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Three-dimensional shape of polyethylene single crystals grown from dilute solutions and from the melt[☆]

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Abstract

Three-dimensional morphology of polyethylene single crystals grown from dilute solutions and from the melt has been examined by atomic force microscopy. The observation of single crystals clarifies the morphology of chair-type as well as hollow pyramidal type for solution crystallization. From the melt, only chair-type was obtained. It has been confirmed that the screw dislocations in the chair-type follow a selection rule of the handedness in a manner to relieve the distortion in the chair-type. The meaning of the selection is discussed in connection with the twisting correlation in the banded spherulites grown from the melt of non-chiral polymers, such as polyethylene.

Keywords: Polyethylene; Single crystal; Dilute solution

1. Introduction

In order to relax the chain folding on the lamellar surface of polymer crystals, in some polymers, e.g. polyethylene and poly(vinylidene fluoride), the chain stems are tilted in the directions nearly perpendicular to the growth faces (Fig. 1(b)). For the chain tilting, chains can be tilted in each growth sector to the respective directions, and hence the single crystal takes a three-dimensional shape. When chain tilting is along the growth faces, due to the disagreement of the directions in different growth sectors, the average shape must be planar with undulation in the tilting direction caused by the buckling of the lamellar crystal [1].

Well-known three-dimensional morphology with the chain tilting nearly perpendicular to the growth faces is a tent-like shape known as hollow pyramidal type (Fig. 1(a) and (b)) [2–4]. Single crystals of a chair-type (Fig. 1(c) and (d)) with each half of the crystal concaving in opposite directions also exist at a rate of 1–1 with the tent type when grown from dilute solution of xylene [3].

The characterization of the three-dimensional shape is mainly based on the observation of the diffraction contrast of each growth sector by transmission electron microscopy (TEM) with the single crystals collapsed on a substrate [3,5–8], while the direct observation of the three-dimensional shape in the suspension by optical microscopy [3] suffers from low resolution of optical microscopy with polymer single crystals in the scale of μm. Therefore, the direct observation of the three-dimensional shape before the collapse with higher lateral resolution is much more preferable.

In a previous paper [9], we have examined the morphology by atomic force microscopy (AFM) and reported a successful observation of the three-dimensional shape of single crystals of polyethylene grown from dilute xylene solution by placing the single crystals on a soft substrate of aqueous solution of poly(vinyl alcohol) (PVA). Similar method has been applied by Geil [10] and Ishihara and Imura [11], and the three-dimensional shape of polyethylene has been observed by the shadowing contrast with TEM. Our aim was the detailed examination of the three-dimensional shape of chair-type single crystals with direct observation by AFM.

By the AFM observation, we have confirmed the two types of the three-dimensional shapes: the tent type and the chair-type. Chair-type is formed by the two halves

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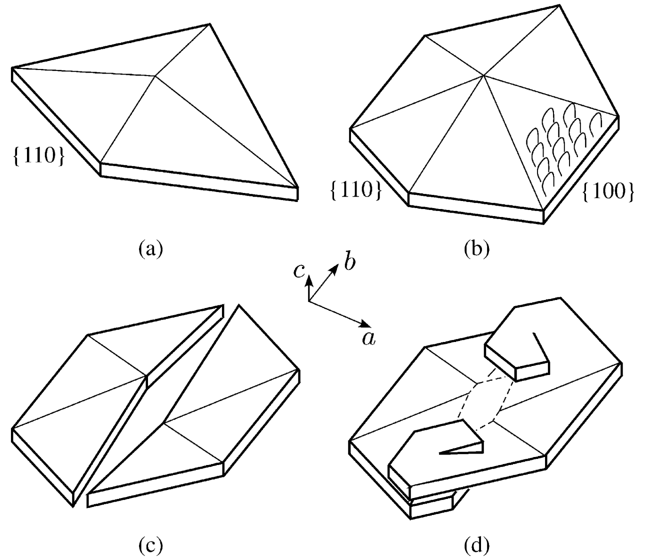
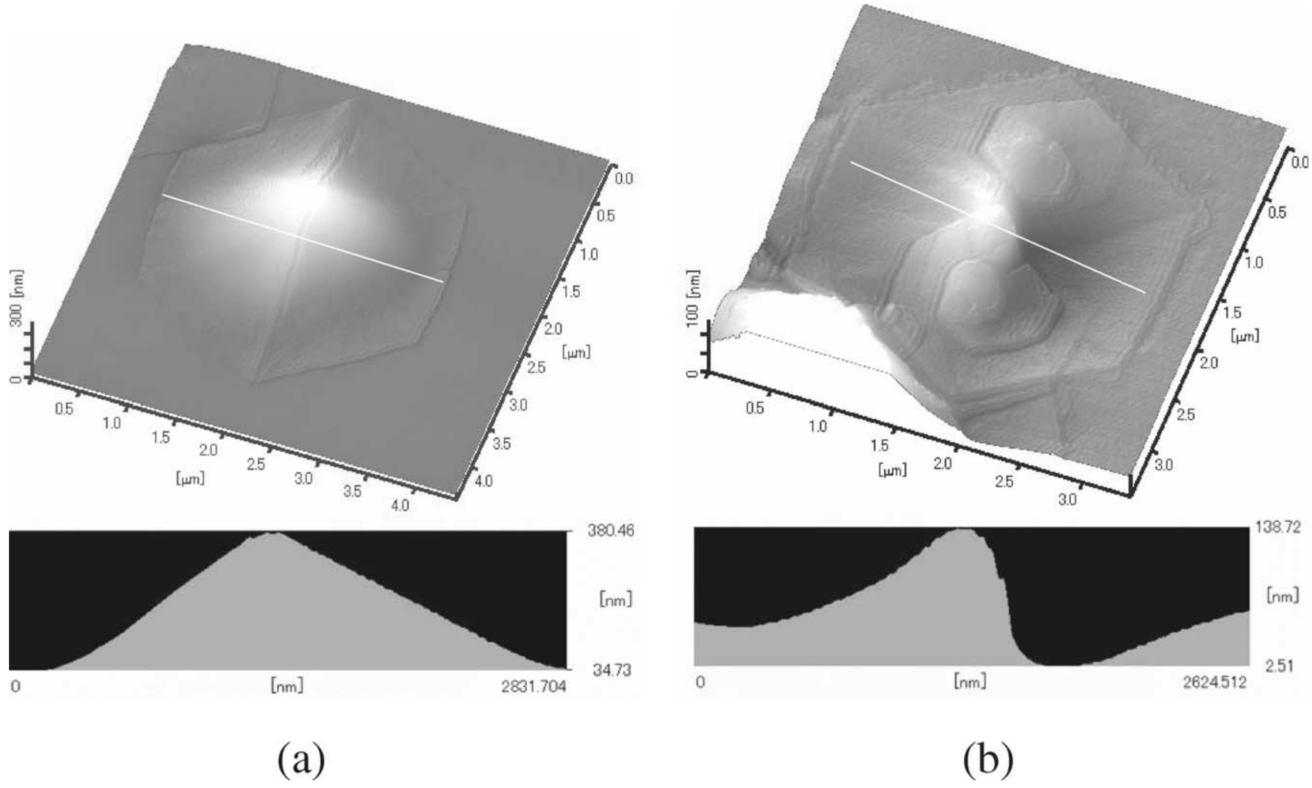


Fig. 1. Schematic representations of polyethylene single crystals: (a) lozenge-shaped tent type, (b) truncated-lozenge-shaped tent type, (c) two halves of truncated-lozenge-shaped chair-type, and (d) truncated-lozenge-shaped chair-type with spiral terraces from screw dislocations, the handedness of which is selected to relieve the distortion in the chair-type. The drawing assumes the {312} folding surfaces of the {110} growth sectors and the {201} surfaces of the {100} sectors [4].

concaving in opposite directions (Fig. 1(c)), and hence strain along the joints parallel to the *b*-axis is inherent in this morphology. The strain may be minimal by staggering in the central portion, but that cannot be the case in the outer region. In the chair-type crystals, we have confirmed spiral terraces formed by screw dislocations selecting the handedness in a manner consistent with the release of the strain in the chair-type shape (Fig. 1(d)).

The selection of handedness can be related with the handedness of the twisting correlation of crystallites in a banded spherulite with periodic ring pattern of extinction under polarizing microscope. Actually for polyethylene and PVDF, it is known that polymer molecules and their crystal structures are non-chiral, and hence the selection of the handedness of the twisting in their banded spherulites must be introduced by a higher order structure [12], such as the three-dimensional shape of single crystals. As we have pointed out in our recent papers [8,9,13], the consecutive formation of spiral terraces [14] in the chair-type can be one of the candidates to produce the twisting correlation in the banded spherulites of polyethylene and PVDF.

In the present paper, we report the extension of our previous study to the single crystals grown from dilute octane and hexadecane solutions and from the melt. Banded spherulites are mainly obtained from the melt, and hence the direct confirmation of the three-dimensional shape of the crystals grown from the melt is quite important. The crystals from octane and hexadecane solutions have been examined



(a) (b)

Fig. 2. Topographic images of polyethylene single crystals of 32 K fraction grown from dilute octane solution of 0.005 wt% at 94.0 °C: (a) convex tent type and (b) chair-type. The height profiles shown below are for the white lines in the images.

because the crystallization temperature is closer to melt crystallization than that of xylene and the lateral shape of those crystals are the type of truncated lozenge with the axial ratio elongated to the *b*-axis, which is similar to the shape of the crystals grown from the melt.

For the melt crystallization, the method to prepare single crystals with soft substrate does not work properly because the quenched portions surrounding single crystals had to be removed before the preparation. Therefore, chemical etching has been applied to observe the isothermally crystallized single crystals embedded in a matrix of amorphous and small crystallites regions formed on quenching after the isothermal crystallization; the single crystals become visible due to preferential etching of the quenched portions surrounding the single crystals. Similar observation with the shadowing contrast of the surface replica by TEM has been made by Patel and Bassett [15]. Our aim is to identify the chair-type shape and to make the direct observation of the three-dimensional shape as a height image by AFM.

2. Experimental

Polyethylene was NIST SRM 1483 of $M_w = 32{,}100$ and $M_w/M_n = 1.11$ (32 K fraction), and NIST SRM 1484 of $M_w = 119{,}600$ and $M_w/M_n = 1.19$ (120 K fraction).

From octane and hexadecane solutions, single crystals were obtained by isothermal crystallization at 94.0 and 99.0 °C, respectively. After the crystallization, the dispersion of single crystals was dropped on an aqueous solution of poly(vinyl alcohol) (PVA). Aqueous solution of PVA is from Diax Co., Ltd, and was 7 wt%. After drying PVA at room temperature, the single crystals distributed on the surface of PVA were observed with an atomic force microscope (SPI3800N, Seiko Instruments Inc.) in a dynamic force mode in air. Silicon cantilevers (SI-DF20, Seiko Instruments Inc.) with a resonance frequency of 110–150 kHz were used for the observations.

For the crystallization from the melt, polyethylene film of several μm thick was crystallized isothermally at 124.0–130.0 °C, and then quenched in a freezing acetone (~ −90 °C). The sample was subsequently subjected to permanganic etching [16] for the observation of single crystals by AFM.

3. Results and discussion

Figs. 2 and 3 show the topographic (height) image of

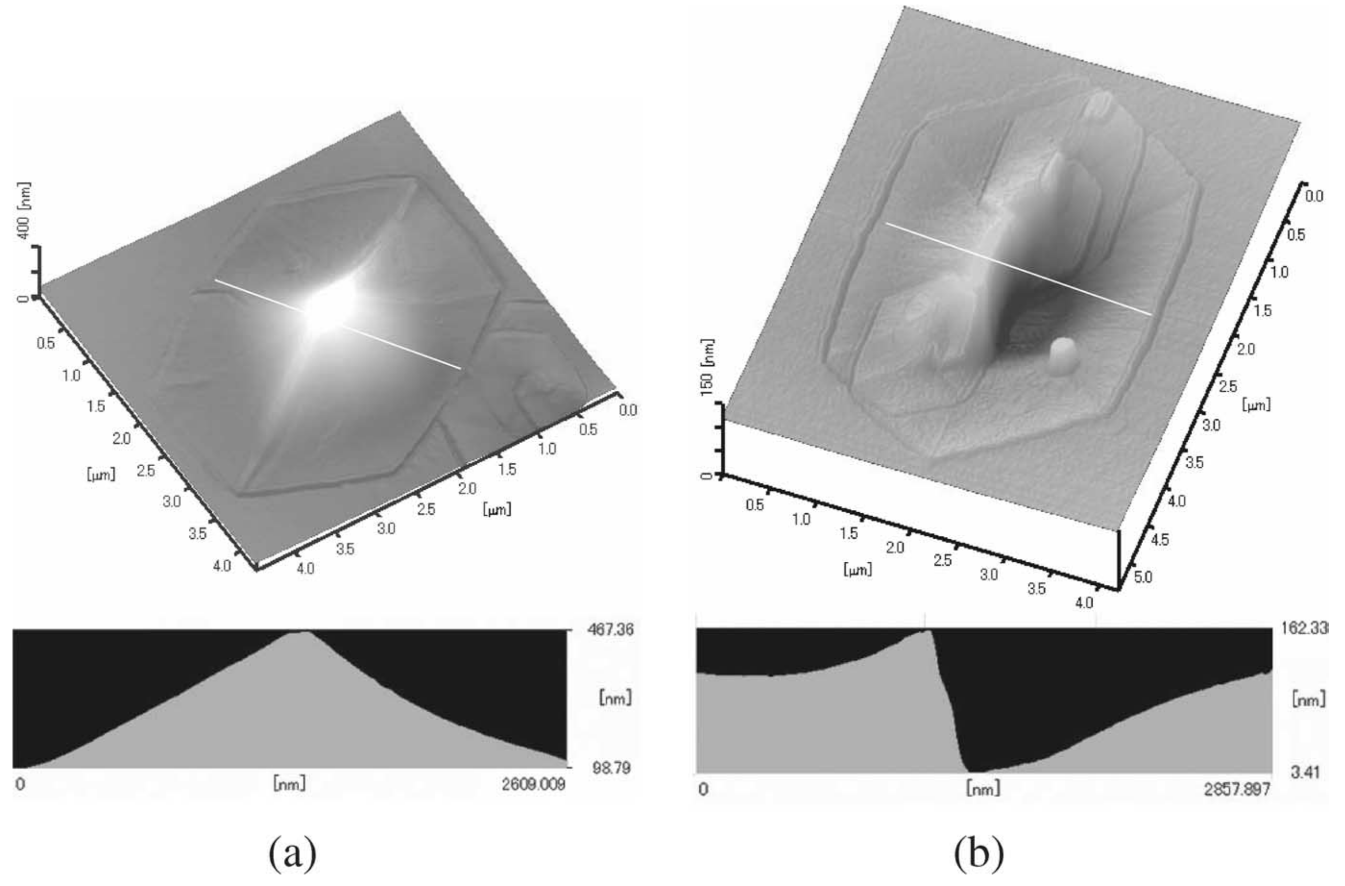


Fig. 3. Topographic images of polyethylene single crystals of 32 K fraction grown from dilute hexadecane solution of 0.05 wt% at 99.0 °C: (a) convex tent type and (b) chair-type.

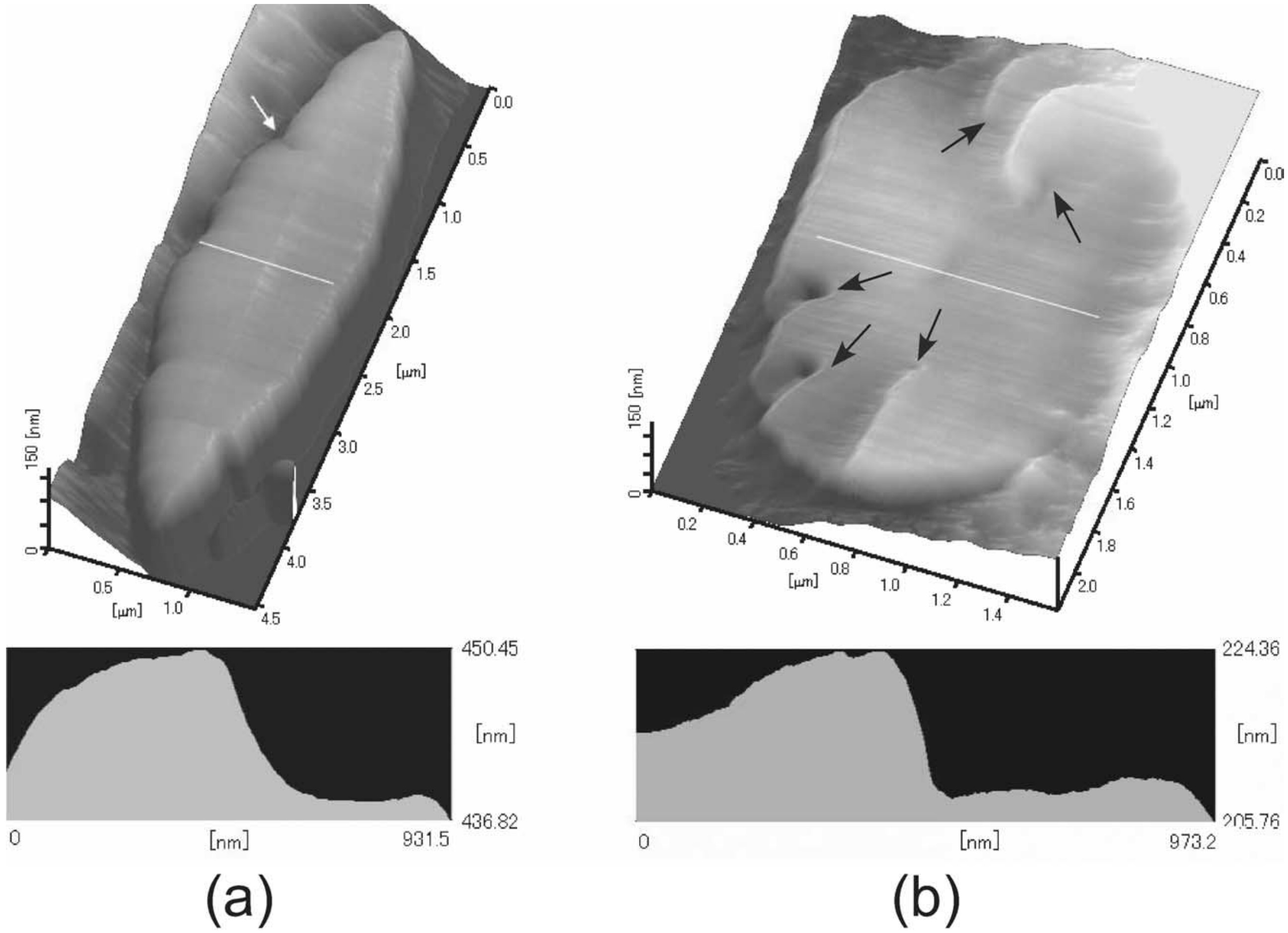


Fig. 4. Topographic images of polyethylene single crystals of 32 K fraction grown from the melt (a) at 130.0 °C for 10 min, (b) at 126.0 °C for 10 s, and (c) at 127.0 °C for 30 s.

single crystals grown from octane and hexadecane solutions; Figs. 2(a) and 3(a) show the convex tent type, and Figs. 2(b) and 3(b) the chair-type. It is noted that partial collapse near the edge of single crystals on PVA solution is seen in Figs. 2 and 3. The lamellar thickness of those single crystals was about 12–15 nm. The observed average tilting angle of each growth sector in the tent type was 16 and 18° for the {110} and {100} sectors from octane solution and 18 and 18° from hexadecane solution, respectively; the observed tilting angle in the {110} sectors is close to that of {314} (∼14.4°) which is calculated from the crystal structure, while the observed angle in the {100} sectors is close to that of {101} (∼19°). The angle in the chair-type is not available because of its three-dimensional shape with the same direction of chain tilting in the facing sectors. As an observation result of several tens separate single crystals, the ratio of the tent type and the chair-type was about 1–1 for the growth from octane solution and 3–7 from hexadecane solution.

Similar to the lozenge shaped single crystals grown from xylene solution, the shape of the chair-type of the truncated lozenge shown in Figs. 2(b) and 3(b) is greatly distorted in the central region from the two halves of convexo–concave form. The detailed molecular modeling of this distortion remains as future works. As seen in Figs. 2(b) and 3(b), we have confirmed the selection rule of the handedness of the spiral terraces, for which the distortion in the chair crystal is relaxed (Fig. 1(d)). Spiral terraces contrary to this rule have not been observed.

It is also noted that corrugations of folding surfaces have not been observed in those single crystals of several µm in size. The corrugations may be introduced in the later stage of growth with larger size and/or by the annealing at the crystallization temperatures.

Fig. 4 shows the topographic images of single crystals grown from the melt at different temperatures. As shown in the profiles of the cross-section, the crystals of 32 K fraction grown from the melt are all chair-type, as has been reported previously [8], though the height difference of the convexo–concave form in those crystals is smaller than those in the crystals grown from dilute solutions shown in Figs. 2 and 3. The small height difference may reflect the distortion to be kept in minimum. The surprising thing is that the lenticular crystals without appreciable {110} sectors also take the chair-type shape possibly due to the chain folding along the curved growth front in the {100} growth sectors, which

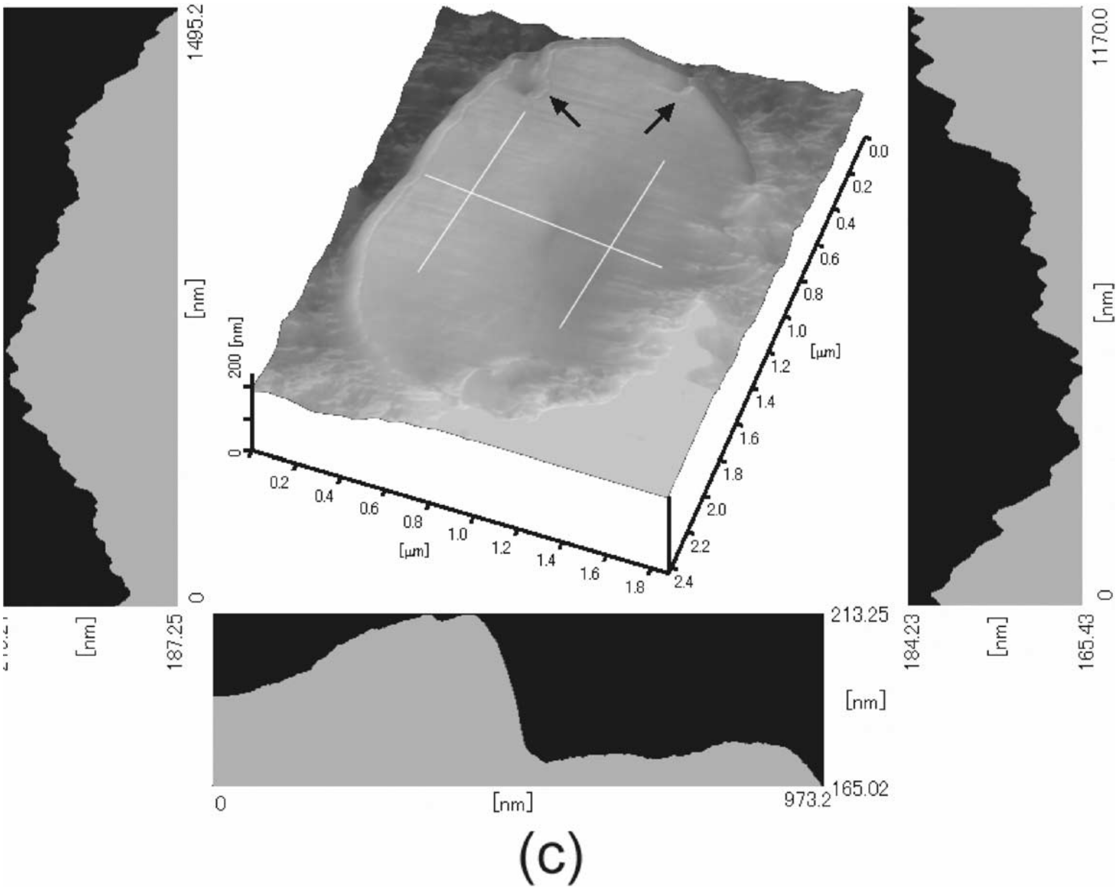


Fig. 4 (*continued*)

plays the role similar to the chain folding along the {110} growth faces in the truncated lozenge shaped single crystals. As is seen in those crystals, the spiral terraces (indicated by arrows in those figures) follow the selection rule of the handedness with the expected manner in which the distortion in the chair crystal is relaxed.

For the growth of only chair-type from the melt, the mechanism should not be due to the stability based on their free energies because the chair-type must be unstable in comparison with the tent type due to excess strain energy in the chair-type. Therefore, the disparity must be caused by kinetic reason. We speculate that the process of dividing of chain-folding direction may be the main cause of the disparity. Our observation of single crystals in the later stage of growth clearly indicates anisotropic morphology and hence the divided chain-folding direction in the later stage of growth. The sectorization and the distinct direction of chain tilting in each growth sector will be the consequence of high regularity of the direction of chain folding along the well defined growth faces, and hence developed in the later stage of growth. On the other hand, in the early stage of growth, e.g. just after seeding process, we speculate that the sectorization may not be strong enough to cause the difference in the direction of the chain tilting. If it is the case, all chains must be vertical or tilted to a uniform direction over the crystal in the early stage of growth (Fig. 5). Then, the evolution of the chair-type of the three-dimensional shape in the subsequent growth will be a natural consequence of the latter case of the chain tilting with uniform direction (Fig. 5(a)); in this case, the formation of tent type needs turn down of one of the halves. The molecular modeling of the crossover change from uniform tilting to the dividing of the direction will be the subject of

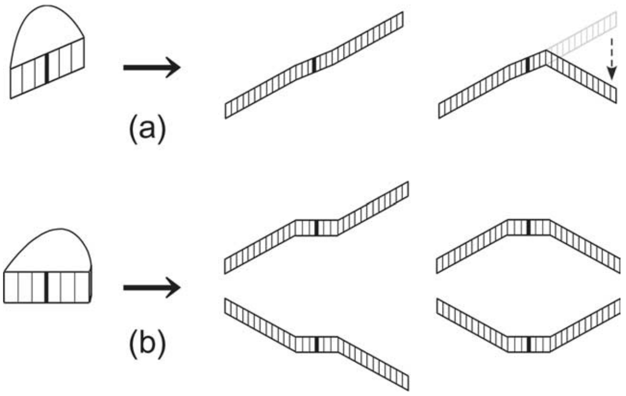


Fig. 5. Schematic representation of possible evolution of three-dimensional shapes from the two types of seeds in the early stage of growth without well-developed sectorization: (a) uniform chain tilting and (b) chains normal to the fold surface.

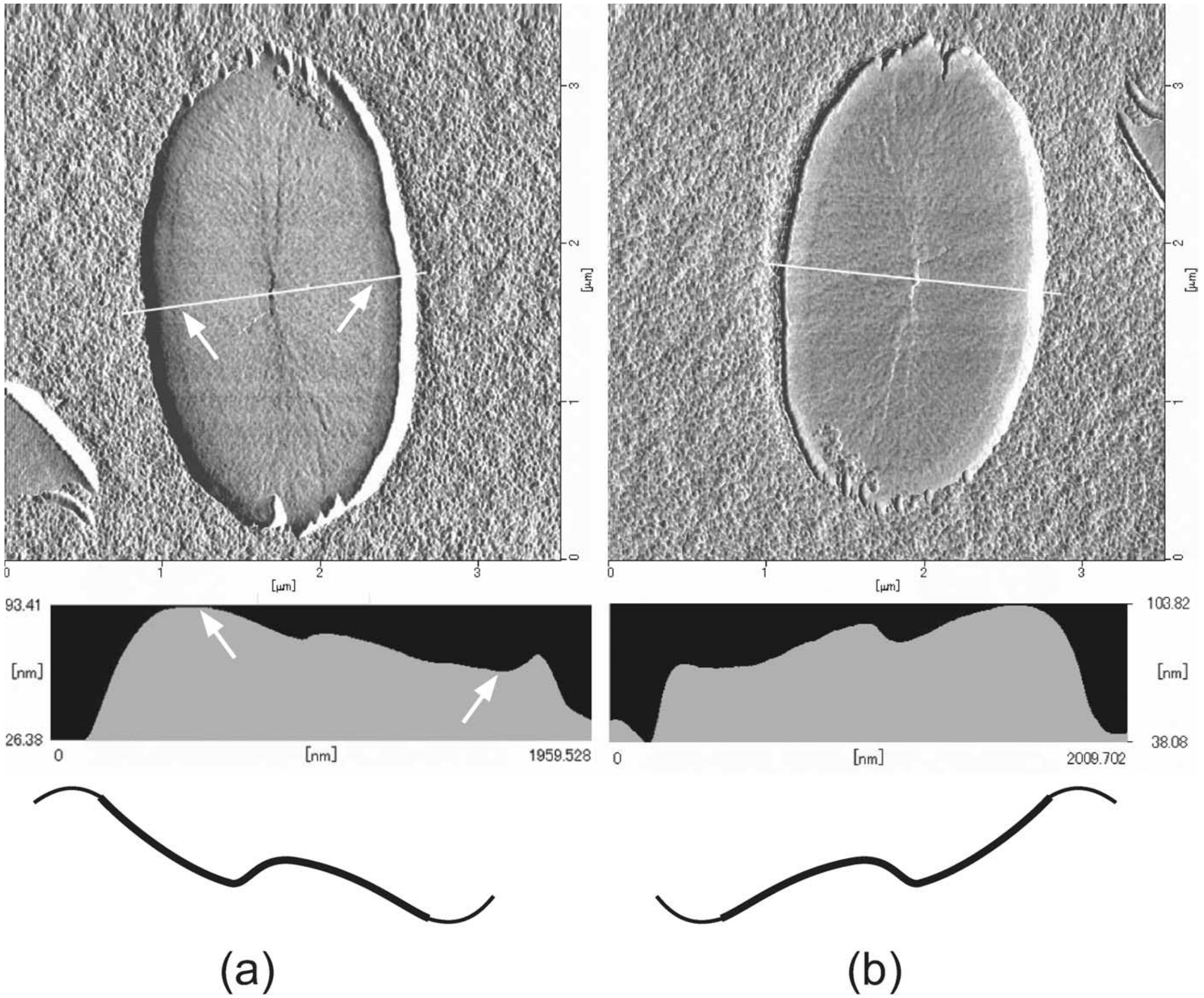


Fig. 6. Phase image and the height profile of a single crystal of 32 K fraction grown from the melt at 128 °C for 10 min, quenched to 120 °C, and immediately quenched in freezing acetone (∼ −90 °C). The scanning direction is horizontal and 180° rotated in (b) in comparison with (a). The schematic drawing shown at the bottom indicates the cross-section of chair-type (thick line) of the inner part and that of the S-shape (thin line) of the outer parts.

our future work. The seed may be made by condensation of single (or a few) molecules with almost random directions of chain folding even though they can be adjacent folding.

For the systematic change in the ratio of the chair-type and the tent type of 1:1 from xylene and octane solutions, 7:3 from hexadecane solutions, and 1:0 from the melt, we can think of the effect of crystallization temperature on the degree of chain titling. With decreasing crystallization temperatures, we expect less active molecular motions in the amorphous folding portions made of irregular folds, loose loops, cilia, etc. As the consequence, we expect a smaller volume of those portions and smaller tilting angle at lower crystallization temperatures [8]. Then, if the chains in the early stage of growth at lower temperatures are all vertical, the 1:1 ratio of the three-dimensional shape will develop subsequently (Fig. 5(b)). Solution growth at lower crystallization temperatures may be this case.

With higher molecular weight fractions or at lower crystallization temperature with smaller molecular weight, it is known that the cross-section of single crystals during melt crystallization take the shape of S [16,17]. For the formation mechanism of the S-shaped cross-section, Keith and Padden [18] proposed a mechanism based on the unbalance of the congestion of the upper and lower folding surfaces of the chain-tilted lamellar crystals. Since, the mechanism is dependent on the balance between the rate of crystallization and the diffusion of polymer molecules, the mechanism will be more effective with faster growth rate at lower temperatures and with slower diffusion of higher molecular weight.

The S-shaped cross-section and the cross-section expected from the chair-type is not consistent with each other in terms of

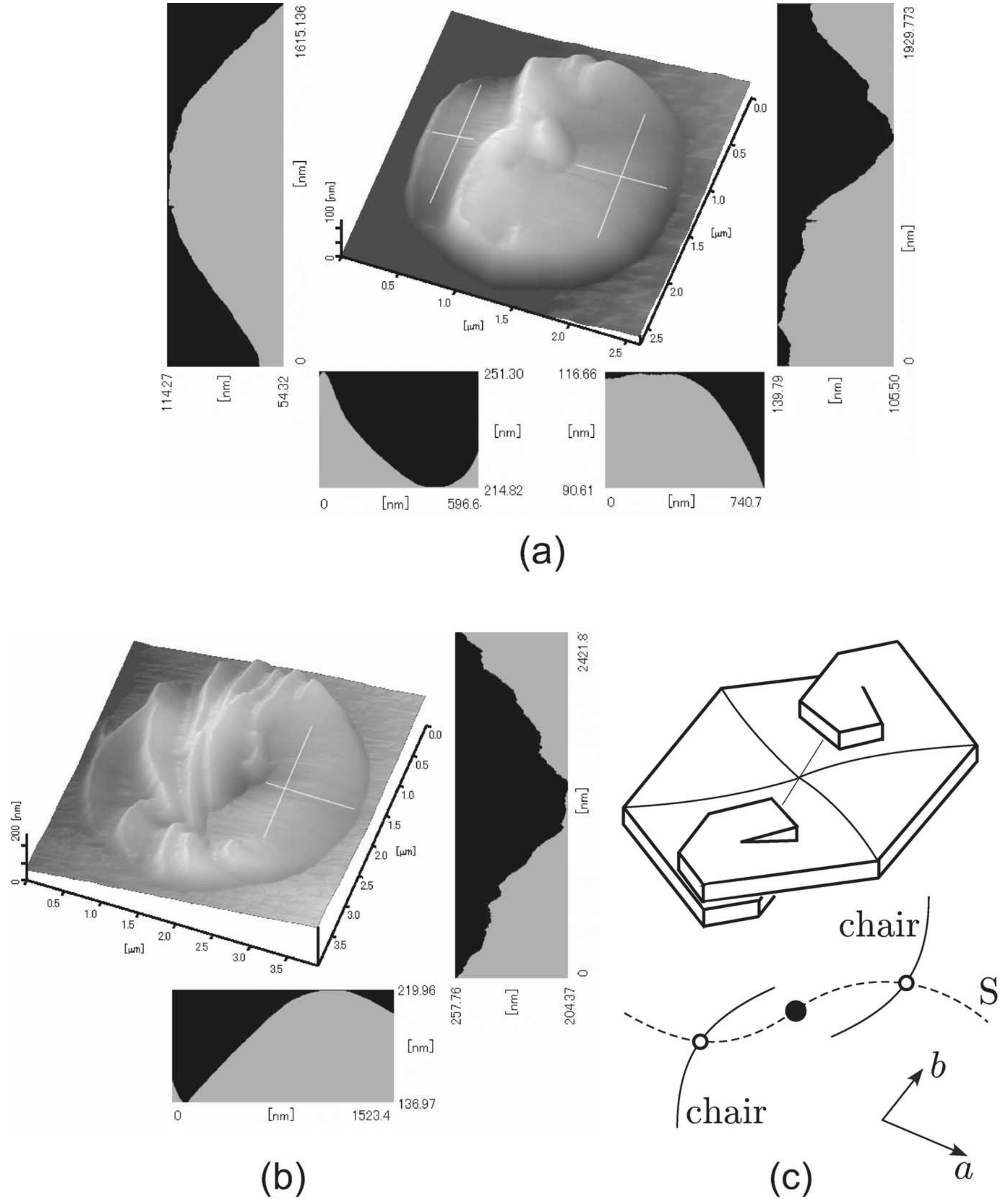


Fig. 7. Topographic images of polyethylene single crystals of (a) 32 K fraction grown from the melt at 124.0 °C for 5 s and (b) 120 K fraction at 125.0 °C for 110 s. Schematic illustrations of those crystals and the curvature with the S-shaped cross-section along the *a*-axis (broken line) and the chair-type chain tilting in the {110} sectors (solid lines) are shown in (c).

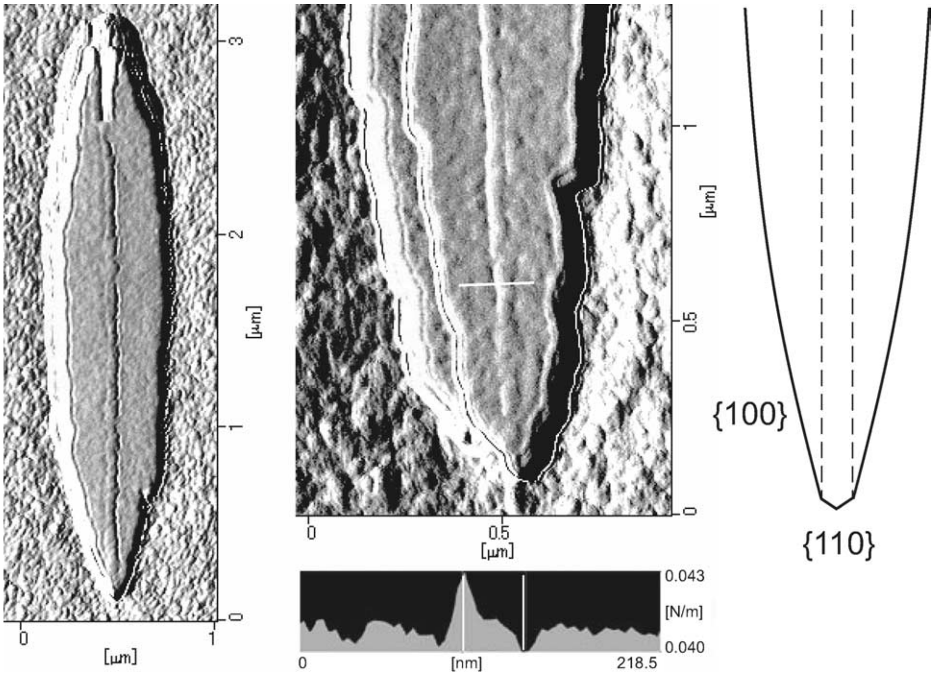


Fig. 8. Amplitude images of lenticular single crystals of 32 K fraction grown from the melt at 128 °C for 10 min.

the direction of chain tilting in those shapes [8]. Fig. 6 shows the crystal of 32 K fraction grown at 128.0 °C and then quenched to a lower temperature (120.0 °C), and finally quenched in freezing acetone (∼ −90 °C); the inner portion is chair-type and the outer edge is expected to have the S-shaped cross-section. Actually, the height profile along the short axis of the crystals shows the expected change from the chair-type to the S-profile; the two images shown in Fig. 6 were obtained with scanning in opposite directions to confirm that the profile near the edge is not the artifact caused by the AFM tip. The change in the contrast of the phase images in Fig. 6 also confirms the abrupt change in the slope of the profile near the edge; if the change is caused by the elastic property of the surface, the contrast must be the same independent of the scanning direction [19].

Fig. 7 shows the crystals of 32 K fraction at lower crystallization temperature (124.0 °C) and of higher molecular weight fraction of 120 K at 125.0 °C, which are expected to exhibit the S-shaped cross-section. In those crystals, the cross-section along the short axis (*a*-axis of the crystal) actually takes the S-shape with concave in the left and convex in the right half, while in the direction of the long axis (*b*-axis) the shape is convex in the left half and concave in the right half with spiral terraces mainly formed in the {110} sectors; the cross-section along the *b*-axis and the handedness of the spiral terraces are not expected from the Keith and Padden's model, but they are consistent with the chair-type morphology. This evidence suggests that the actual three-dimensional shape under these conditions is like a pair of saddles made by the S-shaped cross-section along the *a*-axis and the chair-type shape along the *b*-axis. The S-shaped cross-section will be caused by the mechanism proposed by Keith and Padden, while the chair-type three-dimensional shape along the *b*-axis is inevitable because, even with the S-shaped cross-section in the {100} sector, the direction of chain folding in the {110} and {100} sectors must be different, and the consequent chain tilting must be of the chair-type.

Finally, it is noted that, by chemical etching, the amorphous portions on the folding surface is removed, and hence the anisotropy of the chain packing in the crystals is directly observable with this technique. As seen in Fig. 8, the image of lenticular crystals clearly shows a thin band running through the middle along the *b*-axis. The band region is thicker than the surrounding regions and indicates the existence of the {110} growth sectors [20], which keep their width (∼40 nm) in the lenticular crystals. Because of the narrow width, questions were raised in terms of the existence of this sector in the discussion of the regimes I–II transition [21], which is followed by the crossover of the lateral shape from the lenticular type to the truncated lozenge with curved edges in polyethylene [22]. The present evidence clearly confirms the existence of this sector keeping its width, and proves the required condition for the occurrence of the regimes I–II transition along with the morphological change of the lateral habits [22].

4. Conclusion

We have confirmed the three-dimensional morphology of polyethylene single crystals grown from dilute octane and hexadecane solutions and from the melt. From dilute solutions, the tent-type and the chair-type shapes were confirmed by the direct observation by AFM with the crystals deposited on a soft substrate. From the melt, we have applied chemical etching and confirmed that all examined crystals are chair-type. The difference of the ratio of tent type and chair-type has been ascribed to the difference in crystallization temperatures.

Screw dislocations and the consequent spiral terraces were preferentially produced in the chair-type with the selection of the handedness in accordance with the relief of the distortion. The selection of the handedness in the chair-type, which is the only type developed from the melt, can be one of the candidates of the selection mechanism of the handedness for the twisting correlation of the crystallites in the banded spherulites of non-chiral polymers, such as polyethylene and PVDF.

With higher molecular weight fraction or at lower crystallization temperature with lower molecular weight fraction of polyethylene, S-shaped cross-section lamellae appear, as has been reported by Bassett and Hodge. It is confirmed that the cross-section is S-shaped along the a-axis in the $\{100\}$ growth sectors, while the $\{110\}$ sectors still keep the three-dimensional shape of the chair-type because of the different folding directions in the respective growth sectors.

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