Morphology of iPP Spherulites Crystallized in a Temperature Gradient

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ABSTRACT: The influence of temperature gradient on the lamellar structure of isotactic polypropylene spherulites was studied. Polypropylene films were crystallized in a constant temperature gradient of 35 K/mm with the free surface and studied by means of atomic force microscopy and scaning electron microscopy. Samples crystallized isothermally were also prepared and examined for comparison. The results show that the temperature gradient influenced only the alignment of lamellae within spherulites. The lamellae deviated from a radial direction in a stepwise manner. The lamellae became less and less inclined and finally assumed a direction parallel to the temperature gradient. The change of the lamellae alignment in spherulites was the result of the competition of lamellae to fill the space during growth in the temperature gradient. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 1318–1328, 2002

Key words: crystallization; isotactic poly(propylene); lamellae; spherulites; temperature gradient

INTRODUCTION

The spherulitic and lamellar structures of isotactic polypropylene (iPP) have been studied intensively in the past.[1–7] The studies concentrated primarily on structures formed during crystallization in isothermal conditions. Details of lamellar arrangement in spherulites were disclosed by electron microscopy and atomic force microscopy (AFM) of etched samples. In the α form of iPP, in addition to the long radial lamellae (R-lamellae), the short tangential lamellae (T-lamellae) at an angle of 80° grow epitaxially on the lateral (010) planes of R-lamellae. This crystallographic branching leads to the crosshatching phenomenon. The decrease of crosshatching with the elevation of crystallization temperature is reflected in the spherulite birefringence changing from positive to negative. In addition to the α form, some negatively birefringent β form spherulites, composed of R-lamellae only, were observed in iPP samples crystallized below 140°C. IPP crystallizes in the γ phase only in special conditions, such as crystallization under elevated pressure or crystallization of short molecular chains.[8,9] Also the irregularities of polypropylene chains promote the crystallization in the γ form.[10,11] Lotz et al.[8] observed that tilted γ lamellae can branch from flat-on α-phase crystals. Mezghani and Phillips[9] showed that iPP crystallizes under elevated pressure in the γ-form positively birefringent spherulites, composed of feather-like structures radiating from spherulites centers. The individual γ lamellae inclined at an angle of 70° to the radial direction are supposed to grow epitaxially on earlier formed γ lamellae or on α R-lamellae.

The crystalline forms of iPP can be clearly distinguished by X-ray diffraction. Other techniques, such as Raman[12] and IR spectroscopy,[13] can also be used for this purpose to some extent.

In industrial processes, temperature depends not only on time but also on the position within a bulk of polymer. Hence, the polymer solidifies in a time-dependent temperature gradient. The studies of the influence of the temperature gradient on polymer structure have been concerned primarily with zone-solidified polymers, with iPP among them.[14–21] The zone-solidification technique is based on local melting of the sample. The narrow, molten zone with a steep temperature gradient moves along the sample, establishing the crystallizing front. The motion is slow (e.g., 3 μm/min[17]), which allows for a constant temperature at the crystallization front. Fujiwara[15] and Crissman[16] directionally solidified iPP from the melt and studied its structure by X-ray diffraction and mechanical relaxation. The investigations of iPP by Lovinger et al.[20]

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were aimed at studies of β crystalline form; nevertheless, some other observations concerning the structures crystallized in the temperature gradient were made. The anisotropy of spherulite growth, the quasiparabolic shapes of interspherulitic boundaries, and also the change of lamellae growth trajectories in the motion direction were revealed by means of light microscopy. Schulze and Naujeck[22] predicted the spherulite shapes and growth trajectories in a unidirectional temperature field based on the assumption of minimum growth time along each trajectory, and they confirmed the predictions experimentally by light microscopy studies of the growth of iPP spherulites in a temperature gradient. Swaminarayan and Charbon,[23] who conducted a computer simulation of the R-lamellae growth and their branching in a temperature gradient, pointed out that the lamellae branching and selection of the fastest path was the reason for the nonradial lamellae alignment. Pawlak and Piorkowska[24] studied the crystallization of iPP films by light microscopy in a constant temperature gradient up to 37 K/mm. The temperature gradient affected both the formation and the final shape of the spherulitic pattern. It resulted not only in the anisotropy of spherulites shapes but also in nonradial trajectories of the growth. They bent toward the hotter side of a sample until the direction parallel to the temperature gradient was reached. The changes were enhanced by a steeper temperature gradient, and they were also more pronounced at a higher temperature. As in the other studies, it was demonstrated by Pawlak and Piorkowska[24] that the direction of lamellae growth is always normal to the growth front. Spherulites nucleated in the colder part of a sample grow toward the hotter side, where spherulite nucleation is weaker. It results in the structure containing elongated (300–400 μm long) spherulites, forming a joint, flat crystallizing front composed of nearly parallel lamellae.

Lovinger and Gryte[18] explained the curvature of growth trajectories of spherulites in the temperature gradient as the result of the bending of lamellae similar to the lamellar twist that has been observed in banded spherulites. The second explanation for the mechanism of the change of lamellae growth direction in a temperature gradient was also offered in ref. 18: within the stacks of lamellae inclined to the temperature gradient, the lamellae grow at different velocities. Thus, the angle between the lamellar growth front and the direction of lamellar growth decreases continuously. During further growth, the branches of lamellae are preferred that are normal to the growth front. This results in a progressive stepwise change in the growth direction of the entire lamellae stack in a cooperative manner. These explanations of possible mechanisms for the change in lamellae growth directions were based on the examination of spherulite morphology by light microscopy. When those hypothesis were formulated, it was believed that the adjacent lamellae growth faces form a planar surface. The electron microscopy studies of the morphology of etched polyolefins have shown[4] that spherulites are built on a skeleton of individual branching and diverging dominant lamellae. This finding undermines the credibility of the mechanism proposed in ref. 18.

The mechanism of the change of the lamellae growth direction due to the temperature gradient cannot be fully understood without deeper morphological studies; the resolution of polarizing light microscopy employed so far is not sufficient for the observation of individual lamella and the details of spherulite architecture. Although Lovinger et al. applied electron microscopy to zone-crystallized poly(oxyethylene) spherulites, this was done only to the region with lamellae parallel to the temperature gradient.[19] AFM was employed by Pawlak and Piorkowska[24] to study gradient crystallized iPP spherulites but only at low magnification, not suitable for the detailed examination of lamellar structure. The morphology of a crystalline polymer solidified during processing, that is, in a nonuniform temperature field, was also studied and reported in the past.[25] However, the complexity of thermal and mechanical conditions during processing made it difficult to draw decisive conclusions on the influence of a temperature gradient on the resulting lamellar morphology.

This article is devoted to studies of the morphology of iPP spherulites crystallized in a constant temperature gradient by means of microscopy with higher resolution. Special attention was paid to the mechanism of lamellar deviation from a radial direction and bending toward the higher temperature side.

Thin films of iPP were crystallized with a free surface in a constant temperature gradient. Their surfaces were examined by light microscopy, AFM, and scanning electron microscopy (SEM). We also employed other techniques, such as X-ray diffraction and micro-Raman spectroscopy, to characterize the samples. For comparison, isothermally crystallized iPP films were also examined. The results allowed us to reveal the mechanism of the change of lamellar alignment caused by the temperature gradient.

EXPERIMENTAL

The iPP used in this study was a Polysciences (Warrington, PA) product, having a weight-average molecular weight (M_w) of 220,000 and a number-average molecular weight (M_n) of 40,000 (iPP1). Occasionally, samples of Polysciences iPP with a M_w of 220,000 and a M_n of 17,000 (iPP2) were also prepared and examined. The crystallization of iPP1 in the form of 10–12 μm thick films was carried out in a temperature gradient on a hot stage constructed for this purpose and described earlier in ref. 24. The stage comprised two parallel positioned copper blocks with built-in heaters and resistance platinum thermometers connected to two programmable temperature controllers (Cole Parmer 535 process controllers, Vernon Hills, IL). The blocks were placed inside an aluminum cell with glass windows, mounted on the stage of a polarizing microscope (PZO, Warsaw). The controllers enabled temperature control of each block independently with an accuracy of 0.1 K. A gaseous nitrogen flow through the cell protected samples from degradation. A Panasonic BL 202 camera, connected to a video recorder and personal computer made it possible for us to observe spherulite growth and to record images.

The films obtained by compression molding, placed on 5 mm × 5 mm cover glasses, were positioned on the top of the copper blocks, bridging them. To improve the thermal contacts between the lower glass and the blocks, we applied a thin layer of a special paste (Omega Engineering, Inc., Stamford, CT) having heat conductivity of 2.3 W/(m K). iPP films with free upper surfaces were heated up to 220°C, melt-annealed for 5 min, and then cooled at a rate of 25 K/min to a final constant temperature of 170°C for the left block and 100°C for the right block. The distance between the blocks was 1050 μm. A detailed description of the determination of temperature distribution in iPP2 film crystallizing in such conditions is given in ref. 24. In this study, the entire procedure was also performed for iPP1.

The growth rate of iPP1 spherulites was measured during isothermal crystallization in the broad temperature range on a Linkam (Waterfield, UK) hot stage. The constants of the Hoffman equation,[26] g_o and K_g, for regime II and regime III and the temperature of transition between the regimes were determined. During the crystallization in the temperature gradient, the spherulite growth rate was measured on short distances in the direction normal to isotherms and converted to temperature with the help of the growth-rate temperature dependence. The accuracy of local temperature determination was ±0.25 K. As was already demonstrated in ref. 24, the conditions of crystallization chosen for this study led to a constant temperature gradient of 35 K/mm across the sample, except for the narrow regions directly adjacent to the blocks. Thus, a precise constant temperature could be ascribed to each position on the bridging glass.

An additional check of the temperature distribution across the glass bridging the blocks was performed by an estimation of the position of isotherms of the melting temperature (T_m) of three low molecular substances [benzanilid (T_m = 164.2°C), phenacetin (T_m = 135.5°C), and acetanilid (T_m = 115.3°C)] with sharp melting points, determined during heating in a differential scanning calorimetry apparatus and in a Linkam hot stage during heating at the rate of 2 K/min. The obtained results confirmed the temperature distribution obtained by the measurements of the growth rate of iPP spherulites.

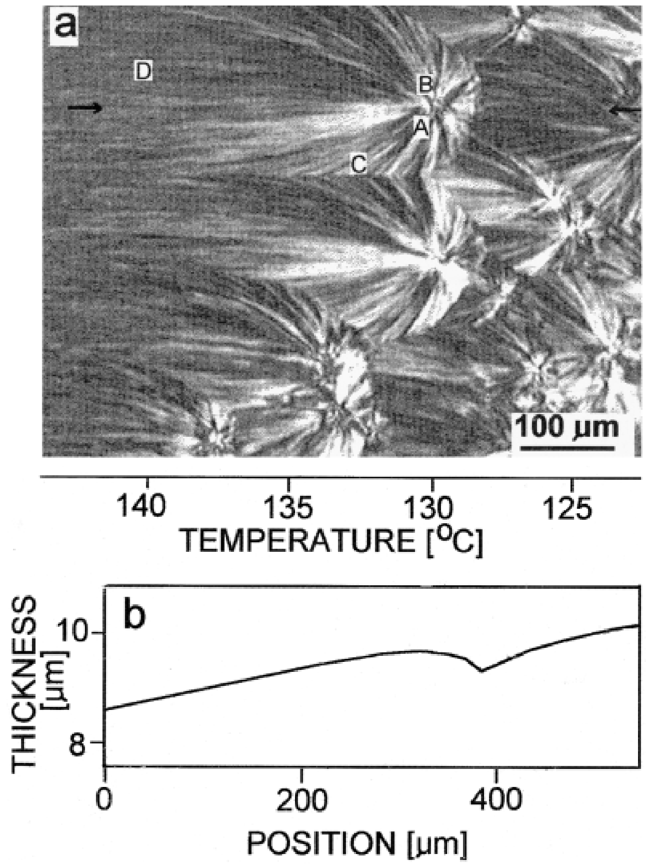

Figure 1 (a) Light micrograph of the spherulitic structure of iPP (Polysciences; M_w = 200,000, M_n = 40,000) film crystallized in a temperature gradient of 35 K/mm. (b) Thickness profile of the film, measured along the line indicated in part a by the arrows.

The isothermally crystallized iPP1 films with free upper surfaces were also prepared for comparison with the gradient-crystallized samples. In this case, both blocks were cooled down at a rate of 25 K/min to the same temperature of 130 or 140°C, at which the crystallization was conducted.

Surfaces of the films crystallized in the temperature gradient of 35 K/mm and crystallized isothermally were examined with an atomic force microscope (Nanoscope III, Santa Barbara, CA). All the scans were performed in air at a scanning frequency of 1 Hz in the tapping mode, with a resonance frequency of 280 KHz The silicone tip (Olympus, Tokyo) had an initial radius of curvature of 15 nm. The amplitude and height images were registered. Height images were used for the determination of structure element dimensions.

A scanning electron microscope (JEOL 5500 LV, Jeol Ltd., Akishima, Tokyo) was also used for the examination of the microstructure of the films that were earlier coated with gold.

The surfaces of iPP1 films were examined by Raman spectroscopy. A microspectrophotometer (The Raman

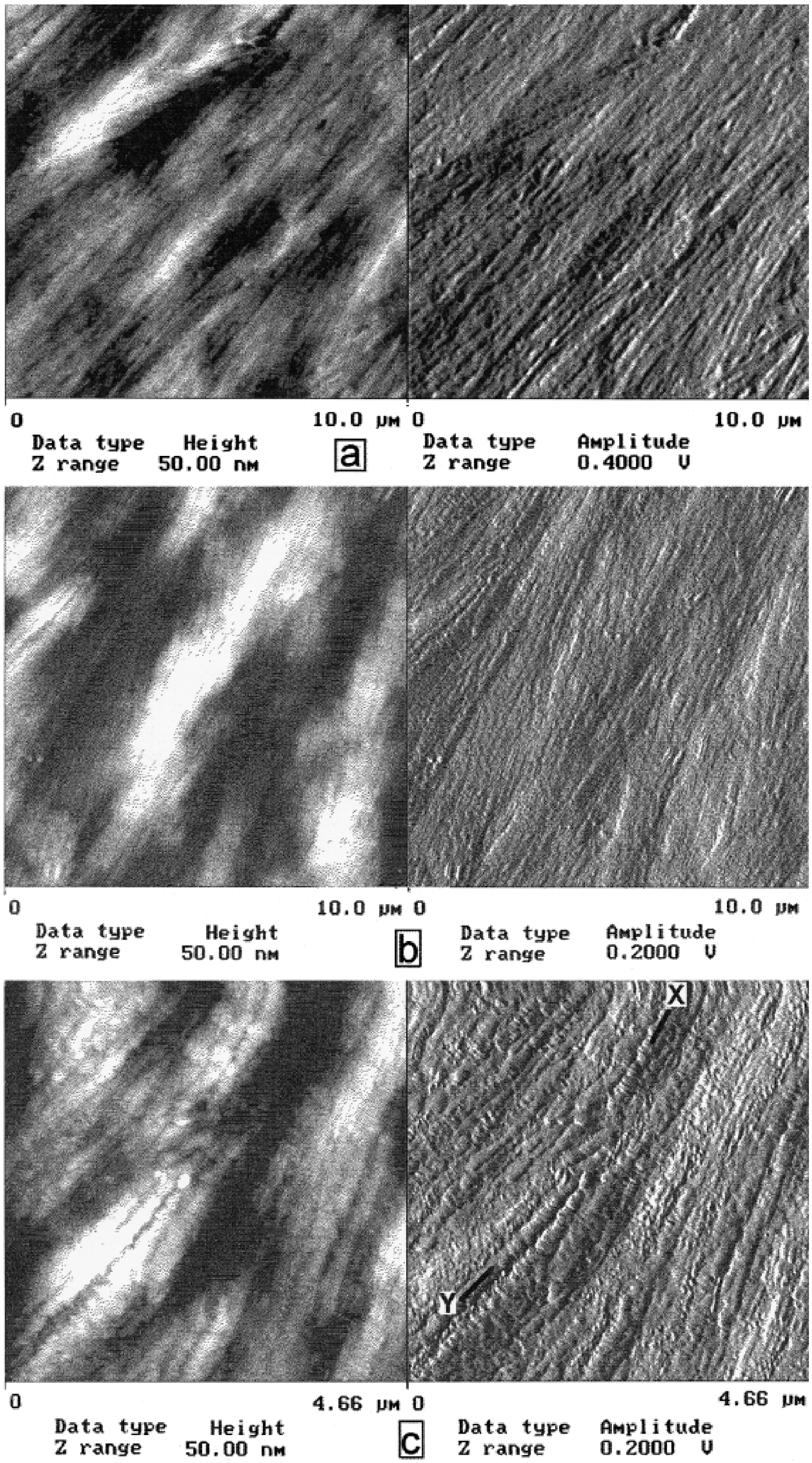

Figure 2 (a,b) AFM images of the region marked by A in Figure 1 and (c) detail of part b.

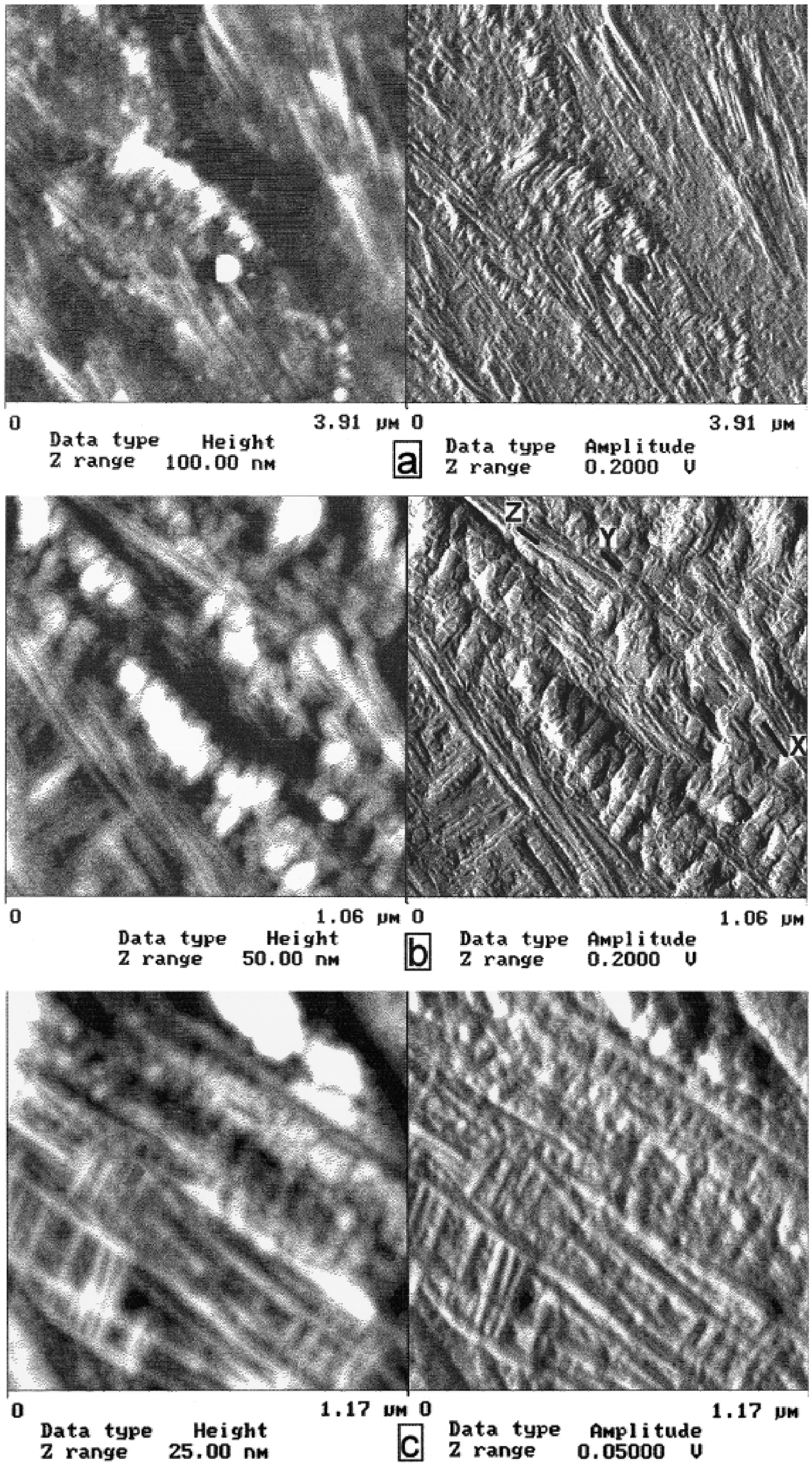

Figure 3 (a) AFM image of the region marked in Figure 1(a) by B, (b) detail of part a, and (c) detail of crosshatching.

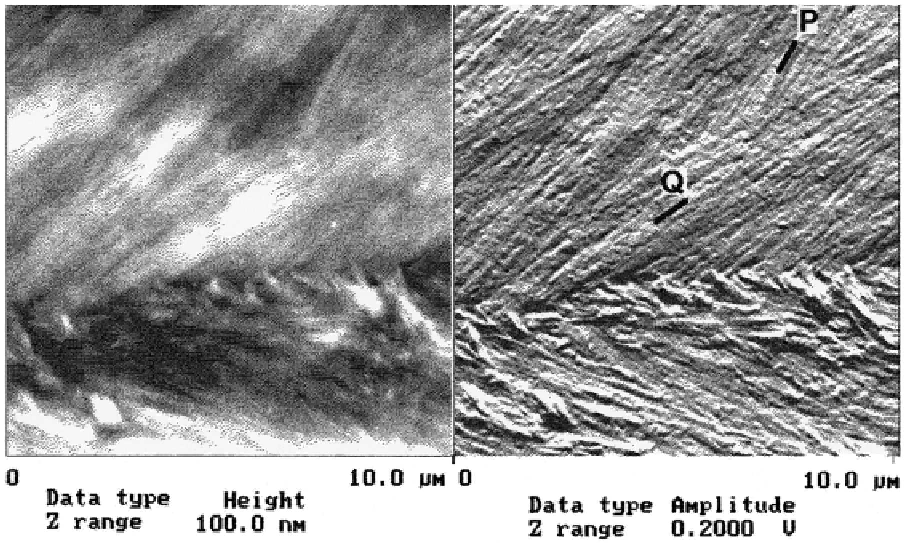

Figure 4 AFM image of the region marked in Figure 1(a) by C.

System T6400, Jobin-Yvon/SPEX, Longjumeau, France) with confocal optics was used for the detection of spectra in the range of 2650–3150 and 1000–1500 cm^{-1}. The signal was collected from an area of 2 μm × 2 μm, with a depth of penetration 2.5 μm. An argon laser with power of 200 mW at an excitation wavelength of 488 nm was the source of light. The 3 samples crystallized isothermally at 130°C and 12 samples crystallized in the temperature gradient were examined. In the latter case, the spectra were collected along the line parallel to isotherms in the region crystallized approximately at 140–141°C.

The wide angle X-ray diffraction of the high-temperature part of the gradient-crystallized iPP1 film was also performed. A wide-angle X-ray scattering system consisting of a computer-controlled wide-angle goniometer coupled to an X-ray generator operating at 30 kV and 30 mA (Cu Kα radiation filtered electronically and by a Ni filter) was used. A range of 2θ between 12 and 24° was selected for the identification of the crystalline forms of iPP1. The examined area was limited to a 0.3 mm wide stripe, selected by a 0.3 mm × 2.0 mm slit opening in a brass plate.

RESULTS AND DISCUSSION

The typical spherulitic structure of the iPP1 film crystallized in a temperature gradient of 35 K/mm is shown in Figure 1(a). As was similarly observed for iPP2 in ref. 24, the iPP1 spherulites in gradient-crystallized films were predominantly of the α crystallographic form with β-form spherulites visible only sporadically. The spherulites seen in Figure 1(a) were elongated in the direction of the temperature gradient, and they reached a length of 300–400 μm. As we determined by focusing the light microscope on the surface of the film, the thickness of spherulite changed slightly with increasing distance from its center [see Fig. 1(b)]. Initially, it was caused by the pulling of some material by crystallization forces on top of the film, which caused thickening of the film near the spherulite center. Further thinning of the film resulted from volume contraction during crystallization and from the transport of melt material toward the crystallization front.

The change in the direction of lamellar alignment within spherulites is clearly visible in Figure 1(a). The lamellae bent toward the hotter region of the film. On the left side of Figure 1(a), only the lamellae parallel to the temperature gradient direction are discernible.

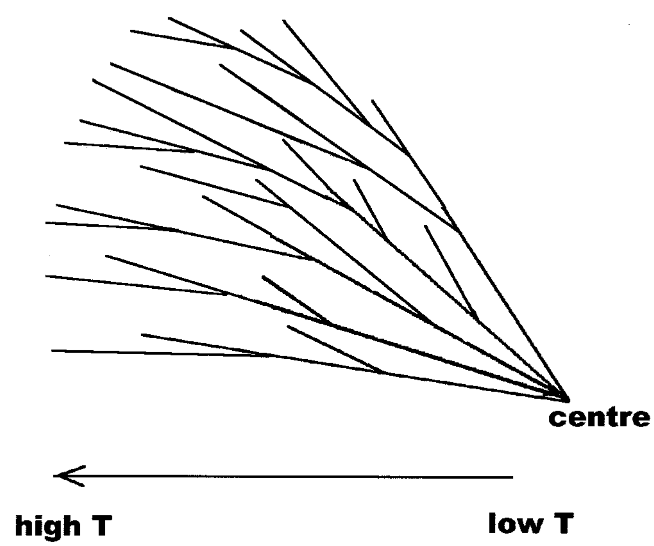

Figure 5 Scheme of the lamellar growth paths in a spherulite crystallized in temperature gradient.

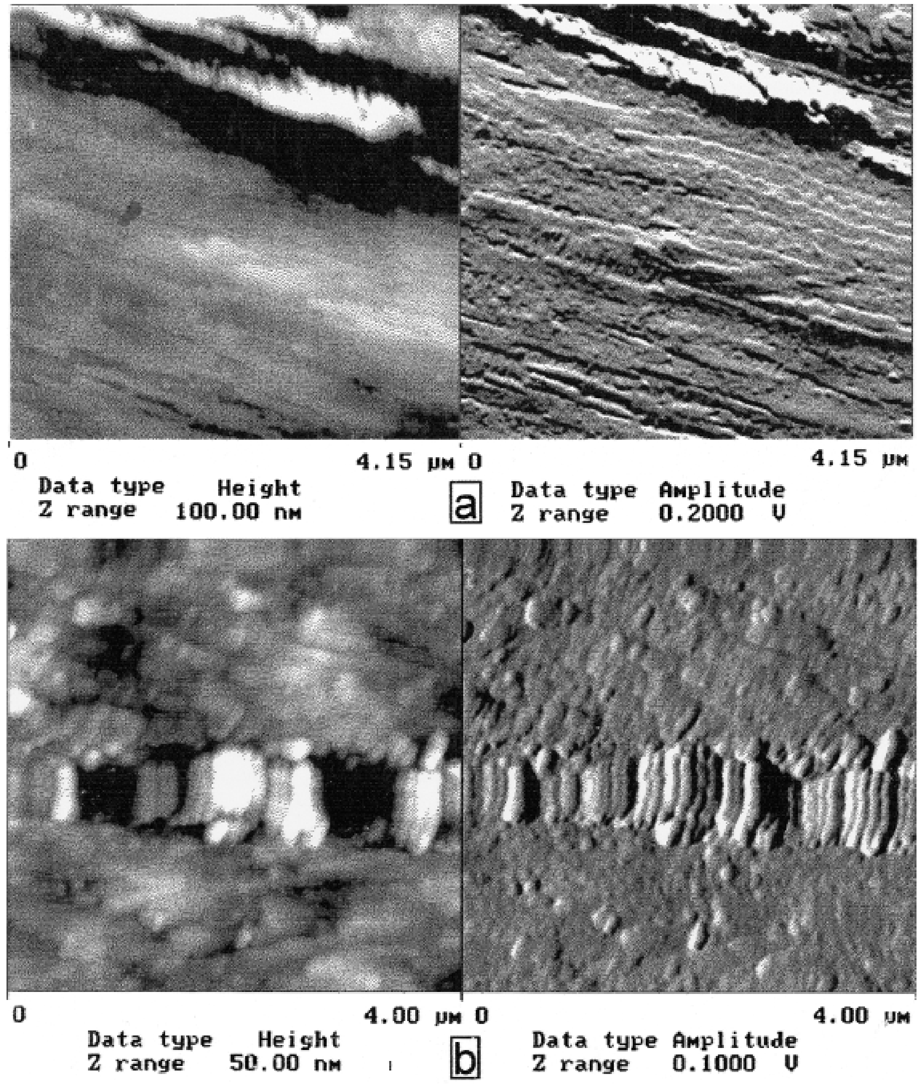

Figure 6 AFM images of the region marked in Figure 1(a) by D and (b) details of the stack of plate-like T-lamellae in the high-temperature region of the gradient-crystallized sample of iPP1.

Preliminary AFM examination of films crystallized in the temperature gradient showed the gradual change of morphology with the crystallization temperature. The change of the lamellar direction visible in a light microscope seemed to be a continuous process leading to curved-shaped lamellae, but detailed AFM images did not support this impression. Figures 2–4 show series of the AFM images in the regions marked in Figure 1 by A, B, and C, in which a pronounced bending of lamellae was observed in the light microscope. Nevertheless, in Figures 2–4, only straight lamellae are discernible, however, differently inclined to the temperature gradient, that is, to the direction of the fastest temperature increase. The change in the direction of lamellae occurred in a stepwise manner. This is clearly recognizable in Figure 2(b) and also in Figure 2(c), where the angle between the lamellae alignment directions X and Y equals approximately 14°. Figure 3(b) illustrates the details of the stepwise change of the lamellar orientation toward the direction of the temperature gradient: the angles between lamellae Y and X and between lamellae Z and Y are nearly 12 and 14°, respectively. The change in lamellae direction occurred twice (from X to Z) over the distance of only 1 μm.

In Figure 2(a), the differently oriented stacks of R-lamellae are within a close distance. Some of them vanished instead of changing the direction of growth in a cooperative manner, as suggested in ref. 17. The termination of lamellae was frequently seen on the impingement with lamellae stacks inclined to the temperature gradient at smaller angles, which extended from the colder region of the spherulite. This is also clearly visible in Figure 4, which shows the vicinity of the boundary between spherulites in the region marked in Figure 1(a) by C. Within the upper spherulite, the lamellae were differently oriented: the angle between the directions P and Q equaled 24°. The ex-

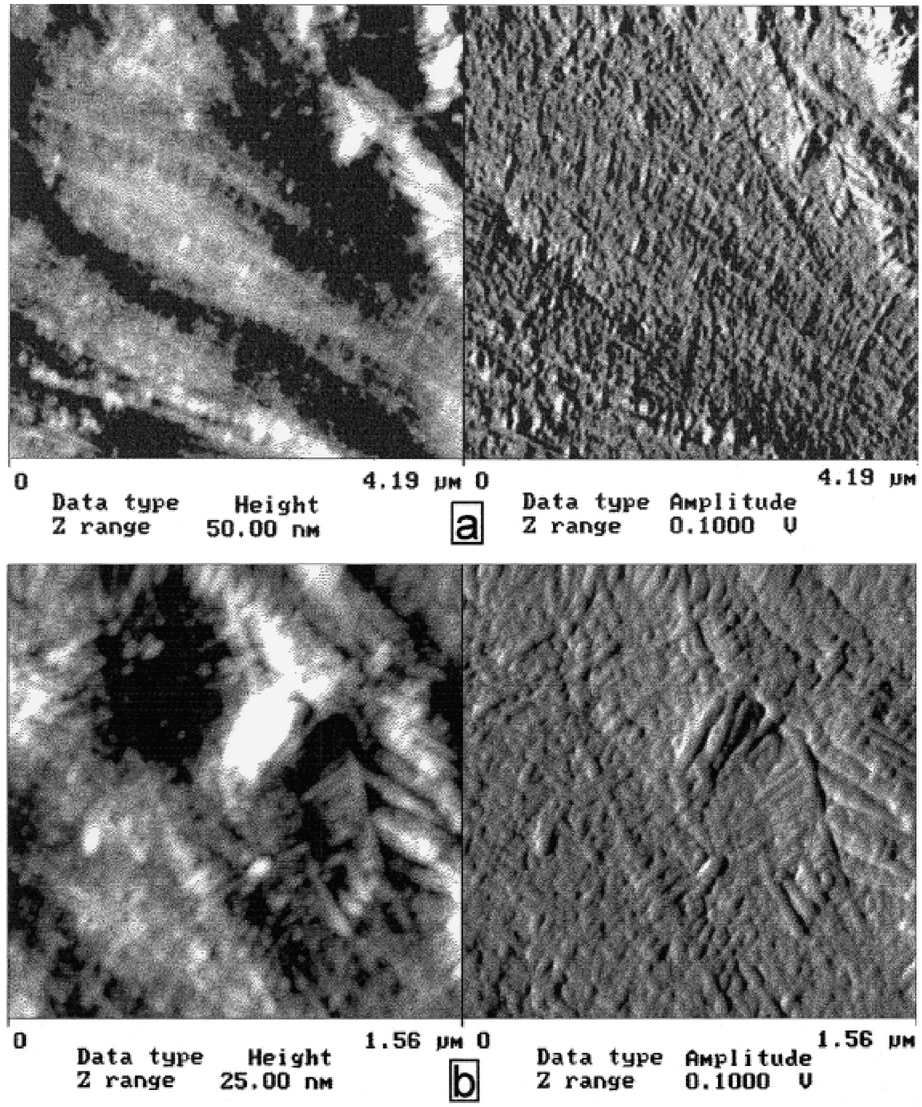

Figure 7 AFM images of the film of the iPP1 crystallized isothermally at 130°C: (a) overview and (b) detail.

tension of lamellae in the direction of P was inhibited by the lamellae propagated in the direction Q, inclined to the temperature gradient at a smaller angle.

New directions of the lamellar growth within a spherulite originated from noncrystallographic lamellae branching at low angles. It follows that the mechanism of the gradual change in the growth direction being the result of a preferred orientation normal to the growth front, as suggested by Lovinger and Gryte,[17] was an oversimplification. The growth trajectories normal to the growth front, as visible in a light microscope, emerged as a result of the competition between growing and branching lamellae. The R-lamellae filled the spherulite by splaying and repeated noncrystallographic branching at low angles. The growth along paths inclined to the temperature gradient at larger angles was restricted by other lamellae arriving from the spherulite colder side. Thus, the lamellae could propagate from the considered part of a spherulite more freely only at smaller angles to the temperature gradient, as is schematically drawn in Figure 5. This mechanism was probably enhanced by more frequent noncrystallographic branching at lower temperatures, allowing for more intense generation of competitive growth directions on the colder side of the sample. In such a way, the changes of the resultant growth trajectories occurred until the growth direction parallel to the temperature gradient was achieved. However, as it is clear in Figure 1(a), in the sample studied, only the lamellae trajectories inclined initially at angles less than 45° had a chance to become parallel to the temperature gradient, whereas the other stopped at interspherulite boundaries. Such nearly parallel alignment of R-lamellae is visible in Figure 6(a), where the AFM images of the region marked by D, crystallized at 140°C, are shown. Because the growth in the direction less inclined to the temperature gradient was slower, the growth of a spherulite

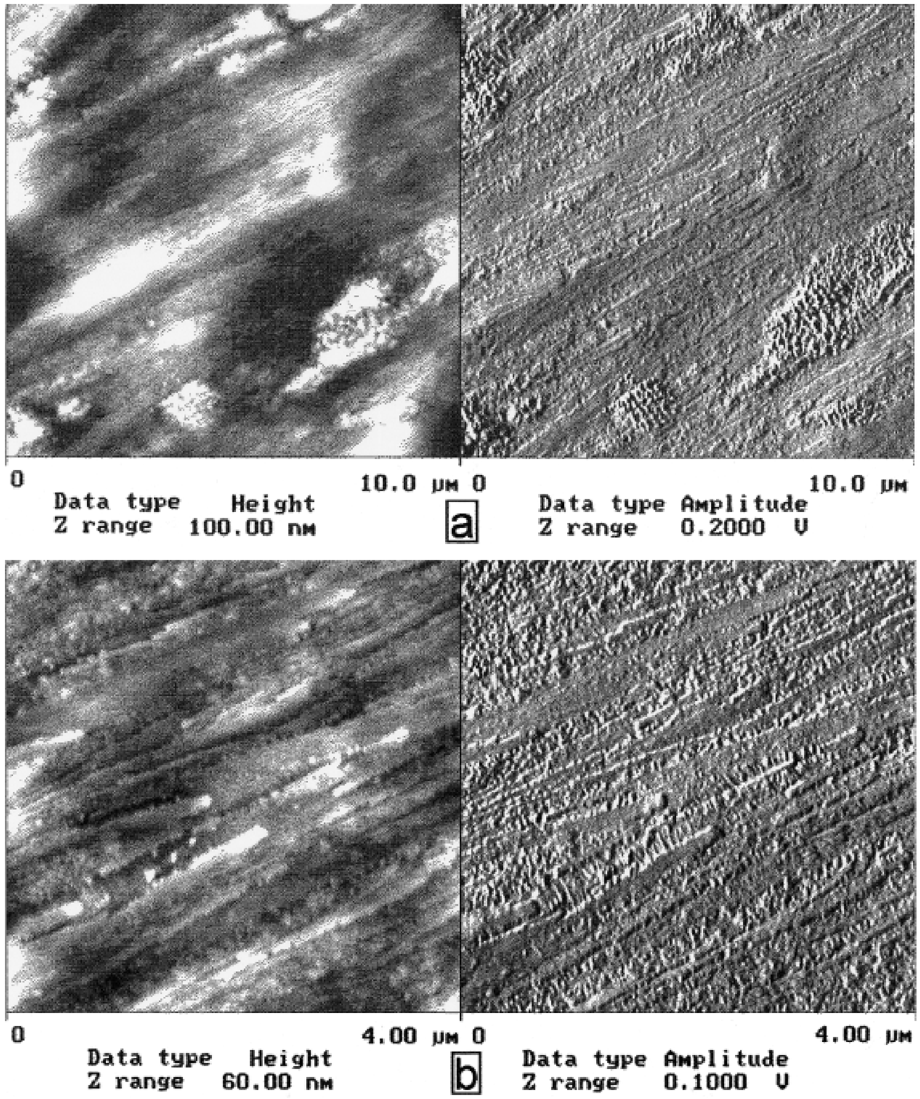

Figure 8 AFM images of the film of iPP1 crystallized isothermally at 140°C: (a) overview and (b) detail.

toward the higher temperature was accompanied by the gradual flattening of the crystallization front as was observed in ref. 24.

The local lamellar structure examined at high magnification was similar in the gradient-crystallized film and in the film crystallized isothermally at a respective temperature. The crystallization temperature of the regions A and B, shown in detail in Figures 3 and 4, was approximately 130°C. In Figure 3(c), numerous T-lamellae are present, branching from R-lamellae at angles close to 80°, as is usually observed for cross-hatched morphology in iPP crystallized isothermally at a similar temperature. In fact, intensive crosshatching was seen in the film crystallized isothermally at 130°C (see Fig. 7).

We attempted to compare the lamella thicknesses in gradient-crystallized and isothermally crystallized samples by measuring the width of height profile of edge-on positioned lamellae, 1.5 nm below the peak. The following average values were obtained for the sample crystallized isothermally at 130°C: 27.0 nm for R-lamellae and 24.5 nm for T-lamellae, whereas the corresponding values for the respective region of the gradient sample were 24.5 nm for R-lamellae and 24.0 nm for T-lamellae. These values were very similar. The small discrepancy for the thickness of R-lamellae could be attributed to experimental errors in the local crystallization-temperature determination or to AFM tip shape rather than to the influence of the temperature gradient on crystal thickness.

Region D of the gradient-crystallized sample (see Figs. 1 and 6), crystallized at approximately 140°C, was composed of long, nearly parallel R-lamellae, with some short and thinner T-lamellae. The average widths of height profiles were 34 and 28 nm for R-lamellae and T-lamellae, respectively. A similar structure at the periphery of spherulites crystallized isothermally at 140°C is visible in Figure 8. In region D

[Fig. 6(a)] and also within spherulites crystallized isothermally at 140°C [Fig. 8(a)], the stacks of plate-like T-lamellae, positioned edge-on and nearly perpendicular to long R-lamellae, were observed. The stacks, partially embedded in the respectively flat surroundings, were several micrometers long and approximately 1–2 μm wide. In the gradient sample, the thickness of lamellae within the stack was similar to the thickness of a single T-lamellae.

The details of the rows of edge-on positioned plate-like T-lamellae in the region of a gradient sample crystallized at 142°C are shown in Figure 6(b). The sizes of these rows of plate-like crystals made them easily discernible also in SEM [Fig. 9(a)]. The rows of T-lamellae were more numerous in those spherulites that were occasionally nucleated at the high-temperature side of the gradient sample. Such a region is shown in Figure 9(b), where the T-lamellae are inclined to R-lamellae at an angle close to 80°. The termination of lamellae growing at a larger angle by the lamellae inclined at a smaller angle with respect to the temperature gradient, illustrated previously for spherulites nucleated in lower temperature regions, is also clearly discernible in this micrograph. Norton and Keller[2] disclosed the rows of T-lamellae branched from some of the long R-lamellae in samples crystallized isothermally at 140°C and permanganic-etched iPP-samples.

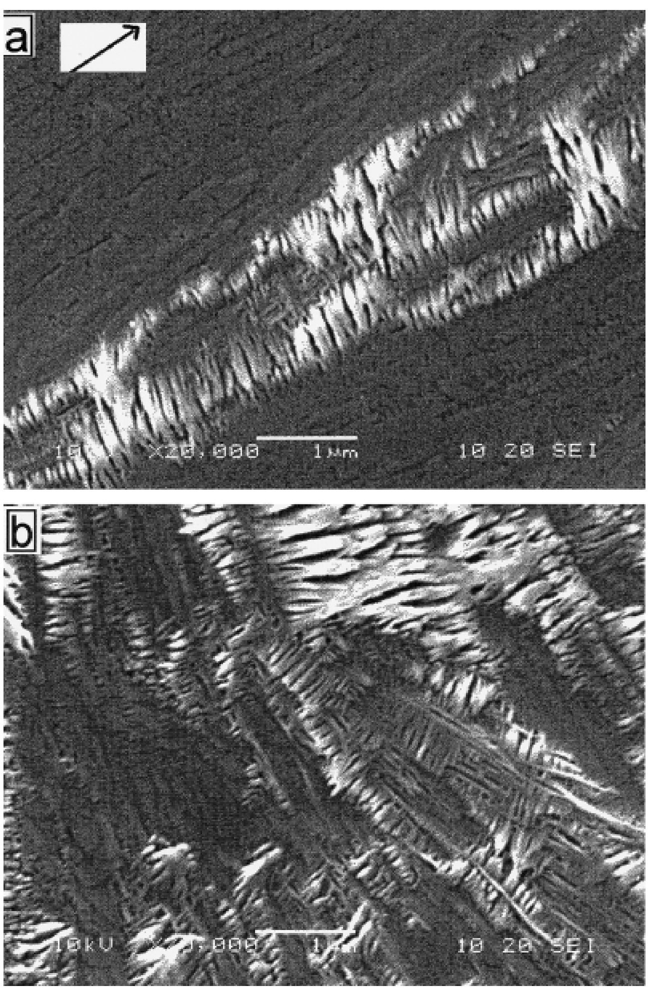

Figure 9 SEM micrographs of the surface of iPP1 film crystallized in a temperature gradient of 35 K/mm in the direction marked by the arrow: (a) stacks of T-lamellae visible in the surface of the high-temperature part and (b) details of crosshatching near the center of the spherulite.

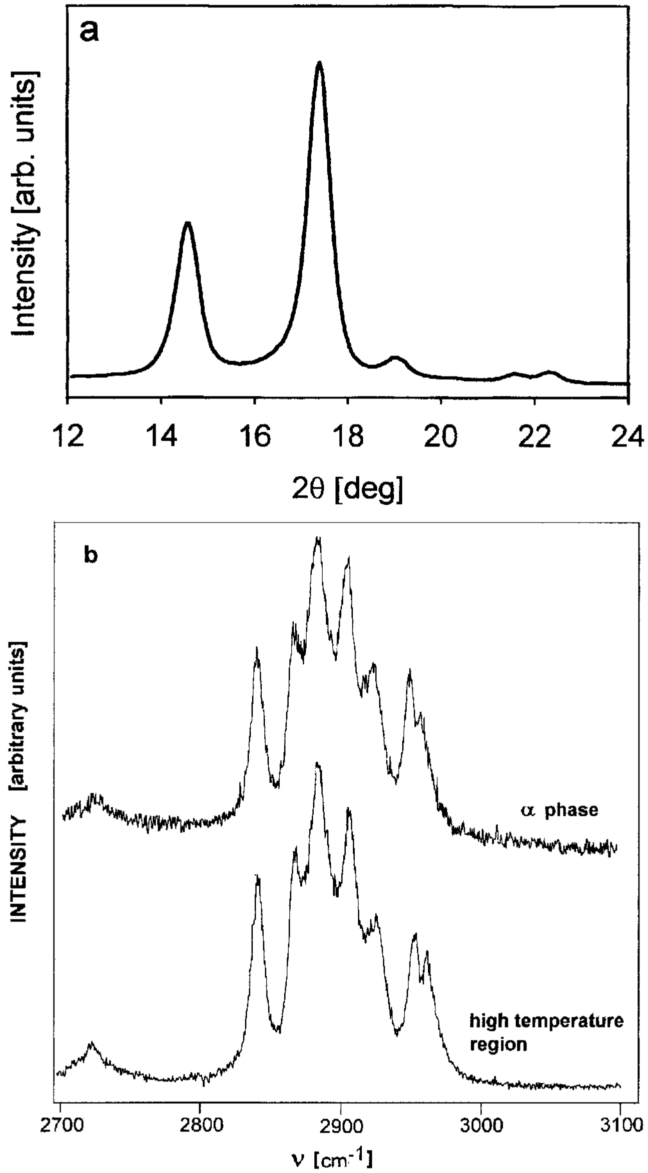

Figure 10 (a) X-ray diffractogram and (b) Raman spectrum of the high-temperature region of the iPP1 film crystallized in a temperature gradient of 35 K/mm.

Although the stacks of plate-like structures showed some similarity to the morphology of the γ form,[8,9] only α-form crystals were detected by X-ray diffraction and by Raman spectroscopy of the high-temperature part of the gradient-crystallized film of iPP1 (Fig. 10). Similar stacks of T-lamellae, even more numerous, were also found in the gradient sample of iPP2.

Between regions A or B and region D (Fig. 1), the gradual evolution of the spherulite structure occurred. In addition to the changes in lamellar orientation, other changes, such as an increase in lamellar thickness, a decrease in crosshatching intensity, and the appearance of stacks of T-lamellae were observed.

CONCLUSIONS

The AFM and SEM investigations of iPP film crystallized with free upper surfaces in a stable unidirectional temperature gradient of 35 K/mm allowed us to explain the mechanism of the change in the lamellar orientation within spherulites. The preferred direction of R-lamellae propagation became less inclined to the temperature gradient in a stepwise manner until the parallel alignment was achieved. The change in the trajectories of growth in the temperature gradient resulted from branching, splaying, and the competition of differently inclined lamellae in filling the space of a spherulite.

Although the trajectory of growth, as visible by light microscopy, was normal to the growth front, AFM and SEM examination revealed differently oriented neighboring stacks of lamellae. Instead of the continuous change in direction, as was suggested in ref. 18, the termination of lamellae by other lamellae, inclined at smaller angles with respect to the temperature gradient, was observed. Obviously, the growth in the directions inclined at larger angles with respect to the temperature gradient was restricted by the presence of other lamellae coming there earlier from the colder side. Thus, the lamellae had more chances to grow, although more slowly, along the paths less inclined to the temperature gradient. The other features of spherulite architecture, such as the intensity of crosshatching and the lamellae thickness as revealed by AFM and SEM studies, were characteristic for the local temperature and were unaffected by the temperature gradient.

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