Polymer Communication

Surface crystallography of polybutene-1 by atomic force microscopy

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Abstract

The surface of ultra-thin polybutene-1 films was studied using an atomic force microscope (AFM) and resolution of individual molecules was achieved. Polybutene-1 can exist in multiple crystal phases. The tetragonal phase, named form 2, is unstable, converting over time to the most prevalent phase, form 1. Comparison of the images with Connolly surfaces enabled identification of which plane of which phase was observed in the AFM images. The samples were prepared in such a way that the bulk would be in the stable phase. It was found that this phase is also stable on the surface. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

For over 40 years it has been known that crystalline polybutene-1 occurs in multiple forms. In 1955, Natta et al. [1] reported the first two forms, with one of these being sufficiently unstable that it converted rapidly to the other, at pressures of around 100 atm. The most common of these, dubbed form 1, was to be extensively studied [1] in 1960. The crystal structure of form 2 was determined 3 years later, in 1963 [2]. This form of polybutene-1 is not stable at room temperature, since it will convert to form 1 without any further treatment. The time scale for this transition has been the subject of a number of studies. Aronne et al. [3], for example, concluded that this transition is complete after approximately 1 week at room temperature. Cojazzi [4] reported a third form of polybutene-1, obtained by evaporation from solution, in 1976.

Form 1 consists of a hexagonal unit cell with parameters $a = b = 17.7$ Å and $c = 6.5$ Å, containing 18 monomers of polybutene-1 (see Fig. 1). Another distinguishing feature of this form is the fact that the molecule lies in a 3_1 helical conformation [1]. This contrasts with the tetragonal form 2, with $a = b = 15.42$ Å and $c = 20.05$ Å, in which the 44 monomers combine to form four 11_3 or 40_{11} helical structures. The two descriptions of the helical structure are equally valid since they represent the nearest ratios of integer numbers [2]. Finally, form 3 has a 2_1 helical chain conformation in an orthorhombic lattice [4].

While the preference for the hexagonal form 1 is well established in the bulk, it is not certain which of these forms is present on the surface. The nature of the surface is of fundamental importance, for example, for the study of adhesion and of crystal growth. For this reason, the current work aims to determine which of these phases is present on the surface.

Other synthetic polymers that have been studied by atomic force microscopy (AFM [5]) up to molecular resolution include polyethylene [6], PTFE [7] and isotactic polypropylene [8]. The study of polybutene-1 crystals using AFM is not new, nor is it exceptional that molecular resolution is achieved on these samples [9]. It is, however, important to be able to interpret these results in terms of the crystal structure.

It has always been the aim of scanning probe microscopists to obtain atomic resolution on the samples that they study. It should be stressed that it is very rare to be able to resolve individual atoms by AFM and at the current stage of development of scanning probe microscopes it appears impossible to achieve this on substances such as synthetic polymers, which have little rigidity when compared to lattices such as mica or graphite. However, the resolution of features within long-chain polymer molecules can be very instructive and such a resolution may tentatively be dubbed near-atomic.

2. Experimental details

For the present study the samples were prepared using the

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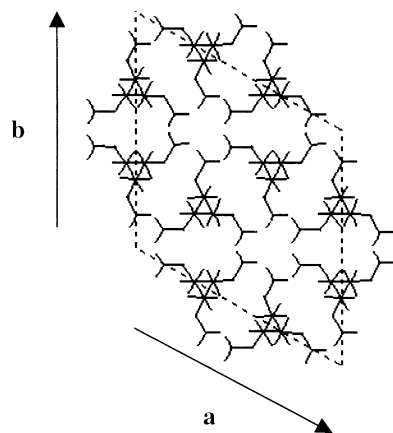*E-mail address:* alex.winkel@bristol.ac.uk (A.K. Winkel)

Fig. 1. The unit cell of form one of polybutene-1. The molecules extend into the page, in the direction of the crystallographic *c*-axis. The crystallographic *a* and *b* axes are indicated.

Petermann–Gohil method for ultra-thin film production [10]. This method involved a thermostatically controlled hotplate with a glass sheet on top preheated to 135°C, on to which a dilute solution of polybutene-1 in xylene (less than 0.6%, w/w) was deposited. Once the solvent had evaporated a spinning roller was introduced and an ultra-thin film was drawn (see Fig. 2). The thickness of these films was of the order of tens of nanometres and the high strain rate applied while drawing the films resulted in a highly oriented film with the molecules aligned in the draw direction [10].

The films were transferred onto freshly cleaved mica and imaged under propanol using a Digital Instruments Extended Multimode AFM. Imaging was performed in a liquid environment to reduce electrostatic interactions and capillary forces between sample and tip, thus reducing sample deformation and increasing resolution.

3. Connolly surfaces and identification

While it is sometimes possible to identify the phase and the crystal plane by measurement of features on the AFM image, this leaves potential for error. It is, for instance,
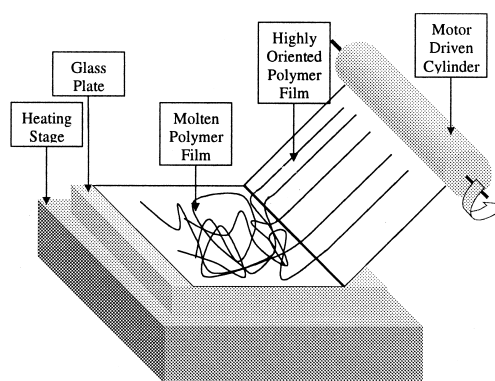

Fig. 2. The Petermann–Gohil method for ultra-thin film preparation.

possible for two closely packed molecules to appear as one in an image. Thus any periodicity measured would be twice the inter-molecular spacing, which could lead to an incorrect conclusion about which plane is being observed. For this reason it is desirable to be able to simulate various crystallographic planes that are likely to be present at the surface and compare these simulated surfaces with the AFM images.

In order to determine the expected appearance in an AFM image of any given plane, it is possible to make use of the crystallographic data [1,11,12] and version 3.5 of the Molecular Simulations software package CERIUS^2. Using the Connolly surfaces routine it is possible to generate a file that details the surface of the CERIUS^2 model. The Connolly surfaces routine essentially rolls a sphere of a given radius over the van der Waals surface of the structure, and plots a certain number of points [13]. The number of points plotted depends on the sampling density. Sixty samples or points per $Å^2$ were chosen as the sampling density and the probe radius was taken to be 2 Å, an adequate approximation for this application.

The generation of the Connolly surface within CERIUS^2 can be very time consuming if large areas need to be calculated. As a means of avoiding this problem a custom written program is used. The combination of two programs, written by Baker [14], essentially tiles any surface generated by CERIUS^2 and converts the whole into an image file, representing a larger area. The length scales in the image were then calibrated using version 0.59 of Jorgensen's scanning probe image processor (SPIP) for Windows NT. The Connolly surfaces can now be compared to the images.

4. Results and discussion

An image of relatively low magnification (1 μm × 1 μm) is presented in Fig. 3. The needle-like morphology observed by Jandt et al. [9] is again apparent. Since the age of the films was in the order of months, the films were sufficiently old that form 1 was expected in the bulk.

Decreasing the scan size significantly and increasing the scan rate facilitates the resolution of individual molecules, as also observed by Jandt et al. [9]. A high-resolution image is presented in Fig. 4(a); Fourier transform analysis indicates that the resolution of this image is approximately 2 Å. This image has been closely compared with the Connolly surfaces generated for low index planes of all three forms of polybutene-1. The only close match is presented in Fig. 4(b); it represents the (110) plane of the hexagonal form 1. While it appears that some molecules have not been clearly imaged, the similarity between the appearance of the repeating units is strong enough to conclude with confidence that this is the (110) plane. It has to be noted, however, that due to the high degree of symmetry in the hexagonal form 1, many faces appear identical. For example, the (110), (010) and ($\bar{1}$10) planes will
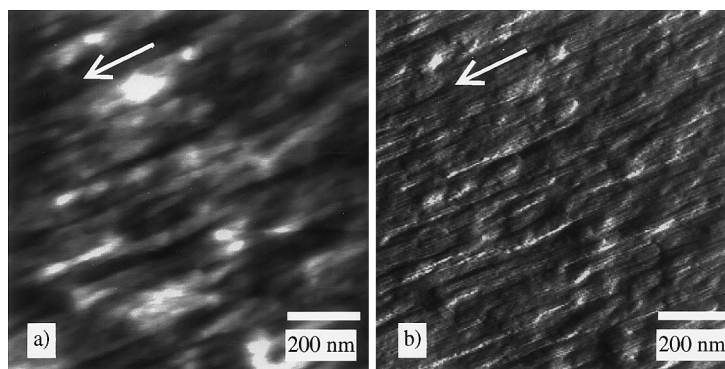
Fig. 3. Height image (a) and corresponding deflection image (b) of polybutene-1. The Z ranges are 15 nm and 0.2 nm, respectively. The bottom left to top right needle like structures (indicated by the arrows) lie in the direction in which the film was drawn.
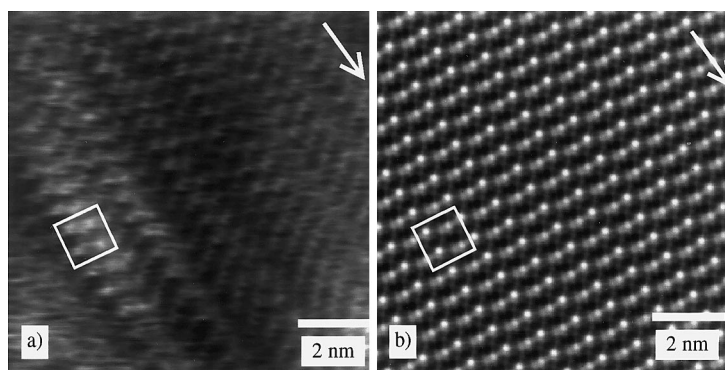

Fig. 4. (a) High-resolution image of polybutene-1. The Z range is 1.8 nm and the image has been enhanced by first order flattening, fitting a plane to first order and low pass filtering once. (b) The closest match of the Connolly surfaces, representing the (110) plane of the hexagonal form of polybutene-1 (form 1). The boxes indicate an area of close resemblance, while the arrow indicates the orientation of the molecules.
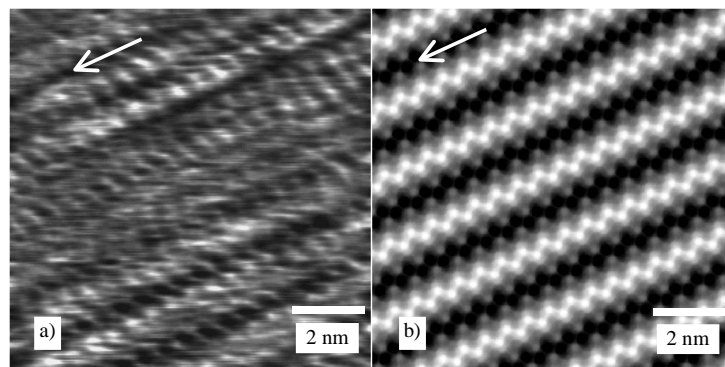

Fig. 5. (a) The Z range of this high-resolution image of polybutene-1 is 0.3 nm. Once again the image has been enhanced by first order flattening, fitting a plane to first order and low pass filtering once. (b) The Connolly surface of the (100) plane looks very similar to the bottom right hand side of the image in (a).

appear identical, as will the (110) and the ($\bar{1}\bar{1}0$). As a result of this degeneracy, any mention of a crystal plane in this work will, in fact, offer only a candidate for the set of identical-looking planes.

The boxes in both Fig. 4(a) and (b) indicate an area where the resemblance is strongest. When the model [1,11,12] is viewed in CERIUS[2], it becomes clear that these boxes represent two repeating units along a single chain. The orientation of the molecules (indicated by the arrow) is

different to that of Fig. 3, due to the fact that the sample was mounted in a different orientation with respect to the scan direction.

A similar result is presented in Fig. 5(a). Fourier transform analysis indicates that the resolution of this image is approximately 2.5 Å. It should be noted that the orientation of the molecules is identical to the orientation of the needle-like structures in Fig. 3; the two images were acquired in the same session. Thus the molecules lie in the direction of the
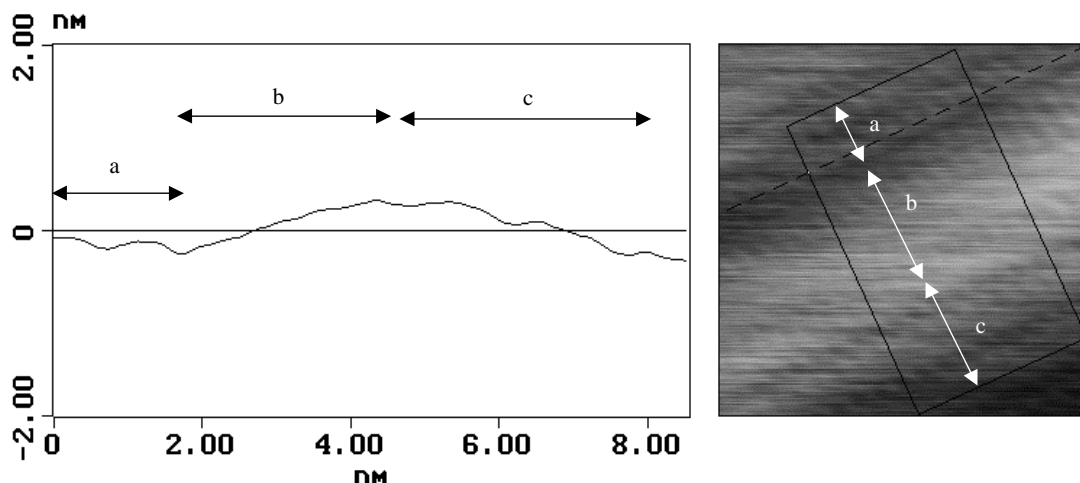
Fig. 6. Section analysis of unmodified version of Fig. 5(a). Area *a* is the (110) area in the image, area *c* is the clear (100) area and area *b* is the region in between. The geometry suggests that region *b* is similar in nature to region *c*.

needle crystals, and not perpendicular. This image also shows two clearly different areas: the top left resembles the (110) plane, while the bottom right looks very much like the (100) plane, the Connolly surface for which is presented in Fig. 5(b). When this plane is examined in cerius[2] it becomes clear that what looks like a single molecule is actually two molecules lying back-to-back. This is, therefore, a situation where simple measurement of features in the image could easily lead to an incorrect conclusion about which crystal plane was being observed.

The presence of two different facets in the same image (Fig. 5(a)) suggests an abrupt gradient in the image. This is confirmed by using the Nanoscope AFM software to perform a section analysis on the topographic image (see Fig. 6). Region *a* is the area previously identified as being (110) or one of the many identical looking planes, while region *c* is the area previously identified as (100) or an alternative. Using the angles measured in this image by the AFM software it becomes possible to be more precise. The crystal structure data define the angle between the $(1\bar{1}0)$ and (100) planes to be 150° (see Fig. 7), while the angle between regions *a* and *b* in Fig. 6 is 165°. Similarly, according to the crystal data, the angle between the (100) and $(0\bar{1}0)$ planes should be 120°, while the angle between regions *b* and *c* is 155°. Given the limitations with the AFM for measuring angles between features in the *z* direction at high scan rates, this is an
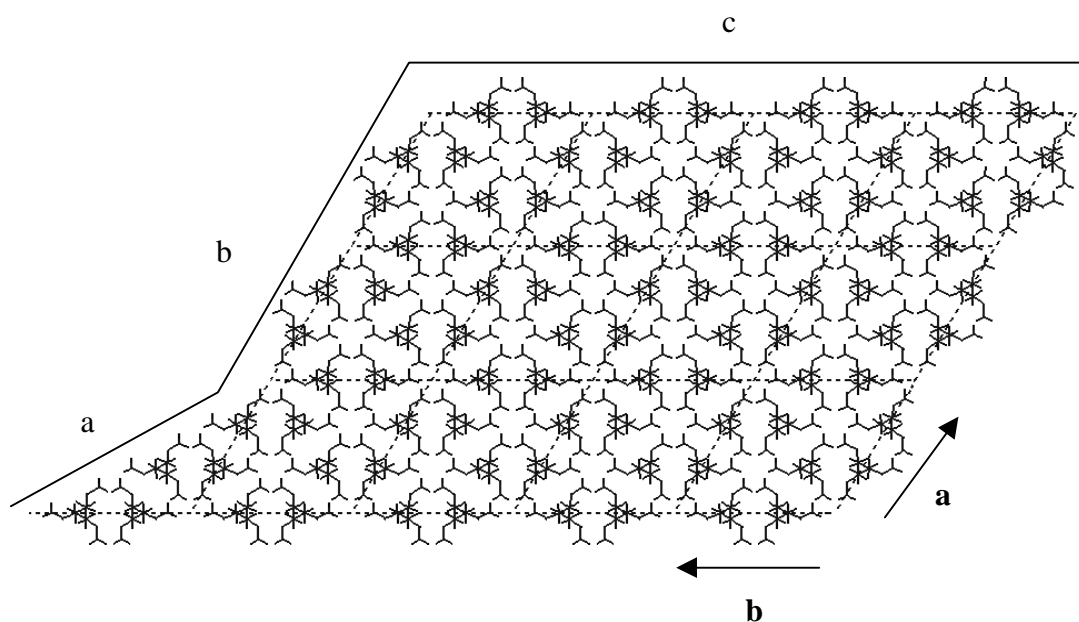

Fig. 7. An illustration of the conclusion regarding which crystal faces are seen in Fig. 5(a). Region *a* is $(1\bar{1}0)$, region *b* (100) and region *c* $(0\bar{1}0)$.
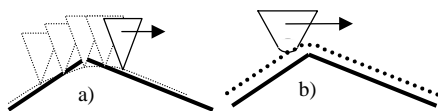
Fig. 8. (a) Limitations in the feedback lead to features in the image being a somewhat flattened version of the actual structure, as the structure is perturbed more at high locations, than at lower ones. This effect will result in measured angles being higher than they, in fact, are. (b) A tip of high radius of curvature will result in the peak being obscured and broadened, so that the exact measurement of angles will be inhibited, leading to higher values of angles measured.

acceptable agreement. This discrepancy in angle may be the result of surface relaxation. It could also be a result of deformation by the tip (Fig. 8(a)), instrumental effects such as tip convolution (Fig. 8(b)) and imperfect feedback response. These effects could combine to give a considerable widening of the angles measured. Therefore, it can be concluded that the only low-index planes that match the data, are as follows: region a is $(1\bar{1}0)$, region b (100) and region c $(0\bar{1}0)$. Fig. 7 illustrates this in terms of the crystal unit cells.

5. Conclusion

The discussion has shown that it is possible to determine the indices of the surface planes of polybutene-1. It has thus facilitated the determination of the phase present at the surface. This has been concluded to be the hexagonal form 1, which is the phase that is stable in the bulk at room temperature. These results show that AFM is a useful tool for polymer surface crystallography. The application of Connolly surfaces to scanning probe microscopy is also a very practical complementary technique.

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