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Unusual crystallization of polyethylene at melt/atomically flat interface: Lamellar thickening growth under normal pressure

A. Tracz*, I. Kucinska, J.K. Jeszka

Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Lodz, Poland

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Abstract

The morphology of polyethylene (PE) crystallized at the melt/atomically flat substrate interface was studied using atomic force microscopy (AFM). Our attention is concentrated on isothermal crystallization of PE on HOPG and MoS_2 substrates at high temperatures up to 135 °C. By quenching after different times of crystallization, it was possible to "freeze" the lamellar morphology at various stages of its development at a given supercooling. After detachment of the PE sample from the substrate, individual lamellae (even 150 nm thick) and stacks of the *edge-on* lamellae after different stages of growth were observed. The similarity of the individual lamellae with those grown from the hexagonal phase under high pressure (characteristic tapered edges), allows to conclude that at the interface, even under normal pressure, the crystallization proceeds according to the mechanism of lamellar thickening growth.
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Keywords: Polymer crystallization; Polyethylene; Atomic force microscopy (AFM)

1. Introduction

The mechanism of crystallization of long chain molecules is complicated and in spite of many experimental and theoretical works it is still controversial and not fully understood [1–6]. It is well known that in most cases crystalline polymers form lamellae, in which the chain is folded. According to the classical model proposed by Hoffmann and Miller [5] the lamella growth proceeds via incorporation of new stems from the melt. Consequently the lamella thickness is determined at the growing edge. Hikosaka et al. described the mechanism of lamellar thickening growth [7,8], based on earlier suggestions by Bassett [9,10] and Wunderlich [11,12]. According to this mechanism the thickness of the lamella gradually increases as its growth proceeds. In consequence the lamella thickness is established only after some distance from the growing front and the edge of the lamella is tapered. This mechanism is well documented for the growth of the PE lamella in hexagonal phase at high temperature under high pressure. In this phase the chain mobility along its axis (sliding diffusion) is high and very intense thickening during growth may occur. The tapered edges of the lamella in the hexagonal phase can clearly be seen even in situ using the optical microscope [7,8]. The lamellar thickening growth of PE lamella under normal pressure was not reported. It was assumed that the sliding diffusion in the case of ordered crystalline phases is too small to enable the intense thickening of lamella at the growing edge.

Verification of the crystallization mechanism operating at given conditions can be made by analysis of the images of growing lamellae at the early stage, when the shape of their edges and thickness are not determined by the neighbouring lamellae. This is hardly possible under typical supercoolings when the growth rate is high and the shape of the edges of thin lamellae (ca 20 nm) is difficult to be identified.

In our previous works we proposed the so-called surface detachment technique, which allows to study the morphology of a contact layer by atomic force microscopic (AFM) imaging

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* Corresponding author. Tel.: +48 42 6803228; fax: +48 42 6803260.
E-mail address: atracz@cbmm.lodz.pl (A. Tracz).

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of a fracture occurring at or very close to the polymer/substrate interface (contact layer). We have studied non-isothermal crystallization of high density polyethylene (PE) on various model substrates like highly oriented pyrolitic graphite (HOPG), MoS_2 or talc [13,14]. In the contact layer, the lamellae are much thicker than in the bulk and form domains as large as several tens of square micrometers.

In this work, we report on the crystallization of PE on HOPG and MoS_2 substrates at high temperatures up to 135 °C. By quenching after different times of crystallization, we were able to ‘‘freeze’’ the lamellar morphology at various stages of its development at a given supercooling, starting from short lamellae. The result of the analysis of the shape if individual lamellae is used as the argument in determining the mechanism of growth. We demonstrate that at low supercooling under normal pressure, PE crystallizes by lamellar thickening growth.

2. Experimental

2.1. Materials and methods

Stabilizer-free HDPE [weight-average molecular weight (M_w) 360 000, number-average molecular weight (M_n) 30 000] provided by BP Chemicals, Ltd. (Grangemouth, UK), by courtesy of Dr. G. Capaccio, was used. Highly oriented pyrolytic graphite (HOPG) ZYB grade and molybdenum disulfide (MoS_2) single crystals used as substrates were purchased from SPI Supplies. The PE samples were investigated using a Nanoscope IIIa atomic force microscope (AFM) (Digital Instruments/Veeco, Santa Barbara, CA), operated in a tapping mode. Rectangular silicon cantilevers of model RTESP7 (Nanosensors, Wetzlar-Blankenfeld, Germany) were used throughout the study. Height and amplitude or phase images were recorded simultaneously. All scans were performed in air with a scan frequency below 5 Hz. The degree of the bulk crystallinity of different PE samples was determined using differential scanning calorimeter DSC 2920 CE (TA Instruments Inc., USA). For melting, annealing and cooling the samples at a controlled rate, a Mettler Toledo (Columbus, OH) hot stage was mainly used throughout this study. Only in some experiments (*vide infra*) a Boetius hot stage was used.

2.2. Sample preparation

A scheme of sample's preparation – a substrate detachment technique – is shown in Fig. 1. The polymer (0.5 mm thick) was melted at 170 °C on a surface of a freshly cleaved HOPG or MoS_2. It was kept for 10 min at this temperature after some slight pressing for good contact. After annealing for 10 min at 170 °C/min (route AB in Fig. 2) three different protocols were used for cooling the samples of PE on HOPG or on MoS_2:

I (route ABC in Fig. 2(left)). The sample was quenched by dropping it into ice water (route BC). In order to make the quenching process reproducible and fast the Mettler Toledo hot stage was placed upside down 20 cm above the container with ice water. At a desired moment, the cover of the hot cell was opened and the sample was dropped into ice water. In this sample was transferred to ice water within ca 0.2 s.

II (route ABDE in Fig. 2). The sample was cooled at a rate of 10 °C/min (part BD in Fig. 2) to a certain temperature T^* ($135\,°C \geq T^* \geq 125\,°C$). As soon as the temperature T^* was reached the sample was quenched by dropping into ice water as described above. Such procedure allowed us to freeze the lamella at different stages of growth.

III (route ABF in Fig. 2). The sample was cooled at a rate of 10 °C/min to room temperature.

IV (route ABGHI in Fig. 2(right)). The molten sample was kept at 170 °C on Boetius hot stage for 10 min. It was then quickly transferred (within 1 s) to the Mettler heating cell stabilized at the crystallization temperature T_c (route BG in Fig. 2). The sample was then kept at T_c for a desired time (route GH in Fig. 2) and then it was quenched by dropping into ice water as described above.

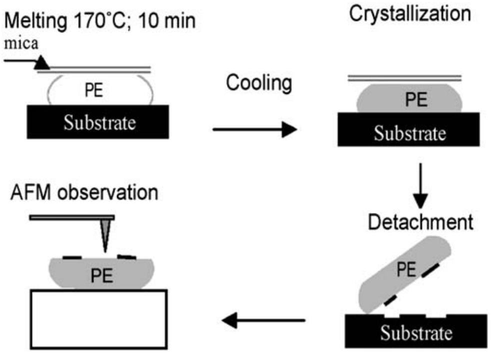

Fig. 1. Schematic illustration of a substrate detachment technique; successive stages of the experiment, from melting to AFM observations.

Detachment of the polymer sample from HOPG results in brittle fracture occurring close to the interface. Usually a part of the fracture surface is covered by the thin graphite flakes (Fig. 3). If necessary some remaining flakes of graphite can be gently removed using adhesive tape. On a thin PE layer, which remained on the detached graphite flakes, protrusions were found corresponding to the pits (missing blocks) on the detached PE surface. The AFM study of these remains is difficult and therefore we concentrate on studies of the surface of the detached polyethylene samples, which are easier to handle.

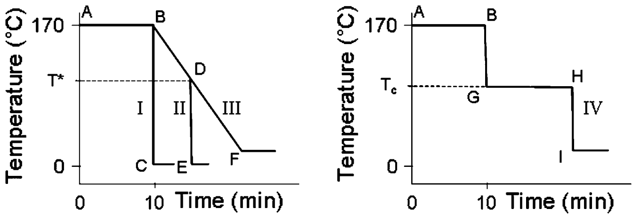

Fig. 2. Scheme of the sample cooling procedures used in this work. Left: protocols I, II and III. Right: protocol IV. Detailed description in the text.

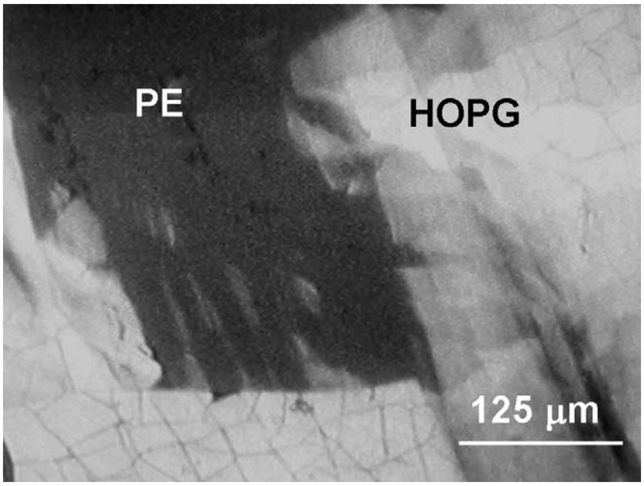

Fig. 3. Typical optical image (reflected light) of the PE sample detached from HOPG. A part of the surface covered by the thin graphite flakes appears bright in the reflected light. The surface of PE without graphite (dark) was investigated by AFM.

Similar preparation procedure was applied for the samples crystallized on MoS_2.

3. Results and discussion

In Fig. 4 AFM images of the fracture surfaces of a sample quenched from 170 °C (protocol I) and of the sample crystallized during cooling at a rate of 10 °C/min to room temperature (protocol III) are shown. The ribbons ≈ 35 nm and ≈ 80 nm in width, seen in Fig. 4(a) and (b), respectively, are in fact crystalline lamellae viewed edge-on. Interlamellar layers are seen in these height images as dark lines. One can see that the morphology of the fracture surface of both samples is qualitatively similar, except for the difference in the lamella thickness (l) (resulting from different cooling rates). Similar morphology was observed by AFM in the case of other polyethylene ($M_w = 193\,000$, $M_n = 82\,000$) crystallized on MoS_2, talc, NaCl [14,16] and on the surface of $C_{390}H_{782}$ detached from HOPG [15].

Typical features of the fracture surface of PE crystallized on atomically flat substrate are narrow block-like protrusions and pits (missing blocks) on the exposed edges of the lamellae, running nearly parallel to the lamella normal. It is important to note here that the width of many block-like protrusions or pits is comparable to the AFM tip radius, therefore they are not equally resolved in images obtained with different tips. In agreement with the earlier finding the height profiles reveal that the smallest steps on the lamellae surfaces are 0.5 nm in height, evidently corresponding to the thickness of one polyethylene chain.

Distinct orientations of the blocks in the neighbouring domains are visible (Fig. 4(a)). These orientations, inclined at 60° to each other, result from the epitaxial relationship with the hexagonal lattice of graphite. The direction of the ridges bound to the protruding blocks and the pits (striations) corresponds to the chain direction. One can see that the polymer chains are generally not tilted with respect to the lamella normal. This is in contrast to the fracture surface of $C_{390}H_{782}$ crystallized on HOPG where a tilt of 30° was found [15].

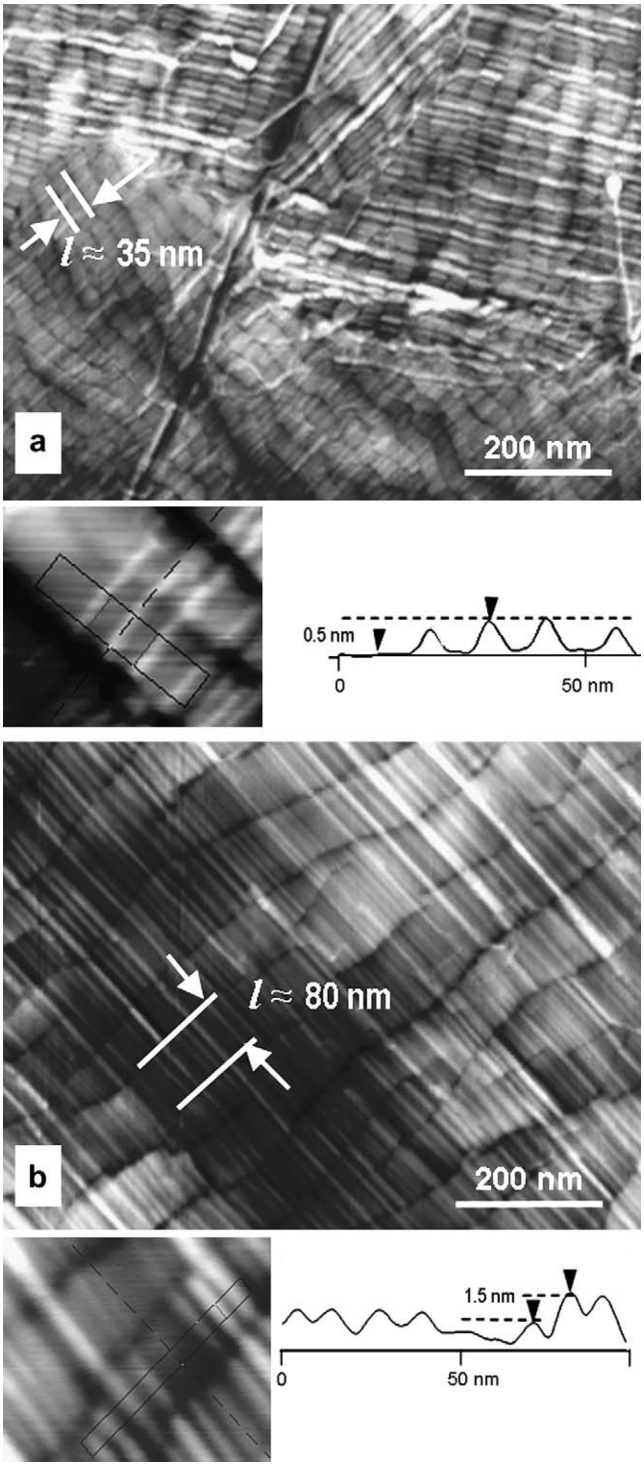

Fig. 4. AFM tapping-mode height images of the fracture surface of PE crystallized from the melt on graphite surface under different cooling conditions: (a) quenching from 170 °C (protocol I); (b) cooling at a rate of 10 °C/min (protocol III). Edge-on lamella is seen. Profiles scanned along the lamella shown at a larger magnification indicate that the height difference between block-like protrusions and pits is a multiple of ca 0.5 nm, that is, a distance comparable to the van der Waals radius of the PE chain in all-*trans* conformation.

Large thickness of the lamellae, reaching 80 nm, on the fracture surface of PE sample crystallized under normal pressure and apparently very high crystallinity in the contact layer are remarkable. The average crystallinity in the bulk of the sample determined from DSC is ≈73%. Taking into account the long spacing ≈30 nm (determined from SAXS) one can calculate that the average thickness of the lamella in the bulk of the sample is ≈22 nm. The lamellar thickness on the surface $l \approx 80$ nm is thus nearly four times bigger than in the bulk. It indicates that crystallization in a polymer layer close to the substrate surface starts at much higher temperature (smaller supercooling) than in the bulk. Taking the ratio of the thickness of the lamella (crystalline fraction) and the thickness of the interlamellar layer (amorphous fraction) as a measure of the crystallinity in the contact layer, it could be estimated to be bigger than 90% (Fig. 4(b)).

Exceptionally large thickness of the lamellae may suggest that they have been formed at high temperature. In order to determine at which temperature the crystallization at the interface really starts, the samples were cooled at a rate of 10 °C/min to a certain temperature T^* and quenched immediately by dipping into ice water (protocol II). AFM images of the fracture surface of such samples are shown in Fig. 5. The topography of the sample quenched from $T^* = 130$ °C (Fig. 5(a)) and of the sample quenched from 170 °C (Fig. 4(a)) is similar ($l \approx 35$ nm). This result indicates that the thick lamellae seen in Fig. 4(a) must form below 130 °C.

On the fracture surface of the sample quenched from $T^* = 129$ °C (Fig. 5(b)), one can see some thick lamellae surrounded by thin ones. Obviously, the thick lamellae formed during cooling at a rate of 10 °C/min before the temperature 129 °C was reached whereas the thin lamellae (similar to those found in the sample quenched from $T^* = 130$ °C) formed later on, during quenching. Thick lamellae have characteristic cigar-like shape − tapered edges. The thickness in the middle reaches 65 nm (Fig. 5(b)). Similar thickness and length of the lamellae indicate that they were formed nearly at the same time. The length of the lamellae is about 1 μm. They were formed during cooling from 130 °C to 129 °C at a rate of 10 °C/min, i.e. during less than 6 s. The minimum rate of the lateral growth of the lamella at this temperature can thus be estimated to be at least 170 nm/s. It is worth to note that the appearance of the fracture surfaces of thick lamella (tapered edges) in Fig. 5(b) is reminiscent of the fracture surfaces of extended-chain polyethylene crystals obtained by the cooling of ordered domains formed under high pressure in the hexagonal phase (Fig. 6).

The chain direction (labelled by the striations seen on thick and thin lamellae) is the same in a very big area, except for a small domain seen in the right part of the image in Fig. 5(b). The orientation of the striations on the surface of all lamellae in this domain differs by 60° with respect to the surrounding. One thick lamella is seen in this domain (marked by a black arrow in Fig. 5(b)). Evidently the lateral growth of this lamella was hindered by the domain boundaries. It could not be a domain of thin lamellae since they were formed later on during quenching. Thus the domain boundaries must label the edges of the pit on the graphite surface. We have shown that even a monolayer deep pits (0.335 nm) on the HOPG surface determine the shape of the PE or alkene domains in the

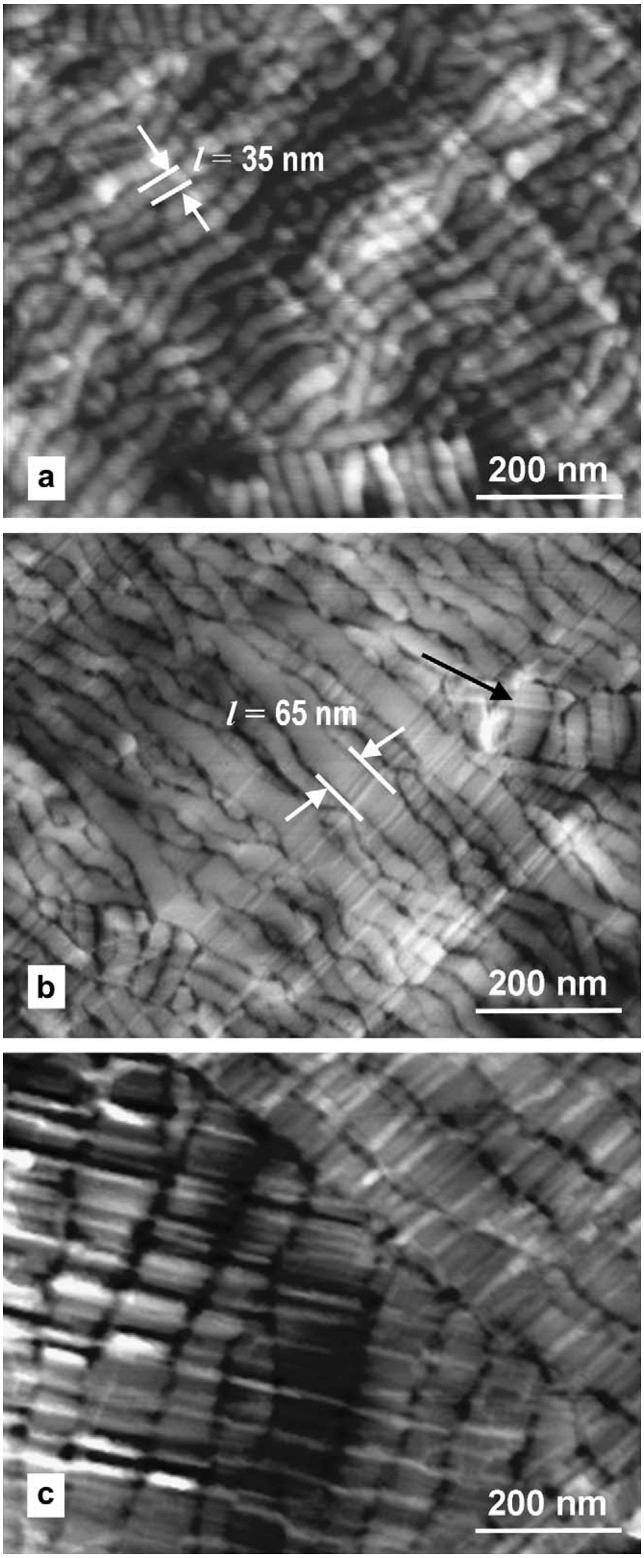

Fig. 5. AFM tapping-mode height images of the fracture surface of PE crystallized on graphite according to protocol II. Samples were cooled from 170 °C at a rate of 10 °C/min until a certain temperature T^* and then quenched. (a) $T^* = 130$ °C; (b) $T^* = 129$ °C; and (c) $T^* = 127$ °C.

Fig. 6. Transmission electron micrograph showing the linear tapered cross section of an isolated extended-chain single crystal (ESCS) of PE (NIST, SRM1483, $M = 32\,000$, $M_w/M_n = 1.11$) crystallized under high pressure, $P = 0.4$ GPa at $\Delta T = 4.6$ K. Scale bar is 1 μm. Sample was pressure-quenched at a stage of growth where ECSCs were isolated with each other and then permanganic etched to make replicas. Reprinted from Ref. [11] with the permission from the editor.

contact layer and the chain orientation in lamellae grown in the pits differs by 60° with respect to those grown outside in the neighbouring domain [13].

The topography of the sample quenched from $T^* = 127$ °C (Fig. 5(c)) resembles the topography of the samples which were cooled at a rate of 10 °C/min to room temperature (Fig. 4(b)). The above results allow to conclude that during cooling at a rate of 10 °C/min, the crystallization at the interface proceeds at temperatures ≤ 130 °C and is completed at 127 °C (i.e. in less than 18 s).

This early stage of PE crystallization at the HOPG surface cannot be detected by a standard DSC measurement. It is demonstrated in Fig. 5, where a corresponding DSC cooling scan of PE sandwiched between thin HOPG plates is shown. Before cooling at a rate of 10 °C/min the sample was thermostated at 170 °C for 10 min as usually done. As one can see, the maximum corresponding to the bulk crystallization is observed at the temperature of 118 °C. Similar result was obtained for the sample not sandwiched between HOPG. On the obtained DSC trace one cannot detect an onset of the crystallization at the interface in the temperature range 129–127 °C (see an enlarged part of the plot in Fig. 7). Obviously the contact layer with thick lamellae is too thin to provide a crystallization heat detectable in a standard DSC experiment. The thickness of this layer is not known. In the case of alkane $C_{390}H_{782}$ crystallized on HOPG it was shown that several tens of nanometers away from the substrate surface the lamella width is already the same as in the bulk [15].

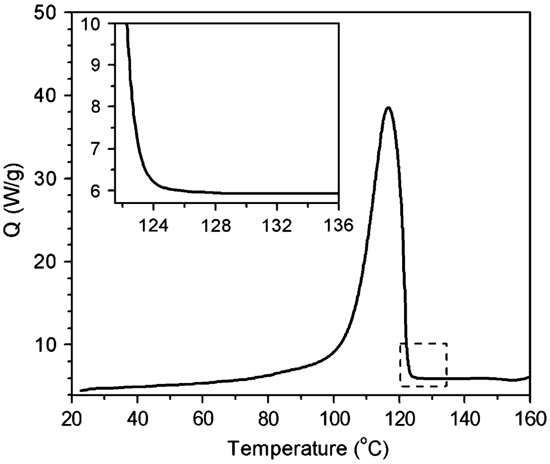

Fig. 7. DSC scan of PE sample sandwiched between two HOPG thin plates. Cooling rate is 10 °C/min.

To study the growth of thick lamellae it is better to perform isothermal crystallization experiment. In such conditions crystallization starts at even higher temperatures. AFM images of the fracture surface of PE crystallized on HOPG at $T_c = 133$ °C for a different time are shown in Fig. 8. After crystallization for 0.25 h (Fig. 8(a)) one can see the domains of thick lamella. They have also tapered edges as in the case of the lamellae found in the samples quenched from $T^* = 129$ °C. The thickness in the middle of the lamella reaches 93 nm. The lamellae in the domain periphery are (slightly thinner and) not tightly stacked. The space between the thick lamellae is filled with thinner lamellae, presumably formed later on during quenching. After 1 h of crystallization (Fig. 8(b)) the domain becomes considerably larger while the average lamellar thickness increased by only 7 nm ($l \approx 100$ nm). In some areas one can see thinner lamellae between thick lamellae (Fig. 8(b)).

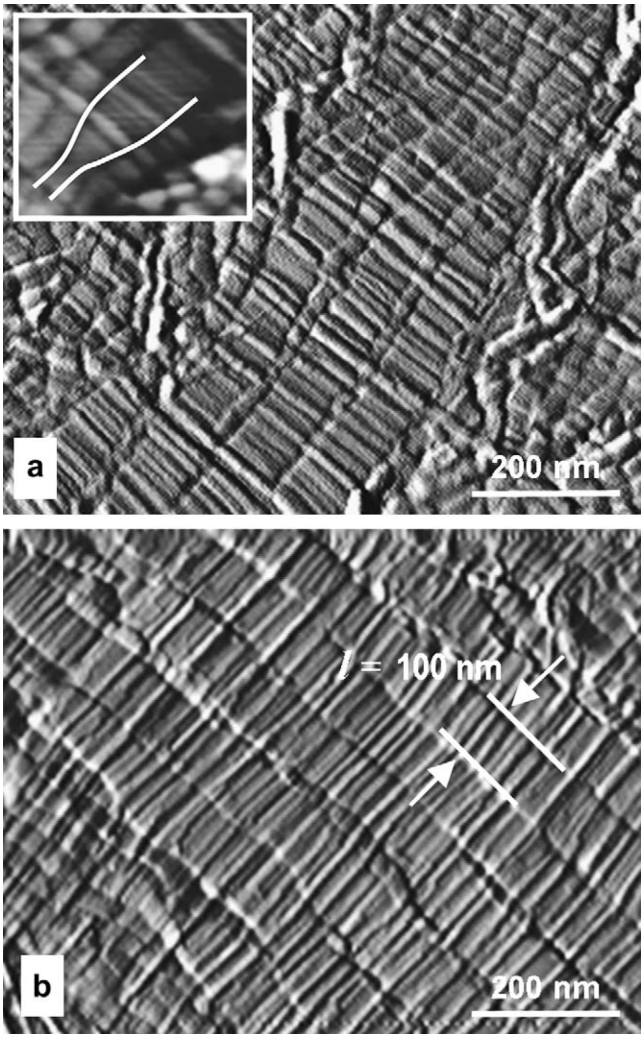

Fig. 8. AFM tapping-mode amplitude images of the fracture surface of PE crystallized isothermally at $T_c = 133$ °C (protocol IV) on graphite for 0.25 h (a) and 1 h (b). In the inset in (a) the tapered edge of the individual lamella is marked by the dotted line. Two thinner neighbouring lamellae are clearly seen.

Still thicker PE lamella could be observed on samples crystallized at higher T_c (Fig. 9). On the fracture surfaces of the samples crystallized on HOPG for 8 h at $T_c = 135\ ^\circ C$ (Fig. 9(a)) short thick lamellae can be seen. Their thickness in the middle reaches ≈150 nm. They have characteristic tapered edge but the tapering angle is bigger than in the case of the lamellae formed at 129 °C or 133 °C (Figs. 5 and 8). So big tapering angle can also be seen in the samples of PE crystallized at 232 °C for 30 min at 5 kbar (see Fig. 8 in Ref. [9]).

After crystallization at 135 °C for 72 h the thick lamellae are much longer and form large domains (Fig. 9(b)). The thickness of these lamellae reaches ≈160 nm. So thick lamellae in PE crystallized under normal pressure were observed for the first time.

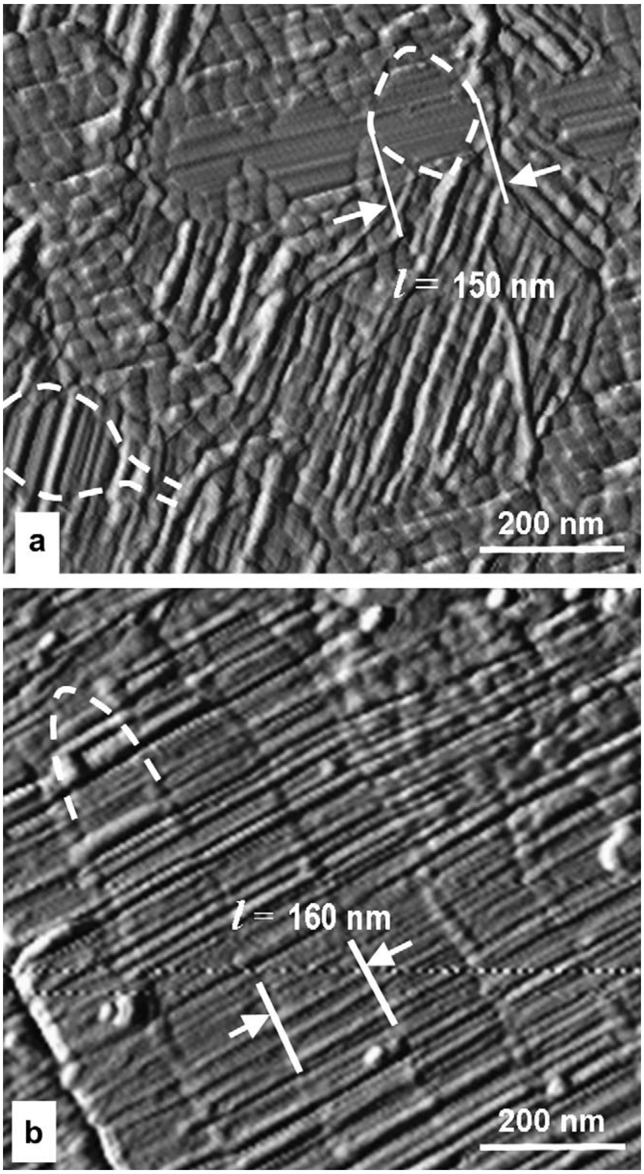

Fig. 9. AFM tapping-mode amplitude images of the fracture surface of PE crystallized isothermally (protocol IV) on graphite at $T_c = 135\ ^\circ C$ for 8 h (a) and 72 h (b).

The images in Figs. 8 and 9 show that the increase in the crystallization time does not result in an increase of the number of separated individual lamella but rather in the enlargement of the domains. Once a lamella is nucleated, the other adjacent parallel lamellae are formed relatively fast. We believe that formation of the domains proceeds according to the following scenario. Part of the chain emerging from growing lamella tends to adsorb on graphite in extended conformation rather than to fold back into the mother lamella. This part of the chain, provided it is long enough, serves as a nucleation site for a new adjacent lamella.

The number and length of the thick lamellae observed after isothermal crystallization at high temperature depended not only on the crystallization time but also on the kind of substrate. On the fracture surface of PE samples after crystallization on MoS_2 for 1 h (Fig. 10(a)) one can see bigger domains of thick lamellae, than on the samples crystallized for 8 h on HOPG. After crystallization for 8 h on MoS_2 thick lamella can be seen on the whole fractured surface (Fig. 10(b)).

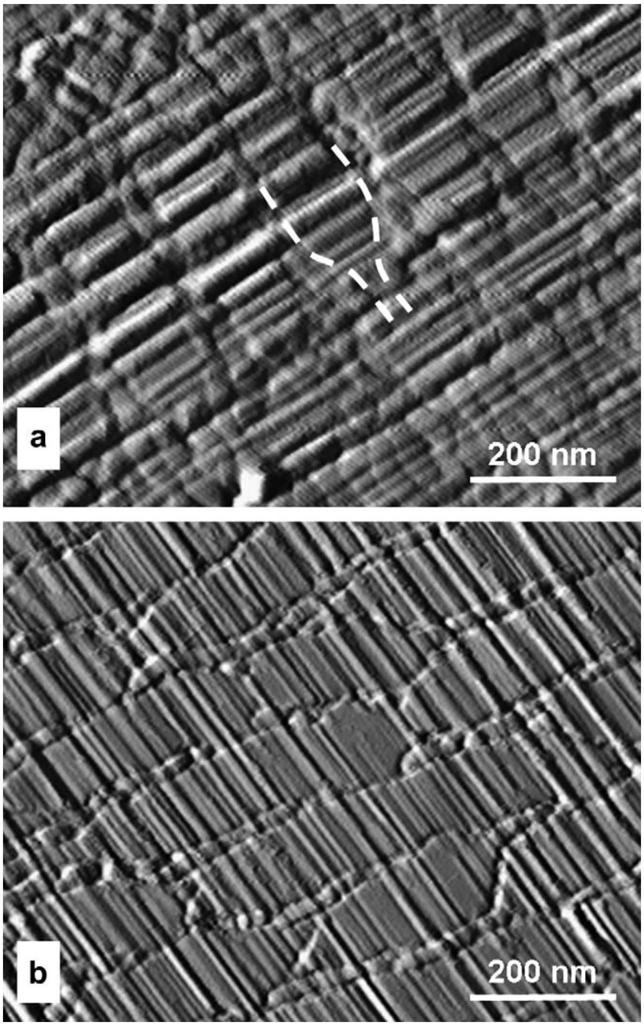

Fig. 10. AFM tapping-mode amplitude images of the fracture surface of PE crystallized isothermally (protocol IV) on MoS_2 at $T_c = 135\ ^\circ C$ for 1 h (a) and 8 h (b).

Comparison of the fracture surfaces of PE samples crystallized for the same time 8 h on HOPG (Fig. 9(a)) and on MoS_2 (Fig. 10(b)) indicates that the crystallization proceeds faster when MoS_2 is used as a substrate. In other words, the atomically flat basal plane of MoS_2 is more effective in inducing PE crystallization than HOPG. This parallels our earlier observation that the lamellae on fracture surfaces of samples of other PE crystallized on MoS_2 during cooling are thicker than on samples crystallized on HOPG at the same cooling conditions [14].

It is worth noting here that the monoclinic not the orthorhombic phase is formed in the contact layer of PE crystallized on HOPG [17]. It was also argued that this phase should form also in the contact layer of PE crystallized on MoS_2 [17]. This assumption is plausible since the lattice mismatch R [18] between the basal plane of MoS_2 and of PE is only -1.2% in case of monoclinic phase (epitaxial relation: $(0001)\langle 2\text{-}1\text{-}10\rangle_{\text{molybdenite}}//(-210)\langle 001\rangle_{\text{monoclinic PE}}$) whereas it is $+8.5\%$ in case of orthorhombic phase (epitaxial relation: $(0001)\langle 2\text{-}1\text{-}10\rangle_{\text{molybdenite}}//(110)\langle 001\rangle_{\text{orthorhombic PE}}$). Moreover the lattice mismatch between the monoclinic PE and the substrate is smaller for MoS_2 (-1.2%) than for HOPG (-5.3%) [17]. Smaller lattice mismatch between PE and the substrate in case of MoS_2 explains why at smaller supercooling the crystallization of PE proceeds on this substrate easier than on HOPG. MoS_2 is also more efficient in nucleating PE crystallization. One can see that the lamellae forming domains seen on sample detached from MoS_2 are shorter. Their growth was stopped by the impingement on other lamella because the nucleation density is much bigger. Impingement of the growing lamella results also in not symmetric shape of their edges (Fig. 10(b)). The tapered edges of the thick lamella formed after 1 h are symmetric (Fig. 10(a)). Before quenching they were freely growing into the melt and their growth was not disturbed by other lamellae.

The temperature of 135 °C was the highest at which we observed PE crystallization both on HOPG and on MoS_2. On the fracture surfaces of PE samples kept at 136 °C even for 63 h we could not find any thick lamellae. The fracture surface was similar to surfaces of samples quenched directly from 170 °C. $T_c = 135$ °C is the highest crystallization temperature of PE under normal pressure reported so far. According to our best knowledge, the studies on the isothermal crystallization of PE under normal pressure were reported for temperatures ≤ 131 °C [19–21]. Samples were crystallized even for several days and the long period determined from SAXS was ≈ 110 nm [19].

Observation of thick lamellae before they impinge on each other makes possible the identification of the shape of their edges, which is important for discussion of the mechanism of the lamellar growth under the conditions studied.

Similarity of the lamella shape in the contact layer and the shape of lamella obtained in hexagonal phase under high pressure (Fig. 6) allows to assume that the mechanism of their growth is similar, namely the lamellar thickening growth. According to this mechanism, the length of the initial chain folding at the tip of the growing front is small but while the lamella is growing its thickness behind the crystallization front increases. The tapering angle φ depends on the ratio of the rate of thickening U to the rate of growth V and increases with a decrease of supercooling [8]. This would explain why the tapering angle of the lamellae formed at 135 °C is bigger than in the case of the lamellae formed at 129 °C or at 133 °C (compare Figs. 5 and 8).

Lamellar thickening growth mechanism may operate effectively only if the mobility of the chains along their long axes (sliding diffusion) in the ordered domain is high (as e.g. in the hexagonal phase). It is assumed that the sliding diffusion of the chains in the growing lamella is dependent on the frictional coefficient between the neighbouring chains. The free energy of activation for sliding diffusion is assumed to be an increasing function of the lamella thickness. In the hexagonal phase, the friction coefficient is low and the thickening rate is practically independent of the lamella thickness, thus formation of very thick lamellae or extended-chain crystals is possible. On the contrary, in the case of tightly packed crystalline phases (orthorhombic or monoclinic) the friction coefficient is assumed to be higher and the sliding diffusion is hindered as the lamella thickness increases. The thickening is thus stopped at an early stage. As a consequence, the lamellae are thin and their thicknesses determined close to the edge are practically the same along the whole of its length. Thus it can be expected that the observation of the tapered edges in the case of lamella growing in orthorhombic phase would be difficult. Indeed AFM images showing various stages of the PE lamellar growth obtained by Hobbs et al. suggest that the lamella thickness does not increase during its growth [22]. The result can therefore be used as an argument that during crystallization of PE in orthorhombic phase, the intense thickening of the lamella is indeed hindered. It is, however, important to note that the lamellae shown in Ref. [22] are relatively thin and the shape of the edge cannot be clearly seen.

Hodge and Bassett found tapered edges in relatively thin PE lamella formed during cooling under pressure 2.3–2.87 kbar when PE is expected to crystallize in the orthorhombic form [23]. They concluded that tapered profiles of the lamellar edges appear to be general to polymeric crystallization from the melt.

Simulations of PE crystallization on or between flat solid walls have shown that the crystallization front is tapered [24,25]. A kind of a tapered edge appears also in Strobl model of lamella growth treated as a multi-stage process, where the thickness and the structure of the lamella are established only after some distance from the growing tip [6].

One should realize that the experimental studies on the shape of lamellar edge are restricted only to a certain range of crystallization conditions when sufficiently thick lamella may grow. Moreover, any relation between the mechanism of lamella growth and the shape of the lamella edge can only be discussed if the lamellae are isolated. It has to be convincing that tapering is inherent and not just a consequence of impingement during growth or thickening of lamellae within a stack. Under some conditions, e.g. at higher supercooling it is impossible to quench the sample at the stage when only few isolated lamella grow in the melt, since fast massive crystallization of numerous thin lamellae takes place within a short range of time. In the case of thin lamella, it is very difficult to determine the shape of its edge precisely using electron or atomic force microscopy. The thin lamellar edge can also be altered by the sample preparation for electron microscopy (etching, staining). On the other hand, when lamella thickness is comparable with the radius of the AFM tip (several nanometers) even a tapered edge would appear rounded.

In our case, we observe exceptionally thick lamellae with clearly seen tapered edges, thus we can unambiguously show that they are formed by lamellar thickening growth. Crystallization under very small supercooling leading to such thick lamellae is possible owing to the strong interaction between PE chains and the substrate. Magonov et al. have shown that melting of the alkane $C_{390}H_{782}$ on graphite is accompanied by the spreading of the alkane onto the substrate and the formation of a thin epitaxial layer. The complete melting of this film occurs at 185 °C, i.e. approximately 55 °C above the melting point of the bulk material [26]. Therefore, we believe that on atomically flat surface of HOPG and MoS_2, even at low supercooling, there exists a ''pre-ordered'' layer of PE before the crystallization starts. Without such order it is hardly possible to explain long-range alignment of chain direction.

At present, it is, however, impossible to conclude the structure of the thick lamellae at the time when they grow. We know that the structure of PE crystallized on HOPG in the contact layer at room temperature is monoclinic, not orthorhombic [17]. Whether the monoclinic phase forms directly from the melt state or the structure of the forming lamella is initially different (e.g. hexagonal) and it later on transforms into monoclinic is an open question. Additional experimental evidences could be provided by in situ structural studies at high temperature.

4. Conclusions

The substrate detachment technique appears to be an excellent tool for studying the early stages of polymer crystallization at the substrate surface. We found that crystallization of the contact layer on atomically flat substrates begins at exceptionally high temperatures: 135 °C under isothermal conditions and 129 °C during cooling at a rate of 10 °C/min. This observation explains why the lamellae formed are very thick. We were able to freeze the lamellae growth at the early stage and their tapered edge could clearly be seen. It indicates that the PE crystallization on HOPG proceeds by lamellar thickening growth mechanism, which under normal pressure leads to exceptionally large lamellae thickness of 160 nm.

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