

Defects in banded spherulites of polymers

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Abstract

In order to investigate the detailed structure of a banded spherulite observed by polarized light microscopy, we develop a new image processing technique that can visualize defects (band defects) in the concentric bands and determine the growing directions of crystals everywhere in a spherulite. This technique is applied to a banded spherulite of poly(vinylidene fluoride) and reveals that the spherulite has many defects (colliding defects), on which crystals collide with neighboring ones. It is found that the band defects are included in the colliding defects. The number of colliding defects increases linearly with the radius to give a constant density. Between the defects, the orientations of crystals are well correlated to form a coherent area. On the basis of these findings, a mechanism of the formation of the coherent band pattern is discussed.

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1. Introduction

The banded spherulite is one of the major morphologies of crystalline polymers and has been attracting many researchers for the beautiful concentric pattern observed by polarized light microscopy (Fig. 1(a)) [1]. Regarding the formation of banded spherulites, two major issues remain unsolved: the origin of a nearly constant pitch of twisting correlation of lamellar crystals and the mechanism of organization of the lamellae on the scale observed by light microscopy. We here treat only the latter issue. Strobl mentioned the issue in his textbook [2] as follows: ‘Really astonishing is the coherence of this texture throughout the whole spherulite, where the orientations of all crystallites are well-determined and exactly correlated. The mechanism leading to this peculiar texture is still under discussion and not yet clarified’.

In order to reveal the detailed structure of banded

spherulites, we have developed a new technique of image processing for polarized light microscopy. We can thereby determine the growth directions of crystallites at all points throughout a spherulite and can make two kinds of defect visible; one is related directly to the concentric bands and the other is a more general one related to the divergence of the growth direction of crystals in a spherulite. On the basis of the analysis of the defects, we propose a mechanism for the formation of the coherent structure in banded spherulites.

2. Experimental

The material used is poly(vinylidene fluoride) (PVDF) (KF1000, $M_w = 2.5 \times 10^5$ and $M_w/M_n = 2.1$) supplied kindly by Kureha Chemical Industries Co. Ltd. A dimethyl formamide solution of PVDF was cast on a glass slide and dried to make a film ca. 2 μm thick. The film was melted at 210 °C for 2 min, cooled down to a crystallization temperature, 168 °C, crystallized for 24 h.

The crystallized film was observed at room temperature with a polarizing microscope (BX51, Olympus Co. Ltd) equipped with a digital camera (DP12, Olympus Co. Ltd).

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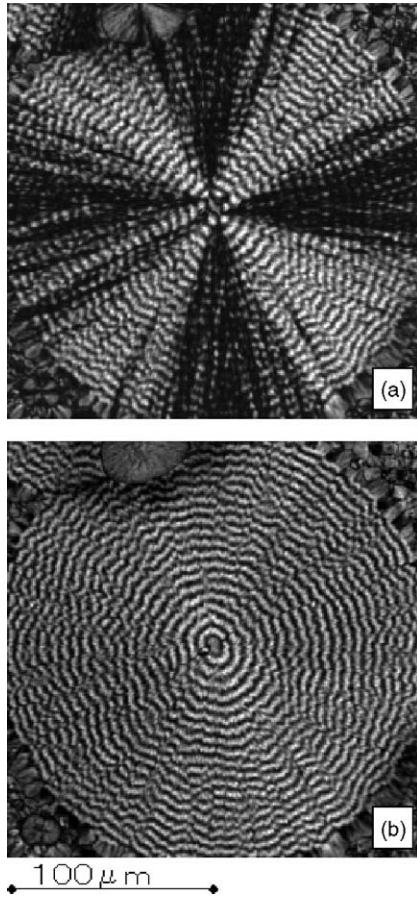


Fig. 1. (a) Banded spherulite image by polarized light microscopy under cross polaroids. (b) Superposition of two polarized light microscopic photographs with the two polarized directions by differing 45° to eliminate the Maltese cross.

The resolution of the image is 2048×1536 pixels; we can get the intensity at each pixel. Keeping the condition of crossed polaroids, we rotated step by step both the polarizer and analyzer by an angle of 5° and took 18 photographs for a spherulite. The reason for rotating not the specimen but both the polarizer and analyzer is the convenience for the image processing; we do not need to coincide the center of a spherulite with the rotation axis of the sample stage in a microscope.

3. Results

For the analysis of the spherulite image by polarized light microscopy, we review the optical properties of a PVDF crystal. The crystal in a PVDF spherulite grown at 168°C has either the alpha form or gamma form. Since the gamma form spherulite is not banded, we investigate here the banded alpha spherulite [3]. The alpha form was the monoclinic structure [4]. The unique b -axis is perpendicular to the chain direction and parallel to the growth direction in

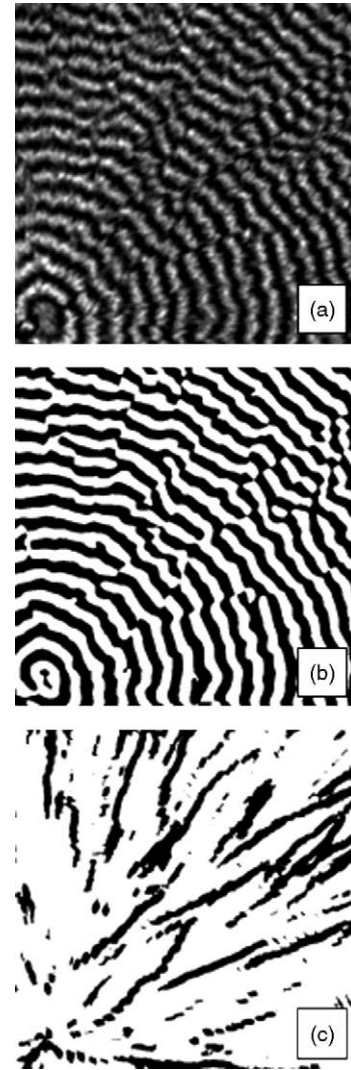


Fig. 2. (a) Enlarged banded spherulite image of Fig. 1(b). (b) Coarse grained image. (c) Band defects visualized by image processing.

the spherulite [3]; namely the growth direction coincides with an optical principal axis. Monoclinic crystals are optically biaxial. However, we can safely treat the PVDF alpha crystal as an optically uni-axial crystal since the spherulite shows not a double but a single band.

For an optically uni-axial crystal, the intensity by polarized light microscopy is described by the following equation,

$$I(\theta, \varphi) \propto \sin^2(2\theta)\sin^2(\varphi) \quad (1)$$

where θ is the angle between the polarizer and one of the optical axis (b -axis) and φ is the angle of rotation around the axis. Eq. (1) shows that the θ dependence of the intensity determines the growth direction of a crystal in a spherulite and the φ dependence does the rotation angle around the growth direction.

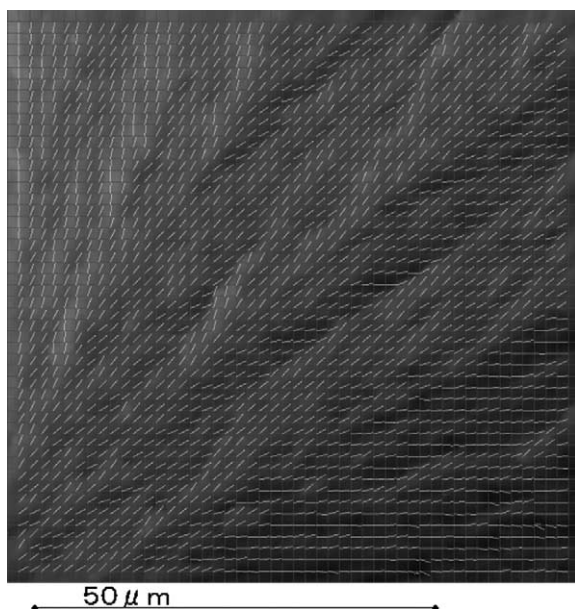


Fig. 3. The distribution of the growth directions (*b*-axis) expressed by white arrow of unit vector \mathbf{u} . Background contrast expresses the direction of the vector in gray scale; white, vertical; black, horizontal.

3.1. Defects in concentric bands

Firstly we analyze the concentric bands. A spherulite should have radial symmetry as a whole. The Maltese cross reduces the symmetry to four-fold symmetry under crossed polaroids. To eliminate the Maltese cross, we simply add the intensities of the two images of a spherulite at two angles of polarizer and analyzer by differing 45° . The factor including

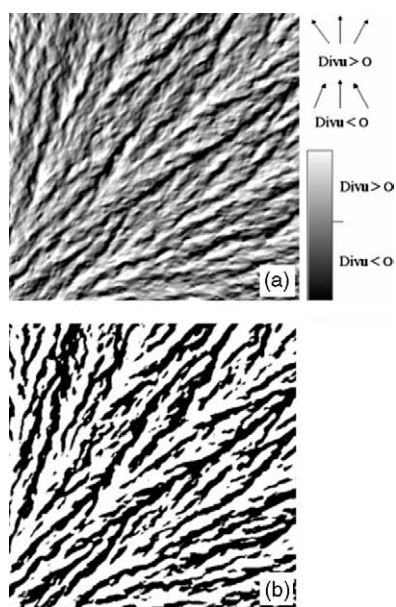


Fig. 4. (a) Gray scale image of distribution of $\text{div } \mathbf{u}$. White area corresponds to the area where growth directions diverge or spread. Black area corresponds to the area where growth-directions converge collide with each other. (b) Binarized image of (a); white area: $\text{div } \mathbf{u} > 0$, black area: $\text{div } \mathbf{u} < 0$.

θ is thereby eliminated (Eq. (1)). The added image (Fig. 1(b)), therefore, has only the information about the rotation angle around the growing directions. Observing the details of the pattern, we notice that the concentric bands are not perfect concentric patterns but have many disturbances. Most noticeable are the line faults almost parallel to the radial direction like the faults of geometrical strata. The length of the fault is much longer than the band spacing. We call this fault the band defect.

To make the band defect clearly visible, we perform the image processing for Fig. 2(a) in two steps. Each step is a kind of local filtering. The first step is a coarse graining process of the band pattern to neglect the fine structure at the scale of $1 \mu\text{m}$ or shorter (Fig. 2(b)) and the second is the visualization of the irregularity of a band along the tangential direction (Fig. 2(c)). In the first process, we take a small square around a point on the image of Fig. 2(a), the side length of which is one half of the band spacing, divide the square into the two same rectangles by a line perpendicular to the radial direction, compare the average intensity in each rectangle. When the intensity at the inner rectangle is larger than that at the outer one, the point is determined to be white, and when the intensity at the outer one is larger than that at inner, the point is black. We made this coarse grained process to all points and binarized band image (Fig. 2(b)). In the second process, we take, in this coarse grained image, the same box as in the first process, divide the square into the two same rectangles by a line parallel to the radial direction, then counted the number of pixels of black point in each rectangle, subtract the number at one rectangle from that at the other and square the difference. When the squared number is larger than a threshold number, the point is determined to be black, and the point is white otherwise. Adjusting the threshold, we can visualize the band defect (Fig. 2(c)). Such a defect was mentioned by Keith and Padden [5]. However, the structure and its role in the formation of banded spherulites have not been investigated.

3.2. Defect of colliding growth direction

Secondly we analyze the growth direction of a crystal at every point in a spherulite. In the 18 photographs described in Section 2, the light intensity becomes minimum when the direction of the optical axis coincides with that of the polarizer or analyzer (Eq. (1)). Accordingly we can determine the growth direction of crystals at all points in a whole spherulite. We cannot decide the growth direction uniquely since there are four angles, θ , $\theta + 90^\circ$, $\theta + 180^\circ$ and $\theta + 270^\circ$ for one angle θ giving the minimum intensity. However, the deviation of growth directions from radial directions is not so large as 45° that we can decide the growth direction uniquely. In Fig. 3, the distribution of the growth directions (*b*-axis) determined is expressed with unit vectors in a quarter of the spherulite. We can see that the growth directions diverge or spread in one area, and converge or collide with neighboring directions in another area. In order to treat these features quantitatively, we

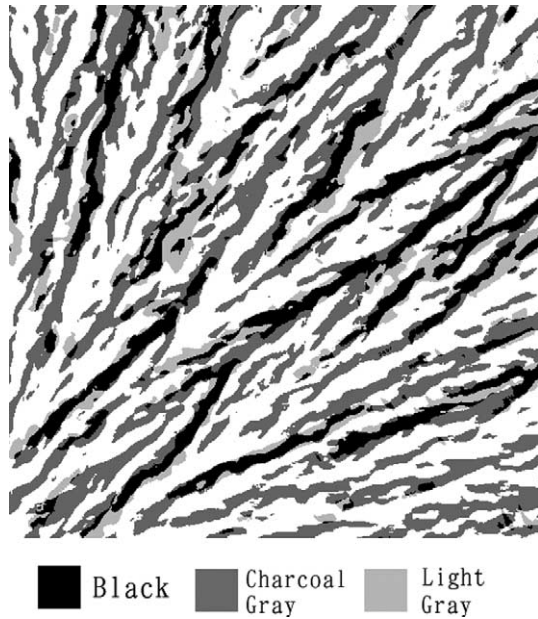


Fig. 5. Superposed image of band defect (Fig. 2(c)) and colliding defect (Fig. 4(b)). Black areas show coincidence of both defects. Light gray areas show only the area of band defect and charcoal gray areas show those of colliding defect. Light gray areas exist only around the black areas. It means that the areas of band defect are included in the areas of colliding defect.

calculate the divergence of this unit vector field $\mathbf{u}(\mathbf{r})$, $\text{div } \mathbf{u}$ (Fig. 4(a)). In Fig. 4(b) the black lines correspond to the converging areas ($\text{div } \mathbf{u} < 0$) and the white areas to the diverging areas ($\text{div } \mathbf{u} > 0$). We call the long line of collision the colliding defect. The short converging line, that merge into the colliding defect is called the colliding line. We focus on the colliding defects in Fig. 4(b) and compare them with the band defects in Fig. 2(c). The result is shown in Fig. 5. We can conclude that the band defects are included in the colliding defects.

In Fig. 6 are shown schematically the two kinds of defect in a banded spherulite. At the black line, the band defect, the concentric bands are dislocated along the radial direction in

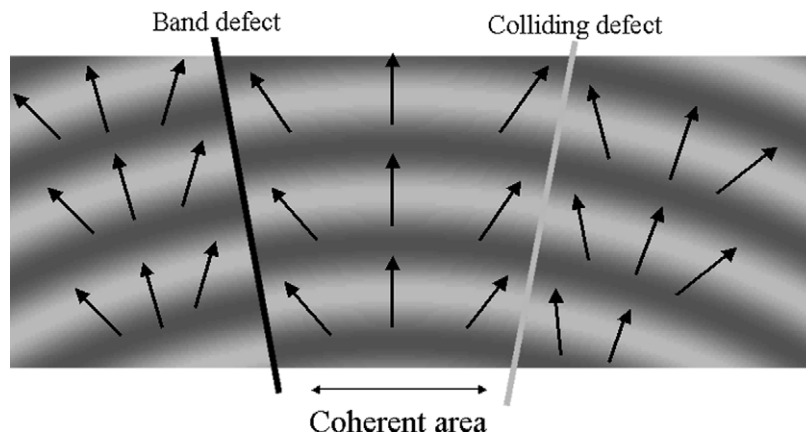


Fig. 6. Schematic drawing of the two kinds of defect in a banded spherulite. Black line: band defect, dislocated concentric bands along the radial direction. Gray line: colliding defect. Crystals collide with neighboring ones and the band pattern happens to be smooth with no band defect. Between the defects are coherent areas.

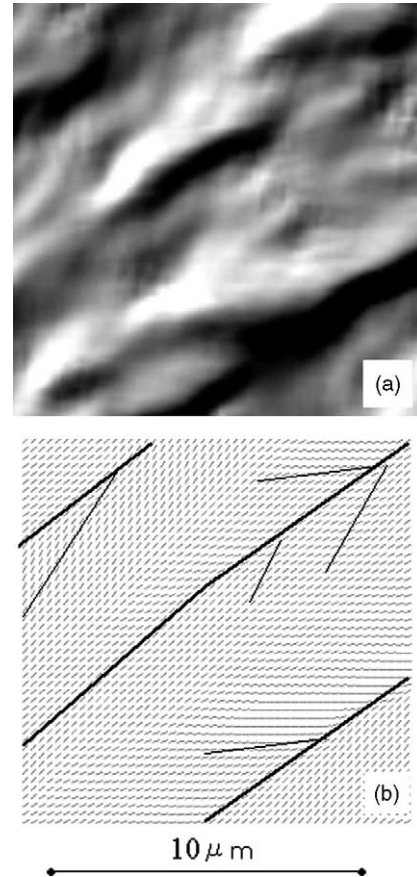


Fig. 7. (a) Enlarged part of Fig. 4(a). (b) Schematic picture of colliding defects and colliding lines with growth directions of crystals in a coherent area. Heavy black lines indicate colliding defects and thin black lines indicate colliding lines.

the spherulite. At the gray line, the colliding defect, crystals collide with neighboring ones and the band pattern happens to be smooth with no band defect. Between the colliding defects, the crystals grow in the diverging growth directions and branch frequently. We call the area between the adjacent colliding defects the coherent area. Even in the

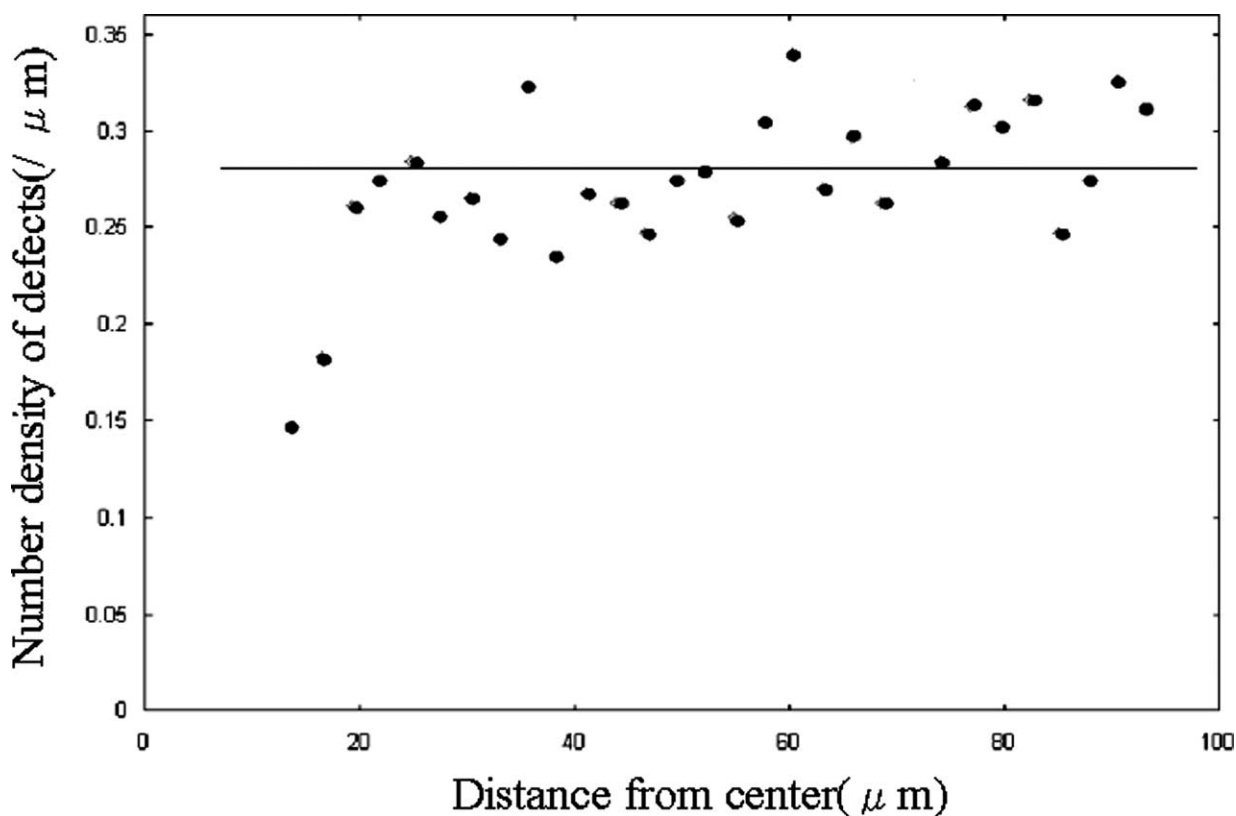


Fig. 8. Number density of colliding defects plotted against radial distance from the spherulite center.

coherent area are many colliding lines (Fig. 4(b)). In Fig. 7(a), which is a zoomed image of Fig. 4(a), there are white diverging areas. The corresponding distribution of growth directions in the coherent areas is shown in Fig. 7(b). This figure indicates that only the crystals, which grow faster than the neighbors can continue to grow to prevent the growth of slower crystals. This competition for growth plays an important role to form banded spherulite as discussed later. By this competition, the band pattern is disturbed and colliding lines are formed.

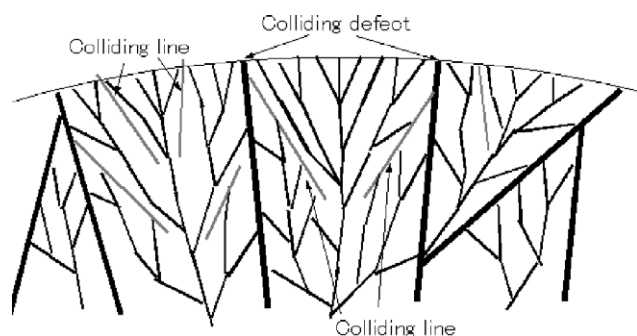


Fig. 9. Schematic picture of branching crystals, colliding lines (gray lines) and colliding defects (heavy black lines). Fast growing crystals survive by winning in the competition against neighboring crystals. The disturbances of the band patterns are extinguished on the colliding defects.

3.3. Distribution of defects

Finally, we examine the distribution of the colliding defects to reveal their role in the formation of the banded spherulite. In Fig. 8 is shown the number density of the defects plotted against the radial distance from the center of a spherulite; the number of defects increases linearly with the radius to give a constant density. Accordingly the average width of a coherent area is constant: ca. $3\mu\text{m}$. In Fig. 4(b), we can see that several new colliding defects are generated and two colliding defects merge into one as a spherulite is growing. Consequently the mechanism keeping the defect density constant may be relevant to the fluctuation in the growth rate of crystals.

4. Discussion

We have treated the spherulite as a two-dimensional object in the analysis of the image. Hence it is required that the film thickness is thinner than the length of the coherent area. The PVDF film is $2\mu\text{m}$ thick and the coherent area is about $3\mu\text{m}$ in the present work. Consequently the effect of the third dimension of the film on the analysis may be small.

We now discuss the mechanism of the concentric pattern formation in a banded spherulite. We have confirmed that there are more colliding defects in the banded spherulite than the band defects observed by polarized light

microscopy. There seems to be no relation between micro-crystallites at both sides of a colliding defect. Therefore, there is no such long-range interaction to make the band pattern coherent in the tangential direction. We have confirmed that the averaged width of a coherent area is constant. Hence we concentrate our attention on the coherent area and the correlation along not the tangential but the radial direction.

In Fig. 9, we summarize the mechanism of keeping the coherence of the band pattern in a coherent area. As described in Section 3, the value of $\text{div } \mathbf{u}$ can change even in a coherent area (Fig. 7(a)). In the region with a large value of the $\text{div } \mathbf{u}$, fast growing crystals survive and branch frequently. The spatial fluctuations of the growth rate may disturb the coherence in the coherent area. However, slow crystals collide with the fast ones, which have grown and occupy the space, to form colliding lines and they are eventually extinguished on a colliding defect as the spherulite grows. The disturbances by the fluctuation, therefore, do not affect the coherence in the coherent area. It is concluded that the coherence in a coherent area can be maintained by the fast growing crystals, which survive by winning in the growth competition; no attractive or repulsive interaction is required for the observed beautiful banded pattern.

The idea that crystals in a spherulite do not have any attractive or repulsive interaction was proposed by Keller and Waring [6] for the morphology of the center of spherulites; crystals branch when they grow by a constant length: regular branching model. Bisault et al. proposed a more realistic model [7]; the growth rate of crystal has a fluctuation and only the fastest crystal can grow. The fluctuation of growth rate was reported by Hobbs [8]. As described above, the present observation is consistent with the model by Bisault et al. If the fluctuation of the growth rate occurs stochastically, the colliding defect should not be

as straight as observed but would curve irregularly. One possibility of the origin for the fluctuation would be the fluctuation in the diffusion field of non-crystallizable species as discussed by Keith and Padden [9]. It is to be noticed that the pattern of colliding defects (Fig. 4(b)) is important to decide the origin of the fluctuation since the generation of new coherent areas requires a large fluctuation. However, what controls the fluctuation of growth rate is yet to be investigated.

We have discussed on the banded spherulite of PVDF with many band defects. There have been reported more beautiful or coherent banded spherulites [1]. If the more beautiful or coherent banded spherulites have many colliding defects, the present discussion on the PVDF spherulite can be applied to banded spherulites of polymers.

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