrated (15 wt-%) and the dilute (3 wt-%) sulfuric acid solutions, respectively. The x-ray diffraction pattern of the PPTA film coagulated with methanol does not change essentially upon annealing at the temperatures in the range from 373 to 773 K, although the intensity and sharpness for each reflection are increased by annealing. These annealing effects are independent of the polymer concentration. On the other hand, the x-ray diffraction pattern of the PPTA film coagulated with water considerably changes upon annealing; and further, it is noted that the annealing effects differ with the polymer concentration of the solution used.

Figure 3(a) shows the annealing temperature dependence of the spacings of the "inner", (110), (200), and (004) planes for the PPTA film coagulated with water from dilute solution (3 wt-%) and annealed for 30 min at different temperatures. The following changes were observed upon annealing: (1) the "inner" reflection does not disappear but attains strong intensity by annealing at temperatures below 450 K. The intensity of the "inner" reflection gradually decreases with increasing annealing temperature above 550 K and almost disappears when annealed at a temperature higher than 720 K. (2) The x-ray diffraction corresponding to the (110) reflection of modification I, which is not observed for the original film, appears upon annealing at about 550 K, and its intensity gradually increases with increasing annealing temperature. The appearance of the (110) reflection coincides with the disappearance of the "inner" reflection. The Bragg spacing of the (110) reflection approaches the value calculated by the lattice constants of Northolt³ and Tadokoro et al.⁴ (modification I) with increasing annealing temperature. (3) The Bragg spacing of the (200) reflection slightly decreases with increasing annealing temperature above 550 K and approaches the calculated value of the (200) spacing of modification I. (4) The (014) ($d = 0.27$ nm), (022) ($d = 0.24$ nm), and (310) ($d = 0.23$ nm) reflections of modification I appear upon annealing simultaneously with appearance of the (110) reflection. These observations indicate that modification II for the film prepared from a solution of low polymer concentration (3 wt-%) by coagulating with water is transformed to modification I.

The annealing effect on the transformation of modification II to modification I for the films obtained from solution of high polymer concentration (above 8

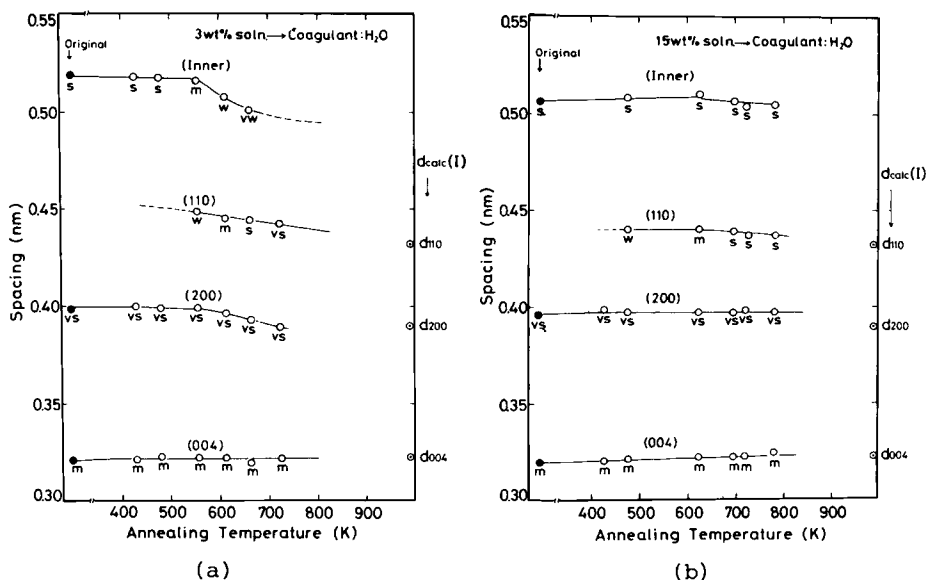


Fig. 3. Annealing temperature dependence of lattice spacings. Films were prepared by coagulating with water from solutions of polymer concentrations of (a) 3 wt-% and (b) 15 wt-%. Symbols represent x-ray diffraction intensity (vs = very strong, s = strong, m = medium, w = weak, vw = very weak).

wt %) by coagulating with water is different from the dilute solution mentioned above. The x-ray diffraction pattern in Figure 2 (a-2) is for the PPTA film coagulated with water from concentrated solution (15 wt-%) and annealed at 718 K. Figure 3(b) shows the annealing temperature dependence of the spacing of each reflection in this case. The following changes upon annealing are observed: (1) the "inner" reflection does not disappear but remains distinct even for film annealed at 773 K. The intensity of the "inner" reflection changes very little by annealing at 773 K. The spacing of the "inner" reflection remains almost constant. (2) The Bragg spacing of the (200) reflection remains constant, too. (3) The (110), (014), (022), and (310) reflections of modification I, which cannot be observed for the original film, appear upon annealing at 473 K, and their intensities gradually increase with increasing annealing temperature. These observations indicate that modification II scarcely transforms to modification I and that a part of the original film transforms to modification I. The appearance of modification I may be explained by the crystallization taking place in the amorphous region upon annealing.

These differences in annealing effects indicate that the crystal of modification II found in the film prepared from a 15 wt-% solution is more thermally stable than that from a 3 wt-% solution. This may be attributed to the difference in the *b*-axis dimension which is represented as the spacing of the "inner" reflection as mentioned in the next section, that is, the *b*-axis dimension for the film prepared from a 15 wt-% solution is slightly smaller than that for the film prepared from a 3 wt-% solution as shown in Figure 3.

The effect of coagulant was also observed by means of infrared spectroscopy. Figure 4 shows the absorption spectra in the range of 300 to 800 cm^{-1} for the original and annealed films coagulated with water and methanol from a 3 wt-% solution. The infrared absorption bands at 720 and 730 cm^{-1} are found to be

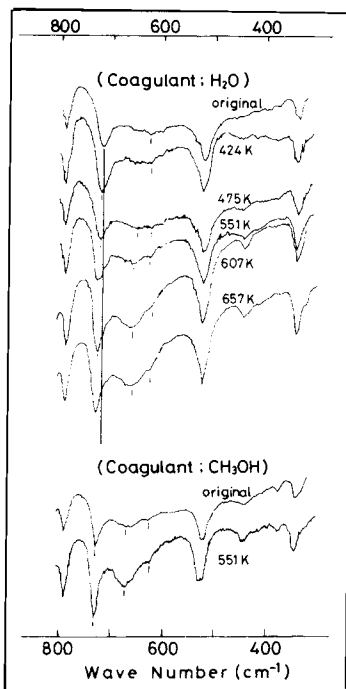


Fig. 4. Annealing temperature dependence of infrared spectra in the range of $300\text{--}800\text{ cm}^{-1}$ for the PPTA films prepared from a solution of 3 wt-%. Upper figure is for water as the coagulant, and the lower figure is for methanol as the coagulant.

very sensitive to the crystal modification. The band at 730 cm^{-1} is sensitive to modification I, and the band at 720 cm^{-1} is sensitive to modification II. The absorption band at 720 cm^{-1} for the film coagulated with water gradually approaches 730 cm^{-1} with increasing annealing temperature, as shown in Figure 5. On the other hand, this band for the film coagulated with methanol almost remains constant at 730 cm^{-1} , being independent of annealing temperature. The

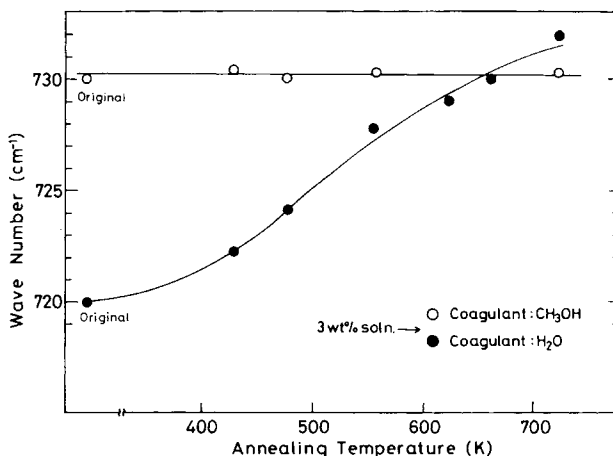


Fig. 5. Variation of wave numbers of 720 and 730 cm^{-1} of the original sample with annealing temperature. Open circles are for methanol, filled circles are water as the coagulant.

bands at 630 and 673 cm^{-1} also show variations similar to the 720 and 730 cm^{-1} bands, as shown in Figure 4. These variations upon annealing are consistent with the results of x-ray diffraction measurements on the crystal modification.

Some absorption bands which might be assigned to the O—H stretching vibration of the bound water molecules are observed as shoulders at ca. 3450, 3290, and 3190 cm^{-1} for film coagulated with water, as shown in Figure 6. These absorptions do not disappear upon annealing at temperatures below 400 K but gradually disappear with increasing annealing temperature above 400 K, as shown in Figure 6. From the elemental analysis of the original films coagulated with water and annealed at various temperatures, it was found that the water content of 3–4 wt-% was removed upon annealing. Also, the annealing films lose the weight, about 3 wt-%. The apparent loss of weight of the annealed film may be explained by the removal of bound water. These facts indicate that water molecules are tightly retained in the original PPTA film coagulated with water and annealed at temperatures below 400 K, and also that the water molecules are gradually removed upon annealing at temperatures above 400 K.

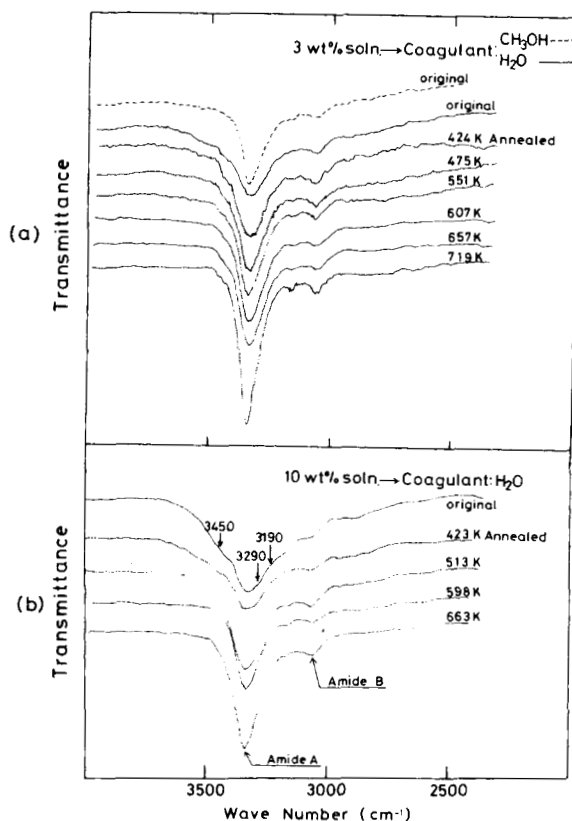


Fig. 6. Annealing temperature dependence of infrared spectra in the wave number range of the amide A band for the PPTA films prepared from solutions of (a) 3 wt-% and (b) 10 wt-%.

Possible Crystal Structure of Modification II

The (200), (004), and (006) reflections of modification II coincide to those of modification I. The (110) reflection of modification II is clearly different from that of modification I. Hence, it can be inferred that the crystal structure of modification II has almost the same a - and c -crystal lattice dimensions and the same molecular packing along the a - and c -axes as those of modification I, and also that the b -crystal lattice dimension or molecular packing along the b -axis of modification II is different from that of modification I. These facts are conceivable when we take into account the fact that the a - and c -axis dimensions are little affected by water since they correspond to the van der Waals and the covalent bond directions, respectively, whereas the b -axis direction is easily influenced by water molecules which invade the hydrogen bonded plane along the b -axis.

Figure 7 shows the x-ray diffraction patterns for the moderately oriented fibers prepared by means of wet spinning from the isotropic (5 wt-%) and anisotropic (11.5 wt-%) solutions with coagulant of water, which show that the molecular chain orientation is easily induced by spinning an anisotropic solution. In this case, the "inner" reflection appears as a strong equatorial arc, which indicates that the "inner" reflection is one of the $(hk0)$ reflections.

The crystal structure model composed of hydrated molecules is excluded from the crystal structure of modification II on the basis of infrared and density measurements. The observed density for the original film coagulated with water from a 3 wt-% solution of PPTA is 1.385 g/cm^3 , and the observed density of the same one annealed at 703 K is 1.420 g/cm^3 . Also, a small change in position or

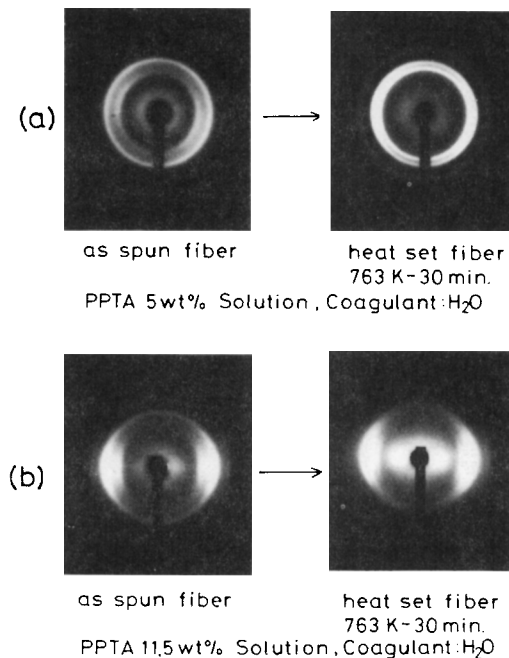


Fig. 7. X-Ray diffraction photographs for PPTA fibers prepared by wet spinning with water from solutions of (a) 5 wt-% and (b) 11.5 wt-%. Left side is for as-spun fiber, and right side is for heat-treated fiber.

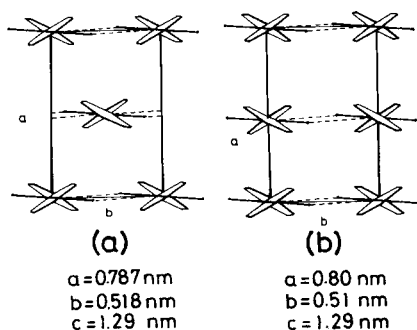


Fig. 8. *c*-Axis projections of the crystal structures for (a) modification I and (b) modification II. Modification I was reported by Northolt.³

orientation of the chain at $(1/2, 1/2)$ in modification I cannot account for the absence of the (110) reflection as shown in Figures 2(a-1) and 7(b).

From these facts, we propose the crystal structure model shown in Figure 8(b) as the most probable crystal structure for modification II, being projected on the paper surface along the *c*-axis, in which the "inner" reflection is indexed to (010). Figure 8(a) is the crystal structure of modification I reported by Northolt.³ The value of the fiber axis (*c*-axis) is assumed to be the same both in modifications I and II. Table I presents the calculated intensities for the crystal structure model for modification II shown in Figure 8(b) and the observed intensities. The calculated and observed intensities are in rather good agreement for the observed reflections of modification II. However, the angular disposition of the chain around the *c*-axis cannot be precisely determined since the number of reflection is limited.

Molecular Aggregation State of Modification II

The film coagulated with water is highly swollen by water before drying. The degree of swelling, which is defined by the ratio of the weight of a swollen film to the weight of the dried film, ranges from 2 to 8. Figure 9 shows the x-ray diffraction photograph of the swollen film. The very strong (200) reflection and the diffuse (004) and (006) reflections are observed. The diffuseness of the (004) reflection may be due to the overlap with the reflection arising from the water molecules ($d \approx 0.3$ nm).⁶ In addition to these reflections, there exists a very diffuse reflection with a spacing of about 0.8 nm, which is characteristic of the existence of water. The rather sharp (200) Debye ring indicates that molecular

TABLE I
Observed and Calculated Intensities for Modification II

<i>hkl</i>	$I_{\text{obs}}^{\text{a}}$	$I_{\text{cal}}^{\text{b}}$
004	m	21
006	m	37
010	s	56
200	vs	100
211	m	39

^a Visually estimated intensities: vs = very strong; s = strong; m = medium.

^b Calculated intensities of the other reflections are smaller than those of the listed reflections.

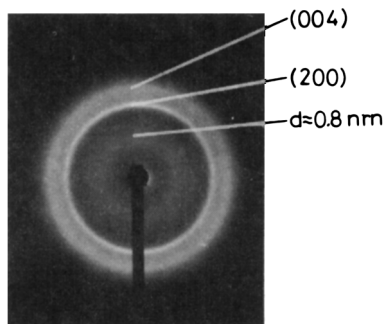


Fig. 9. X-ray diffraction photograph of film swollen by water as coagulant.

chain alignments with regular spacing exist along the a -axis. The absence of the diffraction rings from $(0k0)$ or $(hk0)$ may suggest low regularity in the intermolecular spacing along the b -axis. The appearance of the x-ray diffraction pattern for the film swollen by water makes us speculate that, on the initial step of aggregation of PPTA by coagulating with water from the sulfuric acid solution, the PPTA molecules increase in regularity in the intermolecular spacing along the a -axis along which the PPTA molecules are combined by van der Waals forces. On the other hand, the arrangement of the PPTA molecules along the b -axis may be interfered with by the water molecules bound at the amide linkages. This kind of swollen structure is observed for all swollen films, being independent of the polymer concentration of the solution. The aggregate structure in the swollen film is suspected to be principally similar to the liquid crystalline structure. As the swollen film is dried and the water is removed, the PPTA molecules are put in order along the b -axis. Finally, the crystal structure of modification II is formed instead of that of modification I. This aggregation process is consistent with the result mentioned in the previous section that the "inner" reflection corresponds to that from the (010) plane and it represents the orderliness along the b -axis direction.

Figure 10 shows the schematic representation of the aggregation state of the PPTA molecules in the film coagulated with water. The molecular axes (c -axis) are projected on a paper surface. Figures 10(a-1) and (a-2) exhibit the typical aggregation states of PPTA molecules swollen with water. Figure 10(a-1) is the liquid crystal-like swollen structure having fairly high regularity in intermolecular spacing along the a -axis, which gives the x-ray diffraction pattern shown in Figure 9. In Figure 10(a-1), the arrow along the a -axis is represented by the solid line, whereas the arrow along the b -axis is represented by the broken line, which means that the regularities are high and low along these directions, respectively. Figure 10(a-2) is the amorphous swollen structure in which the PPTA and water molecules coexist in a randomly dispersed state. Figure 10(b-1) shows the crystalline state, in which the PPTA molecules form the crystal structure of modification II. Figure 10(b-2) is the paracrystalline state in which the molecular alignment along the b -axis is largely distorted by the remaining water molecules, which preferably exist between the amide linkages of the PPTA molecules. The inability of thorough removal of water upon annealing at temperatures below 400 K, which is mentioned in the previous section, may be attributed to the water contained in this region.

Finally, in order to discuss the stability of the crystal modification, the transitions induced by various solvent treatments are summarized in Figure 11. On

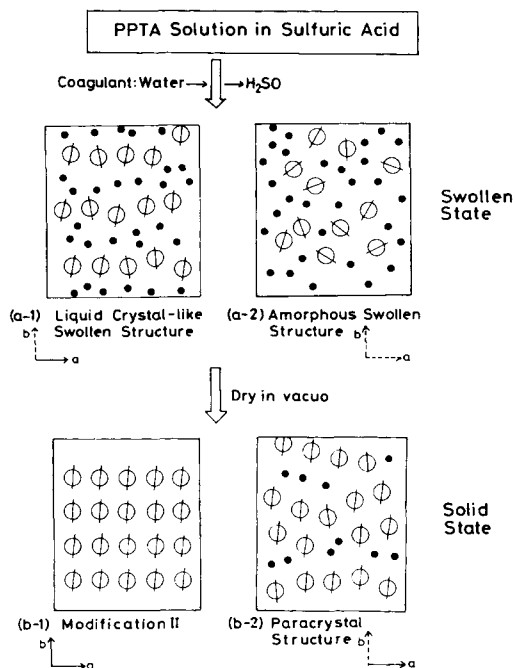
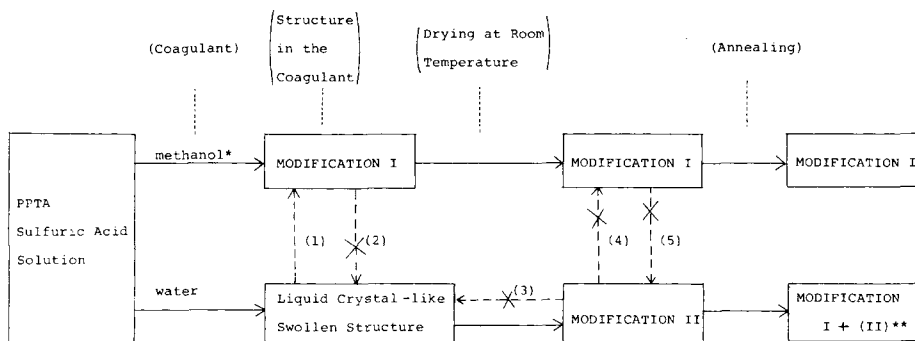


Fig. 10. Schematic representation of the aggregation states of PPTA (O) and water molecules (●) in the swollen or solid phase: (a-1) liquid crystal-like swollen structure; (a-2) amorphous swollen structure; (b-1) modification II; (b-2) paracrystalline structure.



- (1). Treatment in boiling methanol
- (2). Treatment in boiling water
- (3). Treatment in boiling water
- (4). Treatment in boiling methanol
- (5). Treatment in boiling water

* All of the coagulants except water described in the experimental section.

** Modification II scarcely transforms to modification I for the film prepared from the concentrated solution.

Fig. 11. Block diagrams representing the mutual transformations among the liquid crystal-like swollen structures, modifications I and II.

solvent treatment the film is held in boiling solvents for one day. The liquid crystal-like swollen structure containing water molecules changes to modification I by treatment in boiling methanol or acetone (process 1 in Figure 11). This transition is induced by replacement of water molecules in the liquid crystal-like swollen structure with methanol or acetone molecules. Modification I does not change to modification II by treatment with water (processes 2 and 5). Once

films are thoroughly dried, modifications I and II do no longer assume the liquid crystal-like swollen structure by boiling in water (process 3). Modification II in the original or annealed film does not transform into modification I by methanol or acetone treatment (process 4). Thus, modifications I and II in both the original and annealed films, once formed, are stable upon solvent treatment.

CONCLUSIONS

PPTA films are prepared from sulfuric acid solutions of PPTA by coagulating with various coagulants. The coagulants are classified into two groups based on the appearance of x-ray photographs and infrared spectra, that is, water and organic liquids such as methanol and acetone. Water shows its own characteristics in the coagulation process compared with the other coagulants. Film coagulated with water gives modification II, and film coagulated with methanol or acetone gives modification I. Modification I agrees with the crystal structure given in the literature. The crystal structure of modification II is estimated on the bases of x-ray diffraction and density measurements.

The transformation of modification II to modification I by annealing is significant for films prepared from solutions of low polymer concentration, but scarcely occurs for film prepared from solutions of high polymer concentration (above 8 wt-%). These different thermal stabilities of modification II are reflected in the difference of the *b*-axis dimension of modification II.

The liquid crystal-like swollen structure appears in the intermediate stage of formation of modification II from a PPTA sulfuric acid solution with a coagulant of water. In this structure PPTA molecules have a regular intermolecular spacing along the direction of the van der Waals force, and water molecules are included along the hydrogen bond direction between the neighboring PPTA molecules. Modification II appears by drying the swollen film at room temperature.

Both modifications I and II are stable toward treatment in boiling solvents. The transformation of the swollen structure to modification I occurs only by treatment in boiling methanol or acetone. This transformation is induced by replacement of water molecules with methanol or acetone molecules.

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