AN ATOMIC FORCE MICROSCOPY OBSERVATION OF POLY(VINYLIDENE FLUORIDE) BANDED SPHERULITES

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Abstract

We have examined the free surface of a banded spherulite of poly(vinylidene fluoride) (PVDF) by an atomic force microscopy. The directions of the slope of multilayer terraces of lamellar crystals are retained in each half of a banded spherulite; this evidence confirms the macroscopic selection of one handedness in the formation of spiral terraces in each growth direction of the sheaf at the center of a banded spherulite of PVDF. In a previous paper it was confirmed that the three-dimensional morphology of all single crystals of PVDF grown from the melt is chair-type, and hence it is most probable that the stress in the chair crystal is responsible for the formation of spiral dislocations and terraces keeping the same handedness in each growth direction. The chair-type morphology is created because of the chain tilting to the fold surface, which can introduce symmetry breaking and consequently the selection of handedness in non-chiral polymers such as PVDF.

Keywords: AFM, spherulite, banding, PVDF, chair type, spiral terrace

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1 Introduction

Spherulites are composed of small crystallites growing in the radial direction with the formation of branches filling three-dimensional space. With some polymers, a concentric pattern of periodic banding appears in spherulitic crystallization [1]. The formation of banding is not limited only in polymer spherulites. A number of organic compounds exhibit similar types of concentric rings in spherulites [2], and hence this topic has a wider implication in the self-organization process of crystals, in general.

In the banded spherulites of polymers, a twisting relationship of lamellar crystallites in the radial direction has been confirmed experimentally by WAXS [3] and is considered to be responsible for the creation of the periodic extinction banding observed by polarizing optical microscopy.

For lamellar crystallites, twisting must choose one of the two handedness, and the mechanism of the choice has been a challenging topic. With non-racemic chiral polymers, strong evidences suggest that the choice is made by the handedness of the chirality in the polymer molecules [4–8]. For non-chiral polymers, the tilting of polymer chains to the fold surface can be the origin of the choice of the handedness.

Two models of twisting relationship have been proposed, based on the chain tilting. One is proposed by Keith and Padden [9,10] under the hypothesis that the degree of congestion of upper and lower fold surfaces of a lamellar crystal in the melt is different because of the crystallization of polymer chains on the growth face which is tilted to the fold surface. Another possible mode of twisting relationship can be caused by the stress in a chair-type crystal

(Fig. 1a) [11]. Both of the models predict the twisting of a single lamella and/or the consecutive creation of spiral terraces of the same sense in each growth direction (Fig. 1b for chair-type crystal). The accumulation of the spiral terraces keeping the same handedness eventually causes the twisting relationship of crystallites in the growth direction [12], as shown in Fig. 1c.

In a previous paper we examined the morphology of poly(vinylidene fluoride) (PVDF) which is a non-chiral polymer forming banded spherulites [13]. Single crystals were grown from the melt and from the blend with an amorphous polymer, poly(ethyl acrylate) (PEA). The crystals of relatively higher molecular weight ($M_w = 2.5 \times 10^5$) were grown isothermally in the temperature range where banded spherulites are formed with sufficient crystallization time. The crystals were extracted by dissolving the amorphous PEA and PVDF crystals formed on quenching. The three-dimensional morphology of the single crystals was examined by a transmission electron microscopy (bright field, dark field and diffraction) with a tilting stage. For all cases, the titling of chains (25-27 degrees) to the fold surface was confirmed, and the three-dimensional shape of all crystals was chair type for the 30/70 blend and pure PVDF. In chair crystals, it was also confirmed that the spiral terraces keep the same handedness in each growth direction. From those evidences, it was proposed that the chair-type crystals with consecutive creation of spiral terraces of the same handedness are responsible for the twisting relationship of crystallites in the radial direction of banded spherulites of PVDF.

If this is the case, we expect the multilayer terraces of the same handedness in a macroscopic scale of a whole spherulite with the handedness being kept in the respective halves of the banded spherulite. In the present paper, we examine the ordering of the handedness by means of surface observation of banded spherulites with an atomic force microscopy (AFM). From the observation, we confirm that the multilayer terraces are going down in one direction in each half of a banded spherulite, and this evidence shows that the spiral terraces choose one of the two possible handedness in each half of the banded spherulites of PVDF.

2 Experimental

We used PVDF of grade KF1000 ($M_w = 2.5 \times 10^5$ and $M_w/M_n = 2.1$, Kureha Chemical Industries, Co., Ltd.) and PEA of $M_n = 2.9 \times 10^4$ and $M_w/M_n = 2.4$ from Scientific Polymer Products. Two weight ratios were examined: PVDF/PEA = 30/70 and 100/0. The details of the sample preparation was described in the previous paper [13].

The free surface of the sample on a cover-slip was examined by an atomic microscope (Digital Instruments Nanoscope III, Dimension 3100 SPM system). Integrated silicon tips and cantilevers with a nominal spring constant of 30 N m^{-1} were used. The instrument was operated in tapping mode in air. The tapping mode data was recorded in constant force mode. Scanning was performed at a frequency of 1 Hz. The cantilever was oscillated at its resonant frequency of about 250 kHz. In order to examine a wide area of a spherulite, the images of small area (*eg.* 2 μm×2 μm) were taken successively with a parallel displacement of the tip (shorter than the length of the area) for each image. All images were recorded at room temperature. All images represented in the following are of "amplitude" image which is sensitive to the change in sample height; the contrast is similar to that of shadowed image in transmission electron microscopy and suitable for examining the morphology.

3 Results and Discussion

Figure 2 shows an AFM image of the growth tip of a PVDF multilayer crystal grown from the 30/70 blend. Figs. 2a and b, which is an enlargement of Fig 2a, show the arrangement of the terrace of lamellae coming downward in the figure. This arrangement of the terrace clearly indicates that the multilayering was not created by a single spiral terrace but made by a row of spiral terraces keeping the same handedness, as schematically shown in Fig. 2c.

Figure 3 shows the surface profile of a banded spherulite in one period of extinction corresponding to half a period of the rotation of the crystal axis around the radial direction. If the arrangement merely represents the crosssection of stacked lamellae which are rotating around the growth direction, then the arrangement must be the alternation of upward and downward terraces. In fact, this is not the case, since the upward terrace has not been observed. Therefore, it should be considered that the downward terrace which is visible in the figure is what was made by a row of spiral terraces keeping the same handedness like in the growth tip of the PVDF multilayer crystal shown in Fig 2.

Figure 4 is the whole view of a banded spherulite and enlargements of two portions. It is confirmed that the arrangement of the multilayer terraces in both the right and left halves come down from the top to the bottom in clockwise and counterclockwise manners around the center, respectively.

Those observations confirm the arrangement of spiral terraces in PVDF banded spherulites, which we expect for the banded spherulite with rows of spiral terraces keeping the handedness in the respective growth directions.

Figure 5 represents the possible orientations of the banded spherulite formed by this rule and its relation with the handedness of spiral terraces and/or lamellar twisting which will appear on the top surface of the film. As shown in Fig. 5c, only when the seed crystal of the banded spherulite stands up, one of the handedness is chosen on the top surface. There were few cases of standing in this way in fact. However, in almost all cases of the present observation, the arrangement of the terraces corresponds to the case of Figs. 5a and b.

In PVDF, we have confirmed that chair-type crystals grow into banded spherulites in the previous paper [13]. A chair crystal suffers from the consecutive formation of spiral terraces with the handedness chosen to relax the stress in the chair, as shown in Fig. 1b. Therefore, it is reasonable to expect that the consecutive creation of spiral terraces keeping handedness is responsible for the twisting relationship along the growth direction of the banded spherulite of PVDF, as shown in Fig. 1c.

In terms of the possibility of lamellar twisting, the twisting direction of a single lamellar crystal could not be clearly identified because of the multilayering of lamellae by the formation of spiral terraces. On the other hand, there are independent observations of twisting lamellae of polyethylene in literature, as seen in ref. [1]. For this reason, although we have confirmed the row of spiral terraces keeping the handedness, which will be responsible for the twisting relationship in the banded spherulites of PVDF, we cannot come to the conclusion that the origin of the twisting in PVDF is solely due to the formation of this type of spiral terraces in chair crystals. The determination of the mechanism of twisting relationship will therefore need a closer look at the three dimensional shape of a single lamella in the banded spherulites.

Acknowledgements

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Figure Captions

Fig. 1. Schematic representation of (a) halves of a chair crystal of PVDF in a relaxed state, (b) spiral dislocations keeping the handedness in each growth direction, the formation of which can relax the stress in the chair crystal, and (c) the twisting relationship in the radial direction by the consecutive generation of screw dislocations keeping the handedness [12].

Fig. 2. AFM image of the growth tip of a PVDF multilayer crystal grown from 30/70 blend at 165°C for 2.5 h. In (b), a portion of (a) is enlarged. Bar line represents 1 μm.

Fig. 3. AFM image of the free surface of a banded spherulite grown from the melt at 165°C for 2.5 h, showing one period of extinction. Bar line represents 1 μm.

Fig. 4. AFM image of (a) the whole view of a banded spherulite grown from the melt at 165°C for 1.5 h and (b) and (d) the enlargement of portions. In (a), the cross represents the center of the spherulite and the thick line represents the border between the two regions keeping the directions of the slope of the terraces. Bar line represents 1 μm.

Fig. 5. The relationship between the orientation of the banded spherulite of PVDF in a film and the handedness of spiral terraces and/or lamellar twisting which appear on the top surface of the film.

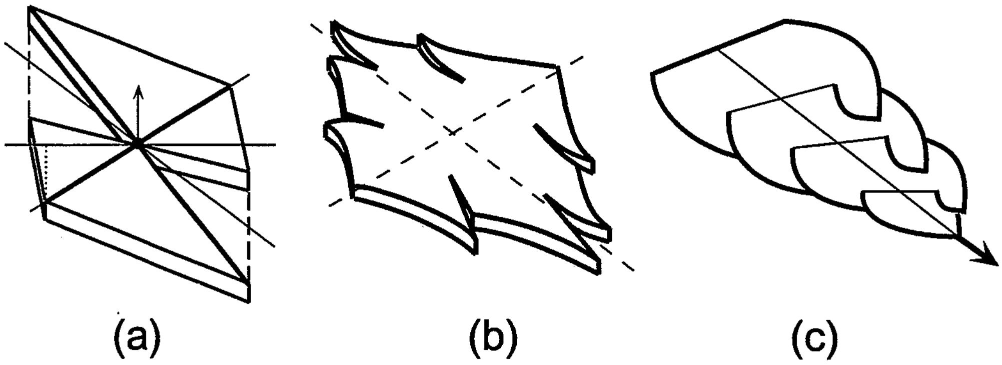

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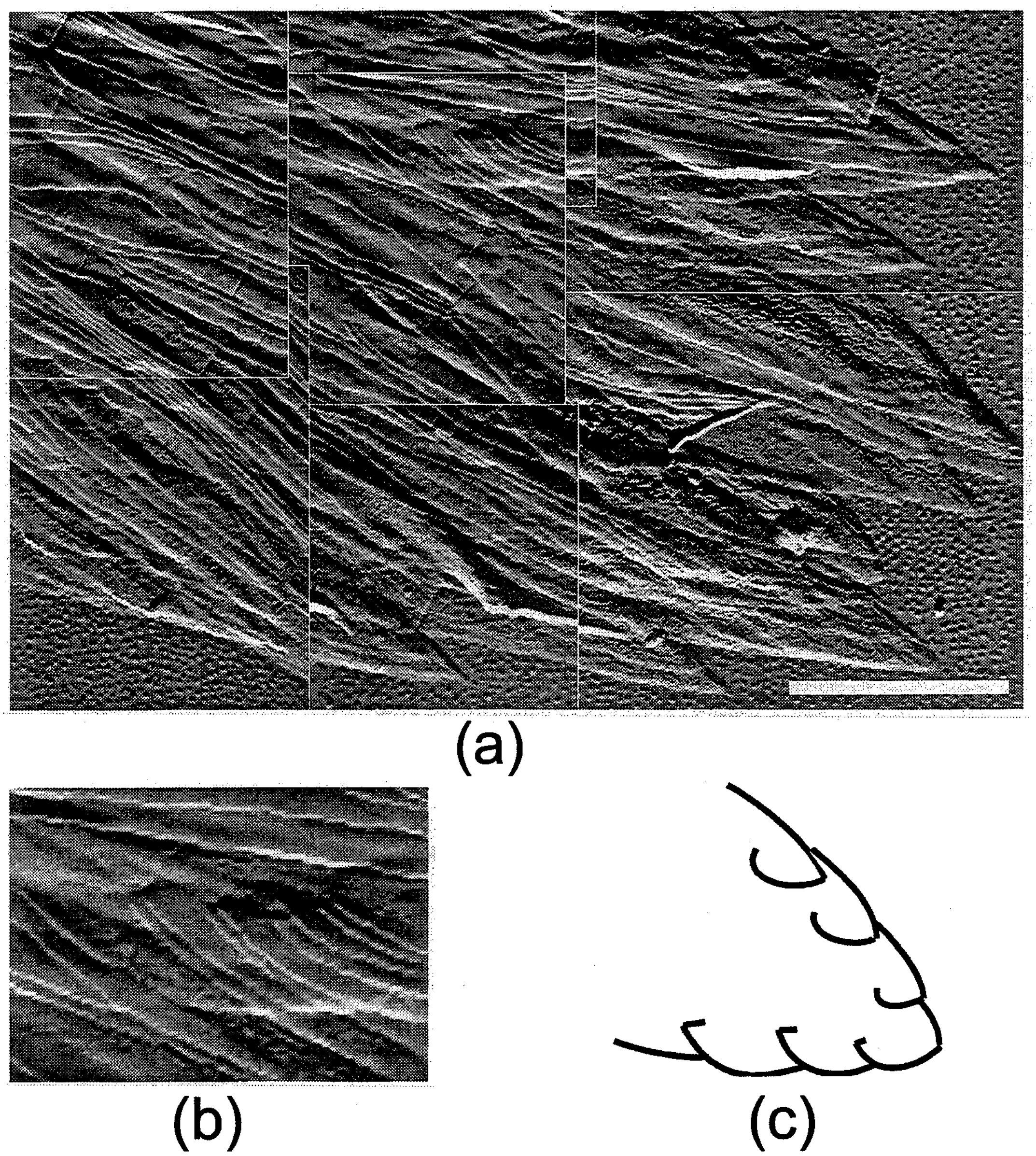
Fig. 1 A. Toda et al.



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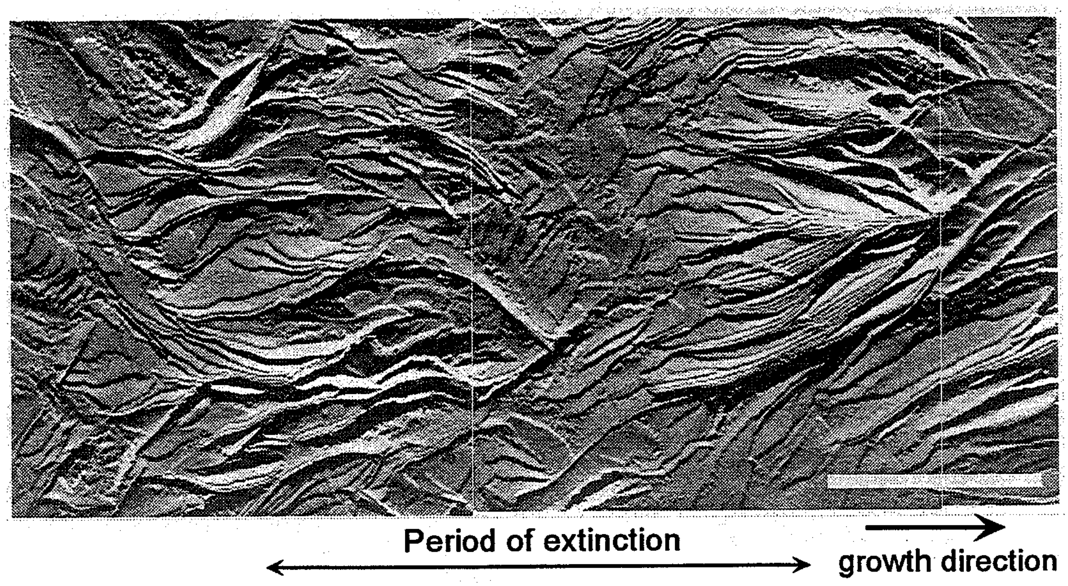

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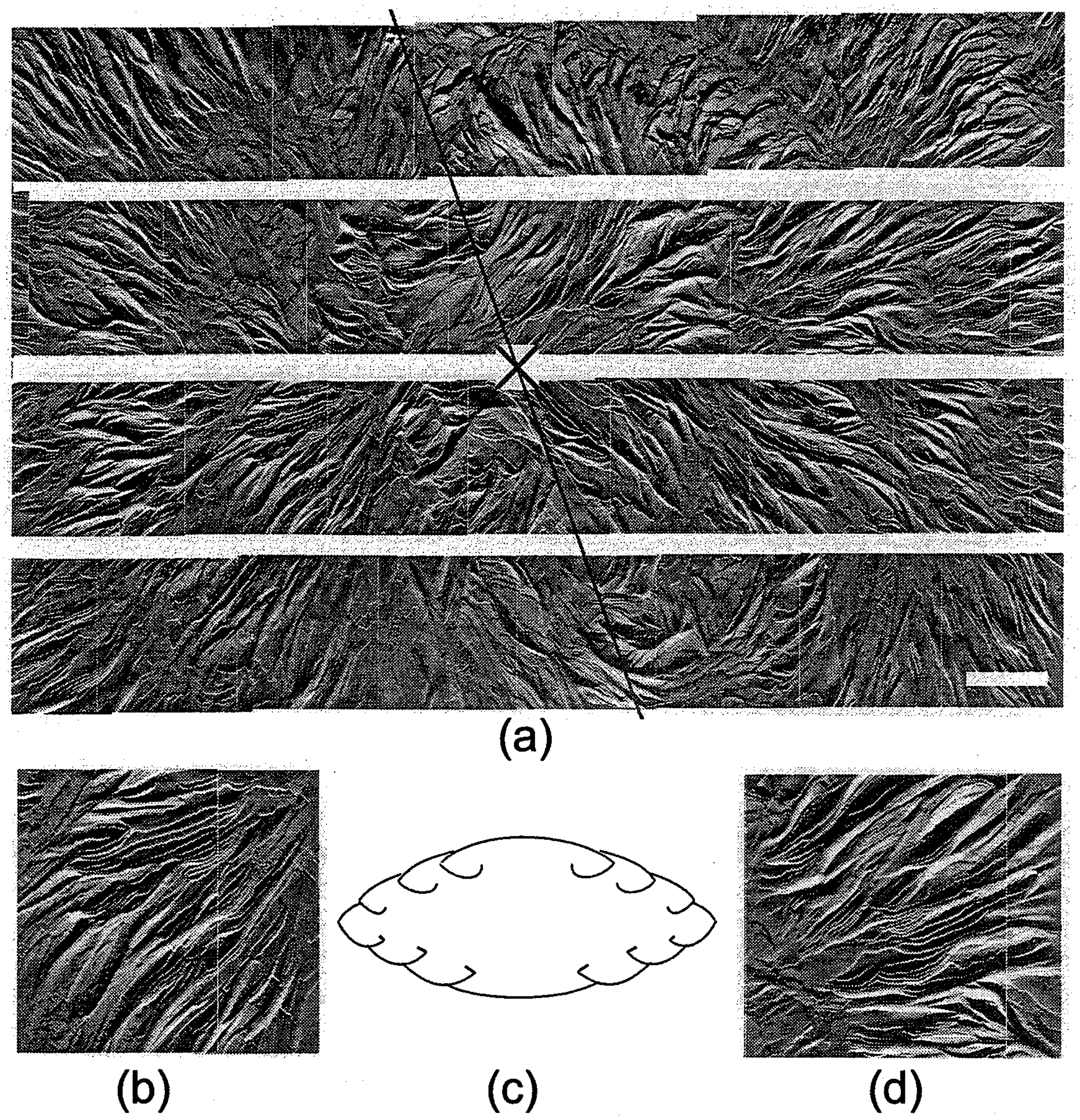

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Fig. 4 A. Toda et al.

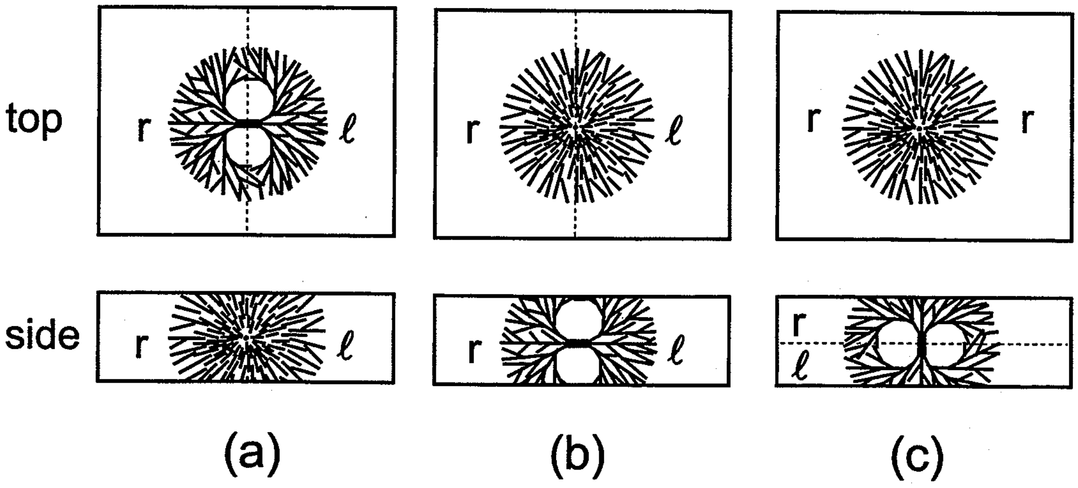

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Fig. 5 A. Toda et al.