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Atomic force microscopy on epitaxially crystallized isotactic polypropylene*

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SUMMARY

Contact faces of thin films of α-phase isotactic polypropylene epitaxially crystallized on benzoic acid are examined by atomic force microscopy (AFM). The AFM images reveal the lamellar structure as well as the methyl side group pattern, thus enabling the discrimination between two structurally different contact surfaces in favour of the 'four' face type, with one methyl group per helix turn exposed. Furthermore it has been verified, that the observed helices are right-handed.

INTRODUCTION

Scanning tunneling microscopy, STM, [1] and atomic force microscopy, AFM, [2] reveal submolecular and even atomic surface features. AFM, however, is more suitable for surface analysis of polymeric materials, the vast majority of which is non-conducting. AFM detection of screw dislocations in dendritic crystals of polyethylene has been reported first [3]. The visualization of polymer chains has been achieved on flat surfaces of cold-extruded polyethylene [4]. Methyl end groups of linear and molecular folds of cyclic alkanes, which form the surfaces of the respective monocrystals, give well defined responses in the atomic scale AFM images [5].

This report deals with AFM studies on isotactic polypropylene (iPP). Its epitaxially crystallized α-phase is highly suited as a model for polymer structure investigation by this new method. In view of its characteristic quadrite morphology [6] it is indeed possible to determine the helical hand and setting of the constituant 3_1 helices and to predict the methyl group pattern in the exposed iPP (010) planes [7].

EXPERIMENTAL

Lower molecular weight iPP is produced by thermal chain scission of high molecular weight iPP under vacuum and vaporization on glass cover slides [8]. No isomerization occurs during this process. The product is comelted with benzoic acid between cover slides and slowly crystallized in a temperature gradient [9]. After removal of benzoic acid by dissolution in hot methanol, the sample is ready for AFM examination.

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*Dedicated cordially to Prof. Henry Benoît to his 70th birthday

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A commercial scanning probe microscope 'Nanoscope II' (Digital Instruments Inc., Santa Barbara, CA, USA) has been used at ambient conditions. 'A' type head and V-shaped cantilever, 200 μm in length, with a force constant 0.12 N/m were used. In AFM images the z-variations (z - the direction perpendicular to the examined surface) in the surface profile of interatomic force registrated during scanning are grey or color coded. The brighter patterns correspond to sites with higher repulsive force. Only low pass filtering was used for large scale images, and filtering in Fourier space was applied for the atomic scale ones.

RESULTS AND DISCUSSION

1. iPP thin film structure

Crystallization on benzoic acid results in the formation of an interwoven array of close-packed iPP lamellae standing edge-on [10], as shown by electron microscopy (Fig. 1). The lamellae are at an angle of nearly 80° (or 100°), in an arrangement very reminiscent of the more loosely interwoven solution-grown quadrites [6]. Electron diffraction patterns of gold decorated thin films indicate that the iPP b-axis is normal to the film surface ((010) faces are exposed) and that the lamellar thickness is ~ 12 nm.

The crystallographic structure of the α-phase of iPP - determined by Natta and Corradini [11] - is characterized by the alternation of (010) layers made of antichiral helices which, in addition, exhibit different settings in the structure (Fig. 2). As concerns the exposed (010) planes, it follows that successive layers are made of helices of alternate hand, with either one or two side chains - methyl groups - exposed. Successive (040) lateral faces thus differ widely in terms of methyl group density and arrangement. The simplest - looser - arrangement corresponds to a lozenge array of methyl groups 0.65 nm apart with an obtuse angle of 99.6° (Fig. 3a). The second -

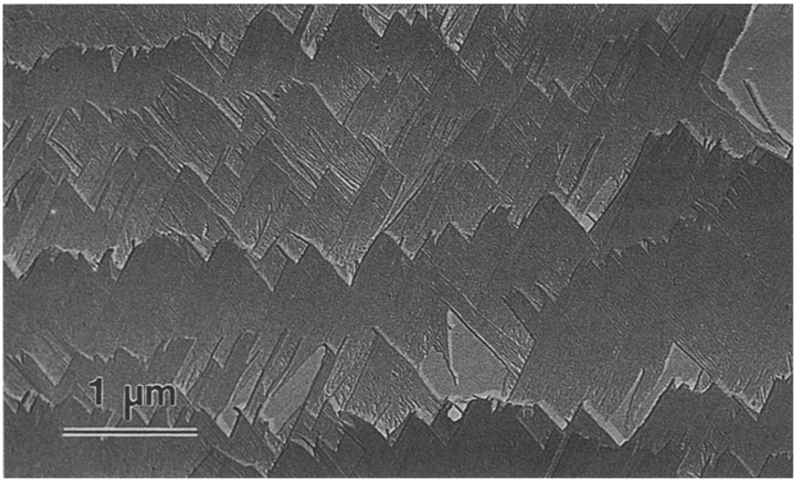


Figure 1: Transmission electron microscopic picture of iPP - epitaxially grown on benzoic acid

denser - arrangement involves a two-fold increase in methyl group density which, is achieved by addition of a methyl group at the center of the previous pattern (Fig. 3b). The two patterns thus resemble the 'four' and 'five' faces of a dice. In addition the principal rows in the 'five' faces, i. e. the short diagonal of the lozenge, are parallel to the helical path and thus materialize the helical hand if these faces are exposed. Whereas the above structural analysis makes it possible to determine the hand and setting of iPP helices in the quadrites [7], neither this analysis nor diffraction evidence indicates which of the two possible (010) faces actually interacts with the benzoic acid substrate surface. The answer to this question was sought by AFM.

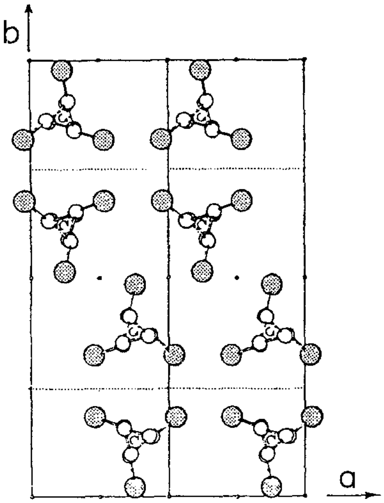


Figure 2: Two unit-cells iPP

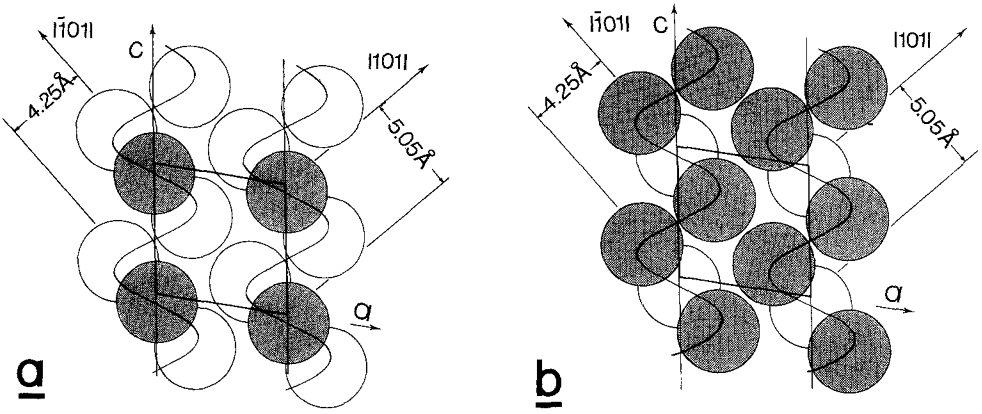


Figure 3: Lozenge array CH_3 groups in iPP

- a 'four' face pattern, one CH_3 group exposed, left handed helices
- b 'five' face pattern, two CH_3 groups exposed, right handed helices

2. AFM examination of iPP contact surfaces

A well resolved and ordered large scale view (340x340 nm) of the contact surface is represented in Fig. 4. A slighty corrugated surface is formed, with several ridges - wide 'hills' and protrusions. The cross-section of the image shows that the 'brighter' rows are separated equidistantly with a periodicity of 12.8 nm. This is demonstrated in the frequency distribution evaluation in Fig. 5. This periodicity corresponds well to the average lamellar thickness determined by low angle electron diffraction of gold decorated films.

The formation of ridges - .04 nm high - rather than depressions has its probable origin in different thermal contractions of the thin polymer film and its support on cooling from ~ 130° C to room temperature. We note that the linear thermal expansion coefficient of benzoic acid is ~ $1x10^{-4}$ cm/°C, which for ΔT ~ 100°C implies a 1 % linear contraction. Since the expansion coefficient of linear crystalline polymers along the chain axis is zero or even slightly negative, the shrinkage of the substrate in a direction parallel to the polymer chain must be accomodated by the interlamellar material only: Due to the resulting compression, this material must bulge, i. e. produces the observed ridge.

Figs. 6 and 7 offer the key for the discrimination between the two structurally different contact surfaces, - the 'four' and the 'five' face type - as well as the verification of the hand of the helices under observation. Fig. 6 presents two lamellae in 48 x 48 nm scale. The molecular structure of the (010) plane of the lamellae has been resolved in the atomic scale images. In Fig. 7 the well resolved patterns are visible, with main periodicities .69 ± .05 nm and .66 ± .05 nm in the directions a and c, with $\beta = 98 \pm 3^\circ$. The picture is reminiscent of the 'four' (010) face of iPP. The repeat distances of the AFM images are close to the corresponding crystallographic parameters, a = .665 nm , c = .650 nm, $\beta = 99.6^\circ$. The comparison of the atomic scale image with the methyl group pattern drawn from the known crystal structure is given by Fig. 3a. Furthermore, the helix axis in Fig. 7 is known to be nearly normal to the lamellar surface of Fig. 6; it is therefore oriented from lower left to upper right corner. Superposition of Fig. 3a on Fig. 7 taking into account the chain orientation indicates that the pattern in Fig. 7 is the mirror image of that of Fig. 3a. As the lattice represents a layer of left handed helices, it follows that helices of Fig. 7, being their mirror images, are right handed. Additionally, Fig. 8 presents a threedimensional atomic scale picture. The Fast Fourier Transform plot in Fig. 9 gives evidence for a monoclinic lattice.

A wide variety of pictures have been obtained on different areas of epitaxially crystallized iPP film. They all indicate 'four' pattern contact surfaces.

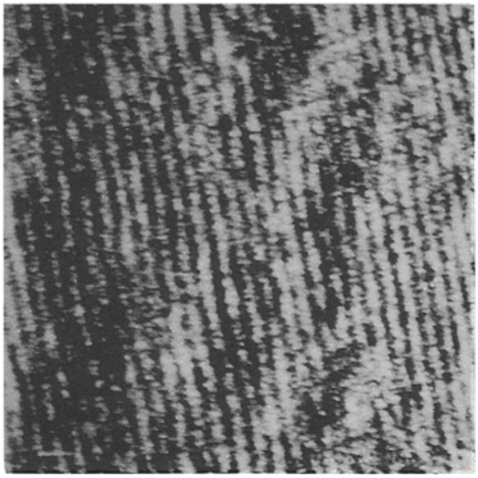
CONCLUSION

AFM of the α-phase of iPP, which was epitaxially crystallized on benzoic acid has been performed with methyl group resolution. The pictures reveal the lamellar surface orientation and the contact face structure. The observed lozenge shaped pattern of methyl groups is consistent with the known crystal structure. It indicates that (010) faces with the lower density of methyl groups are contact faces in the epitaxy. The structural analysis further makes it possible to determine the hand of helices which bear the observed methyl groups. Given the resolution achieved, atomic force microscopy becomes significant tool for structure-related problems of polymers, such as parallel or antiparallel, syncline or anticline arrangement of chains, structural disorder, as well as for analyzing their crystal structure.

Figure 4: AFM large scale top-view of iPP - 340 x 340 nm

Figure 5: Frequency plot of Fig. 4 yields 12.8 nm lamellar thickness

Figure 6: AFM top view iPP - 48 x 48 nm



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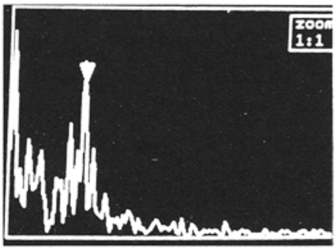

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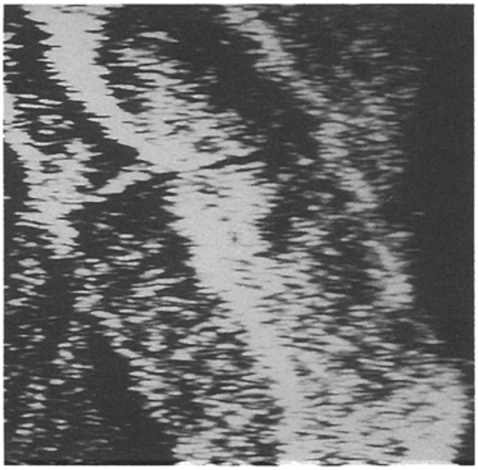

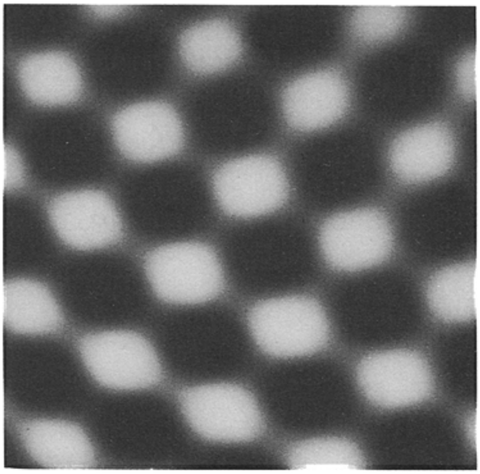

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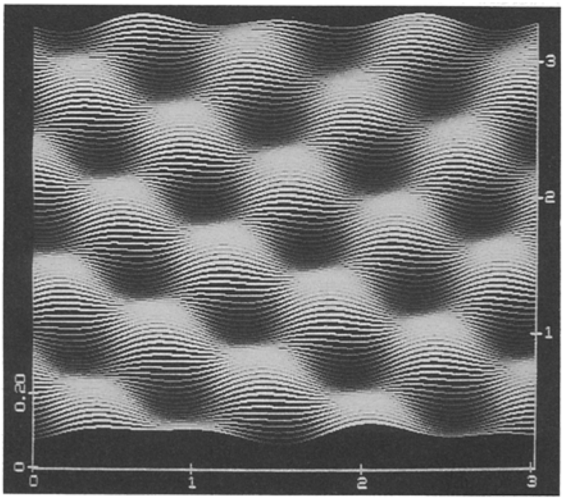
Figure 7: AFM top-view of iPP right-handed helices - 3 x 3 nm - compare Fig. 3a

Figure 8: AFM 3D-plot - scale like Fig 7

Figure 9: 2D-Fourier transform of iPP



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