# Scanning force microscopy of nanostructured uniaxially oriented ultra thin film surfaces of isotactic polystyrene

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Surfaces of ultra thin films of isotactic polystyrene (iPS) drawn from the melt were investigated by scanning force microscopy (SFM). SFM micrographs of iPS surfaces exhibit the morphology of uniaxial orientation resulting from the preparation technique as well as structures pseudomorphic to regularly arranged shish crystals. Their diameters were ~60% larger compared to earlier results obtained from dark-field transmission electron microscopy investigations. Furthermore, different defects of the polymer surface morphology were observed. It is supposed that macromolecules of a lower orientational order cover the shish crystals (hair dressing model).

**(Keywords: isotactic polystyrene; scanning force microscopy; surface morphology; nanostructures; morphological defects)**

## *Introduction*

It is well established that polymer molecules may crystallize from an extented melt in a whisker- or needle-like (shish) morphology. The lateral sizes of these shish crystals depend on both the crystallization conditions and processing techniques as well as the polymer in use. In general, their diameter does not exceed 50 nm. Several models exist for the molecular growth mechanism[1–4] but only a few attempts have been made to explain the limited lateral sizes of these crystals[3–6]. Additionally, the topology of polymeric film surfaces is less elaborated. Surface properties of different polymers determine, for example, the interfacial behaviour of polymer composite materials.

The use of well established transmission electron microscopy (TEM) in polymer science is hindered by the radiation sensitivity of the samples[7]. Additionally, TEM investigations of polymeric surface features are only possible by using replica or metal shadowing techniques (with C, Pt/C, Pt/Ir or Au)[7].

Recent developments in scanning probe techniques [i.e. scanning tunnelling microscopy (STM)[8] and scanning force microscopy (SFM)[9]] now offer the possibility of direct investigations of solid surfaces on the molecular scale. It is thus promising that SFM may yield new insights into the behaviour of organic materials.

This study presents SFM investigations of nanostructured uniaxially oriented ultra thin film surfaces of isotactic polystyrene (iPS). These measurements complement earlier STM/SFM investigations[10–13] performed on other oriented polymer films. The investigations were performed on neat iPS surfaces without any metallic coatings. Therefore, imaging the iPS surface morphology and its defect structures down to a resolution of 2 nm was possible. The SFM measurements are compared with earlier TEM investigations.

## *Experimental*

The oriented semicrystalline polymer substrates were prepared similar to the method of Petermann and Gohil[14]: the iPS granulate (Polysciences Inc.™; $M_w \sim 851\,000$) was dissolved in xylene (~0.1 wt%). Some droplets from this solution were deposited on the smooth surface of a glass slide where the solution dispersed uniformly. On heating the solution between 460 K and 480 K the solvent evaporated. From the resulting melt (thickness $\leqslant 1\ \mu m$) a highly oriented ultra thin film was drawn (thickness $<20$ nm) using a pair of tweezers. Even thinner films may be produced by this technique with careful preparation.

For SFM investigations the film was fixed onto highly oriented pyrolytic graphite. SFM measurements were carried out with a PSI SFM™ using microfabricated $Si_3N_4$ cantilevers having a theoretical force constant of 0.032 or 0.064 N m$^{-1}$. These levers have an integrated pyramidal tip with a square base thus yielding a tip radius[15] of $<40$ nm at a maximum opening angle of 90° at the intersection of the $Si_3N_4$ (1 1 1) planes. Images were collected in the constant force imaging mode.

The SFM micrographs are presented as top-view or pseudo-three-dimensional images. No filtering was used so that all the images are reproduced in the same quality as they were acquired (except for linear plane subtraction to optimize the *z*-scale adjustment).

## *Results and discussion*

Earlier TEM investigations of melt drawn ultra thin iPS films showed that the polymeric material consists of both elongated shish crystals and amorphous regions (*Figure 1*)[6]. From the diffraction pattern in the upper right-hand corner of *Figure 1* the uniaxial orientation of the iPS film is deduced. The diameter of the shish crystals was determined to be $\sim 31.3 \pm 3$ nm.

*Figure 2* shows a $1 \times 1\ \mu m^2$ SFM surface image of an

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**Figure 1** TEM dark-field electron micrograph of an ultra thin iPS film. The arrow in the lower left-hand corner indicates the direction of the molecular orientation. An electron diffraction pattern and a sketch of the morphology are inserted in the upper right-hand and left-hand corners, respectively

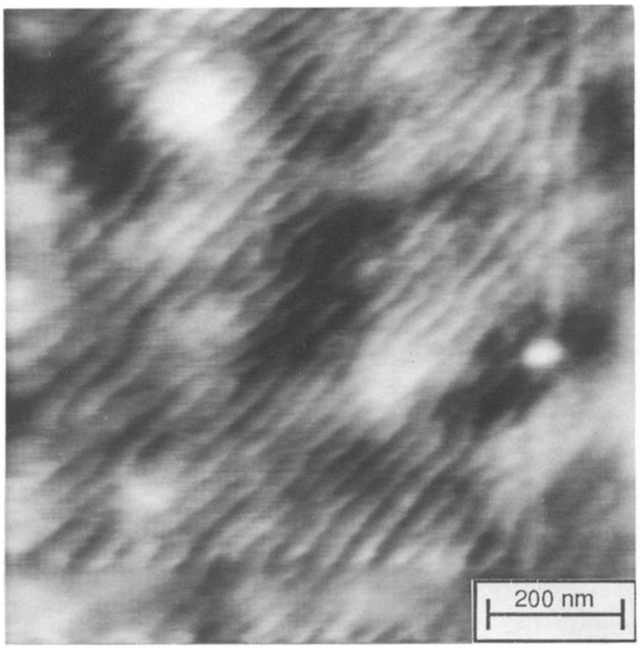

**Figure 2** Top view SFM image taken over 1 × 1 $\mu m^2$ of a highly oriented iPS ultra thin film surface. The surface of the iPS film is characterized by a regular arrangement of close packed highly oriented shish crystals

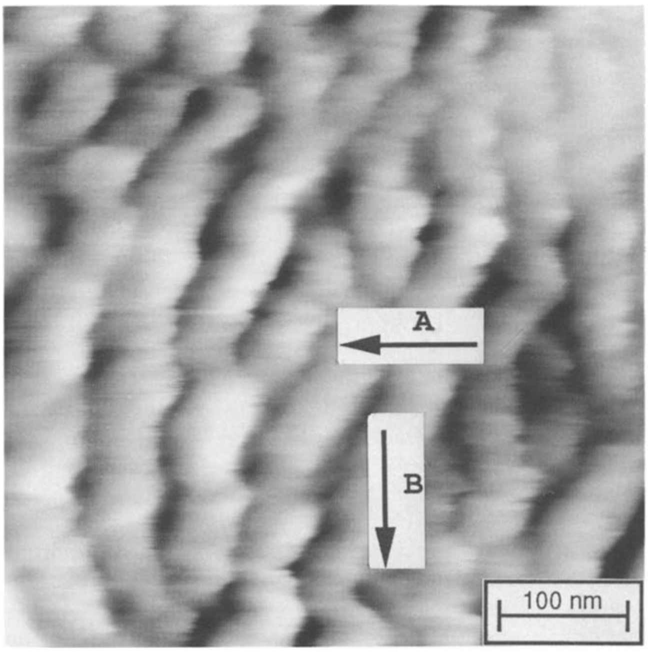

**Figure 3** SFM image taken over 0.5 × 0.5 $\mu m^2$ of the sample from *Figure 2*. The shish crystals protrude a few nanometres out of the surface. By rotating the scanning direction by 90° the latitude of the iPS needle crystals did not change. The structural modulations along the long axes of the shish crystals are also visible. The arrows indicate different regions of disorder as well as deviations from the idealized model of shish crystals: (A) branching of an individual shish crystal; (B) kinks

iPS film. The surface is characterized by a regular arrangement of close packed highly oriented structures pseudomorphic to regularly arranged shish crystals (needle-like crystals). The length of some shish crystals exceeds the dimension of the micrograph ($\sim 1.4\ \mu m$). The average diameter of individual shish crystals at the surface of the iPS film was determined to be $50 \pm 12$ nm which is about two-thirds larger than the needle crystals determined by dark field TEM.

At higher magnification (*Figure 3*) the individual arrangements of ~10 shish crystals and some of their morphological defects are visible. They protrude on average ~4 nm out of the surface (local peak to valley value). The root mean square roughness measured over the whole surface area of *Figure 3* is 4.4 nm.

The needle-like shish crystals do not grow perfectly since they individually deviate from the idealized models (inset in *Figure 1*), as seen in *Figure 3*. Besides local deviations from the uniaxial orientation, kinks (steps in the ledge of a shish crystal), branching and a structural modulation along the long axes of the shish crystals are visible. Similar effects have been observed by TEM[16] (branching) and with SAXS[17] (density variations along the shish crystals).

The different diameters, observed in dark-field TEM and SFM, may be explained by the fact that the dark-field TEM image measures the crystalline part of the crystals only, while by SFM, the whole shish morphology including its surface is imaged. From earlier investigations it was proposed that the shish crystals consist of a crystalline core and a transitional zone of highly oriented molecules (hair dressing model)[18,19]. In the transitional zone, no long range lateral order exists and hence, it is not accessible with dark-field TEM.

SFM investigations have proved to be a supplementary method to TEM, yielding additional information on the morphology of polymers.

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