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TEM Study on Oriented Thin Films of Poly(aryl-ether-ether-ketone) (PEEK)

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High-resolution observation of oriented thin crystalline films of poly(aryl-ether-ether-ketone) [PEEK] was performed by transmission electron microscopy [TEM].

A hot solution of PEEK was sandwiched between two glass slides, and oriented thin crystalline films of PEEK was prepared by displacing one of the glass slides just after evaporation of the solvent. These films showed a stacked lamellar morphology with the long period of about 15 nm or more. The (110) and/or (200) lattice images of the films were successfully obtained, in which (110) lattice fringes of 0.47 nm in spacing and/or (200) fringes of 0.39 nm were clearly identified. Some micrographs showed (002) lattice fringes of 0.50 nm in spacing. These lattice images directly revealed: (1) the thickness of crystalline core in the edge-on lamella is 6~7 nm and less than half of the long period; (2) the crystalline cores, namely crystallites are elongated along the b-axis. Moreover, we directly recognized in some of the images the existence of the "tie-crystallite" connecting successive crystalline lamellae.

KEY WORDS: Poly(aryl-ether-ether-ketone)/ PEEK/ Morphology/ Electron microscopy/ Oriented thin film/ High-resolution image/ Electron diffraction/

1. INTRODUCTION

Poly(aryl-ether-ether-ketone) [PEEK] is one of the high-performance engineering plastics with some excellent properties such as high thermal stability and registance to chemicals. The crystallinity of PEEK products, which were made in a usual way such as melt processing, is rather low and usually below 50%[1,2]. Accordingly, efforts have been still attempted in order to improve the processing procedure by solid-state extrusion[3], zone-drawing/zone-annealing[4,5] and gelation from a PEEK solution[6].

In our previous paper, morphological and high-resolution observations of solution-grown PEEK crystals by transmission electron microscopy [TEM] were reported[7]. The morphological observation showed the following two facts. First, the growth direction of seemingly fibrillar but narrow lamellar crystals as constituents of spherulites corresponds to the crystal b-axis, as also reported by Lovinger and Davis[8]. Second, there exists orientation distribution of crystallites around this b-axis. In the case of high-resolution TEM of the crystal, curved lattice

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fringes clearly denoted the lattice distortion in a crystallite. Moreover, "molecular images" of PEEK crystal viewed along its stem axis (c-axis) were successfully obtained with the resolution limit of 0.296 nm (lattice spacing of (020)), one of which showed a small-angle grain boundary caused by accumulated edge-dislocations. Some of the features mentioned above should be found in bulk materials of PEEK. In this paper, hence, unoriented and oriented thin crystalline films of PEEK cast from solutions are used as models of its bulk materials. Morphologies of the films, especially of oriented thin films are discussed with some results by high-resolution TEM.

2. EXPERIMENTAL

2.1 Sample Preparation

PEEK chips (#450P) were kindly supplied by Sumitomo Chemical Co., Ltd., which are equivalent to the commercial product #450G[9] (melt viscosity of #450P: 4,500 Poise at 400°C). Fine grains selected from the chips were dissolved in α-chloronaphthalene at its boiling temperature, and consequently a 0.1 wt% solution was prepared. Several drops of the hot solution were sandwiched between two glass slides on the hot plate whose temperature was regulated to be constant at 300°C. Just after evaporation of the solvent, a supercooled thin film of PEEK was sheared and crystallized by displacing one of the two glass slides at the temperature. Some of the films thus prepared were annealed at 225°C for 2 hours, but no remarkable change was recognized.

The oriented thin crystalline films were reinforced with evaporated carbon and then floated off from the glass slide in a very dilute aqueous solution of HF ($<0.02\,M$). Then the films were washed with distilled water and mounted with the aid of water surface onto Cu grids for TEM observation: for high-resolution observation, they were mounted onto Au- or Ag-coated microgrids. The specimens were coated with vapor-deposited Al, if necessary, as a reference material in the electron diffraction [ED] experiment. Though several proposals for cell dimensions of PEEK crystal lattice were made so far[2], all the ED patterns in this papper are indexed using the unit cell dimensions reported by Shimizu *et al.*[10]: orthorhombic (*Pbcn*), a=0.780 nm, b=0.592 nm, c (chain axis)=1.000 nm.

2.2 Electron Microscopy

TEM observation and selected-area ED experiments were carried out at 200 kV with a JEOL JEM-200CS equipped with a high-resolution side-entry goniometer SHG-4 (spherical aberration coefficient Cs=1.2 ($\pm$0.1) mm[11]). Images and ED patterns were recorded on Mitsubishi electron microscope films and the films were developed in the full strength of the Mitsubishi Gekkol developer at 20°C for 5 min. Morphological observation was carried out by the defocus contrast method[12]: micrographs were taken at a rather large amount of underfocus of the order of 10 μm. Lattice images were recorded at an electron optical magnification of 100,000, by using a Minimum Dose System[13] without objective apertures. The photographing condition for lattice imaging was practically the same as that in our

previous paper[7].

3. RESULTS AND DISCUSSION

3. 1 Morphological Observation

Figure 1 shows an unoriented thin film of PEEK which was crystallized between two glass slides without being sheared. Dark striations in the figure are crystalline regions with greater density than the surrounding amorphous medium[14]. The ED pattern from the encircled area is set in the figure, indicating that each striation corresponds to an "edge-on" crystalline lamella because the strong arc-shaped 002 reflection appears in the direction perpendicular to the long axis of the striation. Such a striation is curved but seemingly continuous. The average width of the striation measures about 10 nm, but is not regarded straightforwardly as the lamellar thickness because the image was taken at a rather large amount of defocus[14]. A set of striations form an immature spherulite with a sheaf-like appearance. The edge-on lamella, which is observed as a dark striation in the figure, seems to be untwisted along its long axis, as in the case of isotactic polystyrene[15,16]. Directional relationship between the image and the ED pattern in Fig. 1 reveals that the radial direction of the spherulite, namely the growth direction of the lamella is in the direction of crystallographic b-axis[17,24], because the arc-shaped 020 reflection appears in the growth direction of lamellae, and no 110 and 200 reflections

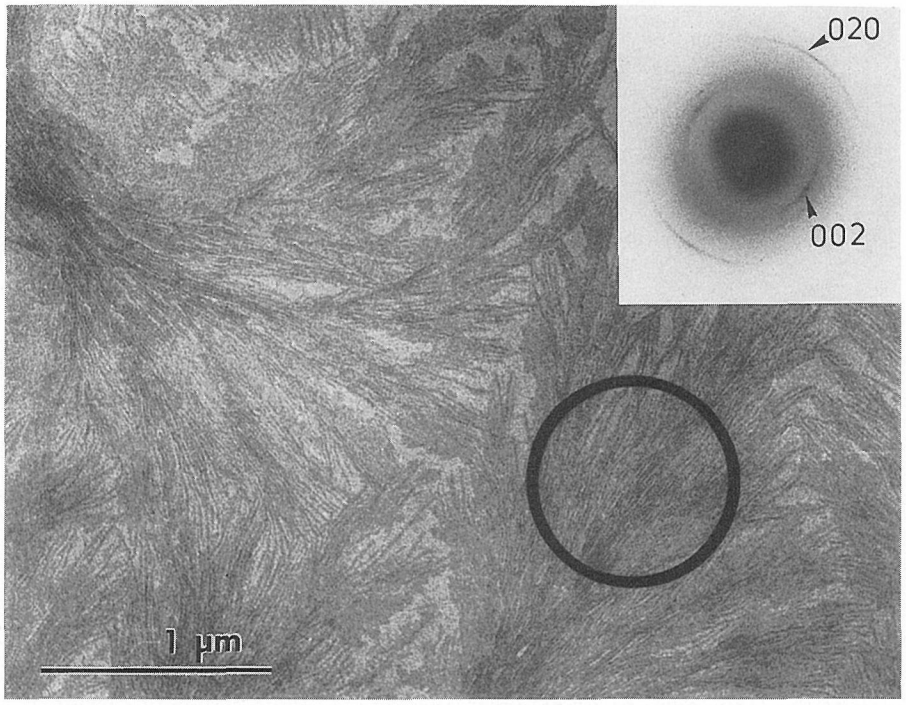

Fig. 1. Unoriented thin film of PEEK crystallized without being sheared. Each dark striation corresponds to an edge-on crystalline lamella. The inset is the ED pattern from the encircled area.

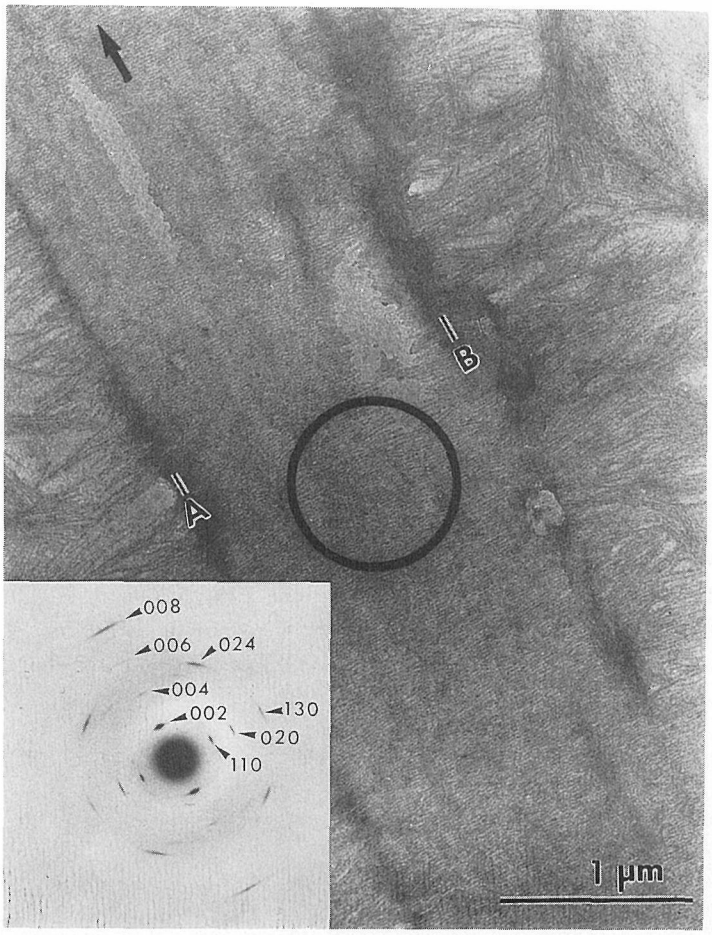

Fig. 2. Partly oriented thin film of PEEK made under a low shear-rate. The black arrow indicates the shearing direction. The inset is the ED pattern from the encircled area.

are observed in this direction. The 002 reflection in the ED pattern of Fig. 1 is broader than 020, which fact suggests a rather small crystallite size in the thickness direction of the lamellae.

Figure 2 is a partly oriented film of PEEK. The band-like region from the boundary indicated by the letter A to the other boundary B in the figure gives the well-oriented ED pattern which is shown in the inset of the figure. The pattern obtained from the encircled area clearly shows the molecular axis (c-axis) orients to the shearing direction indicated with the thick arrow. The band-like region has a stacked lamellar structure, as revealed by parallel dark striations running perpendicularly to the shearing direction. As mentioned already, the width of a striation does not correspond straightforwardly to the lamellar thickness because of the large amount of defocus. Nevertheless, the center-to-center distance between successive lamellae should be less affected by defocus[16,18]. The average value of center-to-center distance between two parallel striations running side by

side is the long period. The value directly corresponds to the average thickness of lamellae, namely the lamellar thickness if they are closely stacked and arranged so as to be similar to a single-crystal mat[16,18]. The lamellar thickness thus estimated is about 15 nm. In the outer parts of the band-like region, the specimen is not oriented except in the narrow zones being in contact with the region. In these narrow zones, lamellae were oriented keeping as good orientation of lamellae as within the region: like transcrystallization[19,25]. In the ED pattern, the 110, 111 and 130 reflections are recognized with fairly strong 00*l*, 020 and 024 reflections, but the 200 reflection is not observed. This demonstrates that c- and b-axes are basically in the plane of the figure, but there exists the angular distribution of the crystallites around the c-axis, probably because of the pleated nature of the film in the direction normal to the shearing direction. In the case of Fig. 2, the angular spread around the c-axis is estimated to be $\pm 37.2°$ at most because the 211 reflection is not identified.

In contrast to Fig. 2, a fiber pattern was obtained from a highly sheared specimen, as shown in Fig. 3 as a typical example. The ED pattern (the inset of the figure) shows a fairly good orientation of the molecular axis (c-axis) along the shearing direction. The *hk*0 reflections appear on the equator with intensities

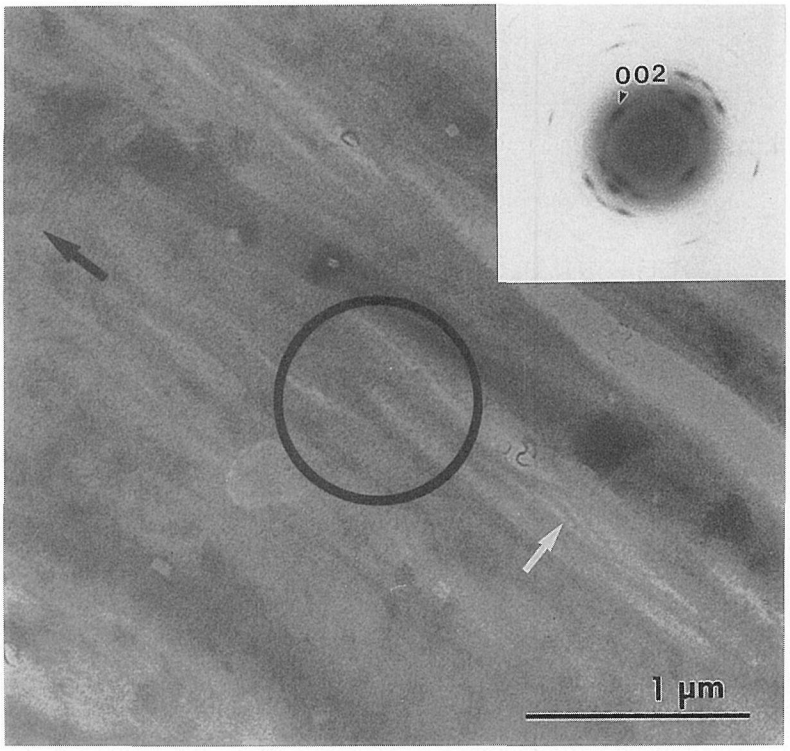

Fig. 3. Oriented thin film of PEEK made under an extremely high shear-rate. The black arrow indicates the shearing direction. The inset is the ED pattern from the encircled area. As for the white arrow, see the text.

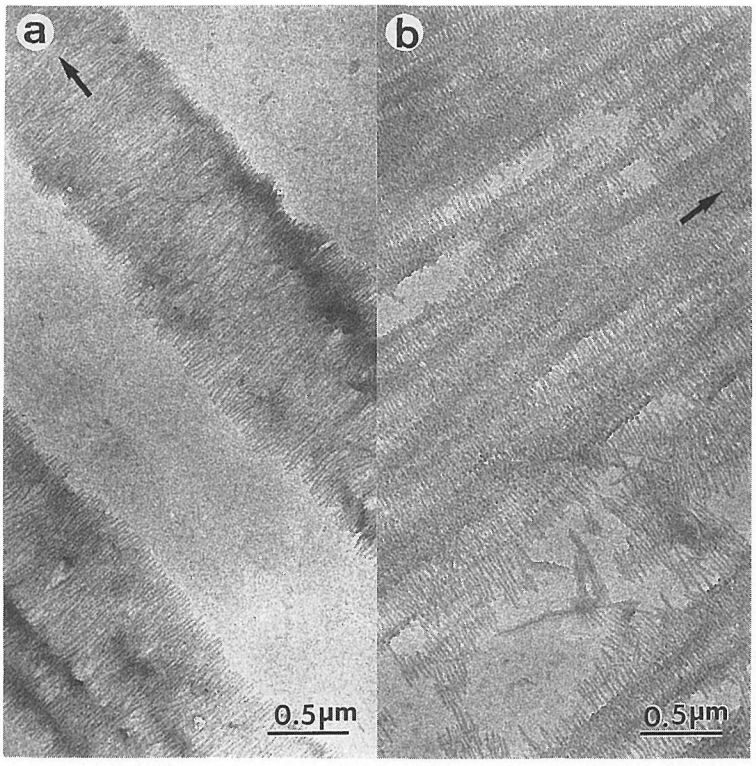

Fig. 4. Oriented thin film of PEEK made under a sufficiently high shear-rate. The black arrow in (a) and that in (b) show the shearing direction.

expected approximately from the structure factor of PEEK crystal[10]. In the encircled portion from which the ED pattern was obtained, there are several fibrils of 100~300 nm in width: each fibril appears to consist of fine microfibrils of 20~50 nm in width (see, for example, the region marked with the white arrow). Such fibrils seem to have a stacked lamellar structure[26]: the long period, namely the lamellar thickness was not measured because of weak contrast, but seems to be more or less greater than 15 nm.

Figure 4 shows intermediate textures between those in Figs. 2 and 3. The texture seen in Fig. 4(a) is very similar to that of the band-like region in Fig. 2, but with no surrounding PEEK medium; the texture in Fig. 4(b) is similar to that in Fig. 3, but with a well-developed shish-kebab structure. The lamellar thickness obtained by measuring the long period in Fig. 4(a) is about 15 nm and that in Fig. 4(b) is also about 15 nm. The texture in Fig. 4(b) might be made by a greater shearing rate than that in Fig. 4(a). The ED patterns corresponding to these intermediate textures, however, were similar to the pattern in Fig. 2: 110 and 200 reflections on the equator were weak or faint, in contrast to the pattern in Fig. 3.

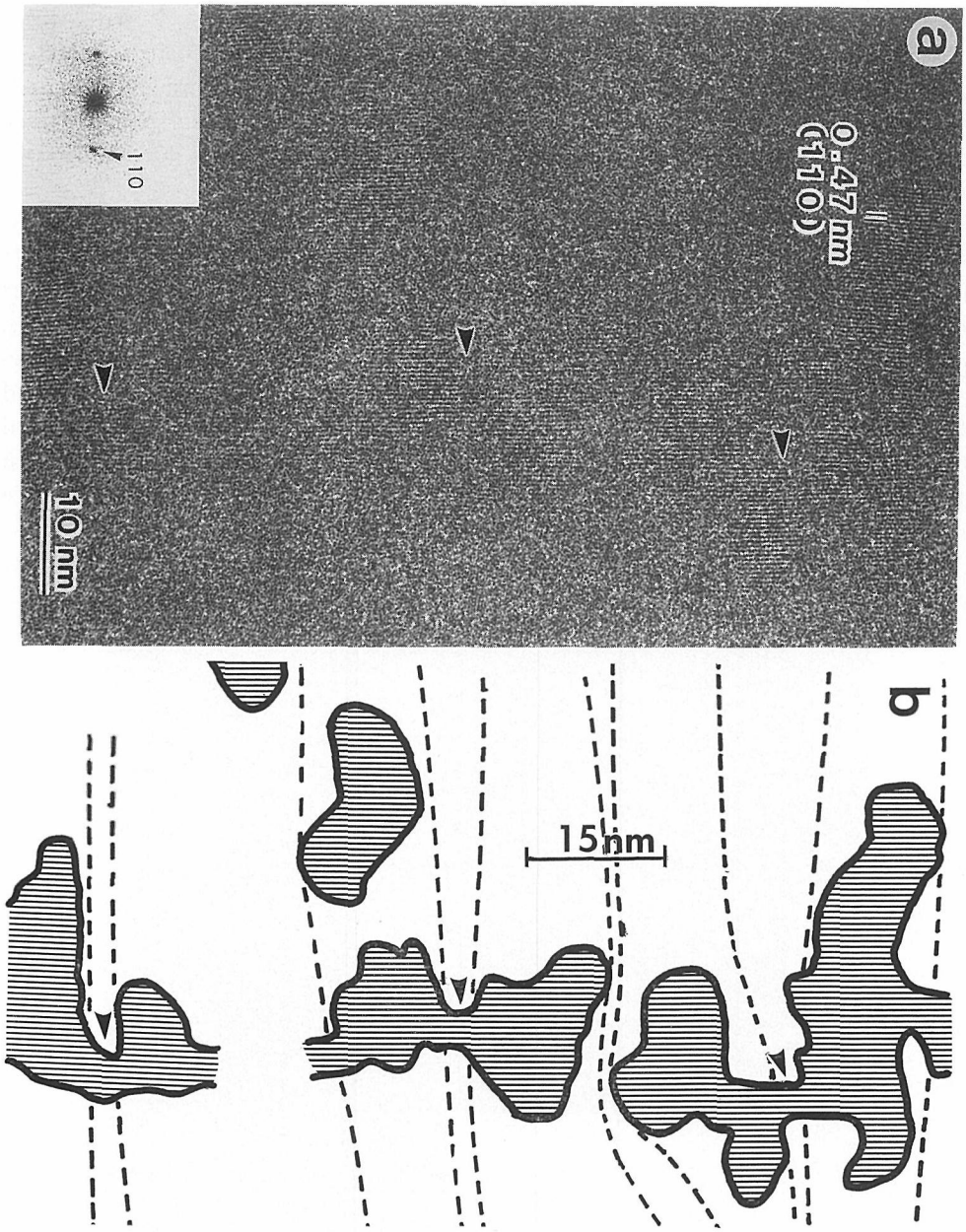

Fig. 5. a) High-resolution micrograph showing the (110) lattice image of an oriented thin crystalline film of PEEK. The shearing direction is vertical. The inset is the OD pattern of the micrograph.

b) Schematic representation of the relationship between stacked lamellae and the domains in which (110) lattice fringes are observed in (a). A region between dashed lines which contains some domains showing lattice fringes corresponds to a dark striation visualized at a large amount of defocus after high-resolution observation. Thick arrows in (a) and (b) indicate the "tie-crystallites" connecting lamellae.

3.2 High-Resolution Observation

As reported in our previous paper, PEEK is one of the less-sensitive polymers against electron irradiation[7]. High-resolution observation was carried out mainly for the oriented specimens as shown in Figs. 3 and 4 because they give a rather strong 110 reflection: this reflection is the innermost and the most durable against electron irradiation of all equatorial reflections[7].

Figure 5(a) shows an example of (110) lattice images (0.47 nm in spacing). As deduced from the slightly arc-shaped 110 reflection in optical diffraction (OD; the inset of Fig. 5(a)), the direction in which the lattice fringes are running varies from domain to domain, and some of the fringes are curved within a domain. Such curved fringes imply the existence of lattice distortion in a crystallite as observed in the case of solution-grown crystal of PEEK[7]. Figure 6 shows (110) and (200) lattice images (0.47 nm and 0.39 nm in spacing, respectively), which reveal the same features as those mentioned above for Fig. 5(a). In the OD pattern (the inset of Fig. 6), the 220 reflection is recognized, but the corresponding lattice fringes of 0.236 nm in spacing could not be observed in the micrograph.

As for (*hk*0) lattice images from a thin film in which the chain axis (c-axis)

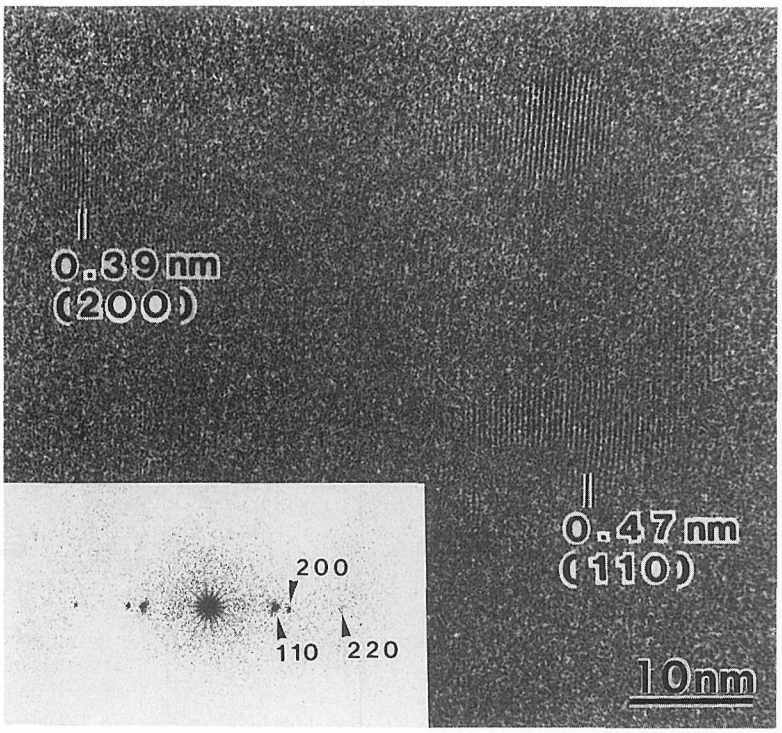

Fig. 6. High-resolution micrograph showing (110) and (200) lattice images of an oriented thin crystalline film of PEEK. The inset is the OD pattern of the micrograph. The shearing direction is vertical. The weak 220 reflection appears in the OD pattern, but corresponding fringes are not recognized in the micropraph.

is oriented in the plane of the film, the length of the lattice fringes in their running direction means the thickness of crystalline core in a lamella[16,18,20]. The number of fringes, that is the lateral width of the domain where the fringes are

Table 1. Thickness and lateral width of crystalline core in the edge-on lamella which were estimated from lattice images of oriented PEEK films.

type of lattice fringes	thickness of crystalline core (nm)	lateral width of crystalline core (nm)
(110)	6~7	~24
(200)	6~7	~10
(002)	~7	—

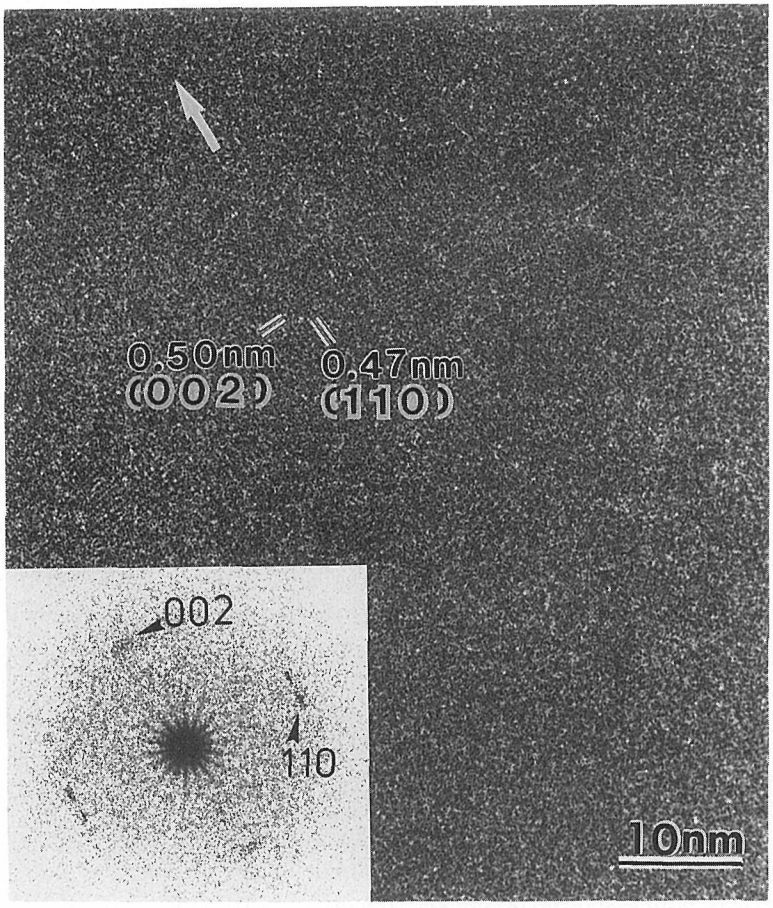

Fig. 7. High-resolution micrograph showing (002) and (110) lattice images of an oriented thin crystalline film of PEEK. The white arrow indicates the shearing direction. The inset is the OD pattern of the micrograph.

observed, corresponds to the crystallite size in the direction normal to the lattice plane in question: the lateral crystallite size. The thickness of crystalline core and the lateral crystallite size thus estimated from (110) and (200) lattice images such as Figs. 5(a) and 6 are summarized in Table 1. Figure 7 is an example of (002) lattice images, in which the lattice fringes (0.50 nm in spacing) are running perpendicularly to the shearing direction. Though the 002 reflection with fairly great intensity was observed in ED patterns set in Figs. 2 and 3, it was not easy to obtain corresponding lattice fringes. The fringe contrast of (002) lattice images obtained in this study was lower than that for (*hk*0) lattice images. The reason for this is to be sought in the "small crystallite size" (small thickness of crystalline core)[21] as well as the much smaller structure factor of 002 reflection than that of *hk*0[10]. The number of (002) fringes, i.e., the vertical width of the domain where the fringes are recognized, indicates the thickness of crystalline core. The thickness thus measured is also shown in Table 1. This table clearly demonstrates the following two facts. (1) PEEK crystallites are elongated along the b-axis, because the lateral crystallite size estimated from (110) lattice images is greater than that from (200) lattice images. (2) The thickness of crystalline core in a lamella is 6~7 nm and less than half of the long period regarded as the lamellar thickness: this agrees with the crystallinity reported so far for melt-crystallized PEEK (<50 %).

Careful inspection of Figs. 5(a) and 6, especially of Fig. 5(a), reveals the followings. In this figure, the domains in which (110) lattice fringes are observed have irregular shapes. If some major domains located at the same height from the bottom of the figure are to belong to a lamella running in the horizontal direction, the average spacing between adjoining domains in the shearing direction corresponds to the long period. The spacing was estimated at about 15 nm, as also schematically shown in Fig. 5(b): this value agrees well with the long period measured from the morphological observation in the previous section. Moreover, as indicated by the thick arrows in Figs. 5(a) and 5(b), adjoining major domains are connected with a small crystallite in the shearing direction: the (110) fringes are running coherently from a major domain to another via the small crystallite. Consequently, such a crystallite should be called a "tie-crystallite". Domains connected with tie-crystallites are in the same orientation to be a microfibril. Similar results were also obtained in high-resolution cryo-TEM of a drawn/annealed thin film of polyethylene[22] and a stretched thin film of poly(4-methyl-1-pentene)[23]: cryo-TEM is needed for high-resolution observation of both materials, because they are much weaker against electron irradiation than PEEK.

CONCLUDING REMARKS

We could obtain (110) and/or (200) lattice images of oriented thin crystalline films of PEEK which showed a stacked lamellar morphology with the long period of about 15 nm. The fringe direction is slightly varied from domain to domain. Some of the lattice fringes were curved within a domain: the lattice distortion accompanied with bending of stems in the crystallite. The (002) lattice fringes

were also observed with or without (*hk*0) fringes in some other micrographs. The lattice images directly revealed the crystallite size: the thickness of crystalline core in a lamella is less than half of the long period, and the crystallite is elongated along the b-axis as in the case of solution-grown crystals[7]. Moreover, we recognized in some of the images the existence of the tie-crystallite connecting crystalline lamellae which were stacked parallelly. In morphological observations, shish-kebab structures were identified in oriented thin films of PEEK. If the lattice images visualizing the existence of the tie-crystallite are taken at the specimen portion with a shish-kebab structure, the tie-crystallite seems to correspond to part of a shish.

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