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Scanning force microscopy of oriented iso- and syndiotactic polypropylene films

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SUMMARY

Different scanning force microscopy (SFM) modes were applied for the examination of drawn films of isotactic and syndiotactic polypropylene, iPP and sPP. Uniaxially stretched films with a draw ratio $\lambda = 6$ were studied at ambient conditions, and under water. In iPP films striated patterns of 40-50 nm in width, which are oriented along the stretching direction, exhibit shish-kebab morphology. The dominating nanoscale features are nanofibrils of 10-15 nm in width, and lamellar platelets, which are 40-50 nm in width and 30-35 nm in length. In many places lamellar platelets are closely packed, and they form periodical sequences with a repeat distance of 30-35 nm, which is consistent with the *long period*. Similar and differing morphological features were found comparing the images of iPP and sPP films. Extended fibrillar patterns of sPP exhibit similar width in the 40 - 50 nm range, while the lamellar structure is more compact, and the platelets are less uniform in length than those in iPP. The length of lamellar platelets ranges from 30 to 60 nm, and they form local periodical patterns.

INTRODUCTION

With the development of scanning force microscopy (SFM) [1] the characterization of polymer surfaces is essentially improved. In first SFM applications to polymers the images showed surface features in the μm scale and the molecular chain arrangement in the nm scale [2]. It was also realized that image artifacts prevent a reliable analysis of the nanoscale surface features. In order to overcome this problem an optimization of experimental conditions is required. Essential progress was achieved by operating under liquid, where the applied force is strongly diminished in comparison with ambient condition experiments [3]. This allows one to enhance the resolution of imaging nanoscale features and to avoid surface modification [4a-4b].

With these improvements we have detected for the first time an organized nanostructure within the topmost surface layer of drawn ultrahigh molecular weight polyethylene (UHMW PE) tapes [4b]. Oriented features as small as

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2-3 nm in width, which are aligned along the stretching direction and perpendicular to it, were resolved in the images recorded with a small force of ~ 1 nN. The found nanostructure was assigned to interfibrillar and intrafibrillar tie molecules, which are present on the nanofibril surface. An increase of the applied force led to a removal of the topmost layer and the observation of the nanofibril core. The periodical profile with a repeat distance of ~ 25 nm was observed along the nanofibril core in the images recorded with the elevated force. It was found that these periodical variations are related to the surface deformation profile, which arises from different indentation depth in hard crystalline and in soft amorphous regions within the core.

The results obtained by the study of drawn UHMW PE tapes motivated us to apply SFM to other oriented polymers, isotactic and syndiotactic polypropylene (iPP and sPP). Images obtained on drawn iPP and sPP films with different SFM modes are presented and discussed in this paper.

EXPERIMENTAL PART

Materials

Polymer films for stretching experiments were prepared by pressing from the melt between glass slides. iPP was fractionated, and the selected polymer fraction exhibits the melting temperature $T_m = 145°C$, 94 % mmmm pentades, $M_n = 1.0 \cdot 10^5$, and $M_w/M_n = 2.0$. Pressing was conducted at 200°C in vacuo, and the obtained film of ~ .1 mm thickness was quenched from the melt. Stretching was conducted at 140°C, with a speed of 2 mm/min. The draw ratio of $\lambda = 6$ was reached in the necked part of the samples. The stripes cutted of the necked part were examined with SFM.

The sPP studied exhibits $T_m = 141°C$, 92 % of rrrr pentades, and $M_n = 1.1 \cdot 10^5$, with $M_w/M_n = 2.5$. Films of ~ .1 mm thickness were obtained by pressing from the melt at 180°C in vacuo. Before stretching, the sPP film was crystallized at 130°C during 7 hours. Stretching was conducted at 80°C, and the oriented material, with $\lambda = 6$, was examined by SFM.

In order to visualize the crystalline structure below the skin layer of unstretched iPP and sPP films, the amorphous surface layer of such films was removed by permanganic etching. The investigated films were received by crystallizing 20°C below the melting point.

Method

SFM experiments were conducted with a scanning probe microscope "Nanoscope III" (Digital Instruments Inc.). Measurements were carried out in the contact and the tapping mode, CM and TM. During operation in the tapping mode height (HT) and deflection (DF) images were recorded simultaneously. In the contact mode we registered simultaneously height and lateral force (LF) images. In both modes the HT images correctly reproduce the height variations, while DF and LF images visualize fine morphological features with a better contrast. Experiments were conducted in air and under water, the latter in a liquid cell filled with twice distilled water. Further details of the SFM experiments can be found in earlier publications [4].

Color-coded SFM images are used in this presentation, brown for iPP and red for sPP. A brighter contrast in HT images is related to higher surface features. In DF images brighter contrast indicates surface features causing larger cantilever deflections.

RESULTS AND DISCUSSION

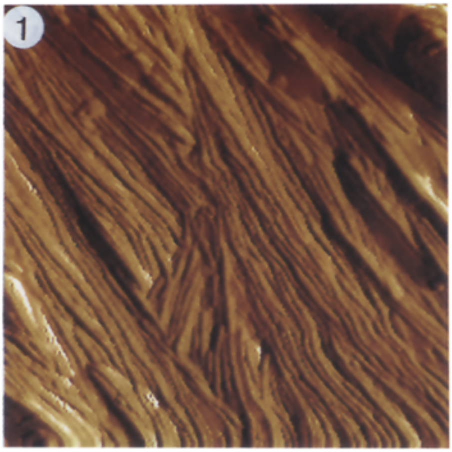
The unstretched films of melt-crystallized iPP and sPP possess surface layers enriched in amorphous material. In order to observe the crystalline structure below the topmost layer, this layer was removed by permanganic etching.

Isotactic polypropylene

A SFM image, which shows the lamellar arrangement of the crystalline spherulitic structures of iPP below the skin, is presented in Fig. 1. Numerous linear patterns with a width in the 100-150 nm range are observed on the etched surface. From smaller scale images it was evident that these patterns consist of several edge-on standing lamellas with a thickness around 15-20 nm. Similar patterns assigned to thicker (mother) and thinner (daughter) lamellas where found in an earlier SFM study of iPP, conducted in air with the contact mode [2d]. Our experience shows that the application of the tapping mode has advantages when studying spherulitic structures. The HT and DF images obtained in this mode exhibit a better contrast than those recorded in the contact mode. However, in both cases the problem of deconvolution of the contributions of surface topography and of hardness to the image contrast is not yet solved [5].

To survey the microscopic features of surface structure of oriented iPP films we selected the SFM images recorded in the tapping mode. In the HT image shown in Fig. 2a one sees a slightly corrugated surface consisting of numerous fibrils with a width in the 20-40 nm range. These fibrils are oriented along the stretching direction. Bright spots scattered over the examined area might be related to surface imperfections, such as ends of broken fibrils. At higher magnification one sees a more detailed nanoscale organization within the fibrillar patterns, Fig. 2b. Many fibrils consist of bright and wide spots, which alternate with thinner and dimmer spots, like beads on a string. These features give rise to the periodical contrast variations with a repeat distance of ~30-35 nm along the individual fibrils. This repeat distance is similar to the value of the *long period* determined by diffraction techniques for iPP films stretched at elevated temperatures (> 130°C) [6].

Details of the surface nanostructure were revealed in the contact mode experiments conducted under water, Fig. 3a - 3c. The HT image registered with small applied force (Fig. 3a) demonstrates thin nanofibrils of 10-15 nm diameter and grain-like patterns attached to the fibrils. These grains are 40-50 nm in width and 30-35 nm in length. This observed nanoscale morphology resembles the shish-kebab structures oftenly found in oriented polyolefins.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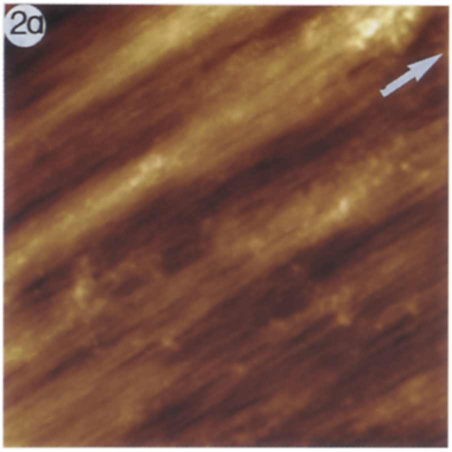
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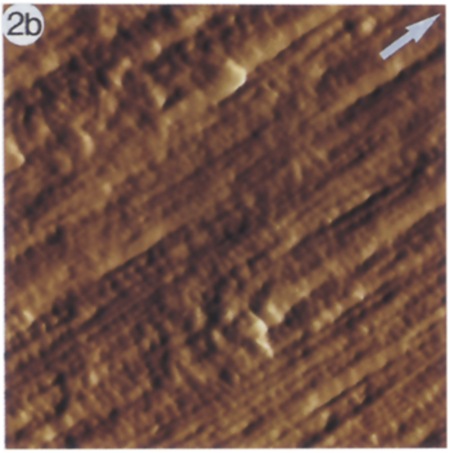
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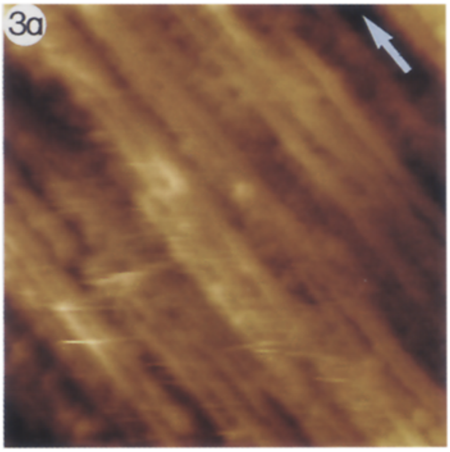
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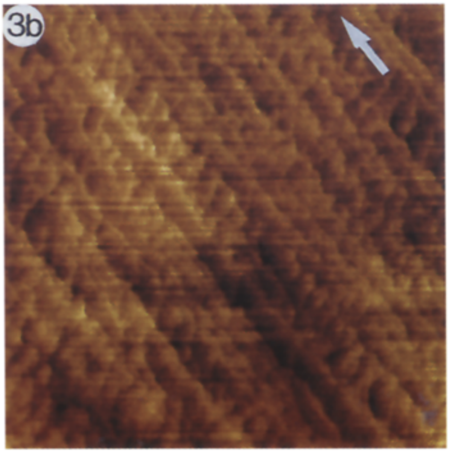
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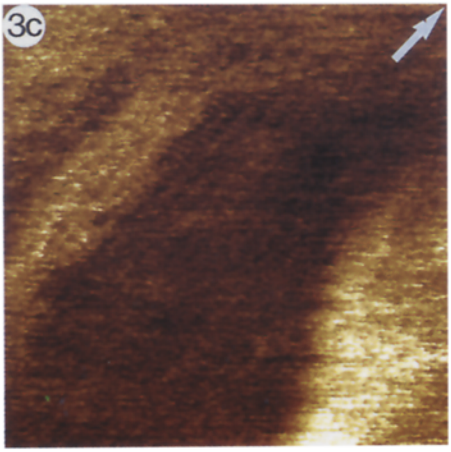
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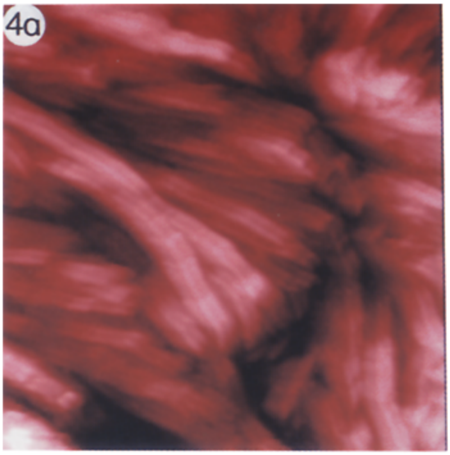
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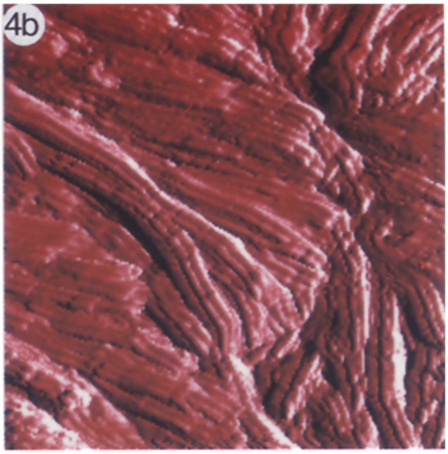
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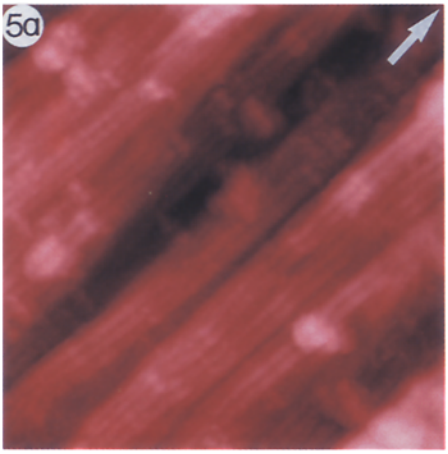
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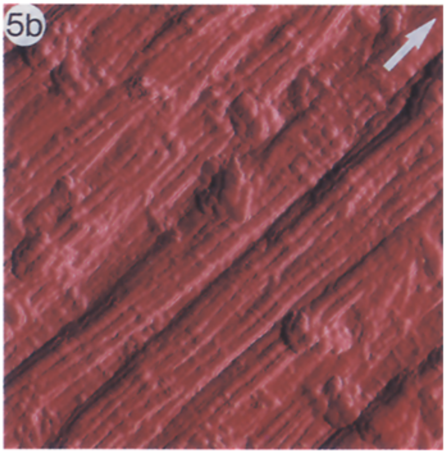
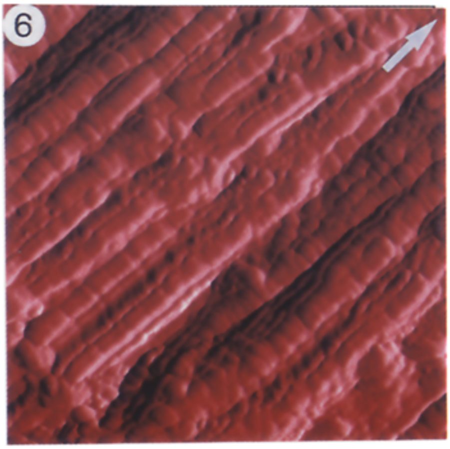

5b

Figures 1 - 6: Size of surface areas
$7.5 \cdot 7.5\ \mu m^2$ in Figures 1 - 2a
$1.5 \cdot 1.5\ \mu m^2$ in Figure 2b
$750 \cdot 750\ nm^2$ in Figures 3a - 3b
$30 \cdot 30\ nm^2$ in Figure 3c
$7.5 \cdot 7.5\ \mu m^2$ in Figs. 4a - 4b - 5a - 5b
$1.9 \cdot 1.9\ \mu m^2$ in Figure 6.
In HT images the contrast covers height variations in the
0-250 nm range in Figure 2a
0-60 nm range in Figure 3a
0-600 nm range in Figs. 4a and 5a.
Other details are given in the text.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By analogy we propose to assign the found nanofibrils to shish crystals, which form a core of the shish-kebab structure, and the grains to the lamellar platelets or kebab elements. The latter present the lamellar blocks epitaxially grown on the shish crystals. These assumptions are confirmed by the following findings.

We found that scanning with an elevated force doesn't change the image features drastically. Only the contrast of the lamellar platelets increased, and they became well pronounced, especially in the LF images as shown in Fig. 3b. Consequently, the patterns observed in the image of an oriented iPP film can be assigned to the surface topography, but not a surface hardness or deformation profile as found in the images of drawn UHMW PE tapes. The image in Fig. 3b shows a surface region, where a compactly packed sequence of lamellar platelets was detected. It demonstrates the periodical arrangement of lamellar platelets, which is responsible for the appearance of the *long period* diffraction pattern. Whilst in drawn PE tapes the *long period* is related to the alternation of hard and soft nanodomains within the fibril core, the *long period* features of drawn iPP films are connected with the formation of shish-kebab morphology during the stretching process. In the UHMW PE tapes intra- and interfibrillar tie molecules, being expelled out of a nanofibril core, form a weakly bounded topmost surface layer with an oriented nanostructure [4b]. We haven't found a similar layer on the surface of iPP films. This might be explained by the presence of tie molecules in the space between neighbouring lamellar platelets.

The important step in the SFM analysis of polymer surfaces is the installation of a relation between molecular ordering and nanoscale features in the 5-100 nm range. One of the images of drawn iPP, where one can distinguish molecular-scale features, is shown in the lateral force image recorded under water, Fig. 3c. Linear striations with a separation of ~ 1 nm, which are visible on the grain surface, demonstrate extended polymer chain structures, probably 3_1 helices. This confirms the assignment of the grains to the lamellar platelets. The resolution of the molecular-scale features in this image is relatively poor. This is a general problem of the measurements with low force, which are conducted under water. It was recognized that the resolution of the molecular scale SFM images of oriented iPP is essentially improved with an increase of the applied force [7]. However, in such a case it appears crucial to assume that the image was obtained from the virgin surface but not from a crystalline block found by the indenting tip within the material.

Syndiotactic polypropylene

The structure of sPP spherulites is studied less intensively than that of iPP. A part of a sPP crystallite demonstrating the arrangement of radial lamellas is shown in the tapping mode HT and DF images in Figures 4a - 4b. In these images one sees numerous blocks, each consisting of several extended patterns. Individual patterns are .5 - 1 μm in length and ~ 150 nm in width. As in the case of iPP these linear patterns are composed of several edge-on standing lamellas, with a thickness of ~ 20 nm. Blocks consisting of tangential lamellas are seen in the lower left part of the image. At other places we found surface patterns, which can be assigned to inclined and almost flat-lying lamellas. The resolution of the SFM images registered in the tapping mode allows one to distiguish the periodical contrast variations along the edge of individual lamellas, which can be assigned to their substructure. These and other nanoscale features detected in the SFM images of several crystalline polymers are discussed in more detail elsewhere [5].

The HT and DF images of oriented sPP film obtained in the tapping mode are shown in Figures 5a-5b. In the large scale image one sees well defined fibrillar patterns with a relatively uniform size. They are arranged within larger extended units containing several individual fibrils. The width of the individual fibrillar patterns ranges from 50 to 60 nm. Similar uniform fibrillar patterns with slightly narrower individual elements (~ 40 nm) were found in the contact mode images of sPP registered under water. These values are closer to the actual dimensions of polymer fibrils. In the tapping mode DF image with higher resolution, Fig. 6, the substructure of individual fibrils is resolved. Closely packed nanoblocks with a length of 30-50 nm are distinguished along the fibrils. A similar, but less pronounced substructure was found in the images recorded under water. These features can be assigned to the lamellar crystals. This assumption was confirmed by the detection of the extended chain order in the molecular-scale SFM images obtained in the contact mode. Because the lamellar platelets exhibit non-uniform length, and they form periodical sequences locally only, one can expect that the related *long period* diffraction pattern should be diffuse.

Comparison of the SFM images of oriented iPP and sPP films revealed the differences in their morphology. Though the shish-kebab morphology of iPP films is evidenced, we have no experimental proof for the same morphology in sPP films. The main difference between the morphologies of oriented iPP and sPP films is related to the arrangement of the lamellar platelets. In iPP films lamellar platelets are loosely packed, and the spacing between the neighboring platelets is variable. Places with a compact arrangement of lamellar platelets (Fig. 3b) are not the dominating the surface features of iPP films. The situation is different in sPP films, where the lamellar platelets are compactly packed. A last point may be considered, however, when comparing the stretched iso- and syndiotactic polypropylene films. Both were obtained by 'cold drawing', sPP at essentially lower temperature, however, than iPP.

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