

A Study on the Appearance of Extended Chain Fibrils of Ultrahigh Molecular Weight Polyethylene at Melt/Solid Interface

S. Masirek,¹ A. Tracz,¹ S. Talebi,² S. Rastogi^{2,3}

¹Center of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Łódź, Poland

²Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven, The Netherlands

³Department of Materials, Loughborough University, Loughborough, England, United Kingdom

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ABSTRACT: Pressing of ultra high molecular weight polyethylene (UHMWPE) melt on a flat substrate of HOPG, Si/SiO₂, or mica resulted into molecular alignment at the polymer melt/solid interface. From the resultant morphology, as visualized from AFM, it appears that the extended chain crystals are formed at the interface. The chain alignment in the extended chain crystals could be preserved even after annealing well above the equilibrium melting temperature (20 h at 160°C). It is thus concluded that the atomically flat surface provides efficient constraint that refrains chain relaxation of the extended chains to random coil state. It is shown that at the melt/hydrophilic

mica interface the extended chain fibrils are formed easier from the polymer obtained from the single-site catalyst compared to the heterogeneous catalyst. The extended chain fibrils at the interface promote the oriented lamella growth. Isothermal crystallization at low supercooling (at 133°C) results in the formation of lamella thicker than 200 nm. The lamellae exhibit a characteristic tapered shape indicating the thickening growth mechanism via chain sliding diffusion. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: polymer crystallization; polyethylene; lamella

INTRODUCTION

Polymer crystallization at the melt/solid interface may proceed differently than in the bulk. Effects reported are heterogeneous nucleation, epitaxy, and transcrystallinity.^{1–3} Solid surfaces may favor heterogeneous nucleation due to reduced nucleation barrier at the melt/solid interface.⁴ In the vicinity of a solid surface, chain configuration and mobility will be different than in the melt. At the solid surface observations on preferential orientation and elongation of polymer coils^{5,6} have been confirmed by simulations.^{7–13} These studies on the polymer interface interactions are of relevance to understand the crystallization process and the resultant morphology, because often a polymer encounters a solid interface in several applications. Crystallization of model crystallizable polymers—high density polyethylenes (HDPE) and ultralong monodisperse alkane C₃₉₀H₇₈₂—on various molecularly flat surfaces of solids (graphite, mica, MoS₂, alkali halides, and others) has been studied.^{14–28} Efficient method that

has been successfully applied in the studies is the substrate detachment technique. The technique allows to study the morphology of a polymer crystallized in contact with a solid substrate. Experimental tool applied for the purpose is atomic force microscopy (AFM), where imaging of a fracture occurring at, or very close to, the polymer/substrate interface is executed.^{14–18,29} Crystallization of the contact layer of HDPE on highly oriented pyrolytic graphite (HOPG) or MoS₂ substrates occurs at exceptionally high temperatures; at 135°C under isothermal conditions¹⁶ and at 129°C while cooling from melt at a rate of 10°C min⁻¹.¹⁴ Moreover, it is found that at atmospheric pressure crystallization at the interface proceeds according to the mechanism of lamellar thickening growth.¹⁶ It is thus well established that some flat substrates may strongly influence the crystallization of polyethylene, at least in the adjacent layer. Epitaxial crystallization of polymer on the crystalline substrates is one of the most important phenomenons that determine the polymer morphology at the interface. In the contact layers of HDPE and C₃₉₀H₇₈₂ crystallized on HOPG or MoS₂, domains with three distinct orientations of the lamellae, inclined at 60° to each other reflects the threefold symmetry of the substrate.^{15–18,29,30}

Correspondence to: A. Tracz (atracz@cbmm.lodz.pl).

The article reports crystallization of ultra high molecular weight polyethylene at the interface, where beside the epitaxial crystallization, the presence of entanglements will have strong influence on the resultant morphology. To investigate the influence of entanglements on polymer crystallization, polymers synthesized via homogeneous and heterogeneous routes have been studied. It is to be realized that while the nascent polymer synthesized via homogeneous (single-site metallocene catalyst) route results into disentangled melt that tends to entangle with time, the melt of the nascent polymer obtained from the heterogeneous (supported Ziegler–Natta catalyst) route is entangled from the very start.³¹

Before studying crystallization at the melt/solid interface a polymer melt is brought in contact with a solid substrate. In many experiments polymers in a form of pellets or reactor powders are pressed in the molten state between the flat substrates. The intimate contact between the melt and a surface occurs gradually, where the flow of polymer molecules is influenced by the atomistic roughness of the substrate. In some local regions, shear forces at the interface are sufficiently high to orient the chains—leading to the shish formation. Because the relaxation time τ increases with the molecular weight (M_w) ($\tau \sim M_w^{3.4, 32, 33}$), it is of interest to investigate the influence of molar mass on chain orientation. Obviously the presence of aligned chains at the interface will have the strong influence on nucleation and crystallization process. It is well established that aligned chains (shishes) in polymer melts serve as nucleating centers. Experimentally, to detect the shish formation is very challenging especially if it is present only at the polymer–substrate interface. Oriented lamellar overgrowth on PE shishes, induced by shearing the melt surface with a razor blade, was observed *in situ* using high temperature AFM.³⁴

In this work we present AFM studies on fibrils of extended chains (EC) of ultrahigh molecular weight polyethylene (UHMWPE) formed at the interface of melt/nanoscopically flat substrates: HOPG, Si/SiO₂, and mica. The substrate detachment technique has been chosen as the most suitable experimental approach. Majority of experiments are performed on ultrahigh molecular weight polyethylene (M-UHMWPE) synthesized using a metallocene catalyst. The polymer is of interest because of the disentangled nature of the melt, where the entanglements per chain could be tailored during controlled polymerization.^{31–33}

EXPERIMENTAL

Materials

UHMWPEs obtained using metallocene catalyst (M-UHMWPE)^{32,33} of molar masses ranging between

2×10^6 g mol⁻¹ and 8×10^6 g mol⁻¹ are used. For a comparison, polymers synthesized using a Ziegler–Natta catalyst are also investigated. Nascent UHMWPEs, as obtained after polymerization, consists of granules. In Figure 1, granules of M-UHMWPE and Z-UHMWPE before and after melting are compared with granular morphology of HDPE.

Because of lower melt viscosity the granules of HDPE undergo substantial shape reorganization after annealing and turn to ball like objects [Fig. 1(a)]. The high melt viscosity of UHMWPE inhibits the polymer to alter its shape, even after melting. In the case of UHMWPE, the melt reorganization occurs only locally within the surface layer and granular, cauliflower morphology remains the same [Fig. 1(b,c)].

For the experiments on substrate, powders are compressed between aluminum or Teflon foils to obtain about 0.5-mm thick films (Fig. 2). M-UHMWPE powders are compressed at ~ 200 bars, for 90 min at 70°C i.e., below the melting temperature. Under such sintering conditions the nascent disentangled state of the polymer is preserved.^{32,33} Z-UHMWPE granules are compressed at 180°C. For crystallization experiments 5 mm \times 5 mm samples are used.

Substrate detachment technique

The morphology of UHMWPE crystallized at the polymer melt/solid interface has been studied using the so-called substrate detachment technique developed for studies of melt-crystallized HDPE. The technique allows to investigate the morphology of a contact layer by using atomic force microscopic (AFM), where imaging of a fracture occurring at or very close to the polymer/substrate interface is performed.^{14–18,29} A scheme of experimental procedure is shown in Figure 3. Because of the high melt viscosity of the UHMWPE, the polymer samples are pressed to ensure a good contact with a substrate (Stages 1 and 2 in Fig. 3).

To ensure the good contact a force of 0.5 kG is applied to the cover of Mettler–Toledo (Columbus, OH) hot stage during heating of the sample. Taking into account the lateral size of samples (0.25 cm²) the overall pressure on the sample is less than 2 bars. Because the cover of the hot stage is not ideally parallel to the substrate, the molten sample experiences a flow in one direction resulting in a deformation of about 10–20 % (Fig. 4).

After pressing the viscous melt two protocols are used for crystallization (Stage 3 in Fig. 3).

Protocol I

The sample is heated to 170°C in steps under the applied pressure. First at a rate of 0.2°C min⁻¹ from

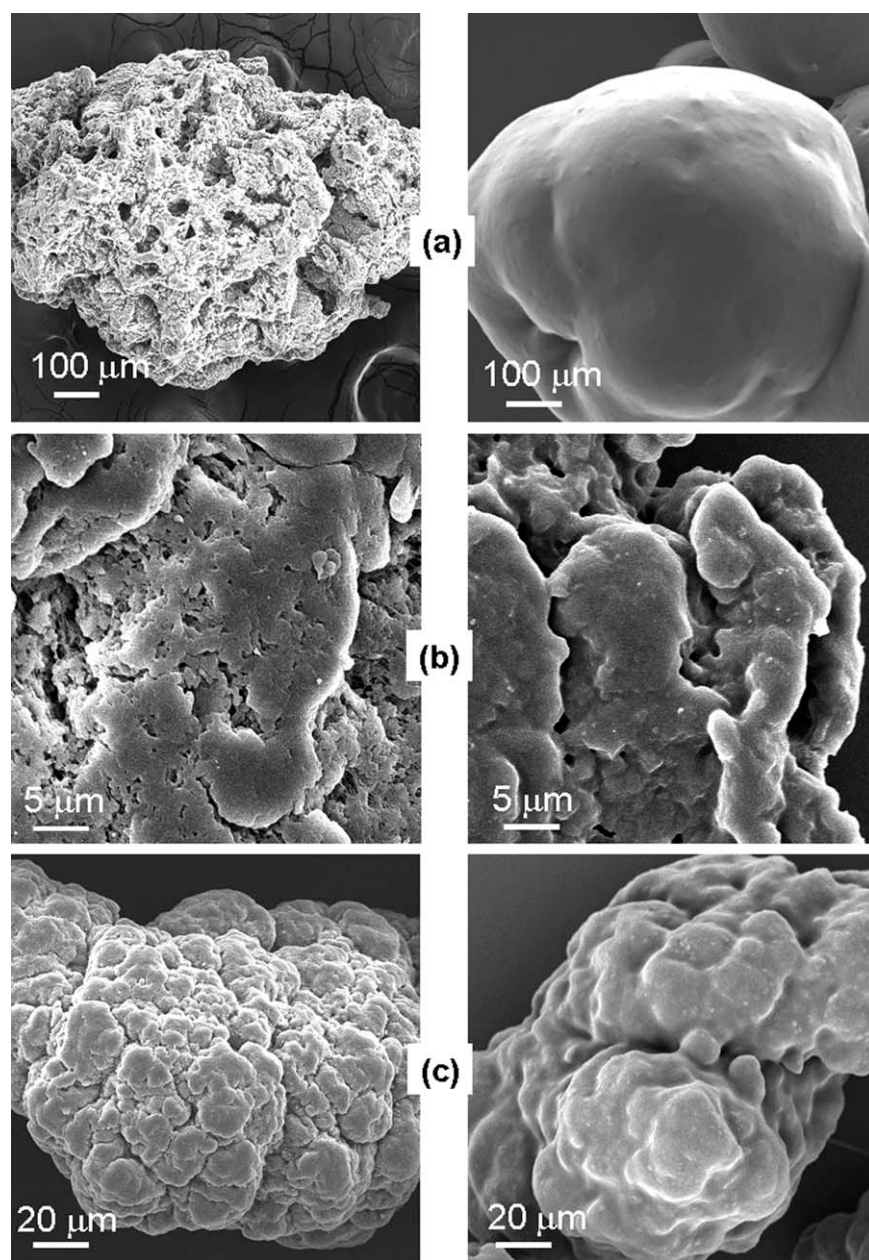


Figure 1 SEM images of reactor powders of three different polyethylenes: (a) HDPE (M_w 193,000); (b) M-UHMWPE ($M_w = 8 \times 10^6 \text{ g mol}^{-1}$) and (c) Z-UHMWPE ($M_w = 6 \times 10^6 \text{ g mol}^{-1}$); Left side figures represent SEM images of the reactor powders as obtained, whereas images on the right side are of the powder after annealing for 10 min at 170°C.

130 to 150°C followed by rate of 1°C min^{-1} up to 170°C. After reaching the desired temperature, the pressure is released and the sample is kept for 10 min at the temperature. Finally the sample adhered to the substrate is quenched by dropping it into ice cool water.

Protocol II

Sample is heated to 170°C at a rate of $\sim 60^\circ\text{C min}^{-1}$. Once the temperature is reached the pressure is applied. After 10 min at this temperature, the pressure is released and the sample attached on the

substrate is quenched by dropping into ice cool water. The difference between the two protocols relies on the different temperature when melt starts to flow under applied pressure. In the case of Protocol I the melt can start flow already above melting temperature since the sample is heated under applied pressure while in case of Protocol II the pressure is applied at 170°C.

The adhered substrate is then cleaved off the sample (Stage 4 in Fig. 3). Prior to cleaving a notch is initiated with a razor blade. Detachment of the polymer sample from HOPG results in a brittle fracture close to the interface. After the detachment

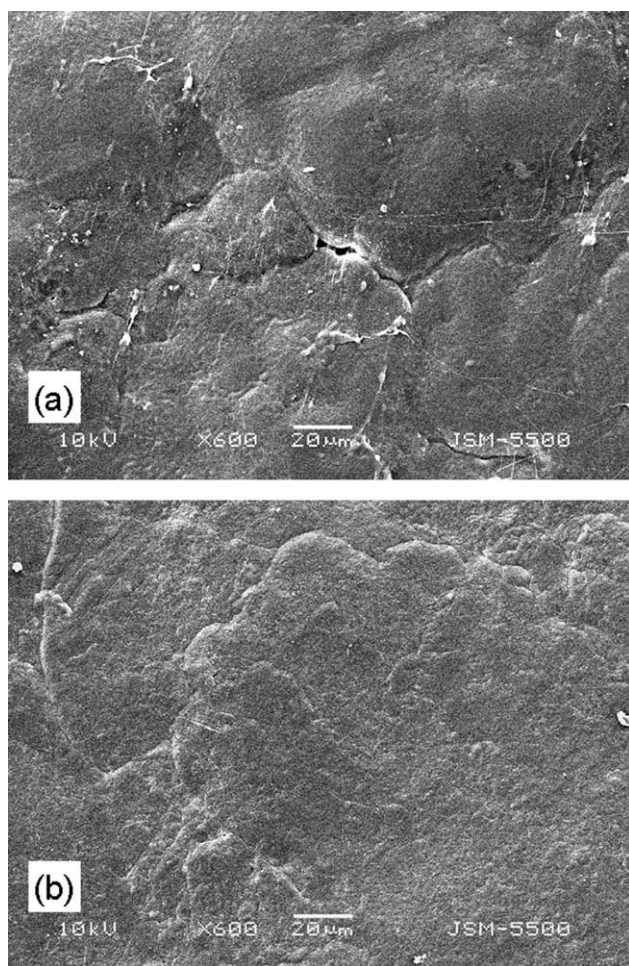


Figure 2 SEM images of the surface of films of UHMWPE used in experiments. (a) Z-UHMWPE ($M_w = 6 \times 10^6 \text{ g mol}^{-1}$) sintered at 180°C , (b) M-UHMWPE ($M_w = 8 \times 10^6 \text{ g mol}^{-1}$) sintered at 70°C . High sintering temperatures for Z-UHMWPE compared to M-UHMWPE are requisite due to differences in the entangled state of the two samples.

most of the HOPG surface is covered by a polymer layer of small nonuniform thickness. In areas where this film is several nanometers thick and flat, morphology similar to that of the surface of the detached sample can be seen. However, the resolution achievable by studying the surface of the detached sample is better, and we therefore concentrate on the latter.

Usually a part of the fractured surface is covered with the thin graphite flakes. If necessary some remaining flakes of graphite are gently removed using adhesive tape. Subsequently, the exposed surface is investigated using AFM. For studies on isothermal crystallization, the samples are cooled from melt at a rate of 1°C min^{-1} to the isothermal crystallization temperature of 133°C followed by quenching in the ice cold water. Highly oriented pyrolytic graphite (HOPG), mica, and silicon wafer with native oxide layer (Si/SiO_2) are used as substrates. HOPG and

mica are freshly cleaved before use. Silicon wafers are cleaned using acetone and ethanol.

Morphological investigations are performed using Nanoscope IIIa AFM microscope (Digital Instruments/Veeco, Santa Barbara, CA), operated in tapping mode. Rectangular silicon cantilevers of model RTESP (Veeco Instruments) are used throughout the study. All scans are performed in air, at room temperature, with a scan frequency below 2 Hz. Scanning electron microscopy (SEM) images are obtained using Jeol JSM—5500LV.

RESULTS AND DISCUSSION

In Figure 5, typical AFM images of the fracture surfaces of M-UHMWPE melted on HOPG, and quenched from 170°C are shown. During melting the sample is slightly pressed following the Protocol I described in the Experimental section. Though the sample is crystallized in contact with a flat substrate, the detached surface is not smooth (Fig. 5). Section profiles imply that the majority of the area in the detached surface is not the first layer that was originally in contact with the graphite surface, where the graphite surface is atomically flat. Fibrils of extended chains (EC) are characteristic of fracture surfaces of UHMWPE molten on a solid surface.

The presence of the fibrils implies that at a certain stage of the experiment the coil-to-stretch transition occurs at the melt/solid interface. During the sample detachment, the fracture occurs through layer of fibrils at different distances from the substrate and/or the EC layer has different thicknesses, which causes topographic variations in different areas of

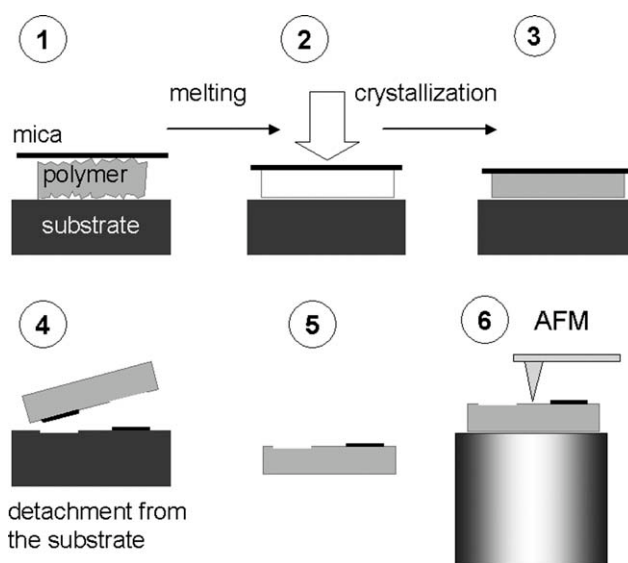


Figure 3 Schematic illustration of the substrate detachment technique. The figure depicts successive stages of the experiment, from melting to AFM observations. Vertical arrow symbolizes pressing.

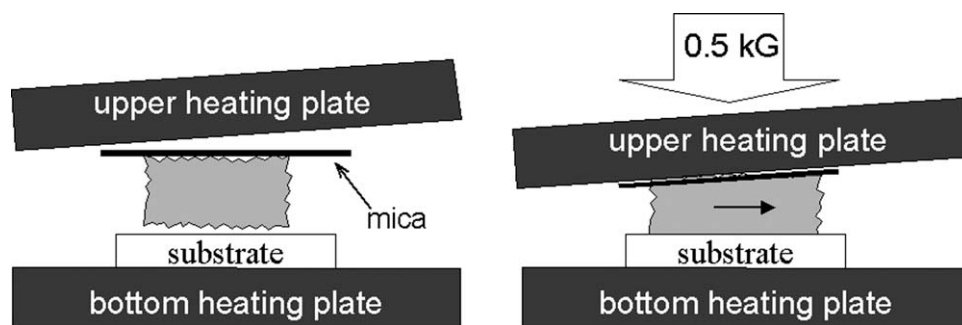


Figure 4 Schematic illustration depicting melting of a polymer sample between hot plates in Mettler Toledo hot stage. After inserting the samples, upper heating plate is not ideally parallel to the substrate. During pressing the molten sample experiences shear deformation in one direction (shown by arrow).

the sample [for comparison see Fig. 5(a,b)]. In some locations, ribbons of fibrils appear to be missing exposing the underlying lamellar morphology thin lamellae are seen between EC fibrils. They are perpendicular to the fibrils axes [Fig. 5(a)]. Obviously

the fibrils acted as nucleation centers. The surface of lamellae is about 3 nm below the neighboring fibrils [Fig. 5(a)]. In other words the lamellae are grown not in the direct contact with HOPG substrate but on the layer of EC fibrils.

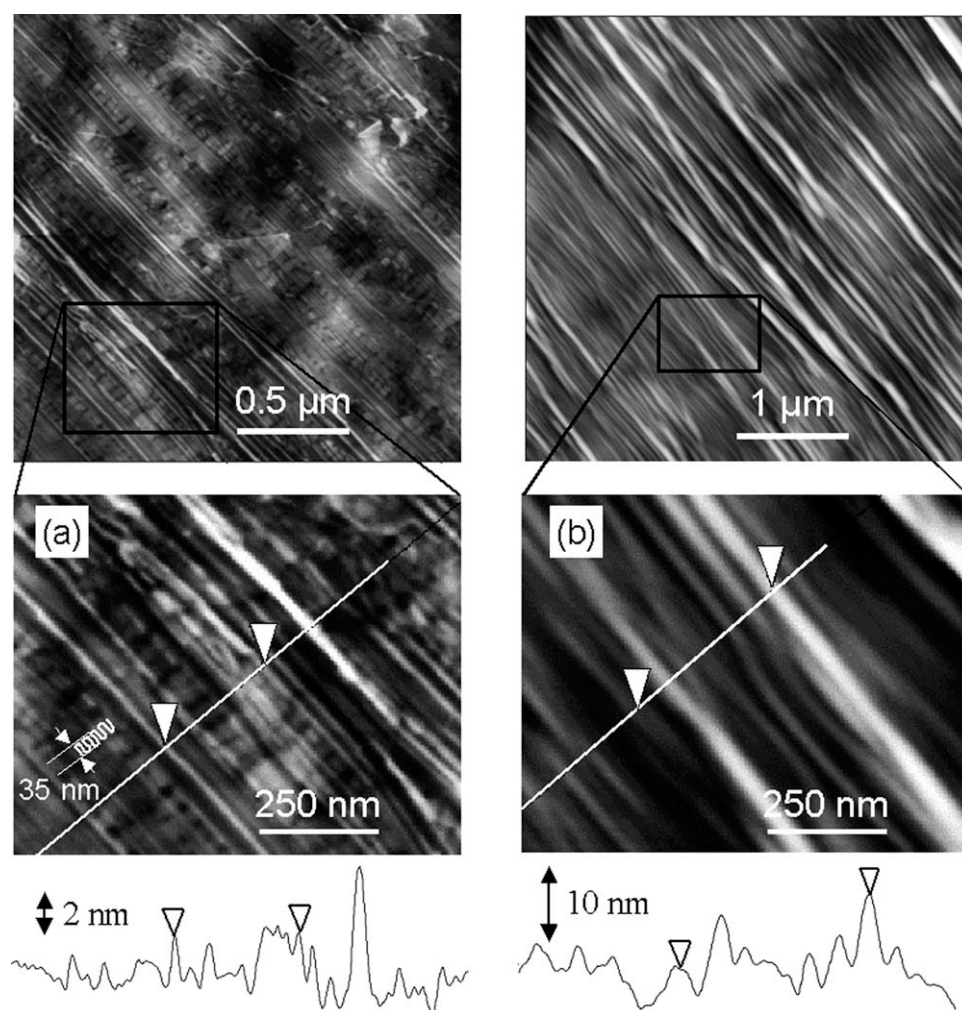


Figure 5 AFM height images of two selected areas of the fracture surface of M-UHMWPE ($M_w = 8 \times 10^6 \text{ g mol}^{-1}$) crystallized from melt on HOPG surface. Samples are slowly heated to 170°C and quenched after 10 min (following Protocol I described in the Experimental section). Fibrils of extended chains running across the images are seen. The height profiles at the bottom of the figures are scanned along the lines indicated in the figures.

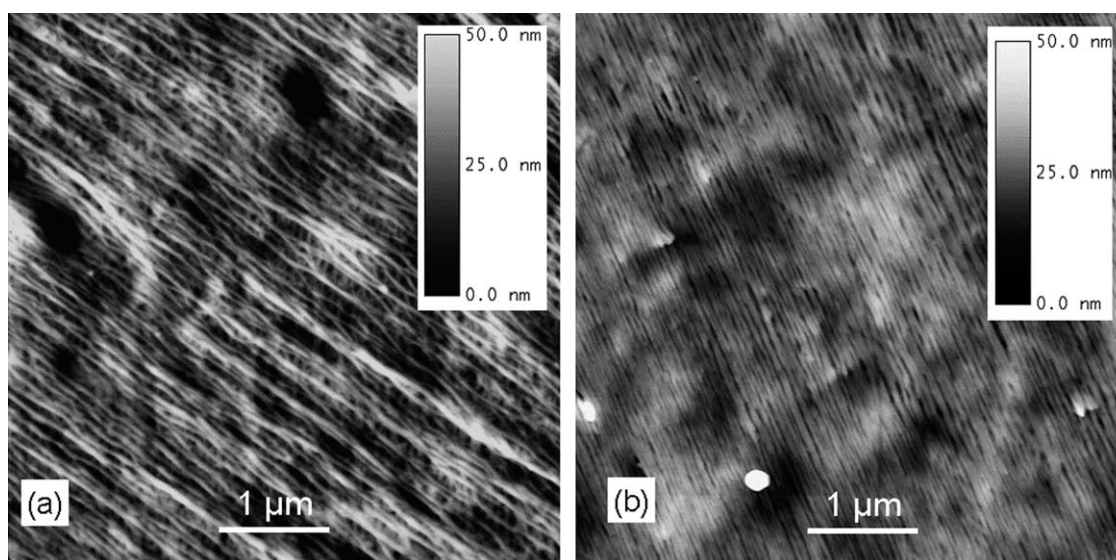


Figure 6 AFM height images of the fracture surface of M-UHMWPE ($M_w = 8 \times 10^6 \text{ g mol}^{-1}$) crystallized from disentangled melt on mica (a), and Si/SiO₂ (b). Samples are slowly heated to 170°C and quenched after 10 min (sample preparation is done following the Protocol I).

In Figure 5(b) a very dense layer of EC fibrils completely covering the underlying lamellar morphology is shown. Relatively big roughness of the surface indicates that also in this case the fracture occurred through the dense layer of EC fibrils. The width of single fibrils seen in Figure 5 (taking into account the effect of finite size of the AFM tip) can be estimated as few nanometers. It is worth mentioning the similarity of highly oriented EC fibrils ones seen on the surface of the UHMWPE gel-spun fiber after splitting.³⁵

Importantly, EC fibrils are observed for samples melted on other substrates used in our experiments (Fig. 6). The results obtained for Si/SiO₂ are of particular interest; as compared to HOPG this substrate is amorphous.

In some images few micrometer long fibrils, evidently pull-out lie randomly on the fracture surfaces (Fig. 7). Some of them split into thinner filaments. The cross section analysis indicates that their thickness ranges from 2 to 8 nm. It implies that the fibrils consist of few chains. One can notice still thinner pull-out filaments protruding by less than 1 nm which may be single chains.

The presence of EC fibrils on fracture surfaces of UHMWPE detached from Si/SiO₂ substrate [Fig. 6(b) and 7], suggests that the long range order and alignment of EC fibrils is not related to epitaxy. Indeed, in previous studies on crystallization of monodisperse long chain alkane C₃₉₀H₇₈₂¹⁸ or HDPE^{14–18,29} on HOPG, the same chain direction in neighboring edge-on lamellae, is detected over distances much larger than the lamella thickness. However, in scale of a few hundred nanometers (up to few micrometers) domains with a distinct chain orientation are seen.

These orientations, in the neighboring domains inclined at 60° to each other, are correlated with the epitaxial relationship with the hexagonal lattice of graphite. Similar results are obtained for samples crystallized in contact with other substrates such are talc or MoS₂ exhibiting threefold symmetry on the cleavage planes.^{15,16,30}

Orientation of UHMWPE EC fibrils in Figures 5–7 is uniaxial in a macroscopic scale, which is preserved over distances of hundreds of micrometers. The chain orientation matches with the flow direction that arose during the sample preparation while pressing the sample on the substrates (Stages 1 and 2 in Fig. 3). It implies that the EC fibrils are formed due to the flow induced orientation during pressing of the molten sample against the substrate, as depicted in Figure 4. Initially, when sample is placed on the substrate and pressed, the contact between the polyethylene melt and a substrate is likely to be established locally only, in a scale of tens of a few nm². The overall pressure applied to the sample in our experiments, calculated taking into account the applied force and the macroscopic lateral dimensions of sample, appears to be low (2 bars). In a nanoscale the molten UHMWPE sample is rough (see Fig. 2). Therefore, the local pressure in contact spots can be orders of magnitude higher, resulting in a shear flow which is sufficient to induce locally the coil-to-stretch transition of UHMWPE chains. Most probably the EC fibrils under constrained conditions form hexagonal phase that provides sufficient chain mobility. It is known that drawing of UHMWPE above melting point leads to crystallization and interestingly the formation of hexagonal phase prior to orthorhombic phase has been reported.^{36,37}

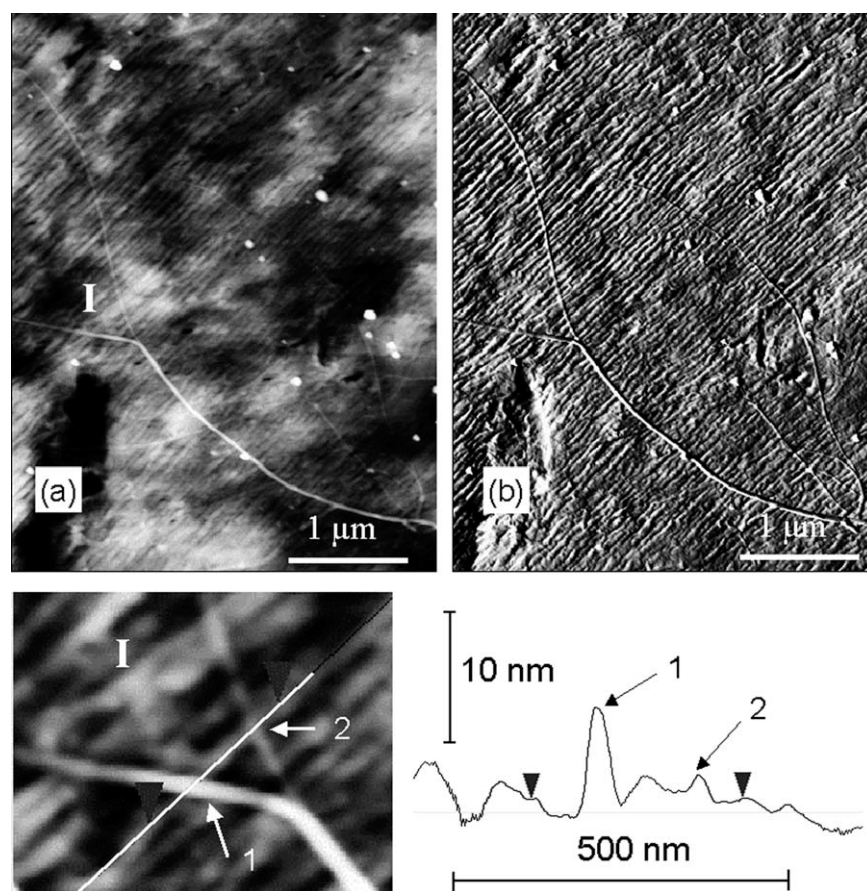


Figure 7 (a) AFM height (grayscale covers 50 nm) and (b) amplitude image of fracture surfaces of M-UHMWPE ($M_w = 8 \times 10^6 \text{ g mol}^{-1}$) crystallized from disentangled melt on Si/SiO₂ substrate. Sample is slowly heated to 170°C and quenched after 10 min (following the Protocol I). At the bottom panel the cross section analysis of magnified area I showing the fibril splits into two is shown.

Formation of EC fibrils on atomically smooth substrates is not evident in previous studies performed on the crystallization of C₃₉₀H₇₈₂ and HDPE.^{15,16,18} Molten alkane C₃₉₀H₇₈₂ spreads spontaneously on a surface. Samples of molten HDPE are also slightly pressed to assure an intimate contact with HOPG, talc or MoS₂ substrates. Obviously, melts of HDPE and C₃₉₀H₇₈₂ also flow on a substrate in a microscopic scale before a full contact with a substrate is established. However, because of lower melt viscosity and shorter relaxation time the flow of these polymers did not result in the formation of clearly detectable layer of EC fibrils.

One could presume that effectiveness of EC fibrils formation should be dependent on various experimental parameters such as temperature, initial state of chains entanglements, molecular weight, properties of the substrate etc. However, the above discussed inhomogeneity of the samples morphology, resulting from locally different deformation conditions at the interface makes the comparative crystallization studies rather difficult. Further studies would be required to gain a better insight into the problem. Preliminary results reported in this publica-

tion indicate that the nature of a solid surface and of the synthesis history of UHMWPE become important parameters if the melt flow at the interface is induced well above the melting temperature (Protocol II described in the Experimental section). On hydrophobic substrates such as HOPG and Si/SiO₂ formation of EC fibrils is observed for the two investigated UHMWPE samples, independent of the stage at which the pressure is applied on the melt. Formation of EC fibrils on pressing of the samples at 170°C, following the Protocol II, is remarkable (Fig. 8). It is worth noting that in most studies performed on relatively low molar mass polyethylenes reported in literature, shishes are induced by shear or flow at temperatures close to but certainly below the equilibrium melting temperature i.e., in a supercooled melt (e.g., Refs. 34,38–40).

On the contrary if Protocol II is applied and hydrophilic mica is used as a substrate, the EC fibrils are found only for M-UHMWPEs [Fig. 8(b)]. Whereas, in the case of Z-UHMWPE disordered lamellar organization is seen and the morphology resembled the one reported earlier for HDPE²⁹ [Fig. 8(c)].

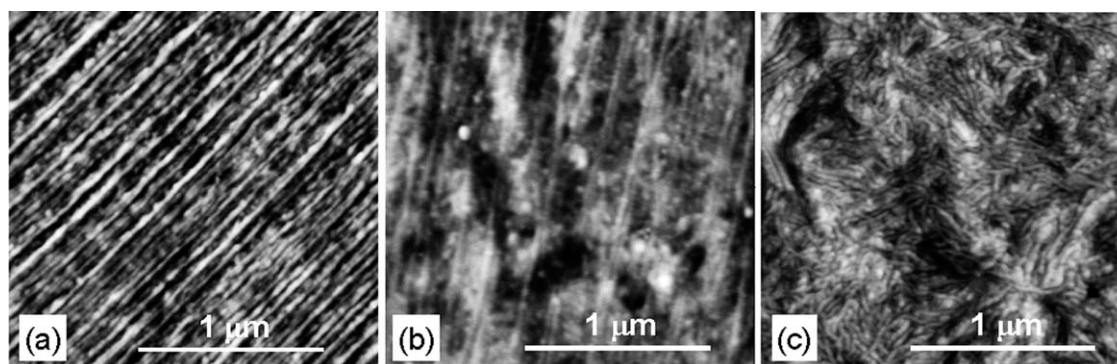


Figure 8 AFM height images of fracture surface Z-UHMWPE ($M_w = 3.6 \times 10^6 \text{ g mol}^{-1}$) crystallized in contact with different substrates. Samples are pressed on different substrates at 170°C (following the Protocol II). (a) Z-UHMWPE ($M_w = 3.6 \times 10^6 \text{ g mol}^{-1}$) on HOPG, (b) M-UHMWPE ($M_w = 8 \times 10^6 \text{ g mol}^{-1}$) on mica, (c) Z-UHMWPE ($M_w = 3.6 \times 10^6 \text{ g mol}^{-1}$) on mica. It is apparent that on mica substrate while M-UHMWPE forms fibrillar morphology, the Z-UHMWPE forms thin folded crystals. Grayscale covers a corrugation of 30 nm.

The results reported in this publication demonstrate the role of friction resulting from the interaction of aliphatic chains with a substrate surface. For hydrophobic HOPG and Si/SiO₂ substrates friction between polymer chains and a substrate surface provides the force high enough to align the chains from melt initiating formation of EC fibrils both for M-UHMWPE and Z-UHMWPE. Mechanism involved in the chain alignment appears similar to the formation of highly oriented thin polymer layers on substrates by so-called friction-transfer method. However, in the latter the process takes place below the melting temperature of a polymer.⁴¹ The friction between aliphatic chains and hydrophilic mica is probably smaller. On pressing at 170°C the EC fibrils can be formed only from the melt of M-UHMWPE [Fig. 8(b)]. This suggests that formation of EC fibrils is easier for M-UHMWPE than the Z-UHMWPE.

This difference in chain orientation can be attributed to the presence of lesser entanglements per chain in the melt of M-UHMWPE compared to the Z-UHMWPE. Assuming that transient metastable hexagonal phase plays an important role in EC fibrils formation, the result is in agreement with the reported observations that during melt drawing of the UHMWPE, transient metastable hexagonal phase is formed easier in the polymers synthesized using metallocene catalyst.⁴²

The EC fibrils thus formed on the surface of HOPG, silica or mica are very stable. Even after annealing above the melting temperature (160°C for 20 h on HOPG) the layer of fibrils can still be seen on the fractured surface of M-UHMWPE sample [Fig. 9(a)]. Similarly, EC fibrils can also be seen on the detached surface of M-UHMWPE sample which, prior to detachment from mica [Fig. 9(b)] or from

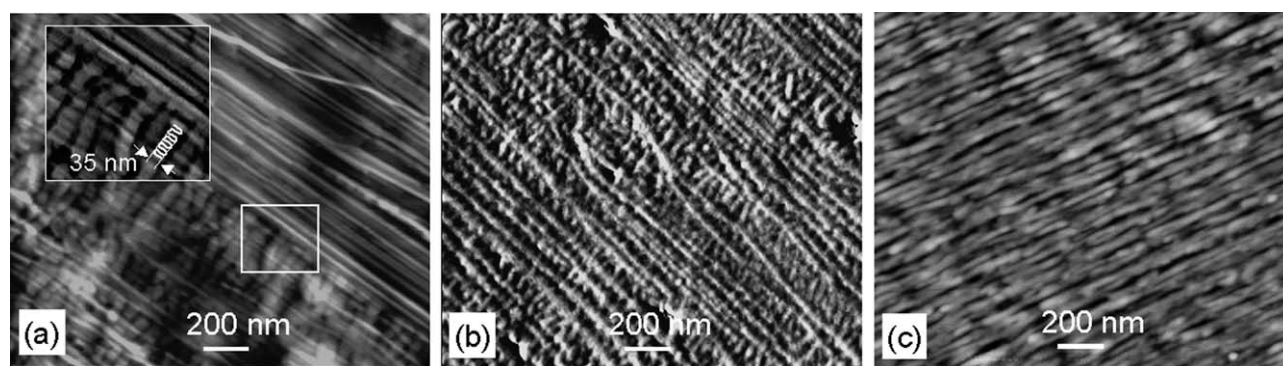


Figure 9 AFM height images of fracture surfaces of M-UHMWPE ($M_w = 8 \times 10^6 \text{ g mol}^{-1}$) prepared under different conditions. (a) Sample is slowly heated on HOPG to 170°C and after annealing for 10 min at this temperature, the sample (without detachment from the substrate) is left to anneal at 160°C for 20 h and subsequently quenched in the ice cold water. The fracture occurred partially through the EC layer and partially farther away from the substrate exposing thin lamellae (thickness of $\sim 35 \text{ nm}$) seen edge on. Thin lamellae are better seen in the inset showing AFM phase image of small area marked by white rectangle. (b) Sample is slowly heated on mica to 170°C held at this temperature for 10 min. After the isothermal annealing at 170°C the sample is heated to 200°C at a rate of 3°C min^{-1} and subsequently quenched from 200°C to ice cold water. (c) Sample prepared as in (b) but on Si/SiO₂. Grayscale covers a corrugation of 30 nm.

silica [Fig. 9(c)], was annealed at 170°C for 10 min, followed by heating to 200°C at a rate of 3°C min⁻¹ before quenching.

To recall, normally annealing in the temperature region of 160–170°C for much shorter time (several minutes) is commonly applied for erasing the melt history. Though in the bulk PE shishes may disappear after annealing at 154°C for 3 min,³⁹ however from the results shown in this publication it can be stated that the commonly used procedures for erasing the melt memory are not sufficient for the chains aligned on the solid surface.

High stability of the EC fibrils at the interface, well above equilibrium melting temperature of the linear polyethylene, can be explained by the molecular interaction of the polymer with the substrate. Magonov et al. have also shown that monolayers of ultralong alkanes or PE molten on HOPG remains ordered more than 40°C above the equilibrium melting temperature of PE.^{43,44} In this respect our findings for the system UHMWPE/HOPG are in accordance with Magonov et al.

High thermal stability of constrained oriented extended chains of UHMWPE has been recognized long time ago. To recall, fibrillar crystals of HDPE ($M_w = 1.5 \times 10^6$) were studied by Pennings and Zwijnenburg using X-ray diffraction.⁴⁵ They used ultradrawn fibers composed of fibrils of extended chains, with diameter of about 15 nm. It was found that the constrained fibers exhibited relaxation well above the normal relaxation time for the high molar mass PEs. Though the constrained fibers (where the shrinking on heating could be suppressed) at atmospheric pressure, exhibited the transformation from orthorhombic to hexagonal phase around 150°C, their orientation could be maintained at 180°C even on heating the sample slowly at a rate of 0.35°C min⁻¹ from 150 to 180°C.

The phase transition from orthorhombic to hexagonal phase has been also reported on annealing of the drawn UHMWPE fibers under constraint at atmospheric pressure.⁴⁶ To circumvent shrinkage on heating the fibers were wounded around metal holder and the ends were tied tightly. Though, upon slow heating in DSC pan, where constraint is transferred during sample preparation by compression of the lid, the hexagonal phase transforms to liquid around 154°C. These results imply that for the stability of hexagonal phase at atmospheric pressure, sample geometry and “quality” of constraints are of great importance—the constraints should be effective enough to transfer macroscopic stresses to molecular level. Our results indicate that confinement of extended chains at atomically flat solid surfaces provide a very efficient constraint allowing survival of EC fibrils upon annealing up to 200°C.

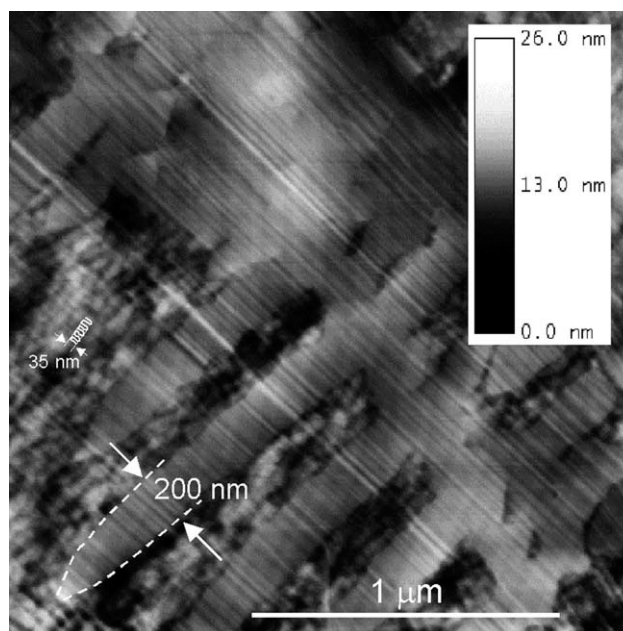


Figure 10 AFM height images of fracture surfaces of M-UHMWPE ($M_w = 2 \times 10^6$ g mol⁻¹) quenched after isothermal crystallization at 133°C for 5 h on HOPG.

From Figures 5 and 9 it is evident that the oriented EC fibrils have an important influence on crystallization. Nonisothermal lamellar crystallization of the melt in contact with fibrils during quenching proceeds directionally, i.e., lamellae formed are perpendicular to the EC fibrils, where the fibrils act as nucleation centers for further crystal growth.

More spectacular influence of EC fibrils on crystallization is observed at low supercoolings, for an example see Figure 10.

More detailed studies on isothermal crystallization of UHMWPE on solid substrates will be a subject of forthcoming article. Isothermal crystallization of UHMWPE at 133°C, in the presence of EC fibrils, results into the formation of very thick lamellae about 200 nm. Tapered edges of the lamellae are indicative of the thickening growth mechanism typical for the formation of ordered domains in pseudohexagonal phase. According to this mechanism the lamella thickness increases gradually.^{47,48} In consequence the lamella thickness is established only at a distance from the growing front, see dotted lines in Fig. 10). The results imply that the flow induced orientation of UHMWPE polymer chains at the melt/solid surface interface facilitates and promotes polymer crystallization from the mesophase.

CONCLUSIONS

Molecular contact between the melt of UHMWPE and a substrate is achieved on application of small load on the sample. The resulting shear flow is sufficient to induce coil-to-stretch transition of the highly

viscous UHMWPE melt, where the extended chain fibrils are formed at the melt/substrate interface. Confinement of extended chains at the atomically flat solid surface provides a very efficient way of transferring the constraint. The chain alignment in extended chain fibrils is preserved even after annealing well above the equilibrium melting temperature. The presence of hexagonal phase at the melt/solid interface is elucidated by the resultant morphologies, comparable to that observed in bulk on crystallization of a linear polyethylene at elevated pressures and temperatures. Results reported here imply that the flow induced orientation of UHMWPE polymer chains at the melt/solid surface interface facilitates and promotes polymer crystallization from the mesophase. The influence of entanglements on the resultant extended chain morphology is observed at the melt/hydrophilic mica interface. The observations are that the extended chain fibrils are formed easier from the polymer obtained from the single-site catalyst compared to the heterogeneous catalyst. These findings shall be of relevance for facilitating the sintering process of UHMWPE reactor powders where the presence of extended fibrils at the interface of the nascent powder may promote the formation of thick lamellae.

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