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Direct observation of the deformation of isolated huge spherulites in isotactic polypropylene

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In situ observation of the uniaxial deformation of isolated individual large spherulites of isotactic polypropylene was performed using films with a few large spherulites embedded in a smectic matrix. The effects of the variation of sign of birefringence in spherulites, which reflects the difference in lamellar morphology within spherulites were examined. In the case of a spherulite with few tangential lamellae, arcshaped cracks appear in the polar zone of the spherulite and then the radial craze-like fracture begins in the equatorial region perpendicular to the stretching axis. In the case of a spherulite with a large number of tangential lamellae, however, the radial crazing appears in the equatorial zone and then straight dark cracks, rather than arcs, running perpendicular to the stretching direction are initiated in the polar region. These results can be explained by considering the mechanical anisotropy in polypropylene lamellae.

1. Introduction

The direct observation of morphological changes induced by the deformation is one of the most important subjects of crystalline polymers such as polyethylene and isotactic polypropylene (PP) for understanding the deformation process [1–3]. A spherulite is the typical superstructure of crystalline polymers in which the crystalline lamellae, composed of folded chains, radiate from its center and amorphous regions exist in the interlamellar regions. Fortunately, a method for preparing films having isolated huge spherulites dispersed in the soft matrix of PP has been established. This enables the direct observation of the deformation and rupture of individual PP spherulites. As is well known, the structural features of PP are highly dependent on the thermal pre-and post-history of the sample. In the case of PP, the difference in lamellar arrangement within a spherulite can be easily identified by the sign of birefringence of spherulites at the level of polarized optical microscopy (POM) [4]. The present work concerns the observation of the deformation process of isolated huge spherulites and particular attention is paid to the effects of the variation of sign of birefringence, which reflects the difference in lamellar morphology within spherulites, during uniaxial deformation.

2. Experimental

The polypropylene used in this study was a commercial grade supplied from TOSOH Corp. (molecular weight $M_w = 260$ K, and $M_w/M_n = 5.7$). Film specimens with a few large spherulites embedded in a soft PP matrix were obtained by pressing the molten sample at 210°C between two aluminum plates and then crystallizing it isothermally, followed by rapid quenching in iced water.

In this work, two types of films were used: one film with negative spherulites was prepared by keeping it at 130°C for 10 min and another film with mixed spherulites of negative and positive sign was prepared by crystallizing it at 145°C for 4 h. The spherulites were observed directly using a transmission optical microscope (Olympus BX-50). The optical character, i.e., the sign of birefringence of the spherulites could be determined by means of a primary red filter (λ-plate) located diagonally between crossed polarizers. The thickness of the samples was around 50 μm.

For direct observation of spherulite deformation, a specially designed tensile testing device was mounted on the stage of the microscope. The clamps to which a film was attached could be manually displaced by means of a screw. At any level of stretching, the clamp could be held stationary so that the deformed spherulite could be observed.

3. Results

Using a polarizing microscopy, the pattern of a spherulite shows a central dark cross (Maltese cross)

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with wings coincident with the respective planes of polarizer and analyzer. The optical character was distinguished using a polarizing optical microscope with a λ-plate. On a spherulite disc, the first and third quarters of the spherulite image are yellow and the second and fourth ones are blue for negative spherulites, while a reversed arrangement of the quarters is observed for positive spherulites.

According to the structural feature of typical spherulites, the molecular chains folded into lamellae are nearly perpendicular to the radius of the spherulites. As the refractive index in the chain direction is higher than the indices perpendicular to the chain direction, the primary lamellae have a negative optical character. The structure of positive and mixed spherulites is interpreted by the formation of a cross-hatched texture consisting of radial (R) and tangential (T) lamellae. The T-lamellae nucleate and grow epitaxially on R-lamellae with a crossing angle of about 80 [5, 6].

The matrix of the films used in this work was soft and transparent. The matrix parts showed two diffuse bands at $2\theta \approx 15^\circ$ and 22° in the X-ray diffractogram, indicating a mesophase structure with intermediate order which is often called smectic [7]. Such a structure is well-known to form on melt quenching. In addition, no spherulites were observed in the matrix by small angle light scattering as well as optical microscopy.

The film crystallized at 130°C has negative spherulites with diameters of about 200 μm embedded in the soft matrix. Fig. 1 shows some stages of deformation in the isolated negative spherulite. In these figures, the microscopic observations were performed between crossed polarizers respectively parallel and perpendicular to the tensile direction. The value of the local longitudinal strain ε was determined from direct measurements of the longitudinal dimensions of the spherulite at each step. As seen in these figures, a few arc-shaped cracks rapidly appear in the polar zone in the initial stage of stretching. With increasing strain, the arc-shaped cracks develop in the polar zone and proceed from the outer to the inner portions of a spherulite. Subsequently, the radial craze-like fracture begins in the equatorial region perpendicular to the stretching axis at around $\varepsilon = 6\%$ and then the radial crazing progressed along with the spherulite radius, resulting in the evolution of the large dark bands in the equatorial region. The dark bands are seen above ca.10% strain, which seems to be almost coincident with the typical yield strain of spherulitic PP materials. These results are consistent with the data previously reported [8–10].

In the case of the mixed spherulite, the radial crazing preferentially appears in the equatorial zone and extends over almost the entire equatorial zone in the initial strain regions as seen in Fig. 2. Then straight dark lines, rather than arcs, running perpendicular to the stretching direction are initiated in the polar region near the spherulite center at 3.7% strain. The straight lines evolve more and more in this region with increasing strain.

4. Discussion

According to Galeski [11], the (110) plane of monoclinic crystals is the growth face at lower supercoolings while at higher supercoolings other planes, including the most probable (040) planes, are the growth faces. This is consistent with the fact that the film prepared at 135°C has negative spherulites having few T-lamellae and the film prepared at 145°C has mixed spherulites having numerous T-lamellae because T-lamellae nucleate only on the surface (040) of lamellae radiating from the center of the spherulite [12]. Thus, in other words, the radial direction of lamellae of the negative spherulite is along the b-axis whereas that of the mixed spherulite is along the a^*-axis.

The important result is that the rupture occurs preferentially in the polar region for negative spherulites and in the equatorial region for mixed spherulites. Before explaining this behavior, the fracture mechanism of crystalline lamellae needs to be considered. It is likely that the strength of lamellae is anisotropic and depends strongly on the axial direction of lamellae. As seen in Fig. 3, when a lamella is uniaxially stretched in the a-axis direction (A-mode), an unfolding process takes place and this leads to a craze-like failure process. When the stress is subjected to the lamellae in the b-axis direction (B-mode), lateral separation between the folding faces composed of (040) planes takes place, leading to the brittle fragmentation due to the weak van der Waals interactions. When stretching the stacked lamellar structure in the chain (c-axis) direction (C-mode), separation of interlamellar amorphous layers occurs, resulting in the strength of lamellae being determined by the cohesive force opposing sliding or pull-out through tie molecules in the amorphous layers. The plastic resistance of the chain sliding or slip motions (C-mode) will be comparable with or slightly greater than that of the lamella unfolding process (A-mode) but both A- and C-modes are much stronger than the separation process between growth planes (B-mode). This is supported by previous observations using POM and SEM [13–15].

It is important to note that the radial crazing process in the equatorial zone can be considered to be associated with the C-mode process for both negative and mixed spherulites. For the negative spherulite, the black arcs initially evolved in the polar zone and then the radial crazing process in the equatorial zone (C-mode) occurs. This is because the growth faces of lamellae of the negative spherulite are predominantly the (040) planes and they are easily ruptured in B-mode. On the other hand, in the case of the mixed spherulite, its polar region is more tough than that of the negative spherulite. Two reasons for the toughened polar region are considered: one is the existence of T-lamellae and the other is that the lamellar growth plane is the (110) plane, which is organized by intrachain folding. In addition, according to experimental [15, 16] and theoretical [17, 18] results, the equatorial region, particularly the center of the spherulite, is subjected to higher strains and stresses as compared with the polar region. Consequently, the rupture occurs preferentially in the equatorial region for mixed spherulites and then the dark straight lines

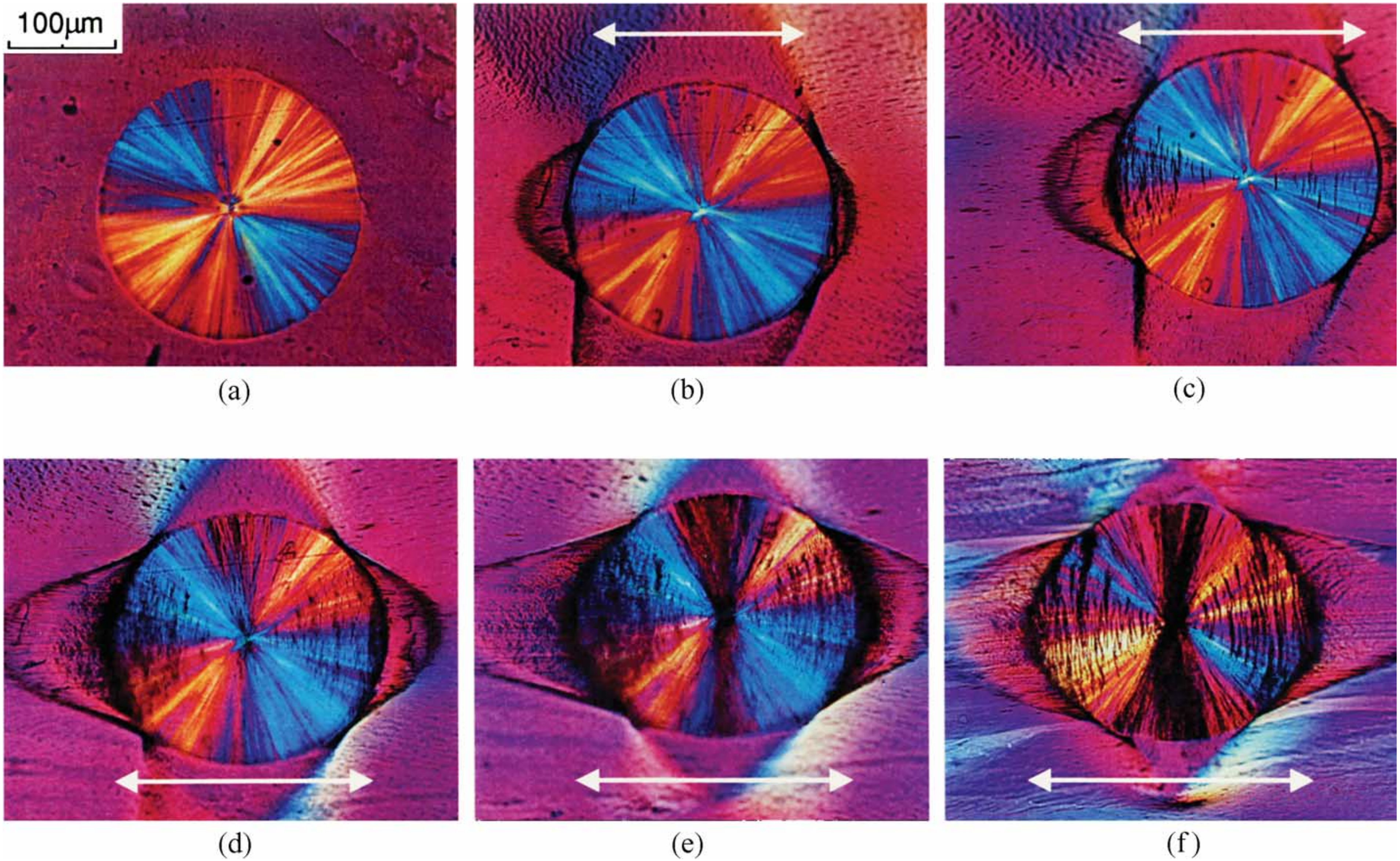

Figure 1 *In-situ* observation of the deformation of a negative spherulite embedded in a smectic matrix of PP. The arrows indicate the stretching direction. For each level of strain, the spherulite was observed with crossed polarizers parallel and perpendicular to the tensile axis. The longitudinal strains were (a) $\varepsilon = 0$, (b) $\varepsilon = 0.021$, (c) $\varepsilon = 0.042$, (d) $\varepsilon = 0.062$, (e) $\varepsilon = 0.101$, and (f) $\varepsilon = 0.12$.

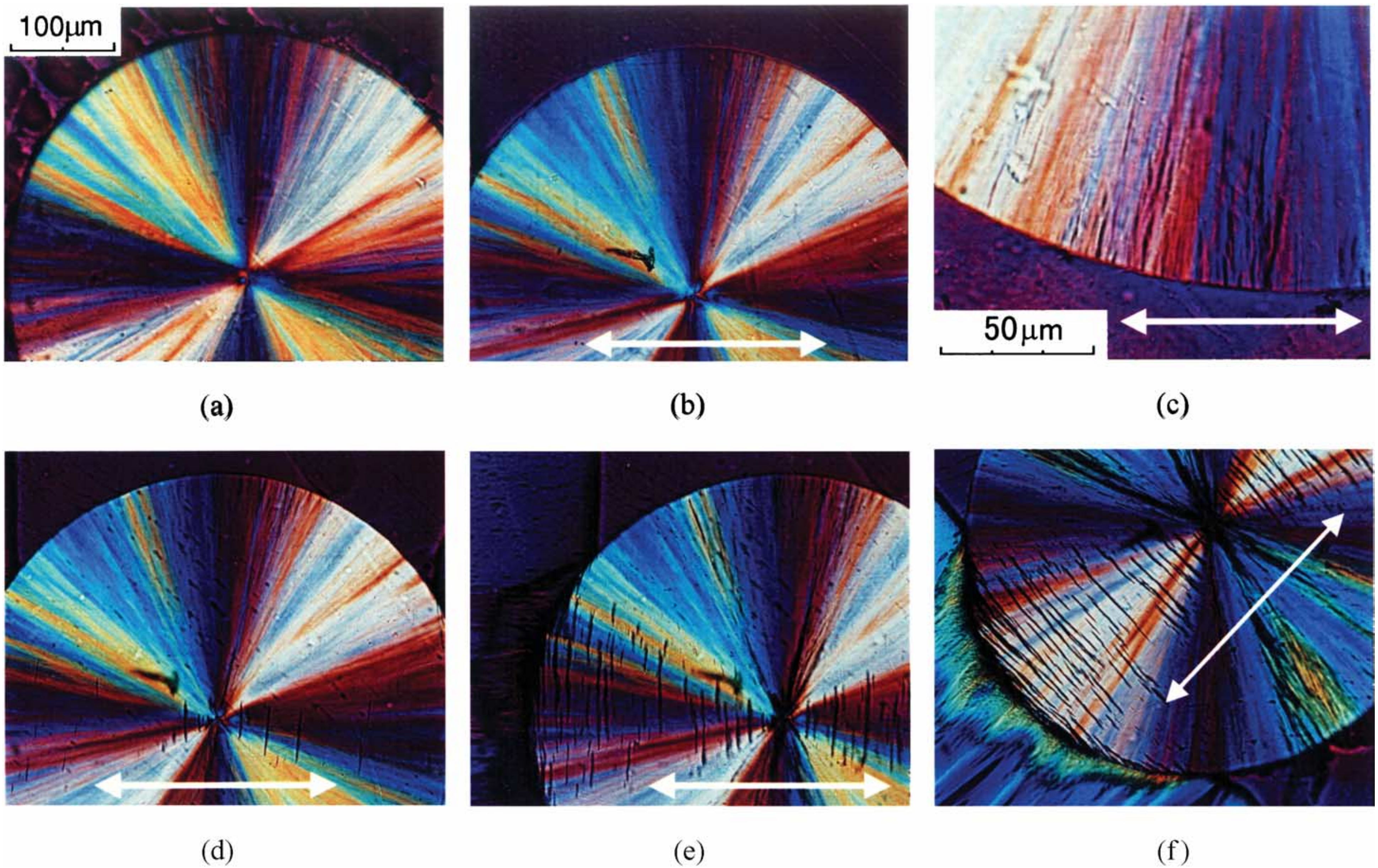

Figure 2 *In-situ* observation of the deformation of a mixed spherulite embedded in a smectic matrix of PP. The arrows indicate the stretching direction. For level of strain, the spherulite was observed with crossed polarizers parallel and perpendicular to the tensile axis for (a–e) and crossed polarizers at 45° to the tensile axis for (f). The longitudinal strains were (a) $\varepsilon = 0$, (b) $\varepsilon = 0.019$, (d) $\varepsilon = 0.037$, (e) $\varepsilon = 0.055$, and (f) $\varepsilon = 0.107$. (c) is a higher magnification image of the equatorial zone in (b).

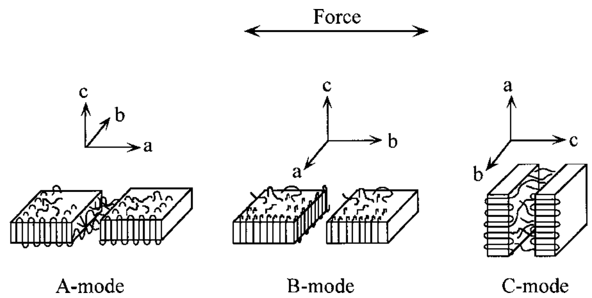

Figure 3 Schematic illustrations of the fracture modes of lamellae.

perpendicular to the strain direction appear in the polar regions.

It has been long recognized that the deformation of crystalline polymers must be considered in terms of various structural factors such as crystallinity, lamellar thickness or long period, spherulite size, and T-lamella content. However, the present study newly demonstrates that the mechanical behavior of bulk PP materials are affected not only by these structural factors but also by the deformation or destruction process caused by the morphological features within spherulites.

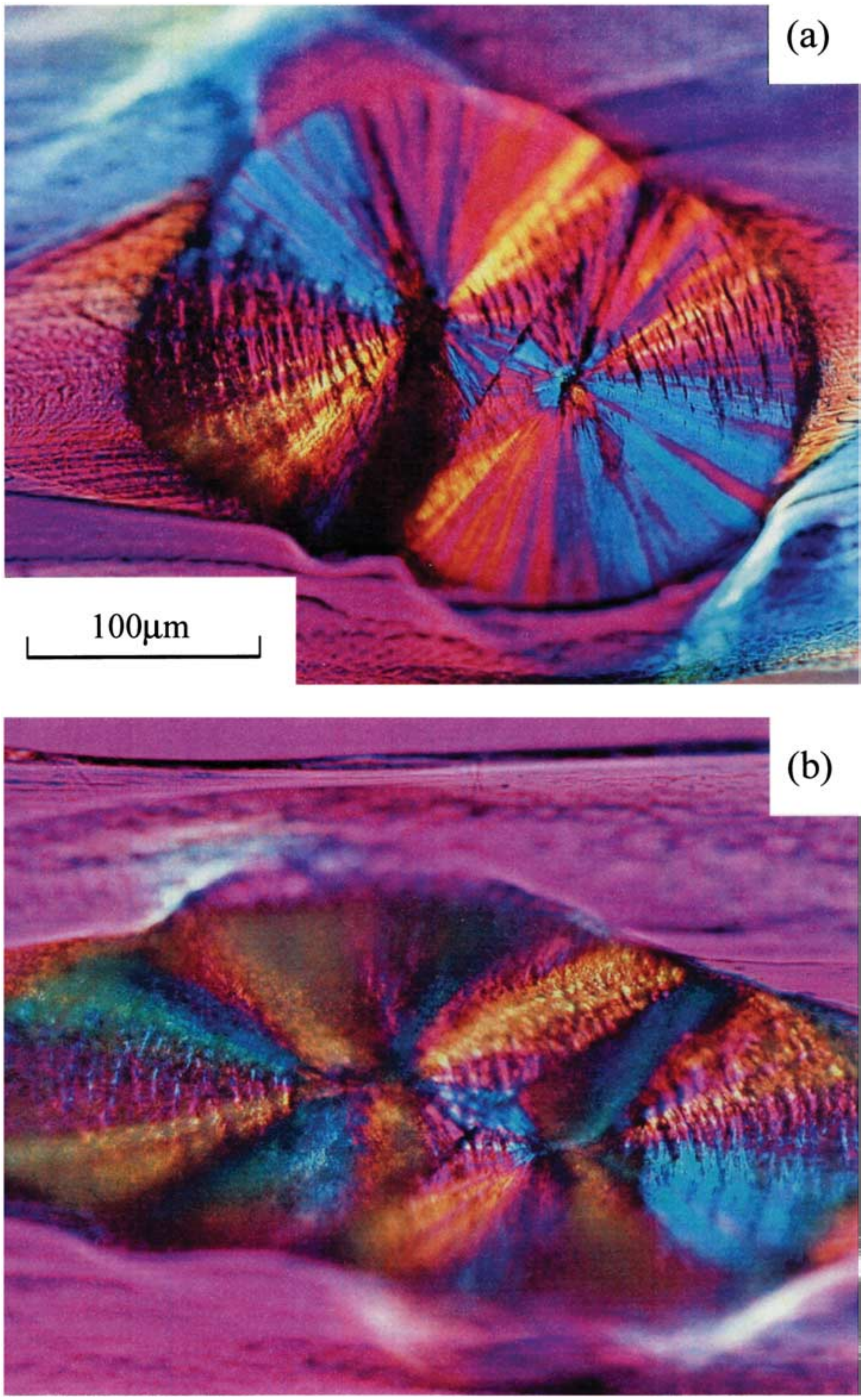

Figure 4 *In situ* observation of the deformed double spherulites at (a) a lower strain level and (b) a higher strain level.

Finally the results relating to the strength of the spherulite boundary are described below. In order to compare the strength of the spherulite boundary with that of spherulite interior, the deformation of the adhesive double spherulites, which evolved in the film with negative spherulites, was investigated. As shown in Fig. 4, the double spherulites elongated more and more in the stretching direction, and the line of the spherulite boundary remains despite a number of cracks appearing within both spherulites. The pictures in Fig. 4 clearly indicate that the boundary of adjacent spherulites is stronger than the inside of the spherulites.

5. Conclusions

In the case of negative spherulites with few tangential lamellae, arc-shaped cracks appear in the polar zone of deformed spherulites and then the radial craze-like fracture occurs in the equatorial region. Conversely, in the case of the mixed spherulite with a large number of tangential lamellae, the radial crazing appears in the equatorial zone and then linear cracks running perpendicular to the stretching direction occur in the polar region. These results demonstrate that the radial direction of lamellae of the negative spherulites is along the *b*-axis whereas it is along the a^*-axis in mixed spherulites. The difference in failure process between negative and mixed spherulites can be explained by considering the anisotropy in strength of crystalline lamellae.

Most previous studies have concentrated on the mechanical properties of bulk PP spherulitic materials, and little effort has been made to directly investigate the deformation mechanism of PP spherulites. In this work, *in-situ* deformation of isolated PP spherulites has been observed and the results provide important information that can lead to an understanding of mechanical properties of bulk PP materials.

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