Atomic force microscopy of polymer crystals: 4. Imaging of oriented isotactic polypropylene with molecular resolution

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Atomic force microscopy (AFM) was used to visualize microfibrils and macromolecules in uniaxially oriented isotactic α-polypropylene. AFM images showed fibrils with a typical average diameter of 150 nm. High magnification scans unveiled individual macromolecules with a 1.17 nm chain–chain distance. Based on this value it is suggested that the (1 1 0) crystal plane was resolved in the AFM images.

(Keywords: atomic force microscopy; orientation; microfibrils; molecular imaging; isotactic polypropylene)

Introduction

The main inspiration for atomic force microscopy (AFM)[1] came from the possibility of imaging atoms and molecules[2,3]; however, morphological characteristics of polymeric materials (e.g. structure and thickness of crystal lamellae[4,5], characteristics of spherulites, microfibrils[6,7], etc.) can also be studied by this technique on the micrometre scale. On the nanometre scale AFM has been successfully applied to visualize various macromolecules[6–10], to observe intra- and intermolecular distances, and to selectively image various atoms in the backbone[6,7]. AFM imaging with molecular resolution obtained from thin films of low molecular weight α-phase isotactic polypropylene (i-PP) epitaxially crystallized on benzoic acid has also been reported[11]. This study interpreted the methyl side group pattern obtained in the AFM images as 'four-face type' structure of right-handed helices.

The AFM probes the sample surface with a very sharp tip attached to a microfabricated cantilever which contacts the surface by a low force[12], typically of the order of 10^{-7} to 10^{-10} N. An optical lever technique can, for example, be utilized to detect the deflection of the microcantilever. Due to the complexity of normal and lateral forces acting on the tip, the inherent many-body interactions involved[13], and the lack of information concerning the arrangement of atoms at the apex of the tip, the imaging procedure is not yet satisfactorily understood. This, combined with problems caused by the square-pyramidal shape of the tip, and other experimental difficulties often results in misinterpretation of the images[14]. Furthermore, in spite of careful calibration attempts using graphite, mica and NaCl images, intermolecular distances obtained by AFM often do not satisfactorily agree with values obtained, e.g. from X-ray analyses[6,10]. Therefore, it seems necessary to obtain more experimental information about AFM, especially concerning atomic-level imaging.

We undertook systematic AFM research aimed at molecular resolution of oriented polymers[6,7] for a variety of reasons. Firstly, AFM imaging of macromolecules of uniaxially deformed polymers with high degrees of anisotropy has the advantage that the direction of the chain axis can be easily identified since it coincides well with the direction of elongation. In addition, polymers with a high degree of uniaxial elongation often have mechanical properties superior to metals, e.g. high modulus and mechanical strength in the orientation direction, and have been the subject of intensive research[15]. Information regarding the molecular architecture and physical properties is indispensable for the design of these new materials. For example, when macromolecules are transformed into oriented, extended-chain structures, the perfection of chain orientation will determine the ultimate mechanical properties of the polymer. Except for the aramids, these high performance materials have only recently been introduced into the marketplace. Therefore, information regarding their molecular structure–physical property relations, design criteria, and performance expectations is largely lacking. For example, highly crystalline aramids and thermotropic copolyesters with much lower structural order have similar mechanical performance[15]. Thus, the role of long-range three-dimensional order to obtain high mechanical properties is controversial. It seems that AFM can yield valuable information about local structural order of polymers with a high degree of anisotropy on the molecular level by directly visualizing the macromolecules.

Experimental

Specimens were prepared from commercially available Propathene® GYM 45 i-PP polymer (ICI, batch no. 93996). Orientation was carried out by using standard tensile test samples which were obtained from injection moulding. Specimens were uniaxially stretched in a tensile test instrument (Schenk-Trebel, model RM-100) at a temperature of 120°C and at a stretching rate of 10 mm min^{-1} until an elongation ratio of $l/l_0 = 6$ was reached. The samples were then quenched under constant stress to prevent relaxation.

Specimens for AFM studies were prepared from oriented i-PP by using a Sorval MT6000 ultramicrotome

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with glass knives. AFM images were taken in air using a NanoScopeII instrument with an A-type scan head utilizing NanoProbe 100 micrometre triangular Si_3N_4 cantilevers with wide legs. The effective spring constant of the cantilever was $0.58\,N\,m^{-1}$. For distance calibration of the piezo controller, mica images with molecular resolution were used.

Samples were characterized by performing differential scanning calorimetry (d.s.c.) and wide angle X-ray scattering (WAXS). D.s.c. measurements were carried out by using a Perkin Elmer DSC 7 device. WAXS experiments were performed on isotropic and oriented samples utilizing a Siemens D-500 instrument and a Huber texture goniometer. Pole figures of oriented specimens were calculated from X-ray intensities. Based on the X-ray diffractogram, the polymer contained predominantly the type-I monoclinic (or α) crystal modification in both the unoriented and oriented states[16,17]. The d.s.c. melt peak temperature of our samples was 161.5°C, which agrees well with literature data[18] for α-PP. Pole figures of the stretched polymer showed a uniaxial texture with chain orientation pointing in the stretching direction.

Results and discussion

AFM images of oriented i-PP on the micrometre scale showed fibrils with a typical average diameter of 150 nm and with an axis aligned in the direction of orientation (*Figure 1*). High magnification scans of the surface of these fibrils unveiled features on the 10–20 nm scale (*Figure 2*). These objects were identified as individual macromolecules since their orientation (marked with a line in the image and two arrows on the margin) coincides with the polymer fibre (or orientation) direction.

The two-dimensional autocorrelation function of six i-PP images with molecular resolution (obtained on two different fibres) were computed to determine chain packing parameters. The value obtained was 1.17 ± 0.03 nm, where error limits correspond to statistical standard deviation and do not include systematic errors.

In order to identify the imaged crystal plane in *Figure 2* we analysed interchain distances of the α-PP crystal structure in the chain perpendicular (1 0 6) plane. Based on the X-ray results[16,17], the value of the chain–chain distance is 1.065 nm in the [1 1 0] facet of the crystal structure which is the closest match to the interchain distance obtained in our AFM experiments. This suggests that the (1 1 0) plane was imaged in *Figure 2*. This seems to be a reasonable conclusion since based on chain packing considerations one would expect that PP cleaves relatively easily in this plane due to a loose interlock between chains in {1 1 0} planes.

In some cases AFM images showed periodic structure also along the i-PP chains, but due to poor image quality a quantitative analysis was not possible. It is worth

Figure 1 AFM image of microfibrils in oriented polypropylene

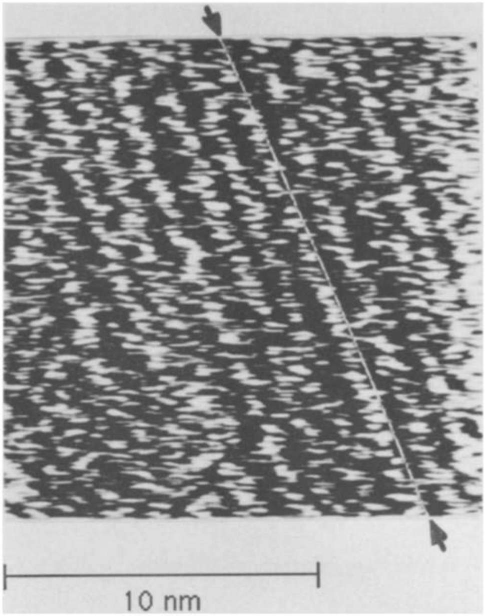

Figure 2 Unfiltered image showing molecular resolution of polypropylene chains obtained on the surface of a microfibril shown in *Figure 1*. The chain direction is shown by the line between the two markers

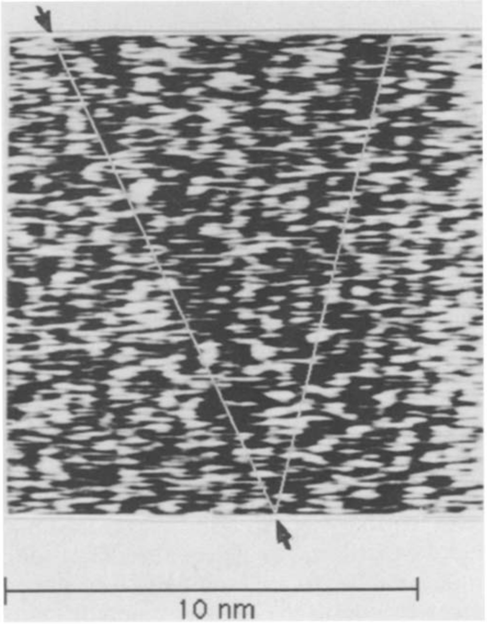

Figure 3 Nanometre-scale features observed at an angle of 39° to the chain (or orientation) direction. The chain direction is shown by the line between the two markers

mentioning that our AFM images of oriented poly(oxymethylene) and poly(*p*-phenylene-terephthalamide) (Kevlar®) fibres yielded images with much better quality, especially concerning chain internal resolution. It is interesting to point out that chain internal structures were seen more often in i-PP if the scan direction was rotated by ~45° with respect to the fibre axis. A similar effect was noted by Hansma *et al.*[10] in an analysis of poly(tetrafluoroethylene) images. For example, in the image shown in *Figure 3* periodic 'rows' cannot be macromolecules since their direction, as shown on the image, makes an angle of 39° with the fibre direction. If the fibre direction had not been known *a priori*, one could have identified these periodic structures as macromolecules. Such *a priori* knowledge is important at the present stage of the AFM technology to identify atomic or molecular details. It seems that depending on the tip–molecule orientation certain periodic features on the nanometre scale are emphasized on the AFM images more than others. This effect could be associated with the shape of the tip and unknown characteristics of the imaging procedure and must be further studied. It is important to note, however, that when our i-PP sample was rotated with respect to the scan direction by ±20°, the image of macromolecules was also rotated by the same extent. In addition, intermolecular distances remained unchanged. Finally, we should point out that even in images such as that shown in *Figure 3*, features in the fibre (or macromolecular) directions can be clearly observed.

To identify these features, the (1 1 0) crystal facet was visualized on a computer workstation using the Schakal 88 software package (Institute of Crystallography, University of Freiburg, Germany). Based on a visual analysis of the molecular packing, we concluded that the features captured in *Figure 3* are associated with 'rows' of methyl groups attached to neighbouring chains, assuming that the individual methyl groups within the 'rows' are not resolved. A quantitative analysis of the AFM images of these features resulted in a packing distance which corresponds to the expected value for the distance between the 'rows' of methyl groups at 40° to the chain axis. A detailed discussion is the subject of a forthcoming paper.

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