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A TEM Study on Poly(tetrafluoroethylene) Heat-treated on Alkali Halides

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Granules of poly(tetrafluoroethylene) [PTFE] wax were heat-treated near/above the melting point on NaCl or KI, and their morphologies were studied by transmission electron microscopy. In the granule, fibrils of 70~120nm in width were observed, exhibiting a pattern of parallel crosses: the fibrils oriented in the <110> directions of the alkali halides. Long fibrils came out of the granule along <110> of the alkali halides, and the cross-sectional shape of the fibrils appeared to be trianglar (or trapezoidal). Electron diffraction patterns from a bandle of the fibrils revealed that the PTFE chain stems in such a fibril are set perpendicular to the fibril axis, and also that the (100) plane of PTFE hexagonal crystal lattice is in contact with the (001) face of the alkali halides. The degree of fibril orientation was better on KI than on NaCl.

Some flat-on platelets of PTFE single crystal were identified in the granules heat-treated on KI, not on NaCl. Lattice images of such a platelet were obtained, and their optical diffractograms clearly showed a hexgonal pattern consisting of three sets of the 100 reflection.

KEY WORDS: Transmission electron microscopy/PTFE/Epitaxy/Electron diffraction/Orientation/Annealing/Sintering/Morphology/Lattice image/

1. INTRODUCTION

When fine granules of poly(tetrafluoroethylene) [PTFE] were heated up near/above its melting temperature[1] for a few minutes on the carbon support film for transmission electron microscopy [TEM] and cooled down to room temperature, fibrillar or rod-like morphologies were observed in the periphery of each granule by TEM. This phenomenon of PTFE by heat treatment is regarded as the case also in the sintered bulk material of PTFE, and should be studied in detail in order to elucidate the relationship between the structure and the physical properties of sintered PTFE. Unfortunately, however, the orientation of fibrils or rods in question was random on the carbon support film, and accordingly the direction of molecular axis in the fibril or rod was not able to be determined.

Alkali halides such as NaCl, KCl, KBr, KI etc. have been widely used as the substrates for epitaxial crystallization of organic and inorganic materials. In the case of crystallizable synthetic polymers, of course, these alkali halides have been used as the substrates in order to controll the chain orientation of the polymers by epitaxy, for example, from solution[2] and from vapor phase[3,4]. In this communication, alkali halides are used as the substrates to controll the chain orientation of PTFE when heat-treated,

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and preliminary results of morphological observation by TEM are reported.

2. MATERIALS AND METHODS

2.1 Sample preparation

PTFE wax L-5 (molecular weight: $4\sim5\times10^4$) was used in this study, which is a product of Daikin Industries, Ltd. As the substrates, newly cleaved (001) faces of NaCl and KI were used.

Granules of PTFE were scattered on the surface of an alkali halide, and then only fine granules were settled there by stroking gently the surface with a fine cotton fiber. Extra granules were removed away from the surface by blowing mildly with a hand blower. The PTFE on the alkali halide was introduced into an electric furnace and heat-treated/annealed at a given temperature. The PTFE was cooled down to room temperature in the air.

2.2 TEM

The PTFE specimens thus heat-treated/annealed on an alkali halide were shadowed with Pt-Pd for morphological observation or with Au or Ag for electron diffraction [ED] experiments, and then coated with vapor-deposited carbon. The specimens reinforced with carbon were floated off on the water surface by dissolving the alkali halide substrate, and mounted on a Cu grid for TEM. TEM was carried out with a Hitachi H-500 (100kV) or a Jeol JEM-200CS (200kV).

3. RESULTS AND DISCUSSION

Figure 1 shows the morphology of granules of PTFE wax L-5, which were heated at 360°C for 2.5 minutes on the carbon support film for TEM and then cooled down to room temperature in the air. Fibrillar or rod-like protuberances are observed in the periphery of a granule of PTFE. Some of them seem to be straight, but the others are curved. Moreover, as shown with arrow-heads, fine rods are also observed here and there independently of the particle. The rod-like protuberances are crystalline because they give arc-shaped crystalline reflections in the selected-area ED pattern. The direction of the chain axis in them and their crystallite orientation, however, were not determined due to their less-defined orientation. In the case of the fine rods, it was difficult to take an ED photograph of them.

Figure 2 shows one of granules of L-5 and its surroundings, which were heat-treated on NaCl at 340°C for 15 minutes and subsequently cooled down to room temperature in the air. The arrow indicates the [100] direction of NaCl and the specimen was shadowed with Pt-Pd in this direction. In the granule, there is seen a pattern of parallel crosses, the constituents of which are fibrils of 70~110nm in width and are lightly oriented in the <110> directions of NaCl. The ED pattern of the granule showed that the *c*-axis, namely the chain axis of hexagonal PTFE is aligned in <110> of NaCl, because the arc-shaped 0015 reflection appeared in these directions. The fibrils in the granule intersect one another approximately at right angles as

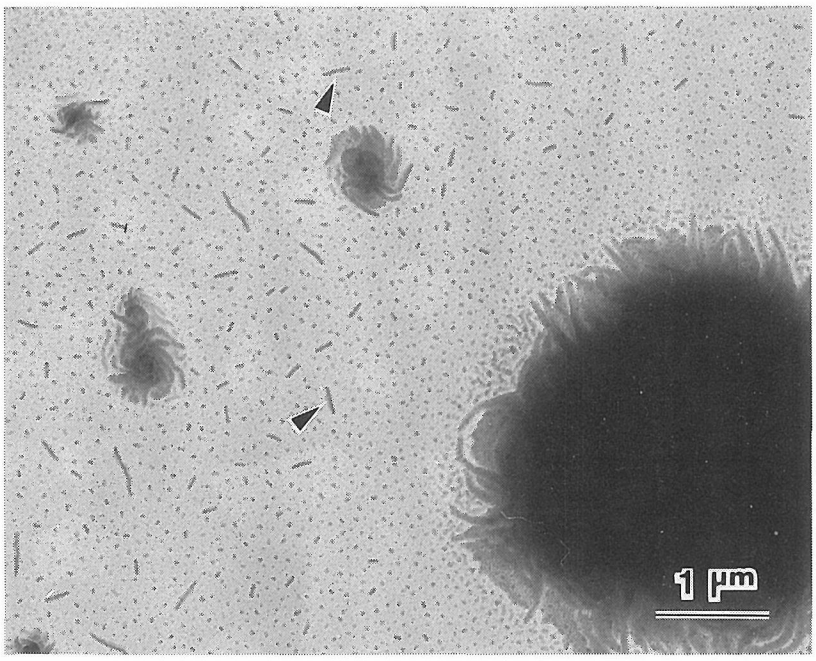

Fig. 1 Granules of PTFE wax L-5 heat-treated at 360°C for 2.5 minutes on the carbon support film for TEM and subsequently cooled down to room temperature in the air (shadowed with Pt-Pd).

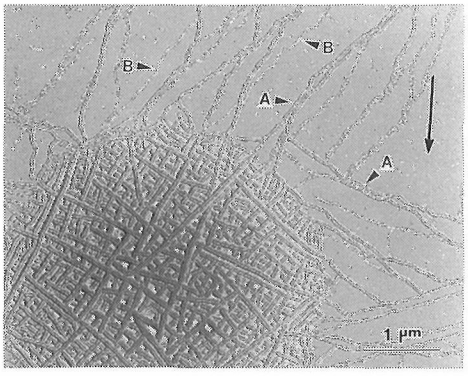

Fig. 2 Granule of PTFE wax L-5 heat-treated on NaCl at 340°C for 15 minutes and subsequently cooled down to room temperature in the air. The arrow indicates the [100] direction of NaCl and also the direction of Pt-Pd shadowing.

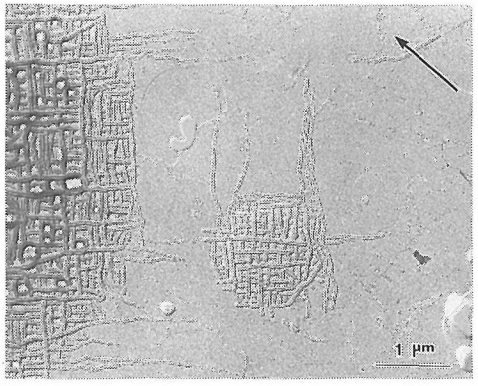

Fig. 3 Granules of PTFE wax L-5 heat-treated on KI at 340°C for 15 minutes and subsequently cooled down to room temperature in the air. The arrow indicates the [100] direction of KI and also the direction of Pt-Pd shadowing.

threads in plain fabrics. Many long fibrils of ca. 70nm in width have come out of the granule, nearly along <110> of NaCl (see, for example, the fibrils marked with the letters A's in Fig. 2). There are also observed finer fibrils of ca. 20nm in width, as indicated with B's in Fig. 2. The outward appearance of the granule and its surroundings resembles a freeway network with multilevel crossings in a modern city and its suburbs.

Figure 3 shows PTFE granules heated on KI at 340°C for 15 minutes. The arrow indicates [100] of KI, and the specimen was shadowed with Pt-Pd in this direction. The morphology is almost the same as that in Fig. 2, but the degree of fibril orientation in granules seems to be better than that of Fig. 2. In fact, ED patterns from the granules on KI illustrated better orientation of chain axis of PTFE than those on NaCl.

In the previous studies, the DSC thermogram of the drawn PTFE tape under the condition of fixed length showed the exotherm peak owing to crystallization at 312°C in the cooling process at the rate of 20°C/min[5]. The thermogram also showed that crystallization started around 327°C. On the other hand, the thermogram of PTFE resins showed in the cooling process that crystallization started at 318.5°C and the exotherm peak was at 315.5°C[6]. Then as the next step of our experiment, annealing of PTFE granules just after heat-treatment was examined at 316°C, below the temperature at which PTFE is to start to crystallize in the cooling process.

Figure 4 shows PTFE heat-treated on NaCl at 360°C for 15 minutes and then annealed there at 316°C for 1 hour. The arrow indicated [100] of NaCl and also the direction of Pt-Pd shadowing. Dark bands are observed in a granule (in the lower-right corner of Fig. 4), which are much wider than the fibrils seen in Figs. 2 and 3 and are ca. 500nm in width. They are roughly parallel to one another and are all lightly aligned in [110] or [$\bar{1}$10] of NaCl in each granule(see also Fig. 7). As for the fibrils of 80~90 nm in width which have come out of the granule, the degree of their orientation along <110> of NaCl has been improved more or less by annealing at 316°C.

Figure 5(a) is the PTFE heated on KI at 340°C for 15 minutes and then annealed at 316°C for 1 hour, indicating that the fibrils are aligned nearly parallel to one another. Figure 5(b) is the ED pattern from the encircled region in Fig. 5(a). The innermost ring is the 111 reflection of Au. The 0015 reflection of PTFE appears in the direction perpendicular to the fibril axis of the fibrillar crystals. This clearly reveals that the *c*-axis, i.e., the chain axis of PTFE is set parallel to the substrate and perpendicular to the fibril axis of the fibrillar crystal. When such a fibrillar crystal of PTFE is tilted in TEM at the angle of ca. ± 30° around the chain axis, the 100 reflection appears with 200 or has its maximum intensity on the equator in the ED pattern (see Fig. 5(c)). Accordingly, it is concluded that the (100) plane of PTFE crystal is in contact with the (001) face of KI, and also of NaCl.

In Figs. 2, 3 and 4, bright striations are observed in all the fibrils of ca. 70nm in width (Fig. 2 and 3) and 80~90nm in width (Fig. 4). The striation is running through and along the fibril. The width of the striation measures ca. 20nm, which is similar to the width of the microfibrils observed in Fig. 2. In Fig. 4, a microfibril of ca. 20nm in width is observed at the tip of the fibril of ca. 90nm in width, for example, at A's. The microfibril appears there as an extension of bright striation out of the fibril. Some

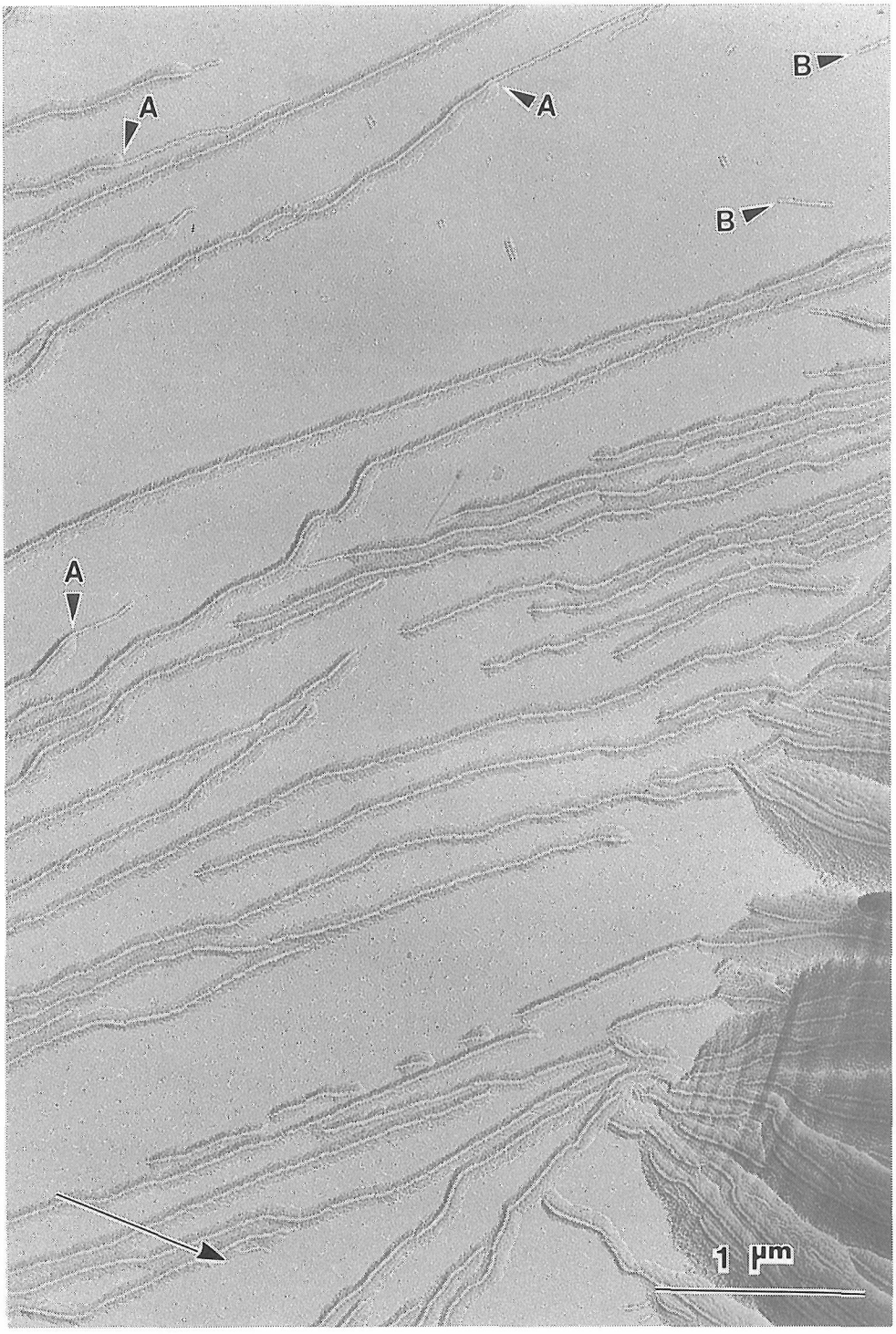

Fig. 4 PTFE wax L-5 heat-treated on NaCl at 360°C for 15 minutes and then annealed at 316°C for 1 hour. The arrow indicates the [100] direction of NaCl and also the direction of Pt-Pd shadowing.

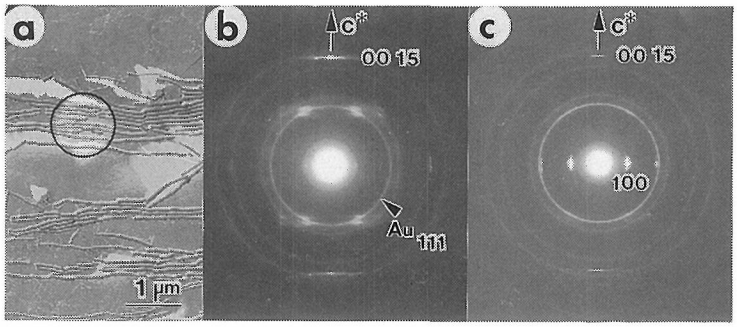

Fig. 5 (a) PTFE wax L-5 heat-treated on KI at 340°C for 15 minutes and then annealed at 316°C for 1 hour (shadowed with Au).
(b) ED pattern from the encircled region in (a).
(c) ED pattern from the specimen tilted at about ±30° around c^*-axis in (b).

isolated short microfibrils of ca. 20nm in width are also observed, as indicated with B's.

Figure 6 shows fibrils which came out of PTFE granules heat-treated on KI at 360°C for 1 hour and subsequently annealed at 316°C for 1 hour. The arrow indicates the direction of Pt-Pd shadowing. As for the fibril indicated with the letter A, at its tip observed in the encircled area of the figure, the shape of the "shadow" of the tip is triangular (or trapezoidal). The fibril indicated with B was shadowed in the direction at an angle of ca. 40° to the fibril axis. Hence, Pt-Pd was thickly deposited onto one oblique side-surface of the fibril, but weakly on the other side-surface. These results suggest that the cross section of such a fibril is approximately triangular (or trapezoidal). The width of the base of the fibrils which is in contact with KI is estimated at 110-120nm. Microfibrils of ca. 20nm in width are also recognized in Fig. 6, as marked with the letter C.

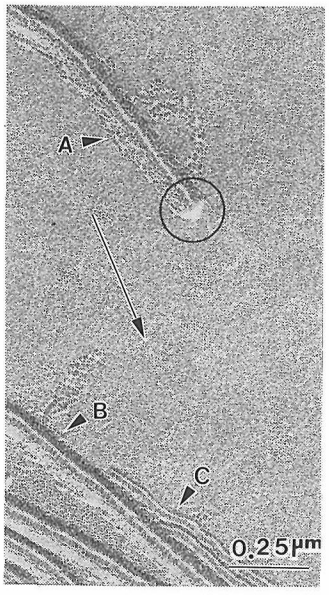

Fig. 6 PTFE wax L-5 heat-treated on KI at 360°C for 1 hour and then annealed at 316°C for 1 hour. The arrow indicates the direction of Pt-Pd shadowing.

In the fracture surface of sintered PTFE, Bunn *et al.* observed the band structure of 100 μm in length by 0.2~1 μm in width[7]. In the bands, they observed fine parallel "striations" perpendicular to the band length, and reported that the distance between "striations" varied greatly, down to 30nm or less. Moreover, they deduced that the chain axis of PTFE was parallel to the "striations" in the band, based on the result of birefringence measurement. Speerschneider and Li also reported the striated band structure, and found that the separation of ca. 20nm between "striations" in the band was not affected by different cooling rates[8]. Melillo and Wunderlich concluded that the chain axis is oriented parallel to the "striations"[9]. Recently, one of us deduced that the "striation" corrresponded to a microfibril of PTFE, the diameter of which was ca. 20nm[10]. Accordingly, the microfibrils of ca. 20nm in width observed in this study seems to be identical with the "striation" observed by Bunn *et al.* and Speerschneider and Li. Hence, the chain axis of PTFE in these microfibrils is deduced to be parallel to their axis. The ED patterns of Fig. 5(b) and 5(c), however, indicated that the chain axis in the fibril of ca. 110nm in width is oriented parpendicular to the fibril axis. The bright striation observed in the fibril whose cross-sectional shape is triangular (or trapezoidal) appears to be identical to the microfibril of ca. 20nm in width, as mentioned before. Seemingly, such a microfibril is set on the top of the fibril which resembles a triangular (or trapezoidal) prism. Now we have no reasonable model to explain these results. Further studies are needed to elucidate the structure of fibrils with a striation.

Figure 7 shows a PTFE granule heat-treated on KI at 340°C for 15 minutes and subsequently annealed at 316°C for 1 hour. In the granule, dark bands which are similar to those in Fig. 4, and fairly wide plate-like parts are observed. The inset is an ED pattern corresponding to such a plate-like crystal of PTFE, showing the *hk*0 net-pattern with the hexagonal symmetry. The pattern indicates that the PTFE chain stems are set perpendicular to the plate surface: a flat-on platelet of PTFE single crystal. In the case of NaCl as the substrate, such a flat-on crystal was never observed. The average lattice spacing of the innermost intense six reflections was estimated at 0.501nm in the inset of Fig. 7. This value gives $a=0.579$nm as the lattice constant, which is slightly larger than the reported value (0.566nm) for the hexagonal modification above 19°C[11]. The cause of this inconsistency is not known at present. Symons

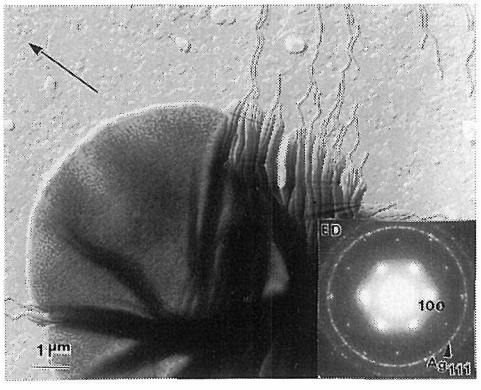

Fig. 7 Granule of PTFE wax L-5 heat-treated on KI at 340°C for 15 minutes and then annealed at 316°C for 1 hour.
The arrow indicates the [100] direction of KI and also the direction of Pt-Pd shadowing. The inset is the ED pattern from a plate-like crystal of PTFE (the innermost intense ring is the 111 reflection of Ag).

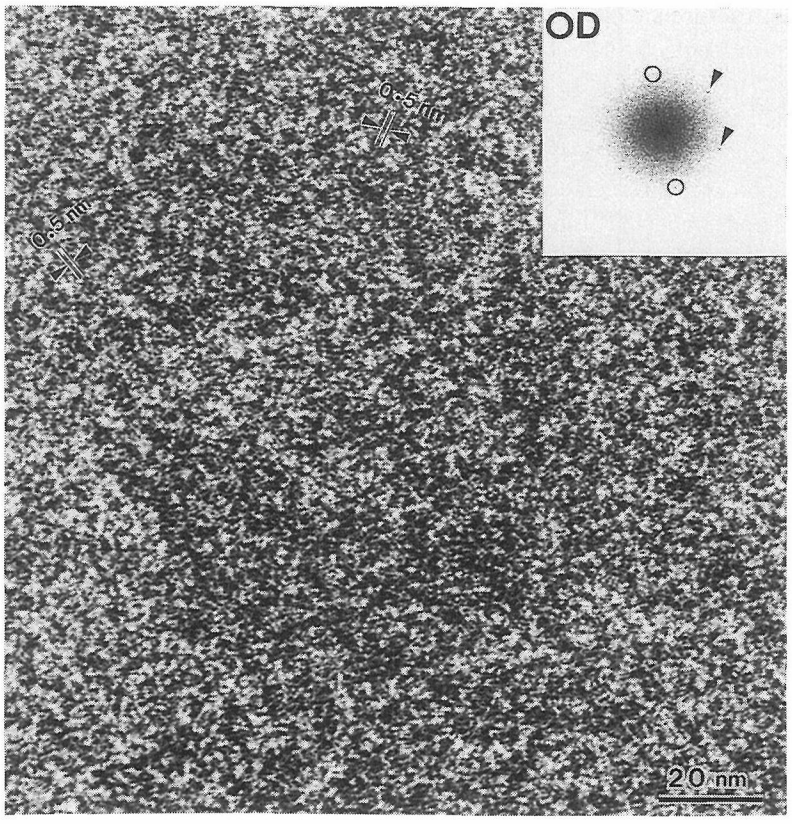

Fig. 8 High-resolution image of a plate-like crystal of PTFE similar to that in Fig. 7. The specimen was coated only with evaporated carbon. The inset is the optical diffraction pattern from the image, showing six 100 reflections arranged in a hexagonal manner as those in the ED pattern (see Fig. 7).

made single crystal plates of PTFE from the melt, and reported that some of them showed their hexagonal outlines[16]. In our samples, however, such a distinct external feature has never been observed.

The total end-point dose of the PTFE crystal for complete destruction of its crystallinity was estimated at ca. 0.008 Coulombs/cm^2 (for 200 kV electrons at room temperature) using fibrous specimens detached from a drawn unsintered PTFE tape. This value is similar to that of polyethylene, indicating that PTFE belongs to a group of radiation-sensitive polymers. However, using a low dose technique, (100) lattice images have been reported so far, of virgin spherical and rod-like particles[12], whiskers[13], and microfibrils in a rod-like particle[14]. Figure 8 shows a high-resolution TEM image of the PTFE corresponding to the plate-like part shown in Fig. 7. The optical diffraction pattern (the inset of Fig. 8) clearly demonstrates that the image has three sets of (100) lattice fringes, which intersect at an angle of 60°.

4. CONCLUDING REMARKS

Granules of PTFE wax were heat-treated near/above the melting temperature (or "isotropization temperature"[15]) on NaCl or KI. In the granule thus heat-treated, fibrils of 70~120nm in width were aligned parallel to <110> of the alkali halides, making a pattern of parallel crosses. Long fibrils came out of the granule, and their cross-sectional shape seemed to be triangular (or trapezoidal). ED patterns revealed that the chain axis of PTFE in such a fibril is set perpendicular to the fibril axis. In order to allow the PTFE particles to coalesce and to endow sufficient toughness and stiffness to PTFE products, preformed PTFE must be sintered above the melting point. When PTFE is sintered, many fibrils come out of each granule. They will reach other granules and break into them. Consequently the granules will be connected one another with these fibrils: PTFE products will become stiff.

By controlling the temperature of heat-treatment/annealing and the cooling condition, flat-on platelets of PTFE single crystal were obtained only on KI. The lattice matching between PTFE and substrates seems to be important to understand this phenomenon and also better orientation of fibrils on KI than on NaCl. At present, these problems are under examination. As for molecular weight dependence on morphologies, we have never recognized any remarkable difference so far between wax L-5 and fine powder F-104 [molecular weight: 4.7×10^6], except the better orientation of fibrils of L-5 than of F-104. The details will be reported elsewhere.

(100) lattice images were obtained from flat-on platelets of PTFE single crystal. Thus this achievement strongly suggests that lattice images are also able to be expected from the striation observed in the fibril and from the microfibrils of ca. 20nm in width, if they are crystalline. The images will directly show us the direction of chain axis in them.

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