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# Three-dimensional morphology of PVDF single crystals forming banded spherulites

A. Toda*, T. Arita, M. Hikosaka

*Faculty of Integrated Arts and Sciences, Hiroshima University, 1-7-1 Kagamiyama, Higashi-Hiroshima 739-8521, Japan*

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## Abstract

We have examined the morphology of poly(vinylidene fluoride) (PVDF) single crystals grown from melt and from blends with poly(ethyl acrylate) (PEA), PVDF/PEA = 0.5/99.5 and 30/70 by weight. The single crystals, of relatively higher molecular weight, were grown isothermally in the temperature range where banded spherulites are formed with sufficient crystallization time. The crystals were extracted by dissolving amorphous PEA and PVDF crystals formed on quenching. The three-dimensional morphology of the single crystals was examined by transmission electron microscopy (bright field, dark field and diffraction) with a tilting stage. For all cases, the tilting of chains (~25–27°) to the fold surface has been confirmed. The three-dimensional shape of all the crystals was chair type for the 30/70 blend and pure PVDF. In chair crystals, spiral terraces keep the handedness in each growth direction. From these evidence, it is proposed that the chair crystals with consecutive creation of spiral terraces of the same sense are responsible for the twisting relationship between crystallites in the radial direction of the banded spherulites. © 2000 Published by Elsevier Science Ltd.

*Keywords*: Spherulite; Banding; Poly(vinylidene fluoride)

## 1. Introduction

Crystallization of polymers from the melt forms spherulites that are composed of small crystallites growing in the radial direction, with the formation of branches filling three-dimensional space [1–4]. With some polymers, a concentric pattern of periodic banding appears in the spherulites. The dynamics of pattern formation [5] under non-equilibrium conditions of supercooled melt has attracted a lot of interest for many years, and recent examination of the banded spherulites formed by non-racemic chiral polymers [6–8] has stimulated workers in this field.

In banded spherulites, lamellar crystallites in the radial direction are in a twisted relationship. As shown in Fig. 1, two possible cases have been postulated. Fig. 1a represents a twist of the lamella itself [9–11] and Fig. 1b shows another case, the consecutive formation of spiral terraces from spiral dislocations keeping the sense [12,13]. The spiral terraces make a finite angle to each other, and hence the consecutive formation results in the twisting relationship between crystallites in the growth direction.

Depending on the specific nature of polymer crystals, the mechanism of twisting relationship can be summarized as follows. Firstly, for non-racemic chiral polymers, Singfield et al. [6–8] proposed the possibility of a twisting arrangement of growth layers, as is the case with cholesteric liquid crystals. Such twisted-ribbon-like cystals have been obtained from a non-racemic chiral polymer [14]. With non-racemic chiral polymers, the sense of twisting is expected to be correspondent with the handedness of chirality in the molecule; experimental observations by optical microscopy [8,15] have shown the choice of sense of twisting throughout a spherulite.

When polymer molecules are non-chiral and the polymer chains are tilted to the fold surface, Fig. 2 shows two possible cases. Fig. 2b–d represents the model proposed by Keith and Padden (KP crystal) [10,11]. They suggest that the chain tilt creates unequal stresses at the two opposing fold surfaces in a given lamella (Fig. 2b), which gives rise to the bending of the two halves of the lamella (Fig. 2c). With the KP crystal, we can expect not only twisting of the lamella but also spiral terraces keeping the sense in each direction of growth (Fig. 2d); the formation of spiral

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* Corresponding author. Tel.: +81-0-824-24-6558; fax: +81-0-824-24-0757.

*E-mail address:* atoda@hiroshima-u.ac.jp (A. Toda).

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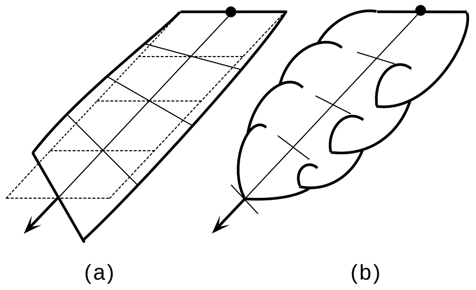


Fig. 1. Schematic representation of two possible origins for the twisting relationship between crystallites in the radial direction of banded spherulites: (a) twist of lamellar crystal and (b) growth of spiral terraces of the same sense by the consecutive generation of screw dislocations keeping the handedness.

dislocations of the specified sense can relax the stress in the lamella [16]. KP crystals must have a S-shaped cross section (Fig. 2b), which has been observed in polyethylene (PE) crystals by Bassett et al. [17].

Fig. 2e–g shows another possibility of chair crystals, which also produces spiral terraces keeping the sense in each direction of growth [16]. The profile of the cross section and the handedness of the spiral terraces in the chair crystals are just opposite to those of KP crystals. In both KP crystals and chair crystals, the sense of twisting is reversed for the opposite growth direction in each lamella (Fig. 2d and g), and hence the models explain the mixture of right-handed and left-handed twisting in banded spherulites of non-chiral polymers [18,19].

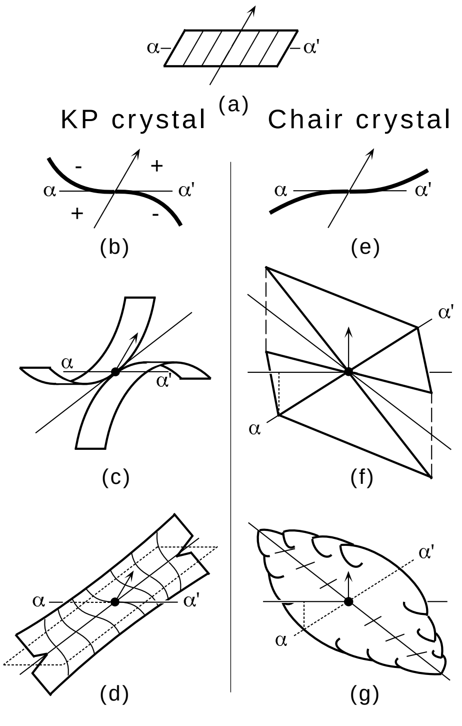


Fig. 2. Schematic representation of KP crystals (b–d) proposed by Keith and Padden [10,11] and chair crystals (e–g) with the chain tilting shown in (a): (b, e) cross sectional view, (c, f) two halves in the relaxed state, and (d, f) twisting and spiral terraces keeping the sense in each growth direction. The symbols, + and −, in (b) represent the stress disparity on the fold surface of the KP crystal. The arrows indicate the direction of chains.

Experimentally, it has been confirmed that all crystals are of chair type when PE of relatively low molecular weight is crystallized from the melt [16]. However, since the temperature range of banded spherulites of PE is lower than the range of chair crystals and the cross section is S-shaped in that temperature range, it is most probable that the KP crystal is responsible for the twisting relationship in banded spherulites of PE.

Spherulites of poly(vinylidene fluoride) (PVDF) are also one of the well-known examples of non-chiral polymers exhibiting concentric banding [20]. PVDF has several crystalline modifications, and the α-phase crystals form banded spherulites. An argument exists in terms of chain tilting in the α phase. When crystallized from dilute solution [21] or from a blend with poly(ethyl acrylate) (PEA) [22], it was reported that chains are normal to the fold surface. On the other hand, when crystallized from a thin film of the melt, chain tilting of about 25° has been recognized [23]. In the case of solution growth, it is probable that the lower crystallization temperature introduced a weaker influence of the steric problem at the fold surface. In crystallization from a blend, the relatively lower molecular weight ($M_w = 4.7 \times 10^4$) of PVDF examined in the experiments may have also brought in the weaker influence of chain folding. With these considerations, we examine the chain tilting with PVDF of higher molecular weight grown from blends as well as from the melt.

Detailed examination of three-dimensional morphology of a single crystal obtained under the condition producing banded spherulites will give us very important information about the twisting relationship between the crystallites. In the present paper, single crystals are extracted from blends and from the melt and observed with transmission electron microscopy (TEM: bright field, dark field and diffraction pattern) to examine the applicability of the above models. The extraction is feasible because amorphous PEA and PDVF crystals formed on quenching are dissolved in a solvent, with isothermally crystallized PVDF remaining intact.

## 2. Experimental

We used PVDF of 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. Dimethyl formamide solution of PVDF and toluene solution of PEA were mixed at the desired concentration at room temperature and then cast on a coverslip. The sample was then dried to make a film of the blend of PVDF and PEA. Three weight ratios were examined: PVDF/PEA = 0.5/99.5, 30/70 and 100/0. The thickness of the 0.5/99.5 blend was uniform at about 50 μm while the

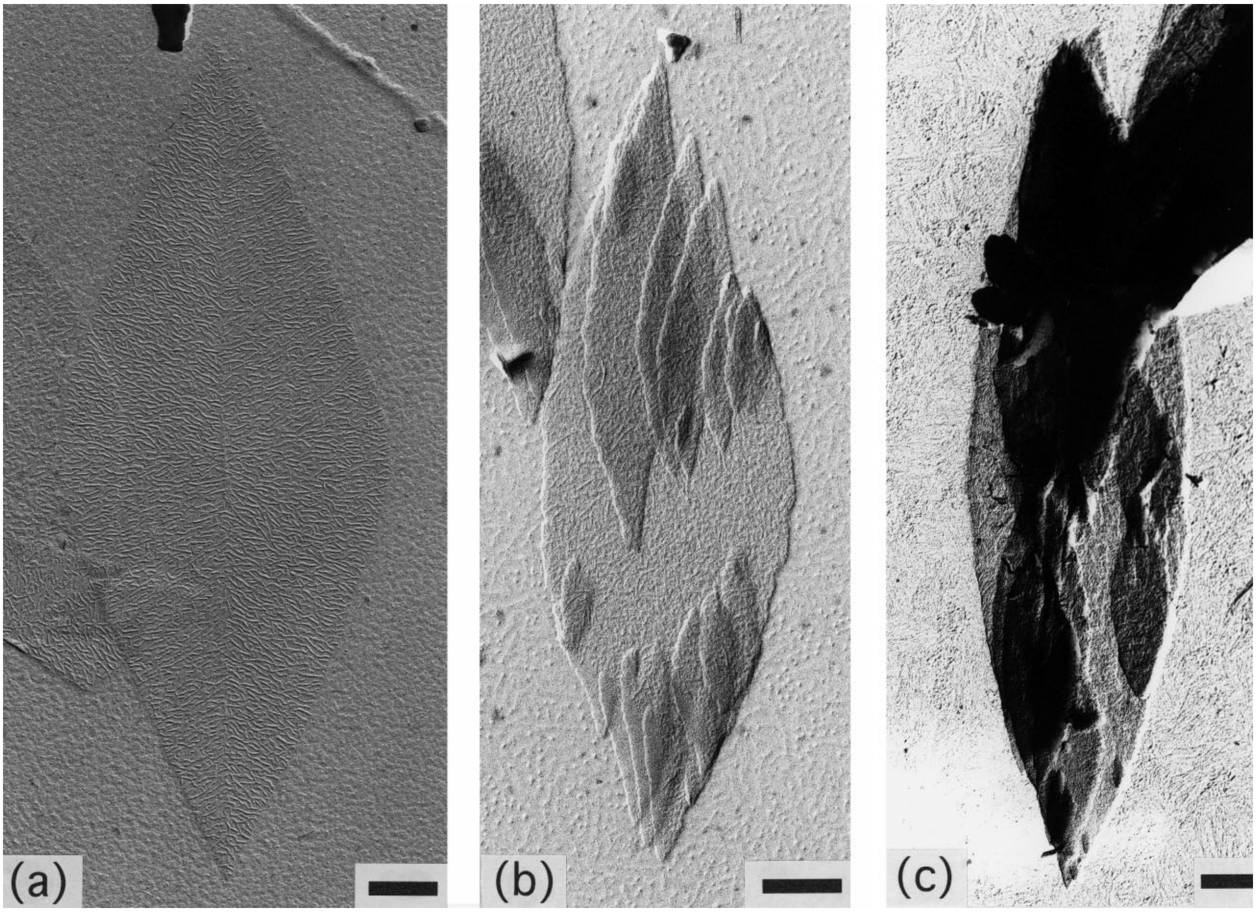


Fig. 3. Electron micrographs of typical single crystals of PVDF: (a) crystallized at 150°C for 2.5 h from the 0.5/99.5 blend and decorated with evaporated polyethylene by the method of Wittmann and Lotz [25], (b) crystallized at 170°C for 2 h from the 30/70 blend and (c) crystallized at 173°C for 1 h from pure PVDF. The *b*-axis of the crystals is vertical. Bar lines represent 0.5 μm.

thickness of the 30/70 blend and pure PVDF were not uniform because of thinner solution concentrations; for those cases, crystals from thicker parts (>10 μm) were examined.

For the 0.5/99.5 blend, the cast film was heated up to 161°C, kept at that temperature for 2 min to melt most of the crystals (self-seeding), and then quenched to preset temperatures to crystallize PVDF isothermally; the obtained crystals were all in the α phase. For the 30/70 and 100/0 samples, it is known that the γ phase crystallizes at higher temperatures (>160°C) [20]. In order to avoid crystallization in the γ phase, the samples were first crystallized into the α phase at 120°C (30/70) or 130°C (100/0), quenched from the liquid state kept at 210°C for 2 min. The samples were then heated up to a self-seeding temperature, and then crystallized isothermally. For the 30/70 blend and pure PVDF, since a higher crystallization temperature is preferable to avoid excessive overgrowth in the crystals, the self-seeding temperature and the crystallization temperature were nearly the same. After isothermal crystallization, the sample was quenched in a coolant (Fluorinert FC-77, 3M Co. Ltd.) kept at about −30°C. The temperature jumps were conducted by sliding the coverslip in a hot stage placed on a steep slope and hence the time required for quenching was less than 0.1 s.

After quenching, the sample was immersed in dimethyl acetoamide for 2 h at room temperature in order to dissolve amorphous PEA and PVDF crystals formed on quenching. The size of extracted PVDF crystals increased with crystallization time and the lateral habits observed by TEM seem to be free from the extraction procedure. Hence, we concluded that the isothermally crystallized PVDF was intact in the extraction process. The extracted crystals on the coverslip were shadowed at $\tan^{-1}(1/1)$ with Pt/Pd and coated with evaporated carbon. The sample on the carbon film was then detached from the coverslip with poly(acrylic acid), relieved on a water surface, and picked up on a copper grid for TEM (JEOL 100CX) observation with an accelerating voltage of 100 kV. The sample was tilted in the microscope with a two axes rotating holder (EM-STH10) or a normal holder with single axis rotation. The bright field and dark field images and the diffraction pattern from the crystals were examined.

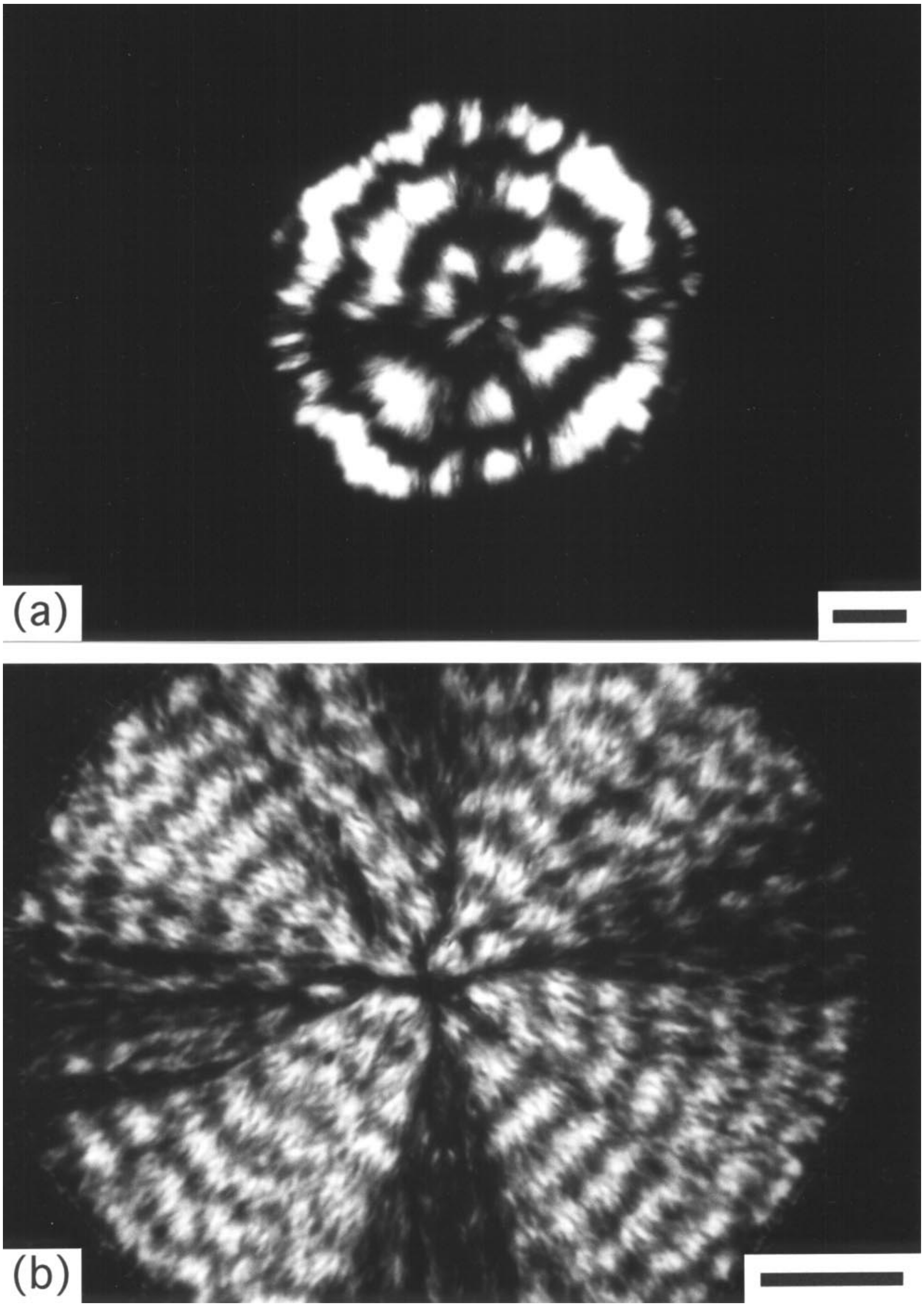


Fig. 4. Optical micrographs of polycrystalline aggregates of PVDF: (a) crystallized at 170°C for 97 h from the 30/70 blend and (b) crystallized at 173°C for 20 h from pure PVDF. Bar lines represent 25 μm.

## 3. Results

Fig. 3 shows typical lateral habits of PVDF single crystals obtained from the 0.5/99.5 and 30/70 blends and pure PVDF. From the blend of lower weight ratio (0.5/99.5), lozenge-shaped single crystals facetted with {110} faces were obtained. This result is in accordance with the results of Briber and Khoury [22]. For those crystals obtained from relatively thick films ($\gtrsim 10\ \mu$m), the influence of the substrate was negligible, while crystals from thinner parts were asymmetric, as reported by Keith et al. [24] for PE. Wittmann and Lotz's decoration pattern [25] in Fig. 3a suggests that the average direction of chain folding is along the growth face in each sector. For the 30/70 blend and pure PVDF, the fold surfaces as well as the substrate were self-decorated with adsorbed polymer that could not be removed by the extraction procedure. Because of the adsorbed layer, Wittmann–Lotz's decoration did not show any preferential orientation pattern for those samples.

Though the lozenge-shaped lateral habits are similar to

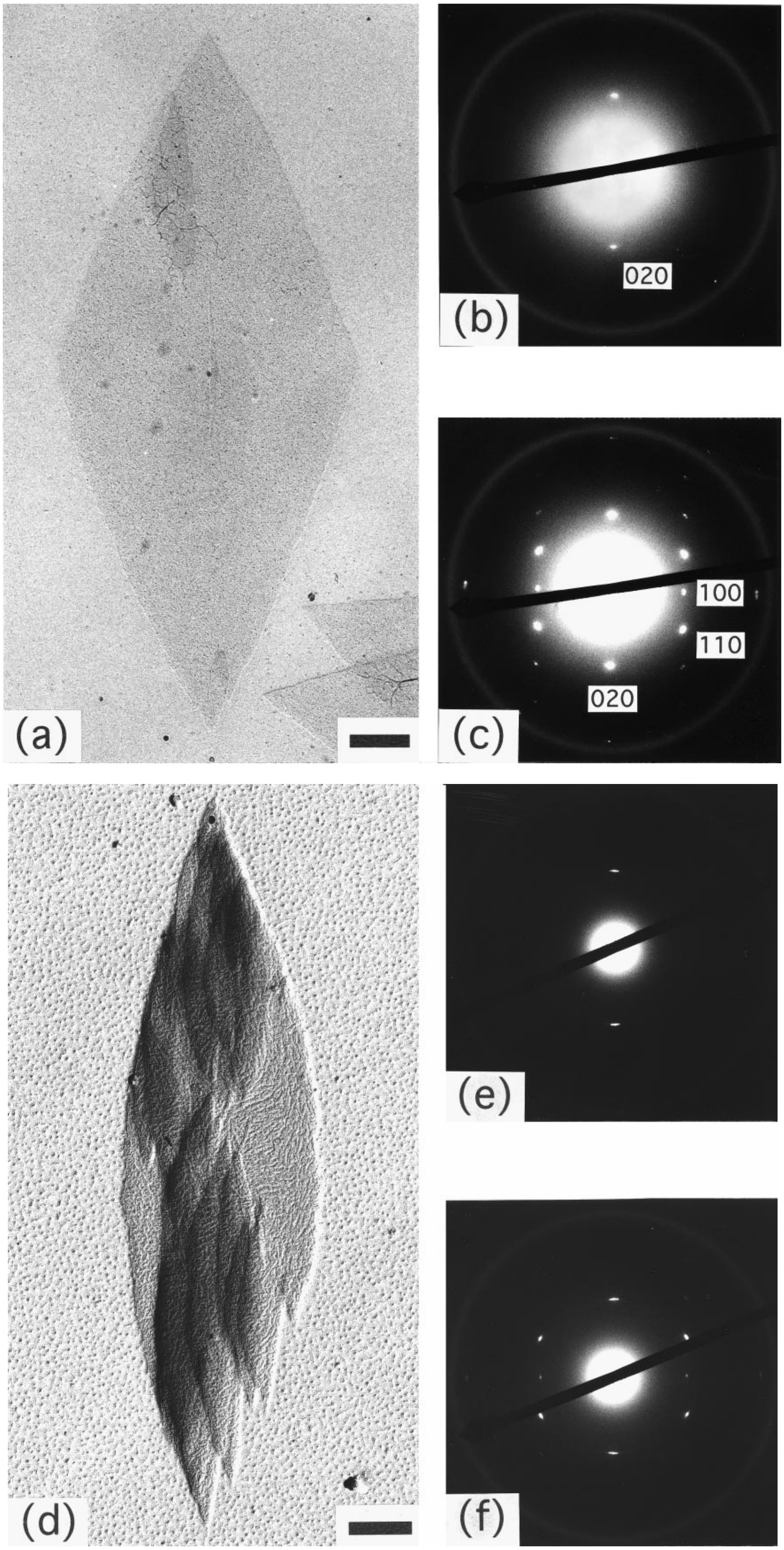


Fig. 5. Electron micrographs and diffraction patterns of single crystals of PVDF: (a–c) crystallized at 150°C for 2.5 h from the 0.5/99.5 blend, (d–f) crystallized at 170°C for 2 h from the 30/70 blend and (g, h) crystallized at 174°C for 1 h from pure PVDF. The specimens are rotated with the axis nearly parallel to the *b*-axis (long axis of the crystals) by 0° in (b, e) and 25–27° in (c, f, h), respectively — right side up and left side down. Bar line represents 0.5 μm.

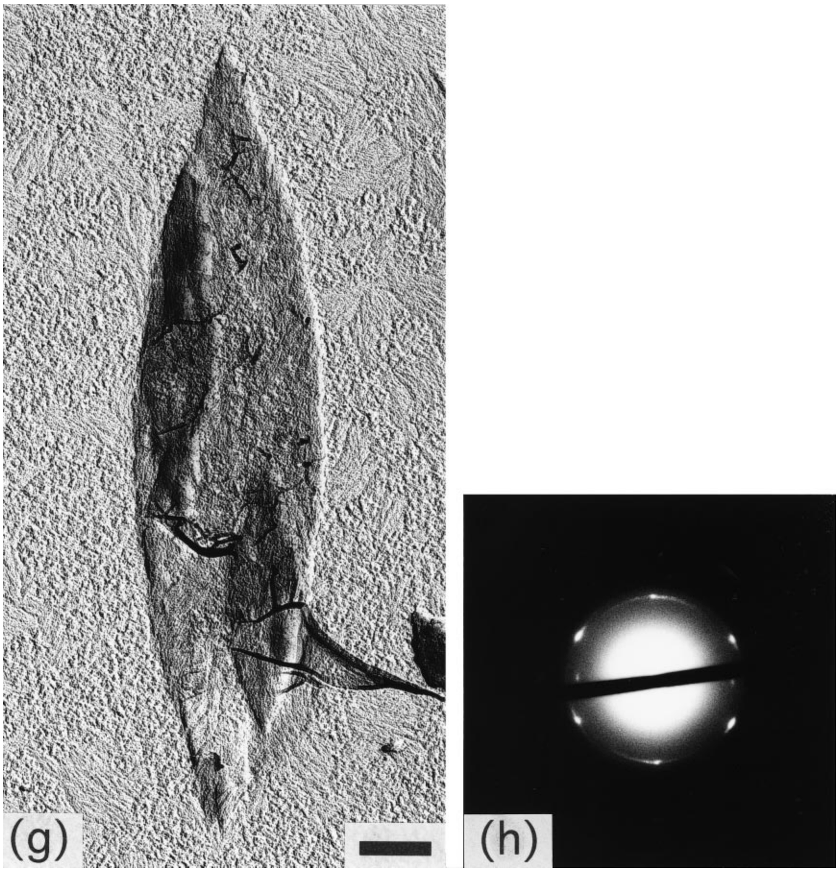


Fig. 5. (*continued*)

those of PE, the preferential growth direction of single crystals and of spherulites is the crystallographic *b*-axis with an acute angle for PVDF ($b/a = 1.94$) and with an obtuse angle for PE ($b/a = 0.67$). The rounded lateral habits for the 30/70 blend and pure PVDF (Fig. 3b and c) are therefore not directly related to the mechanism of the curved {100} faces in PE [2,26–32]. It may also be noted that the spiral terraces with the same sense in each direction of growth are clearly recognized in the crystal shown in Fig. 3b. As shown in Fig. 4, those crystals from the 30/70 blend and pure PVDF form banded spherulites under the respective conditions with sufficient time.

Fig. 5 shows electron diffraction patterns from single crystals. For all cases of blends and pure PVDF, chain tilting of 25–27° has been confirmed; this result agrees with the tilting angle reported for crystals from thin films [23]. The tilting axis for the pattern shown in Fig. 5 makes a small angle with the crystallographic *b*-axis. By examining more than 50 crystals, it is concluded that the deviation is about 6°, and hence a {214} fold surface of each {110} sector is most probable. This result indicates that the single crystals take a three-dimensional shape of hollow pyramidal type or chair type [33]. Fig. 6 shows that a half crystal nucleated on the substrate has a kinked edge line at the boundary with the substrate and supports the nonplanar morphology of single crystals.

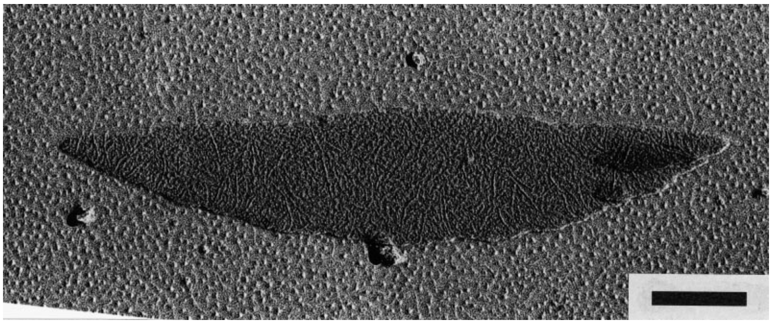


Fig. 6. Electron micrographs of a half crystal of PVDF crystallized at 170°C for 2 h from the 30/70 blend. Bar line represents 0.5 μm.

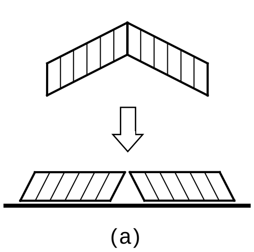


Fig. 7. Schematic representation of the direction of chains in the crystals of (a) hollow pyramidal type and (b) chair type collapsed on a substrate.

Due to the collapse of the three-dimensional shape of crystals placed on a substrate (Fig. 7), the shape can be identified as hollow pyramidal type or chair type by examining the dark field image of tilted crystals [16]. It was confirmed that one half of the crystals was hollow pyramidal (Fig. 8a and b) and another half was chair type (Fig. 8c and d) for 0.5/99.5 blend. On the other hand, for the 30/70 blend (Fig. 8e and f) all crystals were chair type. For the crystals grown from pure PVDF, due to excessive overgrowth and thick lamellae, no direct proof of chair type could be obtained from the dark field image. However, after rotation in one direction for 25–27°, only half of all the crystals show the diffraction pattern such as shown in Fig. 5h. Therefore, the direction of chain tilting must be uniform as shown in Fig. 7b and the crystals must also be chair type for the growth from pure PVDF. These results correspond to the results of PE grown from a dilute solution [33,34] and from the melt [16], respectively.

Figs. 3b, 5d and 8e clearly show the consistent handedness of spiral terraces in the chair crystals grown from the 30/70 blend. Fig. 9 also shows the same behavior of the sense of spiral terraces in the chair crystals grown from the 0.5/99.5 blend and from pure PVDF. The direction of chain tilting and the sense of spiral terraces are consistent with the chair crystals shown in Fig. 2a and g.

## 4. Discussion

In all cases examined in the present experiments (0.5/99.5

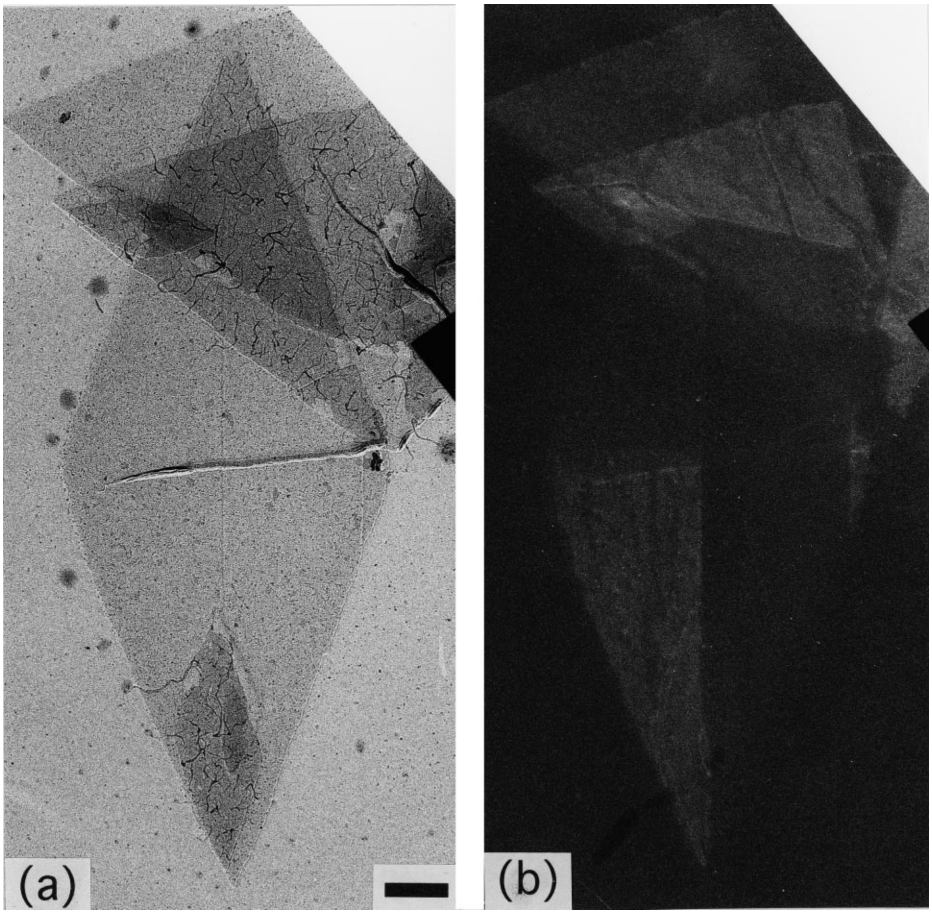


Fig. 8. Electron micrographs of bright field (a, c, e) and dark field (b, d, f) images of single crystals of PVDF: (a–d) crystallized at 150°C for 2.5 h from the 0.5/99.5 blend and (e, f) crystallized at 170°C for 2 h from the 30/70 blend. The specimens are rotated with the axis nearly parallel to the *b*-axis by 25–27° — right side up and left side down. The dark field images are from 110 diffraction. In (b), only one of the sectors is bright, indicating the three-dimensional shape of hollow pyramidal type. In (d) and (f), all sectors are bright and the pair of sectors in the diagonal position is brighter than the others, indicating chair type. Bar lines represent 0.5 μm.

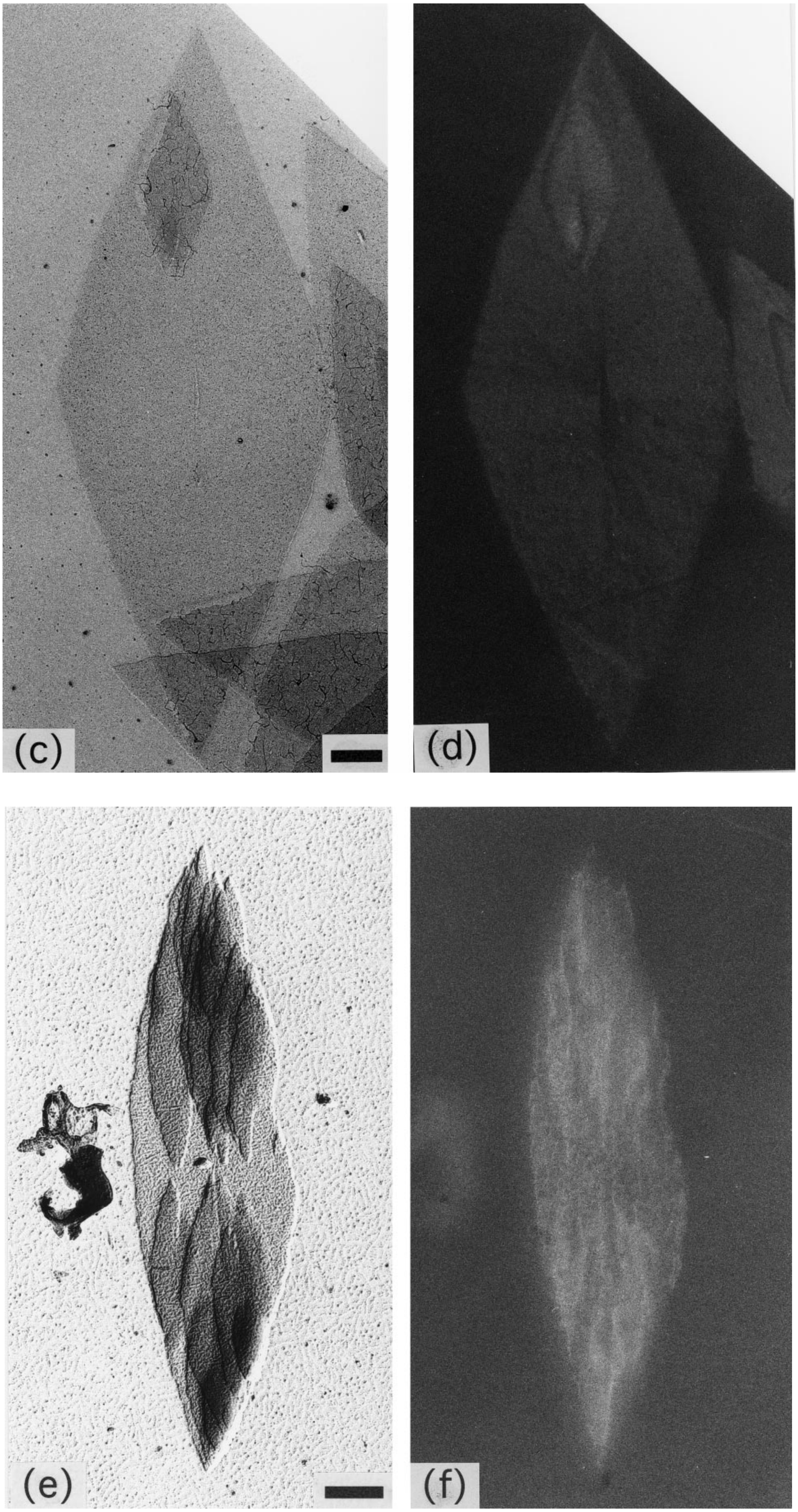


Fig. 8. (*continued*)

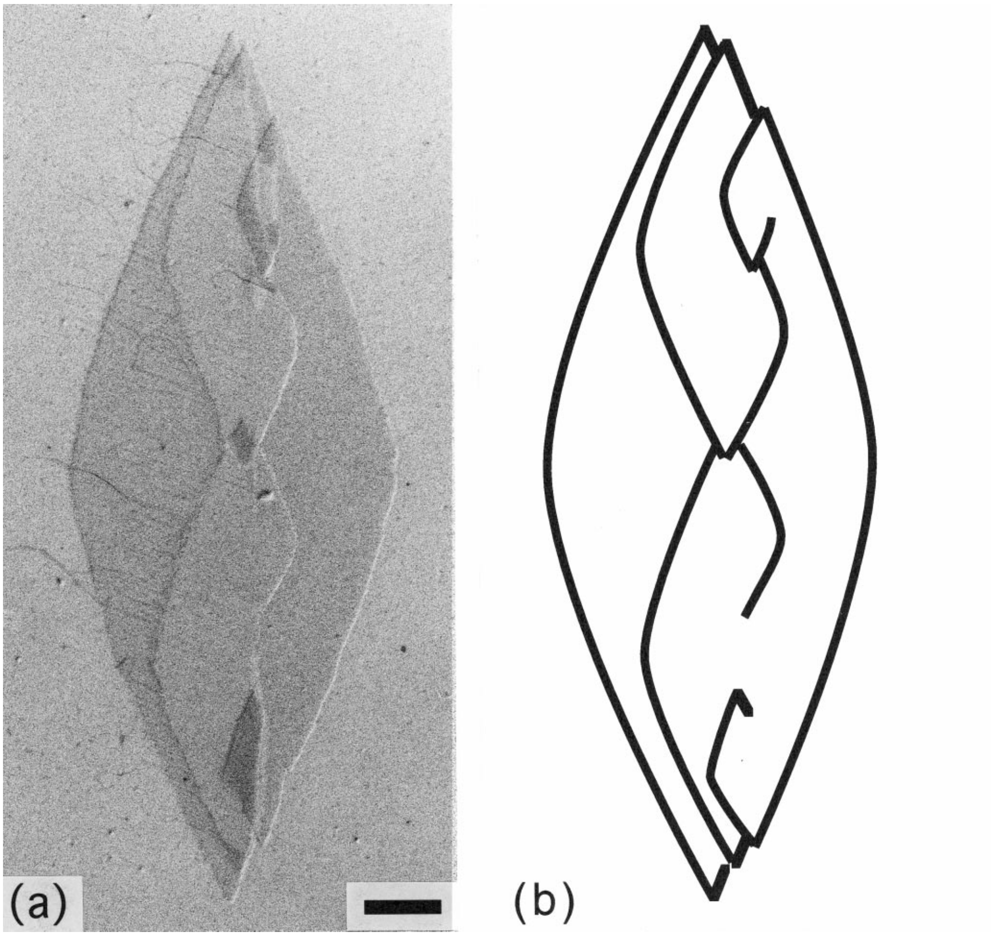


Fig. 9. Electron micrographs and schematic illustrations of consistent handedness of spiral terraces in chair crystals of PVDF: (a, b) crystallized at 150°C for 2.5 h from the 0.5/99.5 blend and (c, d) crystallized at 172°C for 17 min from pure PVDF. Bar lines represent 0.5 μm. The chain tilting is in the same direction as those shown in Figs. 5 and 8, which has been confirmed by the dark field image or diffraction pattern of the tilted crystals — right side up and left side down.

and 30/70 blends and pure PVDF), single crystals of PVDF of relatively higher molecular weight have chain tilting at 25–27° to the fold surface. The fold surface is assigned to be {214} and the crystals are nonplanar. In the cases of 30/70 blend and pure PVDF, the three-dimensional shape is chair type with spiral terraces keeping the sense in each growth direction. Those single crystals were obtained in the temperature range where banded spherulites are formed with sufficient time, and hence it is concluded that chair crystals are responsible for the twisting relationship among lamellar crystallites in banded spherulites of PVDF with consecutive generation of spiral terraces keeping the sense.

Regarding the consecutive generation of spiral terraces and stress relaxation by the creation of spiral dislocations, there can be a critical stress for their creation, and hence we may expect a periodic repetition of the generation of spiral terraces with the relaxation of accumulated stress in chair crystals. This mechanism may explain the repetition of abrupt splaying of fan-like branches in the crystallization from a blend with PEA reported by Briber and Khoury [22].

A question may be raised about the creation of only chair type crystals for the 30/70 blend and pure PVDF. Toda and Keller [16] explained the same behavior observed in PE, as the consequence of the morphology in the early stage of growth. In the early stage, there can be three possible cases, as shown in Fig. 10. Firstly, if the regularity of direction of chain folding is weak and sectorization is not very pronounced, crystals are expected to be planar with a uniform direction of chain tilting (parallel to the *a*-axis for PVDF), as shown in Fig. 10a. For the crystal in an early stage, the formation of a chair crystal in the later stage will be the natural consequence of the development of distinction of sectors. For the transformation of the crystal to the hollow pyramidal type, half the crystal needs to be reversed and the process will need a large plastic deformation and will experience resistance in a viscous polymer liquid. This will be the case in pure PVDF and the 30/70 blend. On the other hand, if the steric problem at the fold surface is less significant, chains in the crystal need not be tilted, as shown in Fig. 10b. In this case, the development of distinction of sectors will result in the formation of hollow pyramidal type and chair type with almost equal probability. Thirdly, if the distinction is developed in the early stage, both types of

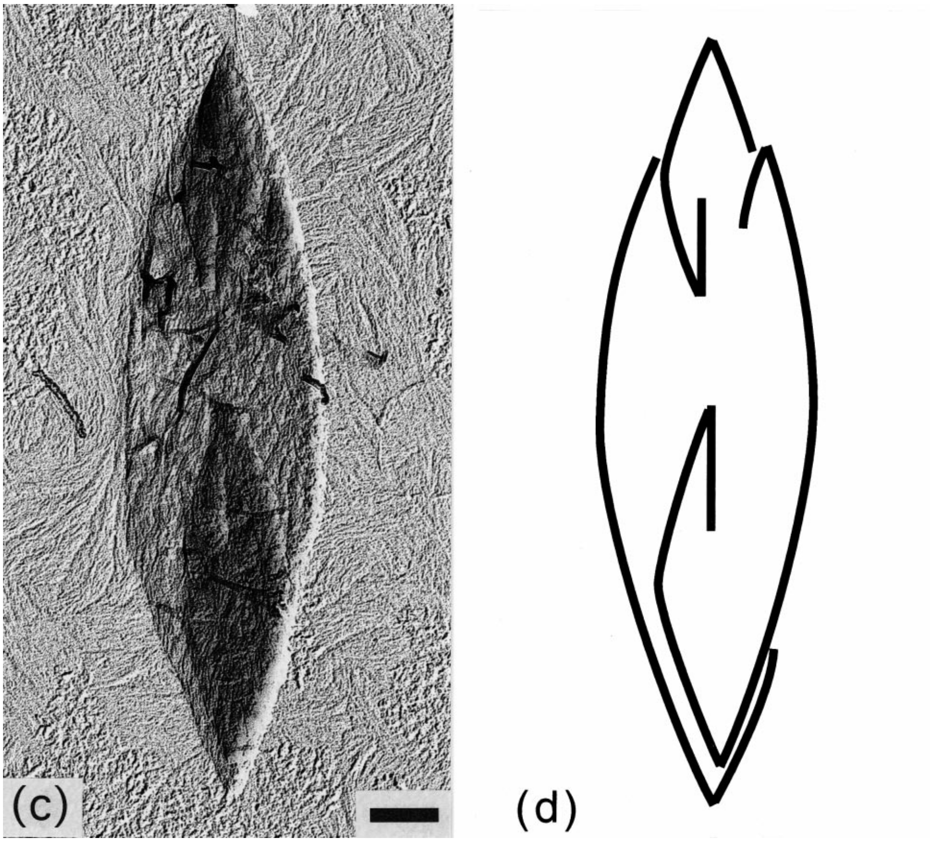
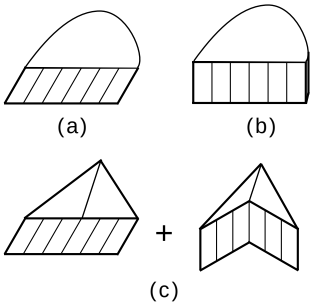


Fig. 9. (*continued*)

crystals will be formed from the beginning (Fig. 10c). For the 0.5/99.5 blend, because of the low concentration of PVDF molecules in the blend, the regularity of chain folding will be better than those of the 30/70 blend and pure PVDF even in the early stages of growth. Then, the second and third cases will correspond to the crystals from the 0.5/99.5 blend. Even for the first case, since the transformation process will be easier for the less viscous 0.5/99.5 blend, the hollow pyramidal type may be obtainable.

The different mechanisms for the twisting relationship in banded spherulites of PVDF (chair crystal) and PE (KP crystal) also needs explanation. The most distinctive difference in the growth will be a much faster growth rate for PE than PVDF in the temperature range where banded spherulites are formed. The stress disparity on the fold surfaces proposed by Keith and Padden [10] is developed for a kinetic reason, and hence the mechanism will be more effective with a faster growth rate. It may also be possible to experience the crossover from chair crystal to KP crystal in PVDF by lowering the crystallization temperature, with faster growth. If this is the case, we will be able to observe a morphological indication of the crossover in banded spherulites, which has not been observed. The nonoccurrence of crossover will also be supported by the fact that the cross section of banded spherulites is not S-shaped even in the ordinary temperature range of growth [35].



It is still unclear why chair crystals of PE do not form banded spherulites. For PE, KP crystals of relatively higher molecular weight do not form banded spherulites either. It is therefore inferred that the formation of banded spherulites needs not only the twisting relationship of crystallites in the radial direction but also coordination in the tangential direction, the mechanism of which is still an open question.

Fig. 10. Schematic representation of three possible cases in the early stages of growth: (a) uniform chain tilting without well developed sectorization, (b) chains normal to the fold surface without sectorization, and (c) coexistence of hollow pyramidal type and chair type with well developed sectorization.

## 5. Conclusion

By examining the three-dimensional shape of PVDF single crystals, we have demonstrated that the twisting relationship in banded spherulites of non-chiral polymers can be introduced by chair crystals in PVDF as well as KP crystals in PE. In both cases, not only the twist of lamellae but also the consecutive creation of spiral terraces can be expected; the essential ingredient in these models is the chain tilting to the fold surface. Fast growth of PE crystals is exceptional among polymers, and it is probable that the chair crystal is a more common origin of the twisting relationship in banded spherulites of non-chiral polymers with chain tilting.

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