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Oriented crystallization of isotactic polystyrene in films prepared by friction transfer

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ABSTRACT

The ability to orient polymer chains by applying external forces opens up the possibility to obtain polymeric surfaces with ordered structures. Here, we employed a friction-transfer approach by moving a pin of isotactic polystyrene (i-PS) across a smooth silicon counterface at controlled velocity, pressure and temperature which led to the deposition of a molecularly thin layer of highly oriented i-PS chains. The observed morphology of the resulting film (ribbons oriented in the sliding direction) indicated that the transferred molecules were highly oriented. This was confirmed after isothermal crystallization which led to the formation of so-called "*shish–kebab*" crystals aligned in the sliding direction. Thus, after crystallization all polymers were preferentially oriented with their chain axis in the shearing direction. Our results strongly suggest that by extending the polymer chain conformations in the shearing direction we can introduce a significant reduction of the nucleation barrier. Accordingly, friction transfer allows to align not only the transferred polymer chains but also the subsequently forming crystalline domains within the transferred films.

1. Introduction

Polymer crystallization is an industrially and scientifically important phenomenon that has been an interesting subject in polymer processing because the final properties of any products are directly related to their anisotropy, crystallinity, structure and morphology. Furthermore, controlling macroscopic orientation of small molecular and polymeric materials represents an important step in the direction of detailed structural analysis and the improvement of their physical properties which may be enhanced by several orders of magnitude with respect to their isotropic counterparts. Moreover, films of oriented polymers may also open up new possibilities for advances in the performance of optoelectronics devices [1–4].

It is well known that crystallization generates striking superstructures on a hierarchy of lengthscales. The application of extensional deformation or shear flow has a strong influence on polymer crystallization, enhancing significantly the growth kinetics [5,6]. From oriented polymer melts highly anisotropic crystalline features, such as "shish–kebab" and transcrystalline superstructures can be easily generated [7]. The shish–kebab morphology was already observed more than 40 years ago [8–10]. Even so, the mechanism of shish–kebab formation is still a topic of ongoing research [5,11,13–17]. Much work has been performed to elucidate the key elements initiating and directing the development of shish–kebab structures, which consist of an elongated long central core (shish) onto which periodically lamellar crystals (kebab) are attached [18].

Several methods for obtaining oriented polymer chains have been reported, such as stretching, mechanical rubbing, or via a liquid crystalline precursor state [19–32]. One of the simplest possibilities to orient the polymer backbone is given by the friction-transfer technique which has been studied in much detail by Tabor [33] and employed in a multitude of cases by Wittmann and Smith [34]. When the solid block of polymer, such as poly(tetrafluoroethylene) (PTFE), is pressed against a clean substrate, e.g. glass, and then moved laterally, a thin film of the polymer is transferred onto the substrate whose thickness is controlled by temperature, pressure and sliding rate. Transfer is basically the result of the competition between adhesion and cohesion, i.e., the interaction strength at the interface between the sliding bodies and the shear strength of the polymer. The friction-transfer technique is useful for the preparation of the thin films of insoluble solid state polymers and for orienting polymer chains already during deposition, i.e., without recurring to a post-deposition treatment like mechanical rubbing.

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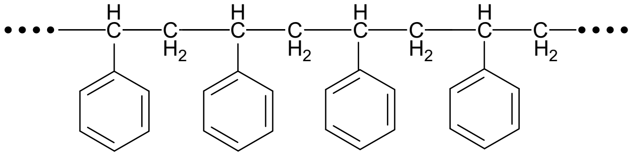

Fig. 1. Chemical structure of isotactic polystyrene (i-PS).

We have applied the friction-transfer approach for the preparation of thin films of isotactic polystyrene of controlled chain orientation. In a subsequent annealing step, we allowed for crystallization of these so deposited chains. The goal is to understand how the preferred chain orientation along the sliding direction induced via friction transfer is influencing crystal nucleation and the orientation of the resulting crystalline lamellae. In particular, we will discuss the relation between the shearing process and the formation and orientation of shish–kebab crystals.

2. Experimental section

In our studies, we started from an isotactic polystyrene (i-PS) powder with a tacticity of 90%, having a weight-averaged molecular weight of $M_w = 400\,000$ g/mol and a polydispersity index of $I = M_w/M_n \approx 2.8$ (purchased from Scientific Polymer Products). The regular chemical structure (see Fig. 1) enables this polymer to crystallize. In order to transfer i-PS onto a smooth silicon substrate (silicon wafer), friction experiments were carried out on a conventional pin-on-disk type tribometer in ambient atmosphere. Silicon wafers were cleaned in water saturated UV–ozone atmosphere. By this cleaning procedure, we created a surface with a high density of hydroxyl groups. A pin of solid i-PS (3 mm in diameter) has been obtained by compression molding of the i-PS powder at 230 °C for 3 min in an inert nitrogen atmosphere. Mechanical deposition of a thin layer of i-PS was achieved by moving such a solid pin of i-PS on a smooth silicon wafer at a controlled rate, temperature and applied pressure, using a pin-on-disk tribometer as shown in Fig. 2. In all friction runs, we performed only a single rotation. Thus, we only deposited i-PS chains on bare silicon surfaces, i.e., multiple depositions on the same substrate site was not allowed.

After this deposition processes, isothermal crystallization of the transferred film was performed by annealing the sample for 12 h at 210 °C in an inert nitrogen atmosphere as schematically shown in Fig. 3. The resulting morphology of the crystalline structure was observed by Atomic Force Microscope (AFM): Measurements were performed with a Nanoscope IIIa/Dimension 3000 (Digital Instruments) in the tapping mode at ambient conditions. We used silicon tips (model TESP) with a resonant frequency of about 160–190 kHz. Height mode (yielding mainly the sample topography) and phase mode data (representing mainly viscoelastic and adhesive properties of the sample) were recorded simultaneously.

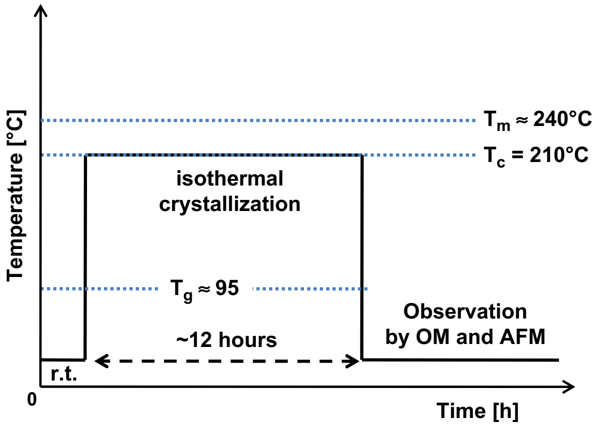

Fig. 3. Illustration of the thermal treatment applied to the i-PS films after deposition.

3. Results and discussion

3.1. Selection of the adequate friction-transfer parameters

Choosing the appropriate experimental parameters for controlling the amount and deformation of transferred polymers represents a crucial step in forming the desired initial structure of a low quantity of deposited i-PS chains on the substrate which would allow a direct correlation between crystal morphology and growth processes. The varied control parameters were pressure (normal load), temperature and sliding velocity. In our experiments, we focused on rather elevated sliding velocities where we could hope that the polymers did not have enough time during transfer to equilibrate these chain conformations completely [35–39]. Fig. 4 depicts the morphology of four i-PS films transferred on silicon substrate under different experimental conditions. Morphological observations of these films clearly indicated the significance of temperature during shearing. Temperature affects the viscoelastic properties of the i-PS pin, in particular relevant at its surface which is in contact with the substrate during shearing. Consequently, temperature controls the probability for detaching i-PS molecules

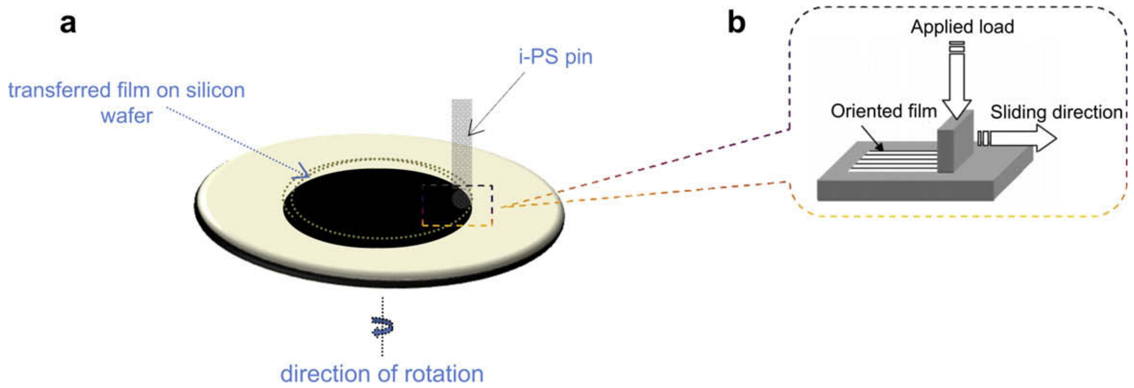

Fig. 2. (a) Schematic representation of mechanical deposition of an i-PS film on a silicon wafer using a conventional pin-on-disk type tribometer in ambient air: a pin of solid i-PS is moved on a smooth substrate at a controlled rate, temperature and applied pressure. (b) Detailed illustration of the mechanical deposition of i-PS film.

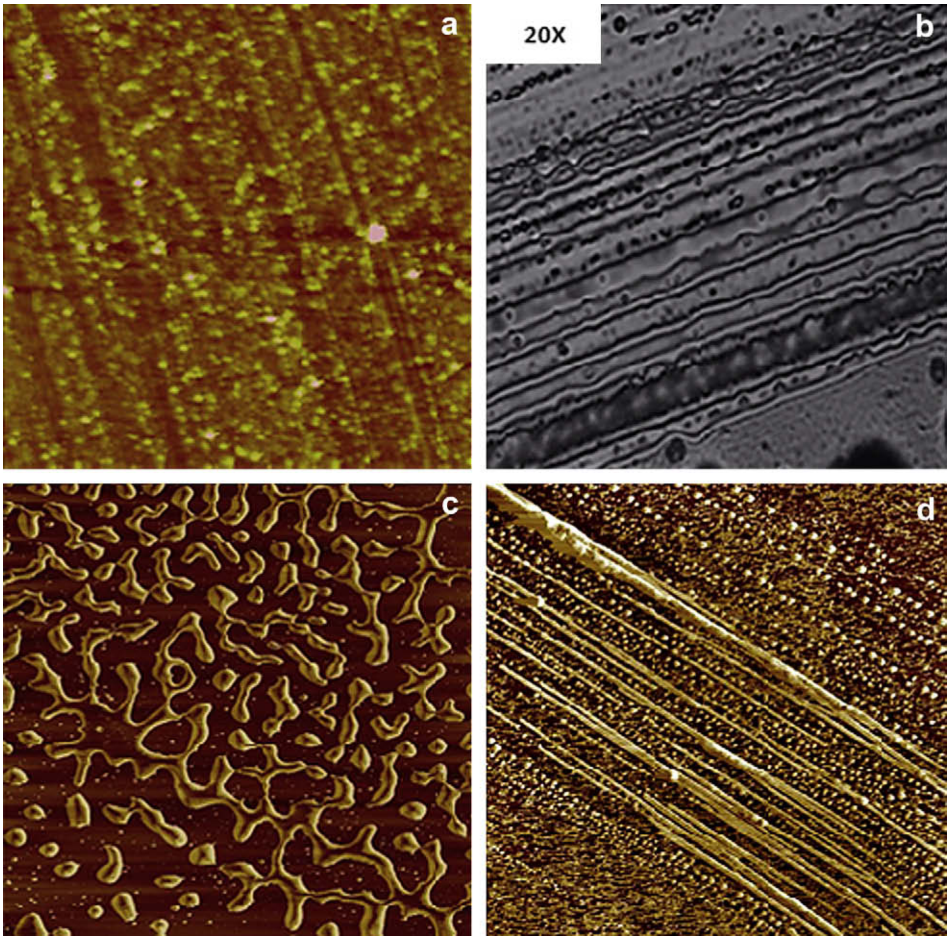

Fig. 4. Morphologies of i-PS films after friction transfer performed under different experimental conditions: (a) friction at a load of 1 N, a sliding velocity of 5 cm/s at room temperature [AFM topography image: 20 × 20 μm^2]; (b) at a load of 1 N, a sliding velocity of 5 cm/s at temperature $T = 150\,^\circ\mathrm{C}$ ($T > T_g$) [optical micrograph]; (c) friction at a load of 1 N, a sliding velocity of 5 cm/s at $T = 150\,^\circ\mathrm{C}$ with a cyclohexanone drop in the contact region [AFM phase image: 10 × 10 μm^2]; (d) friction at very low load (near to zero), a sliding velocity of 5 cm/s at $T = 95\,^\circ\mathrm{C}$ ($T \sim T_g$) [AFM phase image: 10 × 10 μm^2] with a cyclohexanone drop in the contact region.

from the solid pin which leads to the formation of a transferred layer of i-PS on the substrate.

When sliding the pin at room temperature (Fig. 4a) we transferred a high quantity of i-PS in the form of grains having a broad distribution in size: These grains showed a clear preferential alignment along the sliding direction. Moreover, since the temperature in this experiment was much lower than the glass transition temperature of PS ($T_g \approx 95\,^\circ\mathrm{C}$), even the polystyrene

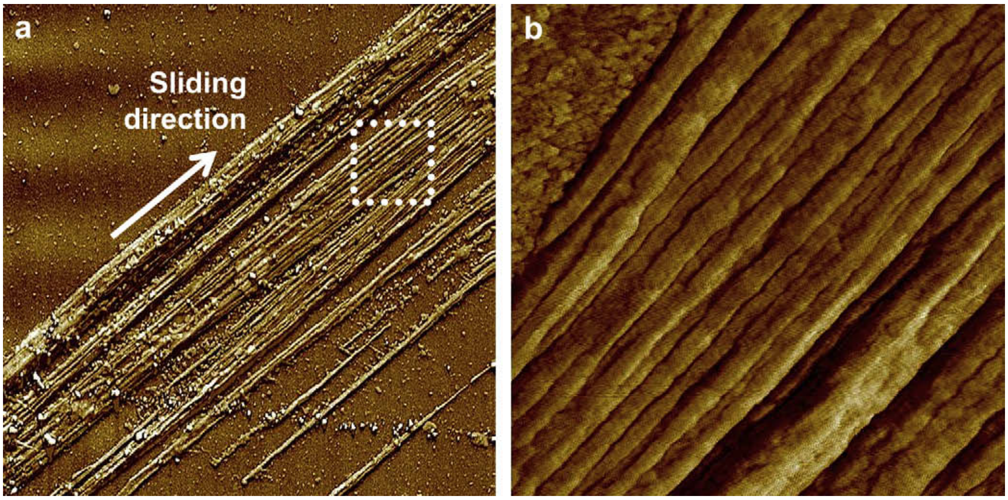

Fig. 5. AFM phase images showing details of the morphology of the layer of i-PS transferred by sliding a solid i-PS pin at a velocity of 5 cm/s at temperature $T = 95\,^\circ\mathrm{C}$ on a silicon substrate at very low applied load (with a small cyclohexanone drop around the contact region). Size of the images: (a) 10 × 10 μm^2; (b) 1.23 × 1.23 μm^2 (zoom of the region indicated by the dotted box in a). The transferred i-PS molecules formed aligned ribbons which were almost equal in width (about 60–90 nm) and comparatively thin (about 15–20 nm, which is comparable to the radius of gyration).

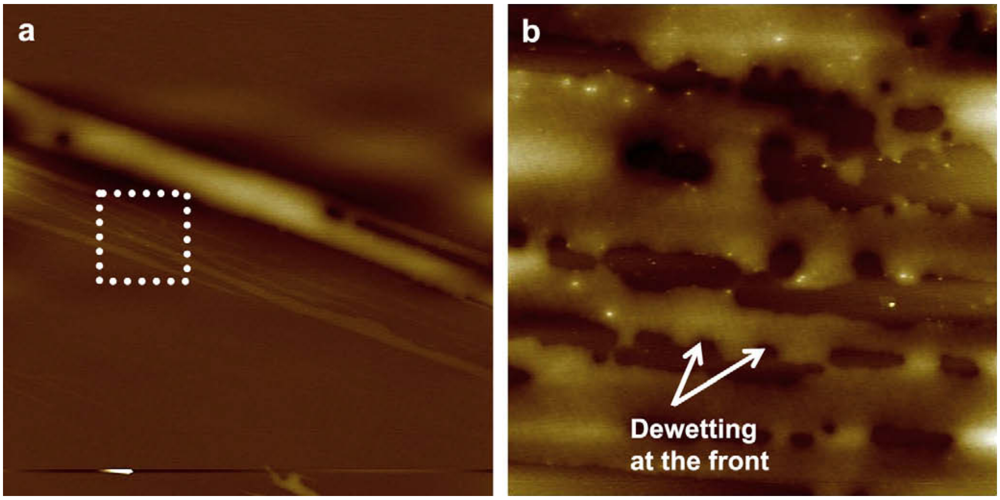

Fig. 6. AFM images of i-PS ribbons (obtained by friction transfer at $T \approx T_g$ in the presence of cyclohexanone around the contact region) which were melted at 270 °C ($T > T_m$) for 15 min. Size of the images: (a) 20 × 20 μm^2; (b) 8 × 8 μm^2 (zoom of the region indicated by the dotted box in a).

chains at the surface of the pin could not be oriented easily by shearing the pin on the silicon substrate [40].

Sliding the solid i-PS pin on the silicon substrate at 150 °C did not allow to deposit an ultrathin layer of polystyrene. Large amounts of i-PS were deposited, both in dry ambient air (Fig. 4b), or by adding a small quantity of cyclohexanone at the position where the i-PS pin contacted the substrate (Fig. 4c), forming a meniscus of cyclohexanone around the pin. (Cyclohexanone is able to dissolve i-PS above ca. 142 °C.)

When friction experiments were performed at 150 °C, the i-PS pin was well above its glass transition temperature (T_g). Thus, we anticipated that a molten film was transferred onto the substrate. In addition, the presence of cyclohexanone favored a dewetting phenomenon (Fig. 4c). Performing sliding at a temperature close to T_g in the presence of a very small quantity of cyclohexanone in the contact region between pin and substrate resulted in a thin transferred layer of i-PS which exhibited clear signs of alignment of extended fiber-like objects (Fig. 4d). Sliding the i-PS pin at temperatures around T_g without the presence of cyclohexanone in the contact area resulted in similar transfer patterns (similar density of particles transferred) as for the experiments performed at room temperature. According to Pooley and Tabor [33], this suggests that cyclohexanone in the contact area may have either acted as a lubricant which lowered the interfacial shear strength (i.e., adhesion) and thereby reduced the amount of transferred wear particles during friction: Alternatively, swelling i-PS by cyclohexanone may have sufficiently lowered the bulk shear strength (i.e., cohesion) which favored the extraction of i-PS chains from the pin and the formation of extended chain conformations (chain segments already adsorbed onto the substrate may act as anchors while the segments still within the pin may be displaced in the shearing direction). These transferred i-PS layers have been subsequently annealed at temperatures close to the melting point T_m of i-PS (around 240 °C) in order to investigate the influence of chain deformation on crystallization behavior.

3.2. Surface morphology of i-PS transferred film just after rubbing

Before allowing for crystallization, we examined the surfaces of the transferred i-PS films in detail by AFM. Fig. 5a shows the typical surface morphology of the films transferred at 95 °C which consisted of ribbons of i-PS, all having about the same width (ca. 60–90 nm) and being aligned along the sliding direction, more clearly visible in the zoom shown in Fig. 5b. The mean thickness of these ribbons was found to be approximately 17 nm which is comparable to the radius of gyration of this polymer (ca. 15 nm). Thus the films were very thin and all polymers had some contact to the substrate. Moreover, such thin films allowed establishing a relation between the preferential orientation of the friction-transferred chains and the orientation of the resulting crystalline lamellae. The clear orientation of the observed surface morphology may indicate strong deformations of the transferred i-PS chains, which under the

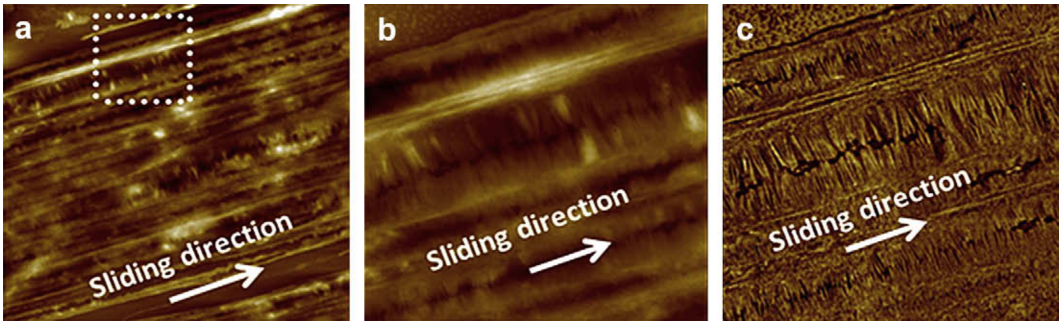

Fig. 7. AFM images of i-PS ribbons after isothermal crystallization for 12 h at 210 °C. (a) Topographic image showing many “shish–kebab like structures” with the “shish” oriented in the sliding direction and the “kebabs” normal to this direction (10 × 10 μm^2). (b) and (c) Topography and phase image showing the region indicated by the dotted box in (a) (3 × 3 μm^2).

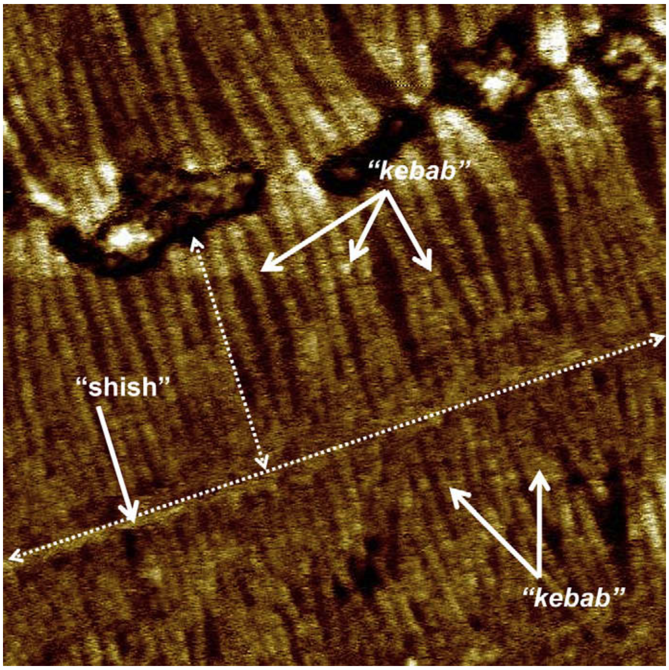

Fig. 8. Overlay of a schematically (by dotted lines) indicated shish–kebab crystals with an AFM image for an i-PS film prepared by friction transfer which was subsequently isothermally crystallized for 12 h at 210 °C (size: 900 × 900 nm^2).

chosen conditions were more flexible than for example rubbed polyimide chains employed for orienting liquid crystals (LC) in LC displays [41].

Annealing these ribbons at high temperatures above T_m revealed their non-equilibrium character. In Fig. 6, these ribbons were annealed at 270 °C (>T_m) for 15 min in an inert nitrogen atmosphere. AFM images of these briefly annealed ribbons demonstrated the onset of a dewetting behavior which eventually would destroy also the alignment over large distances and lead to an inhomogenous film of probably equilibrated chains. Thus, we concluded, in full consistency with the work by Tabor [33] and Wittmann and Smith [34], that friction transfer of i-PS induced strong deformation of the polymer chains which were preferentially oriented in the sliding direction.

3.3. Growth of "shish–kebab" crystals

Isothermal crystallization at 210 °C (as schematized in Fig. 3) of the transferred i-PS film revealed the growth of shish–kebab crystals oriented along the sliding direction as shown in Fig. 7. Such crystallization patterns have only been observed when transfer was performed at a temperature around the glass transition temperature of i-PS and in the presence of a small quantity of cyclohexanone around the contact area. It is well known that applying an external extensional or shear field can have a strong impact on the crystallization behavior of semi-crystalline polymer [17,18,43].

In our case, shear was applied by sliding the i-PS solid pin on the silicon substrate which most likely caused extensive deformation of polymer chains in the sliding direction. The formation of shish–kebab crystals oriented in the sliding direction can be taken as an indirect support for our hypothesis. The shish–kebab crystals generated from the transferred polymer layer exhibited a pattern with a longitudinal axis (shish) preferentially aligned in the sliding direction similar to the situation of shish–kebab structures in the case of melt extrusion [44,45].

AFM images shown in Fig. 7a–c demonstrate that the shish–kebab crystals possess specific anisotropic microstructures, in which probably long chains play an important role to form the shish polymer [44,45]. The formation of edge-on lamellar crystals in the direction normal to the shish direction can be clearly seen. It seems likely that the relatively high polydispersity of the used i-PS ($I \approx 2.8$) which implies the presence of comparatively many longer chains than characterized by the weight average molecular weight of 400 000 g/mol could favor the growth of shish–kebab crystals [45].

In Fig. 8, the AFM phase mode image highlights the closely spaced edge-on lamellae (kebab) which each have a constant width about 16 nm, a value fully consistent with the height of flat-on i-PS crystals grown from spincoated thin films [46]. Obviously, in contrast to flat-on crystals obtained in spincoated films, friction transfer and the thereof resulting anisotropic, deformed chain conformations rather favor the formation of shish–kebab crystals built-up from edge-on lamellae. However, if the film was deposited at a higher temperature under the presence of cyclohexanone (where the transferred chains had a high probability to relax towards equilibrated, random conformations) the preference for shish–kebab crystals consisting of edge-on lamellae was significantly reduced. In fact, as can be seen in

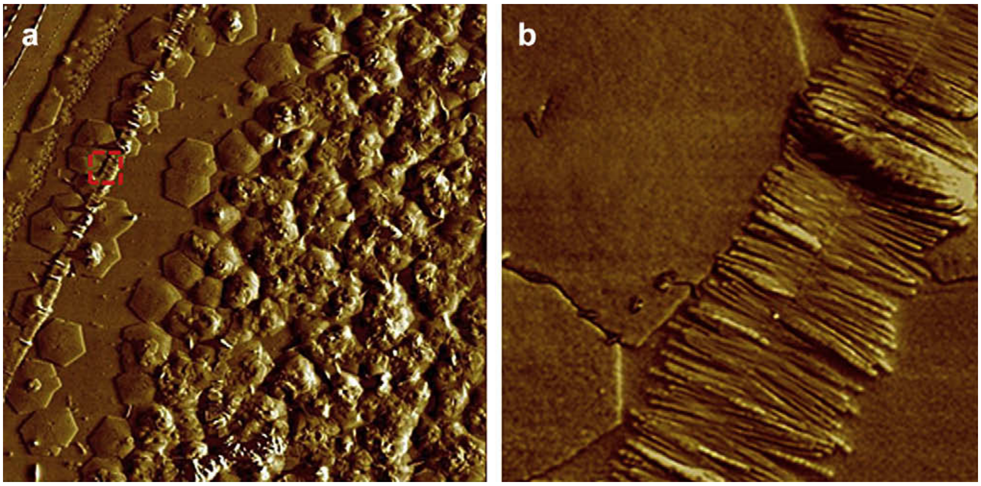

Fig. 9. AFM image of i-PS crystals (coexistence of hexagonal flat-on crystals and shish–kebab crystals) from an i-PS film prepared by friction transfer (at 150 °C in the presence of cyclohexanone in the contact region) which was subsequently isothermally crystallized for 12 h at 220 °C. (b) Zoom into the dotted box shown in (a): the size of the images is: (a) 50 × 50 µm^2 and (b) 4 × 4 µm^2.

Fig. 9, the habit of most of the crystals was mainly hexagonal, again consistent with the results of Taguchi [46]. Very few shish–kebab crystals were formed.

Under the conditions of our experiments, the number of nuclei leading to the growth of kebab lamellae was extremely high. In fact, the distance between individual lamellae was so small that we may have observed the maximum possible number of kebab lamellae per unit length of the shish backbone. In comparison, the in-situ atomic force microscopy (AFM) observations of shish–kebab crystallization of polyethylene by Hobbs et al. [17,47] showed a rather clear separation of the individual kebab lamellae. In addition, in those experiments the shish axis could be clearly distinguished from the growing kebab lamellae. The lower number of nuclei formed might be due to different degrees of chain deformation which could be generated through shear induced either by a moving razor blade or by dragging a glass slide across the polymer surface. Future studies on films prepared by friction transfer under different conditions will be able to find out if a relation exists between chain extension and nucleation probability for edge-on lamellae emanating from a shish backbone.

4. Conclusions

By transferring crystallizable polymers via sliding a solid pin across a solid substrate, we can introduce significant deformations in the conformations of these polymers. When such polymers are allowed to crystallize, one can clearly detect the consequences of the preferred orientation of these transferred chains. In the presented examples we observed the formation of shish–kebab crystals, i.e., a backbone (=shish) formed by preferentially aligned i-PS molecules initiated the growth of a multitude of edge-on lamellar crystals (=kebabs) oriented perpendicular to the backbone. Thus, in both parts, shish and kebab, all polymers were preferentially oriented in the shearing direction. These results strongly suggest that by extending the polymer chain conformations in the shearing direction we can introduce a considerable reduction of the nucleation barrier: This is indicated by the significant number of edge-on lamellae growing in the direction perpendicular to the direction of the solid polymer pin which was slid over the substrate. Accordingly, friction transfer allows to align not only the transferred polymer chains but also the subsequently forming crystalline domains within these transferred films. We believe that this approach can be applied to other crystallizable polymers and is suitable for preparing anisotropic polymer films with a crystalline structure whose orientation can be predetermined.

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