Contact Surfaces of Epitaxially Crystallized α-Phase Isotactic Polypropylene: AFM Imaging with a "Liquid Cell"

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Introduction

A recent paper[1] has shown that atomic force microscopy (AFM) is able to resolve the pattern of methyl groups in the contact face of epitaxially crystallized isotactic polypropylene (iPP) and to discriminate on the basis of structural indicators (i.e., relative chain and lamellar orientation) between the α and γ phases. The contact face is exposed after selective dissolution of the substrate (usually benzoic acid or nicotinic acid) in organic solvents such as methanol.

The purpose of that study was, for both the α and γ phases, to determine the exact nature of the contact face out of two possible crystallographic planes which are structurally different.[2] In these different planes, the patterns of the methyl groups mimic either the "five" or the "four" faces of dice (cf. Figures 1 and 2 in the companion correction[3] showing the set of pictures which reproduced poorly in ref 1). AFM results indicated that the "four" pattern is the actual contact plane.[1] Although this result was arrived at after Fourier filtration of an initial rather poor picture (Figure 7a in refs 1 and 3, which should be looked at a grazing angle from the lower right and left)), the result was unambiguous since the two contact faces differ by their *symmetry*, a feature that is easily accessible to Fourier analysis.

In the present note, we report on further work using related substrates and similar techniques. Significantly improved images have been obtained, mainly by using a so-called "liquid cell" which makes it possible to probe the sample while being immersed in different media. These results illustrate possible routes for easier examination and for achieving better images in AFM investigations of crystalline polymers.

Experimental Section

The polymer samples are identical to those used in the previous work. In addition to benzoic and nicotinic acids, anthracene has also been used in the present study as a substrate for epitaxial crystallization.

AFM experiments were carried out with a Nanoscope III instrument from Digital Instruments, Inc., Santa Barbara, CA. Images were taken with an A-type scan head equipped with Si$_3$N$_4$ tips attached to a microfabricated cantilever (triangular base 200 μm) with a small force constant (0.06 N/m). Images were recorded in both constant force and constant height modes, with scanning line frequencies ranging from 1 Hz at low resolution up to 57 Hz at atomic resolution. Distance calibration was performed using highly oriented pyrolitic graphite. No image processing is used in the pictures presented.

The liquid cell was used as indicated by the supplier. It is limited on its lower face by the sample (usually produced on and supported by a cover glass slide), on its top face by the Plexiglas of the cantilever holder, and laterally by an O-ring. Various

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liquid media have been tested: benzyl alcohol, methanol, and water, which are all nonsolvents of the polymer at room temperature. Although they yield very similar results, water was found most convenient to use and was adopted as a standard environmental medium. It should be noted that stable images can be obtained within a few minutes after adding the liquid.

One drawback of the liquid cell is that, as a result of the elasticity of the O-rings, the area that can be accessed by the tip is significantly smaller than in conventional AFM: ≈1 × 1 mm^2 versus ≈5 × 5 mm^2. However, this is not a serious limitation in our studies since (a) the zones of interest, materialized by the imprints left on the polymer film by the (by now dissolved) substrate crystals, are easy to locate under the optical microscope or binocular on mounting the sample and (b) the epitaxial relationship ensures a constant surface pattern over the whole area investigated.

Results

Resolution of AFM pictures is highly dependent on the tip quality and on the tip–surface interactions. The latter are at the root of a stick–slip process which limits resolution in the scanning direction. Use of a liquid medium reduces the imaging forces typically by a factor of 10, thus limiting the impact of this stick–slip on the resolution.[4] A typical AFM image recorded while probing epitaxially crystallized iPP under water is shown in Figure 1a. The nearly square pattern of methyl groups is clearly visible in the unfiltered image since individual CH$_3$s are resolved: the conclusions of our previous study are confirmed without resorting to the power spectrum and Fourier filtration. The striking regularity of the methyl group pattern which extends over the whole imaged area reflects the constancy of epitaxial interactions in the contact face. Furthermore, the pictures display darker oblique bands oriented at ≈1 o'clock. From their spacing (≈10–12 nm) and general orientation relative to the methyl group pattern, the bands correspond to interlamellar regions, which are visible in epitaxially crystallized polymer films since lamellae stand edge-on.

Both lamellar organization and methyl group organization are revealed by the Fourier transform of the AFM picture (Figure 1b), which displays *both* wide- and low-angle patterns. The six-spot wide-angle pattern is as expected from the nearly square lattice of methyl groups with one pair of 100, one pair of 001 (both at ≈0.65 nm^{-1} spacing), and one pair of 101 spots (note that both 100 and 001 are systematic absences in the X-ray or electron diffraction patterns but are authorized in this surface pattern). As is usual in AFM, slightly better resolution is again achieved in the vertical direction, where it is governed by the density of scan lines; the absence of corresponding 1$\bar{1}$0 spots at ≈2 o'clock confirms lower resolution in the scan direction (horizontal). The low-angle part of the pattern corresponds to the ≈12 nm separation of the darker bands in the unfiltered image and supports its assignment to the lamellar periodicity.

Following the line of reasoning developed in ref 1, it is easy to establish the crystal phase and the hand of exposed helices in the present figure. The phase is α, as indicated by the nearly normal orientation of the lamellae and one set of rows of methyl groups (in the γ phase, both rows would be inclined at 40° to the lamellar normal). Methyl groups of any one of these rows thus belong to the same helical stem. Further, the orientation of the second row of methyl groups (which materializes the *a* axis direction) relative to the lamellar surface clearly corresponds to the situation depicted at the bottom left of Figure 1 in refs 1 and 3: the imaged helices are left-handed.

a

Spectrum 2D

b
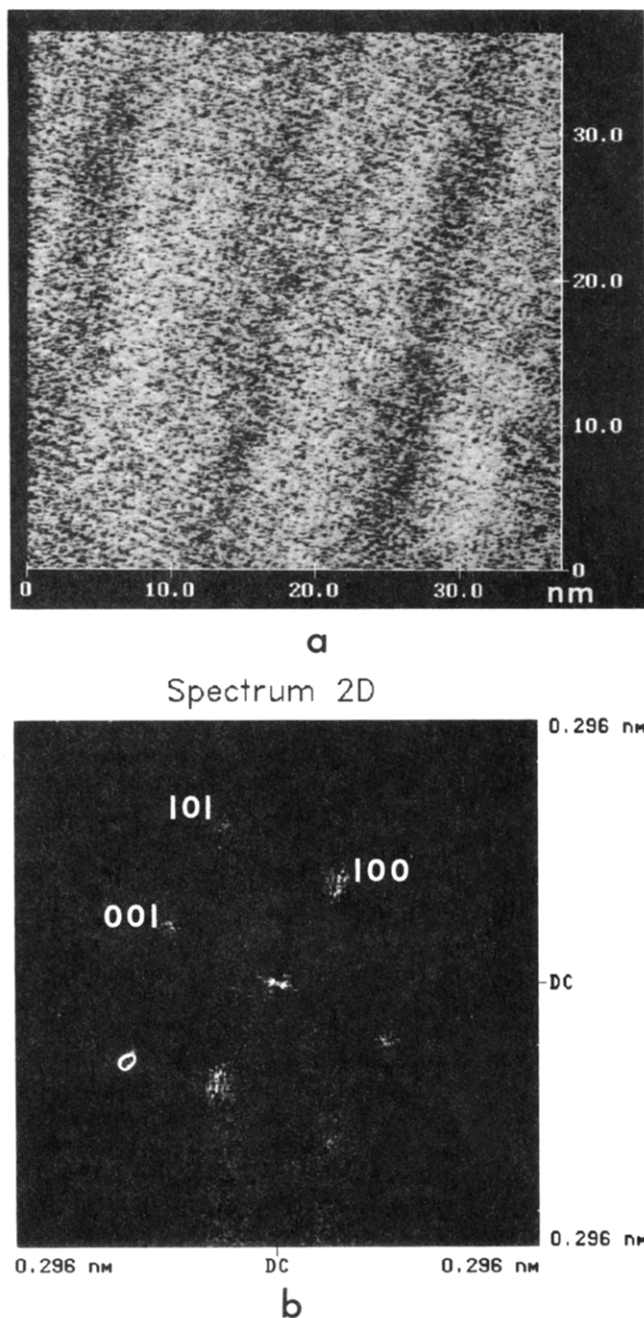
Figure 1. (a) Unfiltered AFM image of an epitaxially crystallized thin film of isotactic polypropylene on anthracene. The nearly square pattern of methyl groups corresponds to the (010) plane of the α phase (cf. Figure 2). (b) Power spectrum of the image in (a). Note the presence of both low- and wide-angle maxima, corresponding to lamellar and unit cell surface patterns. Indexing is given for the monoclinic unit cell of the α phase.

One feature of Figure 1a indicates that we may not have achieved the "ideal" image of the surface: the pattern of methyl groups appears not only on the lamellar core surface but also, although less prominently, in the darker bands which we associate with the interlamellar regions. The methyl group topography is not realistic beyond the lamellar edge and indicates that more than one site of the tip contributes to forming the image. As the tip scans over the lamellar edge, the point of closest range with the sample starts to shift until another part of the tip interacts with the sample (cf. Figure 2). Due to this "tip switch", the topography of the lamellar surface is artificially smeared into the interlamellar regions. To get rid of this relatively minor instrument-generated artifact would
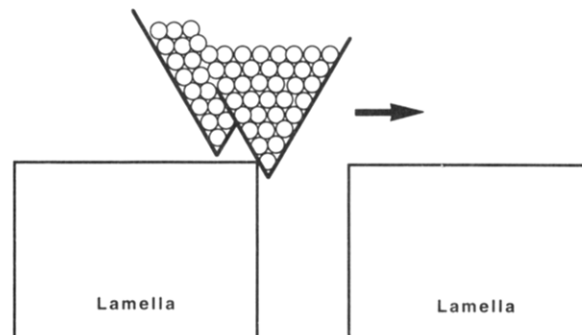
Figure 2. Tip switch: a probable origin of the "smearing" of the lamellar methyl group pattern into the interlamellar region.

require further lowering of the feedback parameters and finding an optimum scan rate.

Beyond this relatively minor point, the present study shows that imaging in a liquid medium enables very *high resolution* (i.e., methyl group) on a relatively *large scale*, compatible with observation of lamellar organization in crystalline polymers: it is therefore possible to directly correlate lamellar and chain features in a single image. This situation contrasts markedly with imaging under dry conditions (cf. ref 1) for which this correlation of lamellar and methyl group organization was only possible by combining information gathered in two different pictures (cf. Figures 6 and 7a, or 10a and 10b, in the accompanying ref 3).

Conclusion

The contact surface of epitaxially crystallized iPP, with its lozenge-shaped, nearly square pattern of methyl side chains, provides a convenient resolution test material for crystalline polymers: the methyl groups attached to the underlying helices stand nearly erect on the surface, and their separation (≈ 0.65 nm) is significantly larger than their diameter (≈ 0.4 nm).

Use of a liquid cell and probing under water facilitate considerably the AFM data collection and, when applied to these epitaxially crystallized films, reveal *both* large arrays of individually resolved methyl groups *and* the lamellar structure in *unfiltered* images. When translated into a 2D power spectrum, this simultaneous imaging of the lamellar and methyl group structure yields an AFM "diffraction pattern" with both low- and wide-angle spots more familiar in X-ray or electron diffraction. However, the original information is contained in a real space surface image which may display structural information beyond reach of techniques based on diffraction, such as helical hand of individual exposed chains.[5]

References and Notes

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