Influence of the Crystallization Conditions on the Morphology of the Contact Layer of Polyethylene Crystallized on Graphite: Atomic Force Microscopy Studies

Adam Tracz,[1] Jeremiasz K. Jeszka,[1] Iwona Kucińska,[1] Jean-Paul Chapel,[2] Giséle Boiteux,[2] Marian Kryszewski[1]

[1] *Center of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Łódź, Poland*
[2] *Laboratoire des Matériaux Polymères et des Biomatériaux, Université Claude Bernard-Lyon I, UMR CNRS 5627, 69622 Villeurbanne, France*

ABSTRACT: The influence of crystallization conditions on the morphology of the contact layer of high-density polyethylene crystallized on graphite has been investigated. The characteristic morphology of the polyethylene contact layer consists of striated, ribbonlike structures organized in domains in which the striations follow the same direction. The directions in different domains reflect the threefold symmetry of the graphite lattice. From the dependence of the width of ribbons on the crystallization conditions (i.e., the cooling rate and annealing), it has been concluded that the polymer chain is aligned parallel to the striation directions and that the ribbon width corresponds to the lamellar width. Therefore, the lamellar width in the contact layer (60 and 80 nm for cooling rates of 10 and 0.2°/min, respectively) is considerably bigger than in the bulk (ca. 26 nm). In addition, the chain orientation can be uniform over large areas, but the domain orientation can be disturbed by the presence of pits only one atomic layer deep (0.335 nm) if they are formed on the graphite surface. These results show the great importance of the nanostructure of the support for polymer chain alignment and epitaxial crystallization of polymers. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 1329–1336, 2002

Key words: atomic force microscopy (AFM); lamellar; polyethylene (PE)

INTRODUCTION

It is well known that the process of polymer crystallization is modified by the presence of solid surfaces.[1,2] This effect can influence the properties of polymer materials, especially composites with fillers such as carbon black, mica, talc, or chalk. With the recently reemerging interest in the field of polymer crystallization from the melt,[3–10] little attention is being paid to crystallization on atomically flat solid surfaces. Atomic force microscopy (AFM) is an excellent tool for observing the morphology of the polymer layer adjacent to the surface; however, only a few studies on this subject have been carried out. Studies on the surfaces of polymer films detached from glass or mica supports[3,11] or exposed by dissolution of the organic crystal on which the polymer was crystallized[12] have been reported. For polyethylene (PE) or polypropylene (PP) crystallized on mica or glass supports, a granular morphology was found.[3,11] These results were considered additional arguments in the discussion of the possibility of the formation of lamellar crystallites via mesomorphic and granular crystalline layers.[3,4]

After detachment from a flat substrate, the surface of a polymer sample is also flat. This is very important because if the sample surface is flat on a submicrometer scale, morphological studies with AFM are much easier and more effective. In most studies published so far, this aspect of sample preparation was the main reason that the surfaces adjacent to substrates were investigated. The influence of the substrate on polymer crystallization was not considered. It can hardly be deduced from the published AFM images because different substrates and different polymers have been studied.

Recently, we published the first AFM images of the contact layers of high-density polyethylene (HDPE) samples crystallized under the same conditions on two different, molecularly flat model supports: graphite and mica.[13] The large differences in the morphologies of HDPEs crystallized on these two supports indicate that the interaction of the polymer chains with the substrate is crucially important.

In this article, we discuss some new results obtained during more detailed experiments on the system men-
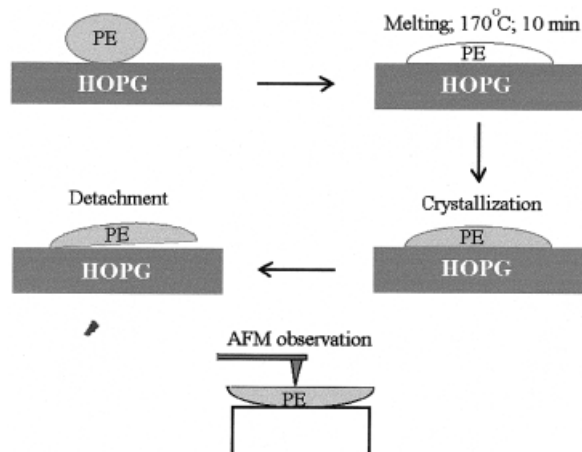
Figure 1 Schematic illustration of the successive stages of the experiment, from PE melting to AFM observations.

tioned in ref. 13, which involves crystallization at different cooling rates and annealing. We demonstrate that AFM provides new information, expanding our knowledge of transcrystallization and epitaxial crystallization of polymers based on earlier scanning electron microscopy studies.

EXPERIMENTAL

A scheme of the sample preparation is shown in Figure 1. The polymer sample (0.5 mm thick) was molten at 170°C on a freshly cleaved highly oriented pyrolitic graphite (HOPG) surface. It was kept for 10 min at this temperature after some slight pressing for good contact. The sample was then cooled to room temperature at different cooling rates on a Mettler Toledo (Columbus, OH) hot stage. The polymer surface obtained by the detachment of the polymer from graphite (and by the eventual, gentle removal of some remaining flakes of graphite) was investigated. The crystallized PE samples could be separated from the support without visible damage to the polymer surface, and flat samples with lustrous surfaces were obtained. In some experiments, PE was molten and crystallized also on an HOPG surface with circular, 0.335-nm-deep etched pits. Such pits were obtained by thermal oxidation of HOPG at 650°C for 10–15 min.[14] The graphite basal plane between the pits and on the bottom of the pits exhibited the same properties as that of a freshly cleaved sample. The bulk properties of the samples crystallized at a 10°/min cooling rate were as follows: degree of crystallinity = 65% [from differential scanning calorimetry (DSC)], long period = 40 nm [from small-angle X-ray scattering (SAXS)], and average lamellar thickness ~ 26 nm.

Stabilizer-free HDPE [weight-average molecular weight (M_w) = 193,000, number-average molecular weight (M_n) = 82,000] provided by BP Chemicals, Ltd.

(Grangemouth, UK), by courtesy of Dr. G. Capaccio, was used. HOPG was provided by Advanced Ceramics (Cleveland, OH). AFM observations were performed with an apparatus made at the University of Łódź and with a Nanoscope III (Digital Instruments, Santa Barbara, CA). Studies were performed in the contact mode [a V-shaped Si_3N_4 tip, radius of curvature (R) ~ 50 nm] or tapping mode (a silicon rectangular tip, R ~ 15 nm; Nanosensors, Darmstadt, Germany), with height and deflection or amplitude images recorded simultaneously. All scans were performed in air with a scan frequency below 5 Hz.

RESULTS AND DISCUSSION

In Figures 2–6, which show AFM pictures of the contact layer of PE crystallized on HOPG under different conditions, one can see striated and banded ribbonlike structures stacking upon one another at relatively large distances. The striations are running more or less perpendicular to the ribbon long axes. They can be well seen, especially at higher magnifications, particularly on pictures made in the tapping mode (Figs. 3–5). The most interesting feature is the alignment of striations (but not necessarily ribbons) in one direction in domains of different sizes. These domains can be best visualized with the friction mode. Figure 2 shows two kinds of such domains. In Figure 2(a), one can see large domains formed on freshly cleaved HOPG. Such domains in many places are as large as several tens of square micrometers. The angles between striating directions in neighboring domains are 60 or 120°, which reflect the threefold symmetry of the graphite lattice. It is not clear if such domains can form also on an atomically flat surface with a perfect lattice or if their boundaries always reflect imperfections of the HOPG basal plane. Figure 2(b) presents domains formed on an HOPG surface with circular, 0.335-nm-deep thermally etched pits.[14] The circular domains of the PE morphological structures evidently reflect circular pits formed on the HOPG basal plane. This means that the organization of PE chains is very sensitive to nanoscopic imperfections of the graphite surface, and even one-monolayer-deep steps disturb the uniform orientation of polymer chains. Another interesting feature in this picture is that the orientation of morphological structures is practically undisturbed by an approximately 30-nm-deep ditch seen in Figure 2(b) as a thick, black line. This means that the ditch was formed because of some stress after the formation of the crystalline structure was completed.

It is not surprising that graphite has an ordering effect on PE chains. An ordering effect of the graphite substrate on alkanes has been proven by calculation,[15] simulation,[16] and scanning tunneling microscopy (STM)[17,18] studies on alkanes adsorbed or evaporated onto an HOPG basal plane. Also, in early studies on
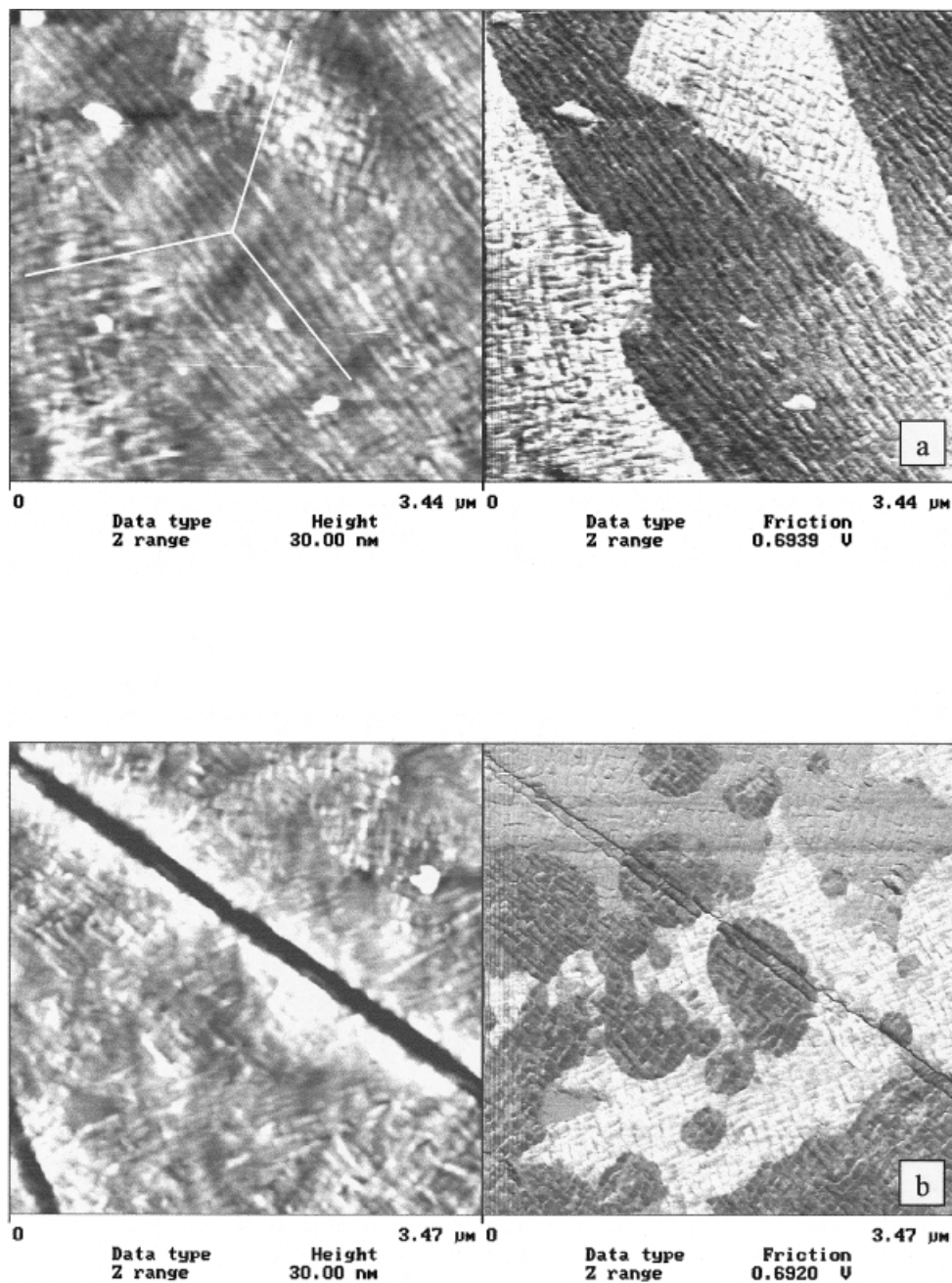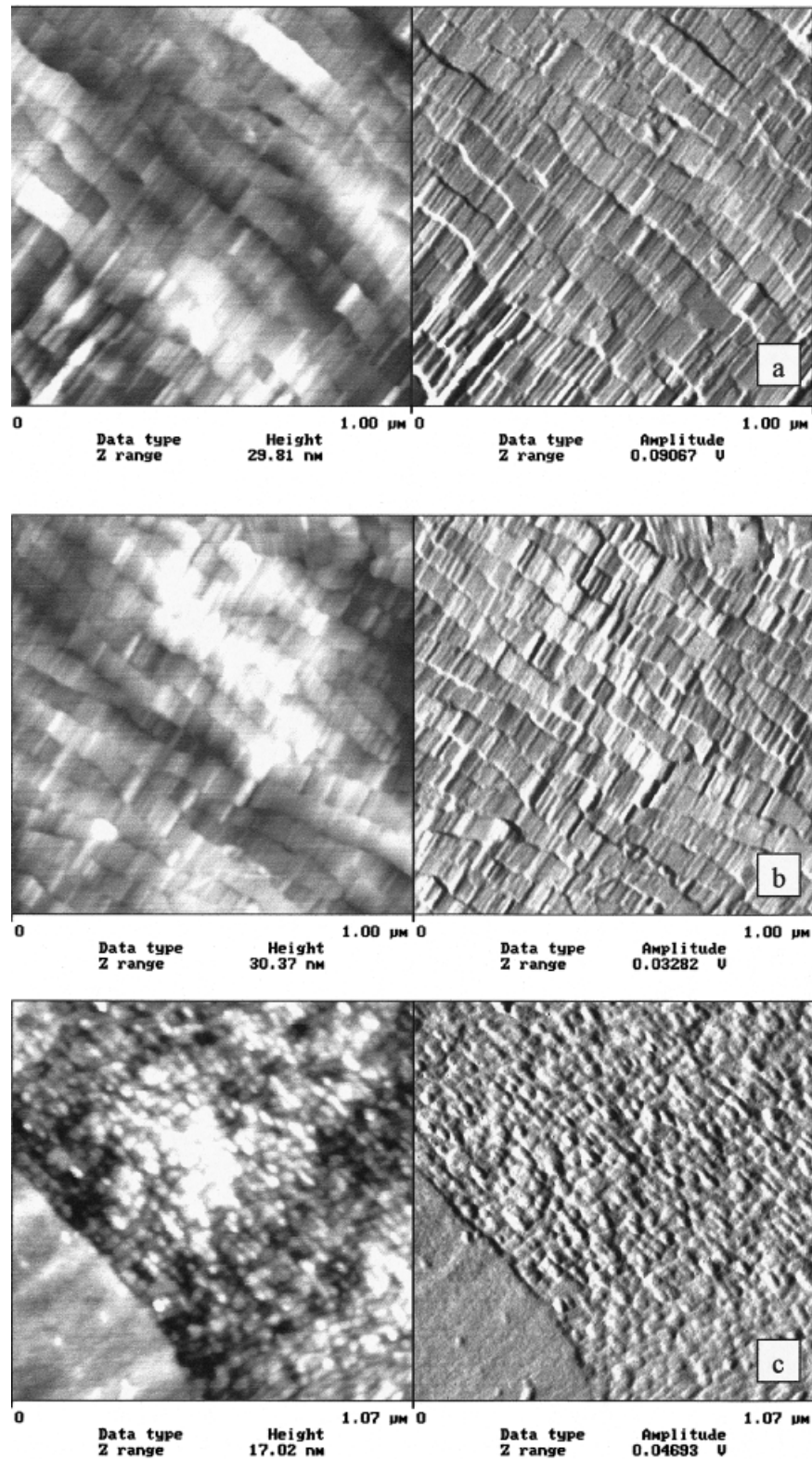
Figure 2 AFM contact-mode height (left) and friction (right) images of the contact layer of PE crystallized on (a) a freshly cleaved HOPG surface and (b) an oxidized HOPG surface (cooling rate = 10°/min).

thin layers of PE crystallized from solution on the basal plane of natural graphite single crystals, it was shown that the rodlike PE crystallites were not randomly distributed but followed the threefold symmetry of graphite.[19]

If we take into account that the striations and not the ribbon edges have uniform orientations over large areas and, as discussed later, follow the threefold symmetry of graphite, it is evident that the PE chain direction should be related to the striation direction. Two possible orientations of the polymer chains should be considered: (1) parallel and (2) perpendic-

ular to the striations. Assuming perpendicular orientation, we arrive at the conclusion that the lamellar thickness would be about 10–20 nm, that is, somewhat smaller than the value of about 26 nm obtained for the bulk with DSC and SAXS for the same sample (cooled at 10°/min). However, in this case it is difficult to explain why the lamellae are so short (ca. 60 nm) and why are they uniformly packed in ribbonlike structures. If we assume the chain orientation is parallel to the striations, the lamellar width is unusually large. The average value of the lamellar thickness in the contact layer determined from AFM would be more
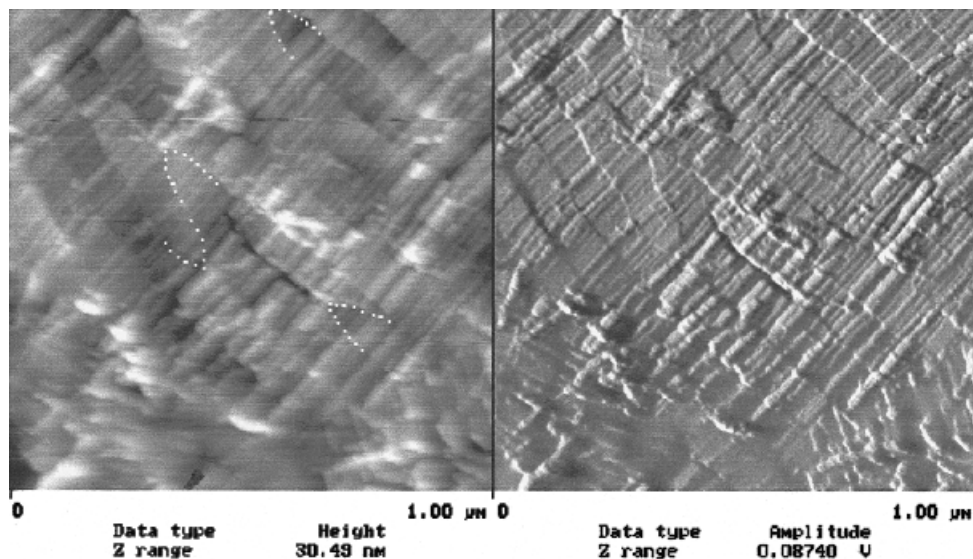
Figure 3 AFM tapping-mode height (left) and phase (right) images of the contact layer of PE crystallized on a freshly cleaved HOPG surface: (a) cooling rate = 0.2°/min, (b) cooling rate = 10°/min, and (c) quenching in water (c).

than 2 times greater than the average lamellar thickness in the bulk.

Because it is well known that the lamellar thickness depends on crystallization conditions and annealing, such experiments can be helpful in choosing one of the aforementioned possibilities. Figure 3 shows AFM images of the contact layers of PE crystallized at different cooling rates (0.2 and 10°/min) and quickly quenched
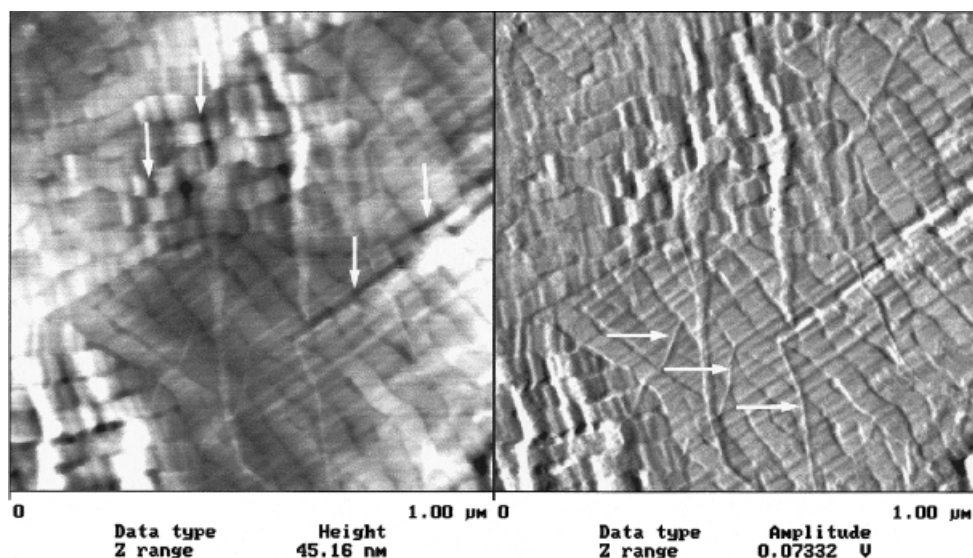
Figure 4 AFM tapping-mode images of the contact layer of PE crystallized on a freshly cleaved HOPG surface. The sample crystallized at a cooling rate of 10°/min and annealed for 10 h at 130°C before the detachment of the graphite. Dotted lines mark the tapered edges.

by immersion in ice-cold water. The morphology of the quenched sample [Fig. 3(c)] is quite different from those of the two other samples. The ribbonlike structures can hardly be seen. It should be noted that the cooling rate in the quenched samples was not known, nor was it reproducible. If we compare Figure 3(a–c), it is evident that the width of the ribbons is dependent on the cooling rate and decreases as the cooling rate increases (ca. 80, 60, and 25 nm for a cooling rate of 0.2°/min, a cooling rate of 10°/min, and fast quenching, respectively). The striation width does not seem to change significantly.

Figure 4 presents AFM pictures of the PE samples crystallized at a cooling rate of 10°/min and then annealed at 130°C for 10 h before graphite detachment. A comparison of Figures 3(b) and 4 shows that the width of the ribbons increased with annealing, from about 60 nm to about 110 nm. Also, in this case the striation width does not increase.

Both the cooling rate and annealing influence the width of the ribbons, not of the striations. On the basis of these results, we interpret the ribbons as lamellae seen edge on with the striations parallel to the chain direction. This conclusion is in agreement with pre-

Figure 5 AFM tapping-mode images of the contact layer of PE crystallized on a freshly cleaved HOPG surface showing fibers on ordered structures of PE, thick blocks (dark spots) removed from PE, and rodlike structures (cooling rate = 10°/min).
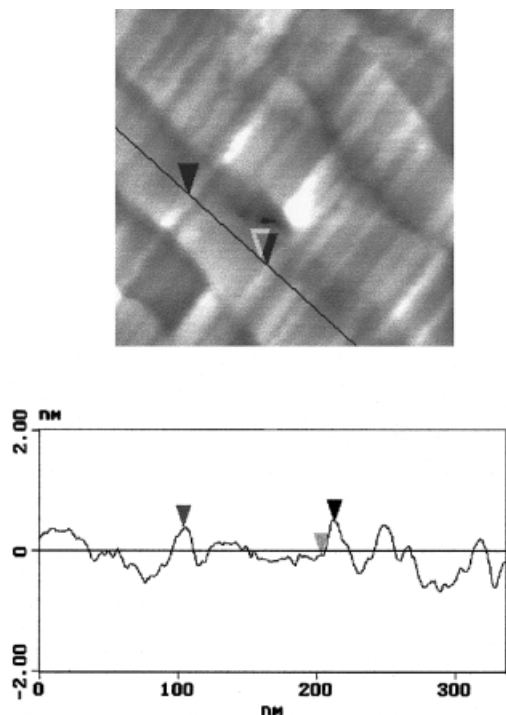
Figure 6 AFM tapping-mode height image [part of Fig. 3(a)] and section analysis of the part indicated by the black line.

liminary molecular resolution observations and Raman studies (which will be presented in detail in a subsequent article). The fact that a contribution of lamellae so thick is observed neither with DSC nor with SAXS implies that they constitute only a very thin contact layer adjacent to HOPG.

AFM pictures at higher magnifications [Figs. 3(a,b) and 4] show a striking similarity to the transmission electron microscopy or AFM micrographs of wide lamellae of PE in samples crystallized under high pressure (via the hexagonal phase)[20,21] or for a long time at a high temperature (130°C),[22] as well as other polymers, such as polybutadiene, crystallized with low supercooling.[23] Fractures of such lamellae display characteristic striations, which label the chain direction. The distribution of their widths is very broad. In our case, the distribution is certainly narrower, and as mentioned before, the average size is about 10–20 nm. It seems possible that at least some elements of the surface morphology are fracture-induced features resulting from a deformation of PE during the detachment of graphite. In some pictures, PE fibers, evidently pulled-out, lie randomly oriented on ordered structures (Fig. 5). In some places, one can also see dark spots that look like thin blocks being removed from PE (arrows in Fig. 5). Such removed blocks should remain on the detached graphite surface, but so far, observations made of detached graphite while the remaining PE structures were sought were not conclusive.

The striations and the boundaries between the lamellae are particularly well seen in the amplitude images; however, an analysis of the height images also provides important information. In particular, section analysis shows that in some places the striations or thin blocks protrude by less than 0.5 nm (Fig. 6), that is, a distance comparable to the van der Waals radius of the PE chain in an all-trans conformation.

The question of whether the width of striations is related to the internal structure of the lamellae remains open. For fractures of extended-chain crystals, it was argued that there was no relation,[20] although the arguments (based on the annealing of fractured samples) were not quite convincing. However, the concept of the formation of lamellar crystals from granular structures was recently considered by Strobl.[4] The striation size could also be related to the L parameter in the Hoffman–Miller (HM) theory of polymer crystallization. It represents the substrate length, reflecting a domain or grain size in the body of the crystal, and according to the HM estimation should be equal to $10/21$ nm.[24] The role and appropriate value of this parameter are, however, not clear, and it is a subject of controversy.[8,25]

The parallel alignment of PE chains along one direction over large areas in many stacked lamellae may suggest the existence of a mobile, columnar (hexagonal) mesophase in the PE melt (at least on the graphite surface) before its crystallization. According to recent considerations of the role of transient metastable phases in polymer crystallization, it is accepted that the growth of PE crystals may initially proceed via a hexagonal phase even in the region of a thermodynamically stable orthorhombic phase in the pressure–temperature diagram. However, the transition to the orthorhombic phase occurs after a certain size is reached.[6,7] It was demonstrated (for an isolated lamella growing in the melt) that such a transition leads to the breaking of the lamella into grains or subunits.[26] It is, therefore, also possible that the striations label the grain boundaries formed during such a transformation.

The phenomenon of the stacking of several lamellae one upon another during polymer crystallization (preserving the chain direction) is not fully explained. For solution-crystallized ultrahigh molecular weight (UHMW) PE, the stacking of the lamellae was explained by the gravitational forces acting on the lamellae during solvent evaporation leading to film formation.[27] For crystallization from the quiescent melt, it was assumed that the stacking was related to the screw dislocation.[9,23,28] However, in no case was evidence shown of the presence of such dislocations in images showing stacked lamella seen edge on. Moreover, the pictures showing stacked lamellae of PE crystallized at high temperatures,[22] polybutadiene

crystallized from the melt,[23] or UHMW PE crystallized from solution[27] are quite similar.

We believe that in our case the stacking of the lamellae is due to the ordering influence of the graphite during the two-dimensional folding of the PE chains on the substrate. Part of the chain emerging from the growing lamella tends to adsorb on the graphite in an extended conformation rather than fold back into the lamella. If this part of the chain is long enough, it serves as a nucleation site for the new adjacent lamella (and possibly also for subsequent lamellar doubling, which is considered later in this article). Such a mechanism can lead to the growth of stacked lamellae, forming large domains in which the chain direction is the same.

However, some rodlike structures running through several adjacent lamellae (as seen in Fig. 5) can also suggest that either some of the primary nuclei on graphite are very long or several blocks (striations) are tightly connected via tie chains. This could explain why the pulled-out fibers (shown in Fig. 5) are of the same width as the striations and are much longer than the width of the lamellae. It should be stressed that the length of the pulled-out fibers seen on fracture surfaces of extended-chain crystals is usually comparable to the length of the striations.[20,21]

Unusually large lamellar thickness in the contact layer is an unexpected result and can be explained in different ways. The first possibility is that it is due to the interaction with the graphite surface, which results in longer stems of the primary nuclei on a large nucleating surface. This situation is similar to crystallization on PE extended-chain crystals.[20]

One has to consider also the possibility that the width of the lamellae in the contact layer is bigger than in the bulk because they were formed at low supercooling. It has been shown that lamellae greater than 100 nm wide can be obtained in the bulk of samples isothermally crystallized from the melt at 130°C.[22] It is also known that at high temperatures the induction time for nucleation is long and that the overall crystallization rate temperature is low. However, the time required to obtain a layer only a few nanometers thick can be very short, especially if practically infinite nuclei (the HOPG surface) exist already at high temperatures. It should also be taken into account that contrary to the crystallization in the bulk, for which the three-dimensional nuclei have to be formed before lamellar growth, for the two-dimensional crystallization on the graphite surface, much lower supercooling is necessary; that is, the beginning of crystallization at higher temperatures can be expected.

When the origin of large lamellar widths is discussed, thickening processes should also be taken into account. The lamellar thickening processes depend on the kind of PE used (M_w, M_w/M_n, and purity) and on the crystallization time. According to Barham and Keller's[29] results for PE (M_w = 119,000), lamellae may reach a thickness of 60–80 nm (via tripling) during isothermal crystallization at 129°C after about 20 min when the initial thickness is about 23 nm. Also, in this case the relatively long time necessary to obtain large lamellae in bulk samples should not be considered a factor precluding their formation in a thin contact layer in our case. It is known that lamellar thickening via doubling can be observed for systems with regular stacking.[27] The regular stacking in our samples is clearly seen in Figures 3–5. One can, therefore, assume that the observed, nearly twofold increase of the lamellar thickness from about 60 nm to about 110 nm with annealing at 130°C can also occur via lamellar doubling. The similar widths of most of the lamellae also indicate that the crystallization at the surface is very fast and occurs practically under isothermal conditions, even when the sample is cooled at a rate of 10°/min.

The crystals growing by chain folding followed by extension[6,7,9] and well-stacked lamellar crystals obtained from solutions of UHMW PE after lamellar doubling[27] show another interesting morphological feature, that is, tapering and rounding of the lamellae toward their edges and frequent reduction in size at the points of intersection. This feature is also observed in the AFM pictures presented in this article (some tapered edges are marked by the dotted lines in Fig. 4). Therefore, it can be taken as a supporting argument in favor of these mechanisms being responsible for large lamellar thickness in the contact layer of PE crystallized on graphite.

CONCLUSIONS

The characteristic morphology of the contact layer of HDPE crystallized on HOPG consists of ribbonlike structures organized in domains in which the striations within the ribbons follow the same direction. From the dependence of the width of ribbons on crystallization conditions (i.e., the cooling rate and annealing), it has been concluded that the polymer chain is aligned parallel to the striation directions and that the ribbon width corresponds to the lamellar width. Therefore, the lamellar width in the contact layer is 60–80 nm for cooling rates changing from 10 to 0.2°/min, which is considerably larger than the value of about 26 nm in the bulk. The large lamellar width in the contact layer can be explained by the crystallization of this layer at low supercooling due to the nucleating and chain-ordering influence of the graphite surface. It has also been shown that the chain orientation can be uniform over large areas, but the domain orientation can be disturbed by the presence of pits only one atomic layer deep (0.335 nm) if they are present on the graphite surface. These results show the great importance of the nanostructure of the sup-

port for polymer chain alignment and epitaxial crystallization of polymers. It is, however, too early to fully appreciate these new results, but they open an exciting chapter in attempting to understand nanoscale interfacial phenomena, which lead to specific phase transitions and result in unexpected surface morphology. In any case, such studies provide a remarkable scientific challenge.

References

1. Wunderlich, B. Macromolecular Physics; Academic: New York, 1980.
2. Sanchez, I. C. Physics of Polymer Surfaces and Interfaces; Butterworth-Heineman: Boston, 1992.
3. Hugel, T.; Strobl, G.; Thomann, R. Acta Polym 1999, 50, 214.
4. Strobl, G. Eur Phys J E 2000, 3, 165.
5. Stocker, W.; Schumacher, M.; Graff, S.; Thierry, A.; Wittmann, J. C.; Lotz, B. Macromolecules 1998, 31, 807.
6. Rastogi, S.; Kurelec, L. J Mater Sci 2000, 35, 5121.
7. Keller, A.; Cheng, S. Z. D. Polymer 1998, 39, 4461.
8. Point, J. J.; Janimiak, J. J. Polymer 1998, 39, 7123.
9. Hikosaka, M.; Amano, K.; Rastogi, S.; Keller, A. J Mater Sci 2000, 35, 5157.
10. Psarski, M.; Piorkowska, E.; Galeski, A. Macromolecules 2000, 33, 916.
11. Magonov, S.; Godovsky, Y. Am Lab 1999, 31(8), 52.
12. Stocker, W.; Schumacher, M.; Graff, S.; Lang, J.; Wittmann, J. C.; Lovinger, A. J.; Lotz, B. Macromolecules 1994, 27, 6948.
13. Tracz, A.; Jeszka, J. K.; Kucińska, I.; Chapel, J.-P.; Boiteux, G. Macromol Symp 2001, 169, 129.
14. Tracz, A.; Wegner, G.; Rabe, J. P. Langmuir 1993, 9, 3033.
15. Baukema, P.; Hopfinger, A. J Polym Sci Polym Phys Ed 1982, 20, 399.
16. Hentschke, R.; Schürmann, B. L.; Rabe, J. P. J Chem Phys 1992, 96, 6213.
17. Rabe, J. P. Science 1991, 254, 424.
18. Ishida, K.; Taki, S.; Okabe, H.; Matsushige, K. Jpn J Appl Phys 1995, 34, 346.
19. Tunistra, F.; Baer, E. J Polym Sci Polym Lett Ed 1970, 8, 861.
20. Wunderlich, B.; Melillo, L. Makromol Chem 1968, 118, 250.
21. Brian, K. A.; Reffner, J. R.; Wunderlich, B. J Polym Sci Part B: Polym Phys 1993, 31, 93.
22. Mandelkern, L.; Price, J. M.; Gopalan, M.; Fatou, J. G. J Polym Sci Part A-2: Polym Phys 1966, 4, 385.
23. Rastogi, S.; Ungar, G. Macromolecules 1992, 25, 1445.
24. Hoffman, J. D.; Miller, R. L. Macromolecules 1988, 21, 303.
25. Point, J. J.; Colet, M. C.; Dosiere, M. J. J Polym Sci Part B: Polym Phys 1986, 24, 357.
26. Basset, D. C. In Developments in Crystalline Polymers; Basset, D. C., Ed.; Applied Science: 1982; Vol. 1.
27. Rastogi, S.; Spolestra, A. B.; Goossens, J. G. P.; Lemstra, P. J. Macromolecules 1997, 30, 7880.
28. Basset, D. C. Polymer 1988, 29, 1539.
29. Barham, P. J.; Keller, A. J Polym Sci 1989, 27, 1027.
30. Rastogi, S.; Kurelec, L. J Mater Sci 2000, 35, 5121.