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Nucleation of branches in elastomeric polypropylene

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ABSTRACT

The formation of a crosshatched morphology during crystallization of an isotactic polypropylene with low crystallinity is studied in detail. Here, a lamella seems to grow through another nearly perpendicular lamella that was crystallized before. The crystallization was observed with in situ scanning force microscopy with a temporal resolution of 3 min per image. After crystallization the volume structure was imaged by nanotomography. A detailed scheme for the nucleation of branches is proposed.

1. Introduction

To examine the microstructure formation of semicrystalline polymers, in particular polypropylene, many different crystallization experiments have been carried out [1]. Some recent research has been focused on observing the crystal growth in situ and in real space by scanning force microscopy (SFM) [2–10]. These experiments gave new insights on individual local events during crystallization. One of the most interesting issues in this context is the nucleation of new crystals or epitaxial branches. Since the nuclei are rather small and are easily influenced by external forces, it is a delicate task to observe these phenomena [8]. However, there exists a structural model which describes the epitaxial branching of α-polypropylene (α-PP) on the molecular level [11]. Up to now it remains unclear what events trigger this branching. Another observation on the mesoscopic structure of α-PP is the so-called crosshatching morphology [9,10,12,13]. The morphology originates in the epitaxial branching of lamella with a typical angle of 80°. In some cases lamellae can be observed which cross two or more different lamellae perpendicular [10]. From a pure branching mechanism one would expect a rather dendritic structure, but no 'real' crosshatching, where lamellae from both directions cross each other without any gaps or interruptions.

In a recent experiment we have observed the crystallization of elastomeric polypropylene (ePP) from the melt at room temperature. The experiments included in situ SFM observations of the crystal growth of the polymer and imaging the volume structure by nanotomography [14] after crystallization was completed [15]. In this work we want to present a mechanism which explains the real crosshatching found in many experiments based on real-time crystallization observations and nanotomography.

2. Experimental section

We study ePP ($M_w = 110$ kg/mol, 28% [mmmm]-pentade content) synthesized by Dietrich et al. [16]. Thin films (thickness ~ 1 μm) of the polymer were prepared on gold coated silicon substrates by dip coating from a 0.5 wt-% ePP solution in decaline.

After melting the polymer for about 20 min at 175 °C under nitrogen atmosphere the samples were quenched to room temperature and immediately transferred into the SFM (MultiMode™ SFM with NanoScope III controller, Digital Instruments, Santa Barbara, USA). Pyramidal shaped silicon tips with a spring constant of ~40 N/m, a resonance frequency of ~300 kHz and a tip radius of 8 nm were used. We have measured height and phase images in tapping mode with an amplitude ratio of $A_{ts}/A_0 = 0.85$ (A_{ts} damped amplitude, A_0 free amplitude). The time period between two successive images was 3 min resulting in a scan rate of 2 Hz. After the crystallization the same sample area was observed by nanotomography. Therefore, the sample surface was imaged by Tapping Mode SFM, then etched by wet chemical etching, and the same area of the etched surface was imaged. Etching and imaging were repeated 42 times. After some image processing steps the phase images were combined with the height information, and the resulting curved images were stacked in distance of the etching rate. Details on the nanotomography are given in Refs. [14,17]. Three-dimensional images were produced by choosing a threshold for the gray values of the curved phase images. All values below the threshold were set transparent, and values at the threshold are combined to a so-called isosurface. This isosurface is an

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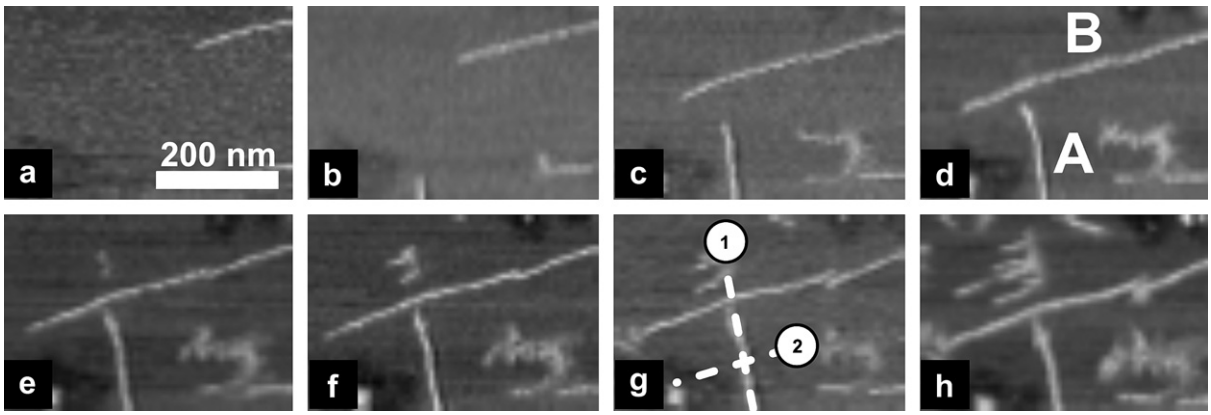

Fig. 1. SFM tapping mode phase images of the crystallization of ePP. The time between two successive images is 15 min, 21 min, 9 min, 9 min, 9 min, 36 min and 105 min, respectively.

interpolated surface, which connects voxels to the surface that have different gray values than the threshold if they are in between voxels that have the threshold value. To remove artifacts from the etching a median filter with a 3×3 kernel was applied in x–z- and y–z-direction.

3. Results and discussion

Bright areas correspond to the crystalline phase; dark areas are the amorphous phase of the polymer. In Fig. 1a and b a lamella growing from right to left can be seen (lamella B). In Fig. 1b an additional lamella (lamella A) appears at the bottom of the image. This lamella is growing upwards (Fig. 1b–d). After 54 min the growth front of A reaches lamella B, which had already formed before (Fig. 1d). We note that the angle between the two lamellae equals 80° which is typical for the epitaxial branching of the α-form of PP [12]. This angle is often used to identify this crystal modification in SFM [3] or electron microscopy images [3,11], but is random here. Nine minutes later a new lamella appears on the other side of lamella B in line with lamella A (Fig. 1e). The newly formed lamella grows on and branches several times (Fig. 1f–h) showing the typical angle of 80° as mentioned above.

Watching the whole time series, it appears as if lamella A had grown through lamella B. This appearance is also favored by the fact that the newly formed lamella appears at the position and time where the growth front of lamella A would be, if a constant growth rate of lamella A is assumed.

To check for tip induced damage or changes of the crystal morphology we have compared the observed area to areas, which were not scanned during crystallization. We found a slight decrease in the roughness of the surface topography of the scanned area, but no notable differences in the morphology of the crystals. Nevertheless, there will always be an influence of the scanning SFM tip even at very high amplitude ratios.

To gain further insight into the growth mechanism of this phenomenon, a volume image of this area was captured with nanotomography.

The left image of Fig. 2 shows the isosurface of the volume image of the two lamellae. Nanotomography was done ~1 month after the observation of crystallization. Therefore, the gap between lamella B and the newly formed lamella that can clearly be seen in

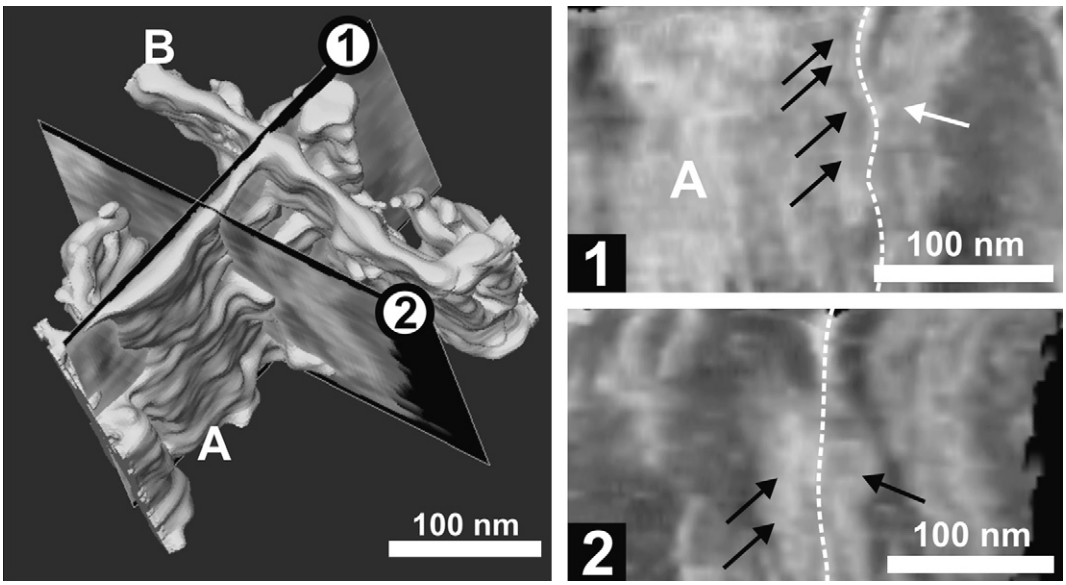

Fig. 2. Nanotomography images of the lamellae in Fig. 1 after the crystallization. Left: isosurface image (threshold 46.8%). Neighboring lamellae are not shown for clarity. Right: Sections 1 (along lamella A) and 2 (parallel to lamella B) parallel to z-direction through the volume image as indicated in Figs. 1g and 2 left. The dotted line in Section 1 indicates the position of lamella B. The dotted line in Section 2 indicates the position of lamella A. The black arrows in Section 1 mark the amorphous region between lamellae A and B. The white arrow marks the nucleation point of the new lamella. The black arrows in Section 2 indicate two tiny epitaxially grown daughter lamellae.

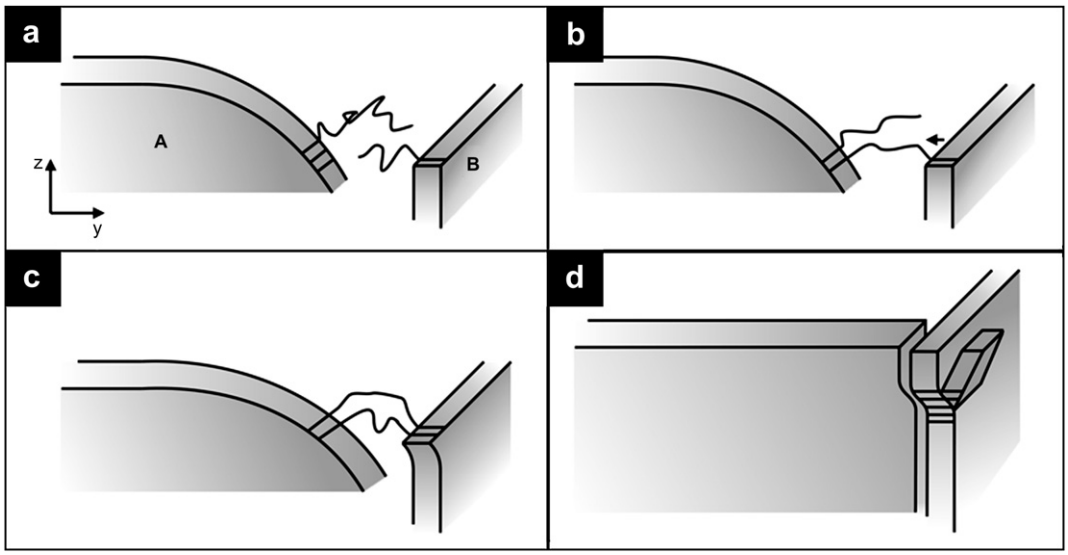

Fig. 3. Sketch of the proposed growth scheme. Note that there is a continuous growth in *z*-direction.

Fig. 1h nearly vanished at the surface of the sample, because of secondary crystallization. As described, the isosurface is calculated from voxels having the same gray value. Since lamellae A and B are nearly connected, they appear connected in the calculated isosurface. Two sections through this volume image as marked in the left image of Fig. 2 and in Fig. 1g are shown on the right of Fig. 2. Section 1 shows the section along lamella A. In the section lamella A is represented by the bright area on the left side marked A. Lamella B is marked by a dashed line. The black arrows indicate a dark region that follows the side of lamella B very well. Since dark regions in the tapping mode SFM phase images correspond to amorphous material, it is obvious that lamella A did not grow *through* lamella B, since it did not even reach the side of lamella B. The amorphous area following the side of B denotes that lamella A stopped growing towards lamella B, before it reached it. Hence, it could not grow through lamella B. In contrast in Section 2 a cut through two epitaxially grown daughter lamellae (black arrows) of lamella A (dashed line) is shown. No amorphous regions between the mother and the daughter lamellae can be observed. Another interesting observation in Section 1 is that lamella B is not straight, but has a curved shape. This shape is neither an artifact of the measuring process nor of the image registration, since the registration was performed on the complete image stack and a larger area [17]. As can be seen from this figure, the newly formed lamella is connected to lamella B at the position of a kink (Section 1, white arrow).

Considering the information mentioned before, we are able to propose the following mechanism (Fig. 3).

The growth front of lamella A is curved which is confirmed by the SFM height images (Supplementary data) (Fig. 3a). This curved growth front reaches lamella B at a point below the observed surface (Fig. 3b). Parts of chains which are built in lamella B can attach to the growth front of lamella A, which leads to a tension between the lamellae [18], caused by entropic effects [19]. The stretched parts of the chains act like entropic springs, i.e., a random coil state of the chain is favored over an elongated chain. Furthermore, chains which are built into lamella B are shifted towards lamella A during the growth in *z*-direction. The growth in *z*-direction and the depletion zone next to a crystal has been confirmed by our previous work [15]. This leads to a tilted growth of lamella B and the formation of a kink (Fig. 3c). The growth front of lamella A develops until it is parallel to the side of lamella B, where it can no longer grow because of a depletion zone of crystallizable material between the two lamellae (Fig. 3d). Lamella A can still grow in *z*-direction, because here no other crystal formed before, so there is still enough crystallizable material to grow on. Short time after the tilt of lamella B has happened, the new lamella which grows in *z*-direction is nucleated on the exposed growth front, i.e., the kink (Fig. 3c). Additionally, the formation of the new lamella is supported by pre-aligned chains in the vicinity of lamella B [20]. Because of the little delay between the development of the kink and the nucleation of the new lamella the appearance of this new lamella fits the time and position of the apparent "break-through".

4. Conclusion

We could show that next to the already known mechanisms of α- and γ-branching, there exist other more complex elementary processes in the structure formation of polypropylene. The branching mechanism described here for the first time differs in the way that the necessary nucleus is provided. For epitaxial branching the nucleus is the growth front of a lamella. In the case observed here, the interaction between two lamellae, i.e., the tension and resulting tilt, provides the necessary branching nucleus by exposing a crystal plane to the amorphous melt. Because of that the apparent 'collision', when the two lamellae meet, triggers the nucleation of a new branch. This branch is in line with one of the two lamellae. Our results also show that the combination of new and innovative techniques leads to new insights into already well studied phenomena.

Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.polymer.2008.08.007.

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