

# Surface Morphology and Crystalline Orientation of Uniaxially Drawn Polytetrafluoroethylene Films

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## Synopsis

For polytetrafluoroethylene (PTFE) films drawn uniaxially at 100, 150, 250, and 350°C, the morphology and degree of crystalline orientation were investigated by electron scanning microscopy and wide-angle X-ray diffraction, respectively. On the surface of the PTFE films which were heat-treated at 350°C for 2 h before the drawing, granules with a diameter of about 2  $\mu\text{m}$  and bands with a width of about 0.3  $\mu\text{m}$  were observed. By the drawing below the melting point, the bands are transformed into fibrils and a porous structure is formed by the drawing above the draw ratio ( $\lambda$ ) of about 1.3. By drawing above the melting point, striations appear perpendicularly to the draw direction, and the collapse of the granules is observed. The orientation of the crystallites increases rapidly with increasing the draw ratio and approaches a plateau at  $\lambda \approx 1.5$  for the films drawn above the melting point and at  $\lambda \approx 2.0$  for that below it.

## INTRODUCTION

Polytetrafluoroethylene (PTFE) is a remarkable material in many ways. Its very high melting point, extreme resistance to solvents and corrosive agents, unique nonadhesion, and very low coefficient friction are examples of these unusual properties. In order to make use of these properties in the form of films, PTFE films are produced by rolling the powder or skiving the sintered block, and the rolled or skived films are sometimes drawn in order to improve the end-use properties.

Because of the technological importance for the PTFE film processing, the molecular orientation has been investigated in the relationship with the macroscopic deformation condition, and its effect on mechanical and other properties has been examined. Wecker et al.<sup>1,2</sup> have studied the orientation and deformation of the crystallites in the uniaxially deformed PTFE by X-ray methods. Davidson and Gounder<sup>3</sup> have studied the orientation in crystallites and the non-crystalline phase of uniaxially drawn PTFE films by IR dichroism and broad-line NMR. Yeung and Jasse<sup>4</sup> have also studied the orientation of chains in crystalline and amorphous regions of uniaxially oriented PTFE by IR measurements. Moreover, Haneda et al.<sup>5</sup> have reported that uniaxially drawn and rolled films of unsintered PTFE (coagulated dispersion PTFE) have a porous fibrillar network structure. Recently we have also reported the morphology of biaxially drawn film of sintered PTFE.<sup>6</sup>

Since PTFE in the melt is not a flowing liquid, the molecular orientation by drawing can occur even above the melting point. In this study, sintered PTFE films are drawn uniaxially below and above the melting point. The morphology of the drawn films is observed by a scanning electron microscope (SEM), and is discussed in relationship to the orientation investigated by wide angle X-ray diffraction (WAXD).

## EXPERIMENTAL

The polymer used in this study was granular PTFE (Polyflon M-12) which has a particle size of about 25  $\mu\text{m}$ . The PTFE powder was charged into a die and pressurized gradually up to 20 MPa at room temperature. The pressure was held constant for 1 h until it was released to atmospheric pressure. The PTFE powder which was preformed thus in the form of 520 mm in outside diameter, 200 mm inside diameter, and 620 mm in length was sintered at 370°C for about 24 h in a circulating-air oven, and then cooled slowly to room temperature. The PTFE films were obtained by skiving the sintered PTFE to 200  $\mu\text{m}$  thickness.

In order to remove the residual stress in the skived films, they were heat-treated in the melt state at 350°C for 2 h, and then cooled slowly. The crystallinity of the heat-treated PTFE films was 65%, which was estimated from density measurement.

The PTFE films were cut to square samples (210  $\times$  210 mm) to fit in a drawing machine (Iwamoto Seisakusho), which can be used for both uniaxial drawing and biaxial drawing of PTFE films. PTFE films with different orientations were prepared by uniaxial drawing at 100, 150, 250, and 350°C. The film width perpendicular to the draw direction was maintained at the original width by gripping with the chucks of the drawing machine. The drawing rate was 5 mm/s. After elongation of the PTFE films, the elongated films were cooled in air to room temperature in a constant elongation. The actual elongation to calculate the draw ratio was obtained by measuring the distance between two marked lines on the drawn film which had been removed from the drawing machine.

SEM (Akashi Seisakusho) was used to observe the free surface of the drawn film. Gold was sputtered on the surface to the SEM observation.

The orientation of crystallites in the drawn PTFE films was investigated by using a WAXD apparatus and fiber specimen attachment (Rigaku Denki). The degree of the crystalline orientation was calculated from the full width of half-maximum intensity of the Debye ring for the (110) plane.

## RESULTS AND DISCUSSION

### Morphology

The morphology of the free surface of the undrawn and drawn PTFE films was observed by SEM. Figure 1 shows the morphology of the free surface for the undrawn film, the starting sample, which was heat treated at 350°C for 2 h and then cooled slowly. Granules with a diameter of about 2  $\mu\text{m}$  and randomly oriented bands with a width of about 0.3  $\mu\text{m}$  can be seen on the film surface, which is smooth before the heat treatment. We suppose that the

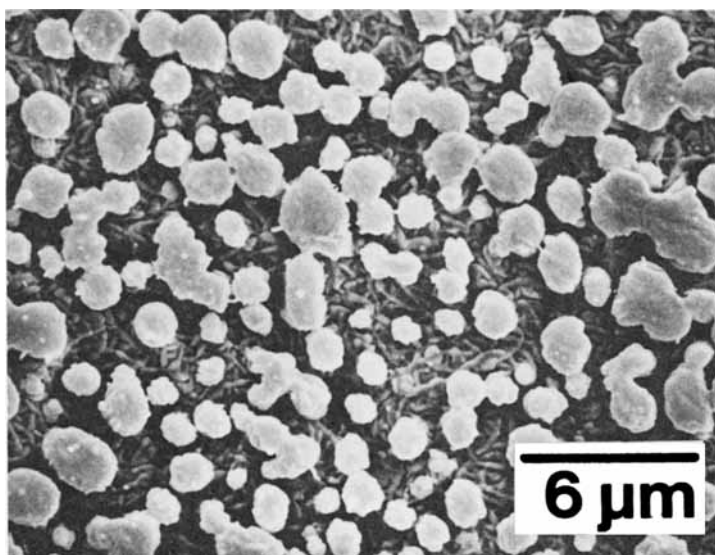


Fig. 1. Scanning electron micrograph of free surface of PTFE films heat-treated at 350°C for 2 h.

bands are essentially same as rodlike or ribbonlike entities observed by Rahl et al.<sup>7</sup> and Chanzy and Smith.<sup>8</sup> They have reported that virgin PTFE consists of two kinds of particles: rodlike and spherical entities. The spherical particles has been suggested to be irregularly folded ribbons<sup>7</sup> or to be composed of similar rodlike entities which are wrapped around themselves in a more or less random fashion.<sup>8</sup> The axis of PTFE chains is parallel to the long axis of the rods or ribbons. When the PTFE powder is compressed and heated above the melting point, the particles may stick each other being imposed strains, but the original groups of the molecules may hardly disperse since the melted PTFE is not a flowing liquid. Therefore, the rodlike or ribbonlike structure of virgin PTFE may be maintained latently in the sintered materials. When the films are heated above the melting point, the stuck particles may put forth in the form of the bands on the free surface being released from stress. The origin of the granules appearing on the film surface is also considered that by the heat treatment above the melting point the latent spherical particles (folded ribbons and/or wrapped rodlike entities) put forth on the free surface or the ribbonlike (or rodlike) entities are further folded or wrapped around themselves.

Figures 2, 3, 4, and 5 show the morphologies of the free surface of the PTFE films obtained by drawing at 100, 150, 250, and 350°C, respectively. The draw ratio  $\lambda$  is the ratio of drawn to undrawn length. The morphological change by drawing is clearly different between the drawing temperatures below and above the melting point.

In the morphology of the films obtained by drawing below the melting point (Figs. 2–4), the granules deform slightly with deformation of the base material. At a higher draw ratio ( $\lambda > 1.3$ ), the bands are transformed into highly oriented ivylike fibrils and a porous structure is formed. The porous structure is similar to the structure as seen in the biaxially drawn PTFE films.<sup>6</sup> For the

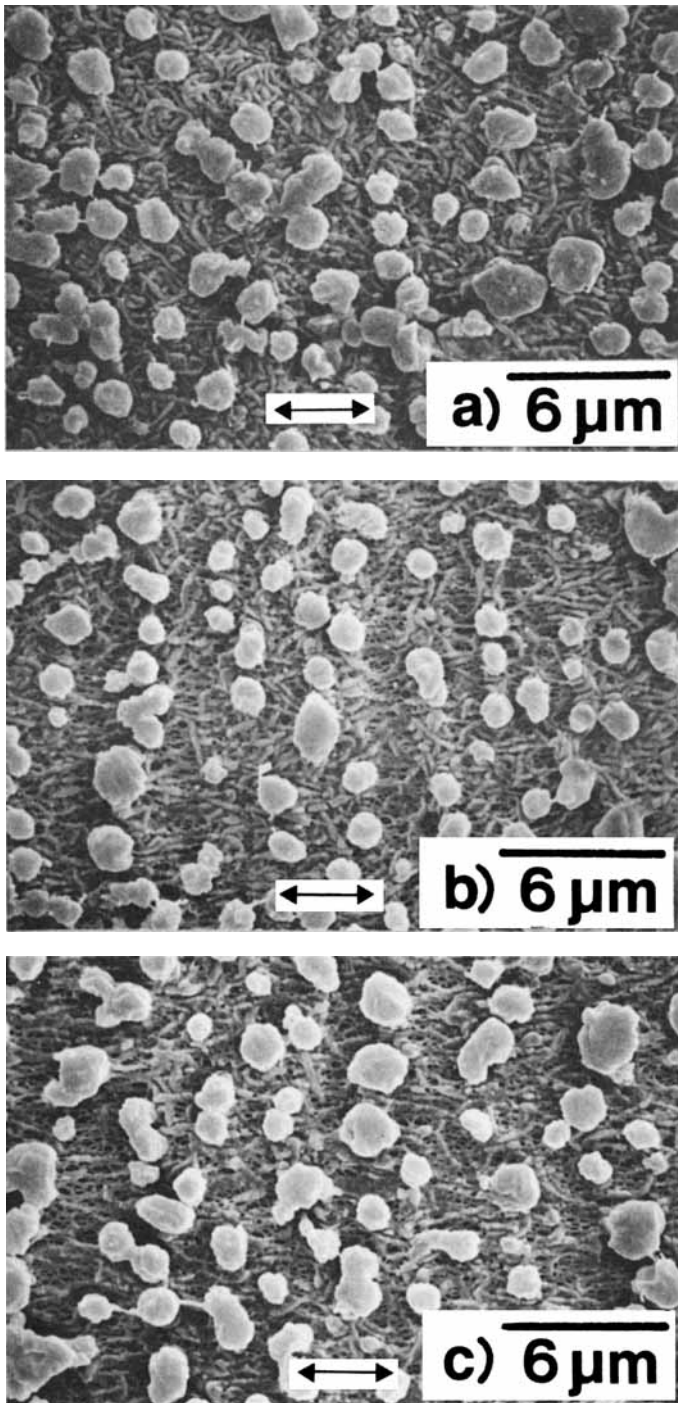


Fig. 2. Scanning electron micrograph of free surface of PTFE films drawn uniaxially at 100°C;  $\lambda$ : (a) 1.3; (b) 1.6; (c) 1.8. The arrow represents the draw direction.

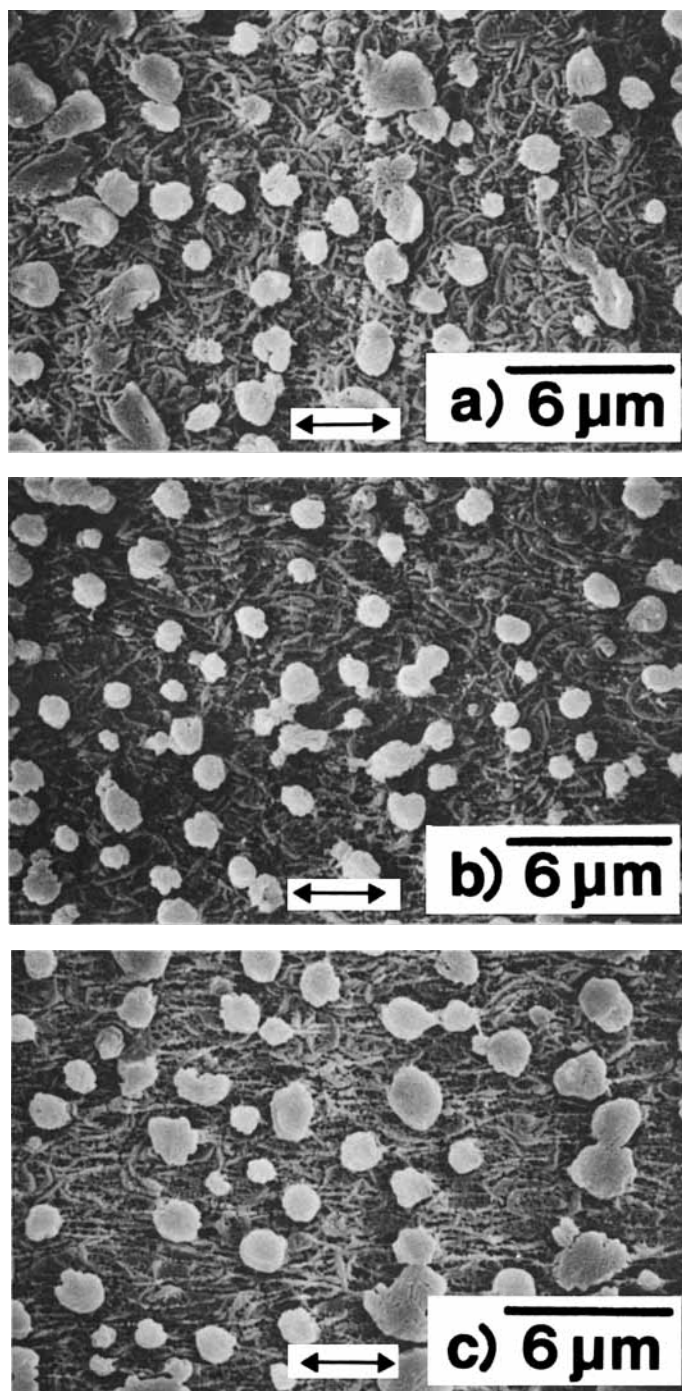


Fig. 3. Scanning electron micrograph of free surface of PTFE films drawn uniaxially at 150°C;  $\lambda$ : (a) 1.3; (b) 1.6; (c) 2.0. The arrow represents the draw direction.

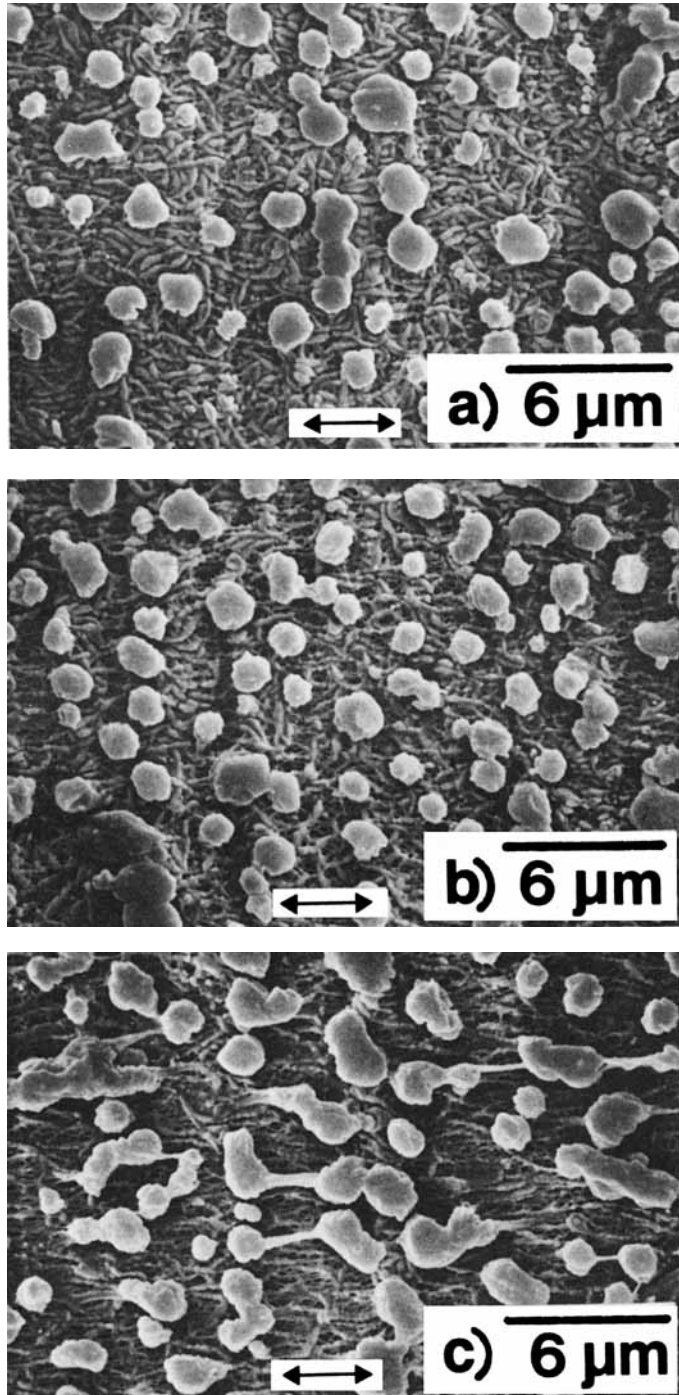


Fig. 4. Scanning electron micrograph of free surface of PTFE films drawn uniaxially at 250°C  $\lambda$ : (a) 1.3; (b) 1.6; (c) 2.2. The arrow represents the draw direction.

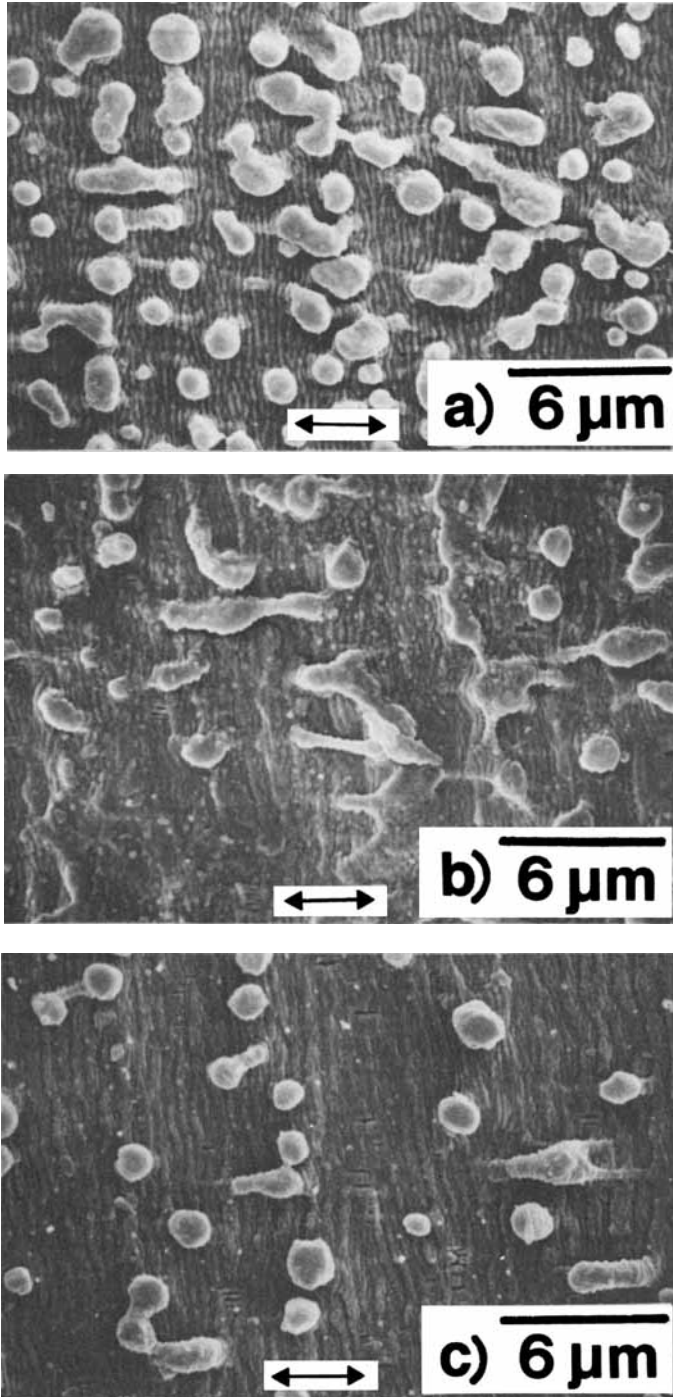


Fig. 5. Scanning electron micrograph of free surface of PTFE films drawn uniaxially at 350°C;  $\lambda$ : (a) 1.6; (b) 2.0; (c) 2.7. The arrow represents the draw direction.

lateral autoadhesion of the fibrils is relatively poor, they can be so easily separated from each other that the voids are formed by highly drawing. The fibrils are often bridged each other by more or less disoriented microfibrils.

By the drawing above the melting point (Fig. 5), striations perpendicular to the draw direction occur at a little draw ratio. At a higher draw ratio, the other broader striations are formed, and microcracks occur in line parallel to the draw direction because the lateral shrinkage of the film was restricted through the drawing and cooling processes. The development of the cracks is restricted to the width of the broad striations. The striations may be slip lines of the stuck ribbons and/or rodlike entities which may remain latently even in the melt. The striations also are observed clearly in the granules deformed by highly drawing [Fig. 5(c)]. The fibril formation as seen in the drawing below the melting point does not occur because of intermolecular autoadhesion in the melt. Moreover, the porous structure is not formed even at a higher draw ratio. The deformation of the granules by the drawing represents that the structure observed below the melting point remains almost even in the melt and changes with the deformation of the base materials, since the "melt" is not a flowing liquid; it has an extremely high viscosity. The formation of the step structure by highly drawing shows that the granule consists of stacked plates which may be the folded ribbons and/or wrapped rodlike entities mentioned above.

### Orientation of Crystallites

The orientation of crystallites in the uniaxially drawn PTFE films was investigated by WAXD. The degree of the orientation was calculated from the full width of half maximum intensity of the Debye ring for the (110) diffraction. Figure 6 shows the relationship between the draw ratio and the degree of

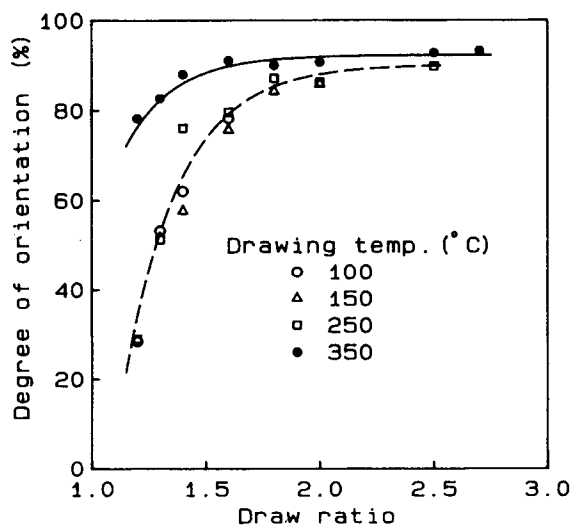


Fig. 6. Degree of crystalline orientation as a function of draw ratio in uniaxially drawn PTFE films. Drawing temperature (°C): (○) 100; (△) 150; (□) 250; (●) 350.



crystalline orientation. It is noticed that the orientation behavior is different between the drawing temperatures below and above the melting point.

For the films drawn below the melting point, the degree of the orientation increases rapidly with increasing the draw ratio and approaches a plateau. This result agrees well with the result by Davidson and Gounder,<sup>3</sup> which has been obtained in the study of the PTFE films drawn uniaxially at room temperature. The crystallites in PTFE reach their maximum state of orientation at a low draw ratio ( $\lambda \approx 1.5$ ) with comparison to many other crystalline polymers in which plastic deformation of spherulitic structure and chain unfolding occur by drawing, since PTFE has nonspherulitic and nonfolded chain crystal structure. The SEM photographs in Figures 2, 3, and 4 show that, in the stage of the rapid increase of the crystalline orientation, the ivylike fibrils form and orient with drawing, and that, in the stage of the plateau, the fibril formation progresses and the porous structure develops.

The very high melting point of PTFE is considered to be due to the unusual stiffness of the fluorocarbon chain. It is reasonable to suppose that in "melted" PTFE the molecules are straighter and tangle less together than in most other polymers just above their melting points. Therefore, the high degree of the molecular orientation can be obtained easily by a little elongation even in the melt state. Figure 6 shows that by the drawing above the melting point the crystalline orientation approaches a plateau at a lower draw ratio than by the drawing below the melting point. It is suggested that in PTFE the molecular orientation occurs more easily at the melt state than the solid state. This is confirmed from the X-ray photograph shown in Figure 7. In the cooling process from the melt the elongated films, which are clamped to maintain constant elongation, crystallize leaving the molecular orientation because of low mobility of the molecules. By further drawing after the

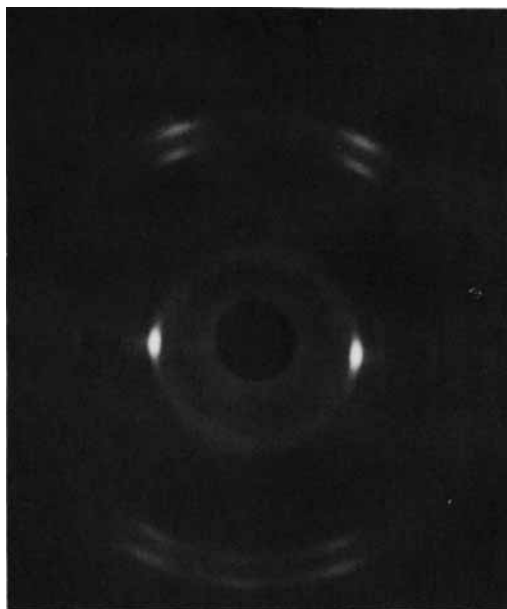


Fig. 7. X-ray photograph of PTFE film drawn uniaxially at 350°C and  $\lambda = 2.7$ .

molecular orientation is almost completed, the cracks occur, as is seen in Figure 5, since the melted PTFE is a jelly with weak cohesion: cheeselike rather than rubberlike.

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