

Formation of Highly Ordered, Unusually Broad Polyethylene Lamellae in Contact with Atomically Flat Solid Surfaces

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Introduction

Crystallization of polymers in the presence of solid surfaces draws considerable attention because of its influence on the properties of composite materials especially containing inorganic fillers. There are numerous works on crystallization of thin layers of polymers on different crystalline substrates, e.g., refs 1–9. Recently some insight into crystallization conditions in the polymer layer adjacent to the substrate (the contact layer) has been obtained by studying crystallization in thin and ultrathin films on crystalline and amorphous substrates.^{8–11} It was found that the film morphology (as observed on the free surface) depends on the layer thickness and crystallization rate decreases in thin layers. However, polymer crystallization in thin, usually not continuous layers may not represent the real conditions of polymer crystallization from the melt. Another approach was described in our previous works.^{12,13} It consists of atomic force microscopy (AFM) studies of the surface of the polymer sample crystallized in contact with an atomically flat substrate. This surface is exposed by gentle detachment of the polymer samples from the support.

Previous reports on polymer crystallization on atomically flat surfaces, e.g., graphite, talc, and alkali halides, have shown that such substrates influence the crystallization and that the orientation of polymer crystals coincides with some crystallographic directions pointing to the importance of the lattice match between the substrate and the polymer.^{1–7} The crucial point in the influence of the substrate on polymer crystallization is the interaction between the chain and the substrate. Monolayers of alkanes and other organic molecules on model molecularly flat substrates have been studied by scanning tunneling microscopy, and it has been found that stable, ordered layers are formed above melting points of bulk crystal phases.^{14–16} Formation of the ordered monolayer in a polymer melt in contact with the substrate might be expected to influence the morphology of the contact layer upon crystallization.

Indeed we discovered very unusual morphology of the contact layer of polyethylene (PE) crystallized on highly oriented pyrolytic graphite (HOPG) (but not on mica).¹² Its characteristic features are: long range ordering of chain direction and wide lamellae 2–4 times wider than in the bulk.^{12,13} While the orientation of polymer chains in edge-on lamellae crystallized on various substrates has been shown for many polymer/substrate systems; e.g.,^{2–8} the influence of the substrate on the lamella thickness has not been clarified yet.

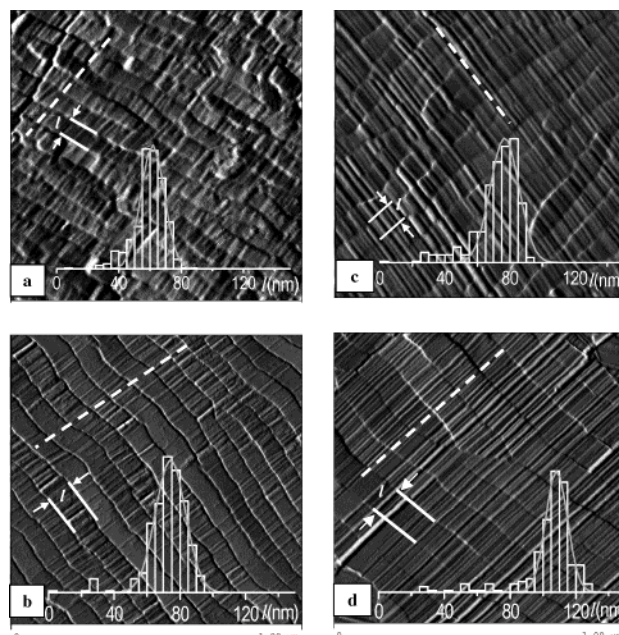


Figure 1. AFM tapping mode, amplitude images of the contact layer of PE crystallized on talc (a and b) or MoS₂ (c and d). The cooling rate was 10 deg/min for parts a and c or 0.2 deg/min for parts b and d. A lamella width l is indicated by two parallel solid lines. The dashed lines show the chain direction labeled by blocks (striations). The histograms show the distributions of the lamella widths.

In the present paper, we show that the formation of such a contact layer is a more general phenomenon occurring during PE crystallization on other atomically flat surfaces such as MoS₂ and talc despite the different chemical composition and unit cell parameters. A mechanism of formation of highly ordered contact layers as well as their fracture mechanism are proposed.

Experimental Section

Linear polyethylene (PE) (HM5420 $M_w = 360\,000$, $M_w/M_n \approx 12$) provided by BP Chemicals (GB), sample (thickness ca. 0.5 mm) was molten at 170 °C in contact with the freshly cleaved substrate surface. After 10 min, the sample was cooled (0.2 or 10 °C/min). The surface of PE exposed after detachment was investigated using a Nanoscope IIIa atomic force microscope (AFM) (Digital Instruments/Veeco, Santa Barbara, CA), operated in tapping mode. Rectangular silicon cantilevers model RTEP7 (Nanosensors, Wetzlar-Blankenfeld, Germany) were used throughout the study. Talc was kindly provided by G. Fourty (Luzenac Europe). Highly oriented pyrolytic graphite (HOPG) ZYB grade and molybdenum disulfide single crystals were purchased from SPI Supplies.

Results and Discussion

Examination of the polymer surface detached from the investigated substrates (Figure 1) reveals an unusual blocklike (striated) lamellar morphology, very similar to that observed on HOPG^{12,13} and similar to that of fracture surfaces of the samples crystallized under high pressure.¹⁸ The lamella width l is exceptionally big, ca. 60–100 nm (to be compared with ca. 25 nm in the bulk). As for the PE/HOPG systems¹³ also for MoS₂ and talc a considerable increase of l in the contact layer with the decrease of the cooling rate is observed. The above results prove that the chain direction also for PE

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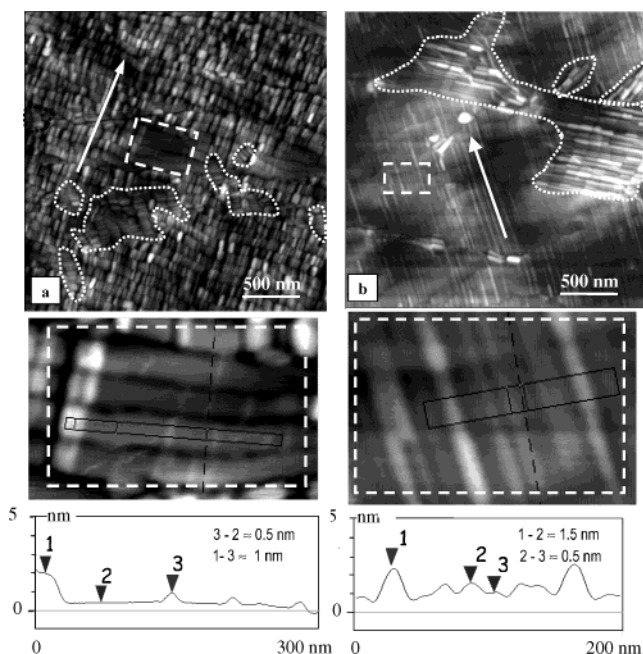


Figure 2. AFM tapping mode, height images of the contact layer of PE crystallized on (a) talc and (b) MoS₂. Smaller domains with striations directions differing from the direction in the large domain (indicated by white arrow) by 60° are indicated by dotted lines. In the bottom part of the figure the cross section analysis of enlarged parts (indicated by white rectangle) is shown. Profiles represent the section averaged over the area within black rectangle.

crystallized on these substrates is labeled by the block (striations) direction.¹³ For all the substrates the chain direction is strongly related to the substrate in-plane symmetry; i.e., in the neighboring domains it differs by 60° (Figure 2). This direction is preserved in domains as large as several tens of square micrometers.

On talc the PE lamellae are thinner and the decrease of the cooling rate from 10 to 0.2 deg/min results in the increase of l by ca. 13 nm (from ca. 62 to 75 nm), similar to that reported for HOPG.¹³ In the case of MoS₂, l is bigger and increases by ca. 30 nm (from ca. 76 to 106 nm). The difference in l on different supports may be related to their different surface energies.

Interestingly, the morphologies of the contact layer crystallized on HOPG, talc and on MoS₂ are qualitatively similar despite different lattice parameters and chemical composition of these substrates.¹⁹ This implies that for formation of such morphology the matching of crystalline lattices of the polymer and of the substrate is of secondary importance.

The strong ordering effect of MoS₂ on PE is in agreement with the results of experimental and theoretical studies on two-dimensional crystallization of alkanes on MoS₂.^{14,17} Crystallization of PE with (110) plane parallel to the substrate (chain folding parallel to the substrate) has been confirmed by electron diffraction studies for PE/talc system,⁷ PE/HOPG,³ and recently also for PE/MoS₂.²⁰

The surface of the lamella on detached PE is exceptionally flat but not molecularly flat. It appears to consist of blocklike structures, and some blocks appear to be missing. In such a case, similar blocks should be found on the surface of the solid substrate. Thin, discontinuous polymer layers were indeed found on HOPG (Figure 3). Similar morphological features are observed both on the surface of the substrate and on

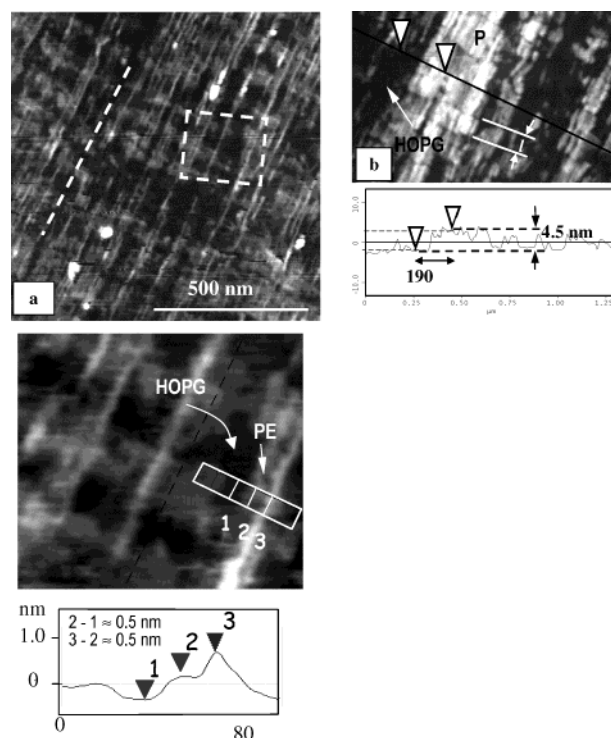


Figure 3. AFM tapping mode, height images of the layer of PE remaining on the surface of HOPG. An enlarged part of the image (a) (dashed rectangle) is shown in the bottom with the section profile averaged over the area within white rectangle. Image b shows the morphology of the thicker region of the layer. A lamella of width l is indicated by two parallel solid lines.

the surface of the polymer detached from it. In different regions of the same sample, the surface roughness is significantly different. It is most probably related to the depth at which the fracture occurs. The most flat regions (like this marked by a rectangle in Figure 2b) result from a fracture at PE/HOPG interface or at most several angstroms apart.

On both surfaces, the blocks protrude by at least multiples of ca. 0.5 nm (chain thickness) (Figures 2 and 3; see also Figure 6 in ref 13 for PE/HOPG).²¹ The thicknesses of long rodlike objects is ca. 1 nm (Figure 3), and their widths can be estimated to be ca. 10 nm.²¹

The fracture should preferentially occur at the polymer/support interface and not in the bulk of the polymer, since neither breaking nor disentangling of polymer chains is necessary in this case. For a substrate that weakly interacts with the polymer chains, no "bulky" fragments of PE should be found on the detached support surface. However, the substrates used in this study relatively strongly interact with aliphatic chains.¹⁴⁻¹⁷ Therefore, the presence of PE particles on HOPG after its detachment is not unexpected. However, the nanoscopic flatness of the fracture surface (no pulled out fibers or local deformations) (Figure 3) is surprising, unless one assumes it consists of highly ordered layered structure with many adjacent reentries and few entanglements. The fracture of PE crystallites should therefore occur along (110) planes so the height difference between the planes should correspond to diameter of one chain. This is in agreement with our finding that the smallest height difference of the blocks is ca. 0.5 nm.

It is also important to note that the length of PE rodlike structures seen both on PE surface detached

from HOPG¹³ (also seen in Figure 1d) and remaining on HOPG (Figure 3) exceeds several times the lamella width. It is a strong indication of their extended-chain structure with relatively few folds. On the other hand, the long and short blocks are apparently weakly connected in a direction perpendicular to their long axes (the chain direction), which suggests high perfection of the folds with many adjacent reentries, characteristic for the crystallization in regime I.²²

It is consistent with the observation that in the contact layer there is very little space left for the amorphous phase (very narrow regions between the lamellae; cf. Figure 1).

Usually many long blocks can be seen on the flat regions (presumably resulting from fracture close to the substrate surface) and not on rough ones. This suggests that extended-chain type crystals are formed at the atomically flat support surface and not a few nanometers apart.

The presented results suggest that in contact with an atomically flat substrate crystallization of PE proceeds in two steps: (1) adsorption of polymer chains on the substrate and formation of domains containing partially folded chains aligned along the crystallographic directions of the substrate; (2) layer by layer crystallization of PE with chain folding preferentially in the plane of the layer, leading to the formation of contact layer with unusual structure and the remarkable flatness of the fracture surfaces.

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References and Notes

- (1) Willems, J. *Discuss. Faraday Soc. Macromol. Liq. Cryst.* **1958**, 25, 111.
- (2) Mauritz, K. A.; Baer, E.; Hopfinger, A. J. *J. Polym. Sci., Macromol. Rev.* **1978**, 13, 1.
- (3) Tuinstra, F.; Baer, E. *J. Polym. Sci., Polym. Phys. Lett.* **1970**, 8, 861.
- (4) Thierry, A.; Mathieu, C.; Straupe, C.; Wittmann, J. C.; Lotz, B. *Macromol. Symp.* **2001**, 166, 43.
- (5) Baukema, P. R.; Hopfinger, J. *J. Polym. Sci., Polym. Phys.* **1982**, 20, 399.
- (6) Rybníkar, F. *J. Macromol. Sci. Phys.* **1981**, B19, 1.
- (7) Wittman, J. C.; Lotz, B. *J. Mater. Sci.* **1986**, 21, 659.
- (8) Bartzak, Z.; Argon, A. S.; Cohen, R. E.; Kowalewski, T. *Polymer* **1999**, 40, 2367.
- (9) Sawamura, S.; Miyajiri, H.; Izumi, K.; Sutton, S. J.; Miyamoto, Y. *J. Phys. Soc. Jpn.* **1998**, 67, 3338.
- (10) Frank, C. W.; Rao, V.; Despotopoulou, M. M.; Pease, R. F. W.; Hinsberg, W. D.; Miller, R. D.; Rabolt, J. F. *Science* **1996**, 273, 912.
- (11) Schönherr, H.; Frank, C. W. *Macromolecules* **2003**, 36, 1188, and *Macromolecules* **2003**, 36, 1199.
- (12) Tracz, A.; Jeszka, J. K.; Kucińska, I.; Chapel, J.-P.; Boiteux, G. *Macromol. Symp.* **2001**, 169, 129.
- (13) Tracz, A.; Jeszka, J. K.; Kucińska, I.; Chapel, J.-P.; Boiteux, G.; Kryszewski, M. *J. Appl. Polym. Sci.* **2002**, 86, 1329.
- (14) Cincotti, S.; Burda, J.; Hentschke, R.; Rabe, J. P. *Phys. Rev. E* **1995**, 51, 2090.
- (15) Magonov, S.; Yerina, N. *Langmuir* **2003**, 19, 504.
- (16) Magonov, S. N.; Yerina, N. A.; Ungar, G.; Reneker, D. H.; Ivanov, D. A. *Macromolecules* **2003**, 36, 5637.
- (17) Claypool, C. L.; Faglioni, F.; Goddard, W. A.; Lewis, N. C. *J. Phys. Chem. B* **1999**, 103, 7077.
- (18) Wunderlich, B.; Melillo, L.; Cormier, C. M.; Davidson, T.; Snyder, G. *J. Macromol. Sci.* **1967**, B3, 485.
- (19) Periodicity of neighboring C atoms on HOPG basal plane is 0.142 nm, of O atoms on talc is 0.263 nm, and that of S atoms on MoS₂ is 0.316 nm.
- (20) Takenaka, Y. Private communication.
- (21) A width of an object of the height h protruding from flat surface is apparently broadened due to final size of the AFM tip by a value $2(2Rh - h^2)^{1/2}$, where R is the radius of the tip. Taking into account that R is ca. 10 nm, the height of nanorods is ca. 2 nm, and taking into account that their apparent width seen in AFM images is ca. 20 nm, the real width of nanorods can be estimated to be ca. 10 nm. The thickness of blocks can be satisfactorily measured only in some regions, where a single block protrudes from a flat part of a lamella. This is illustrated in Figure 2 in case of PE detached from talc. In the places where the AFM tip cannot penetrate between neighboring blocks, the differences between the heights of the blocks are also of the order of multiples of 0.5 nm (Figure 2b).
- (22) Hoffman, J. D.; Miller, R. *Polymer* **1997**, 38, 3151.

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