Polymerization and Crystallization of Polyethylene on a Flat Model Catalyst

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ABSTRACT: A planar $CrO_x/SiO_2/Si$ (100) model for the Phillips ethylene polymerization catalyst, prepared by spin-coating impregnation from an aqueous solution of CrO_3, polymerizes ethylene in the gas phase at 160 °C with a significant and constant activity. After polymerization for 5 min and cooling to room temperature, an approximately 40 nm thick high-density polyethylene layer was formed that exhibits a morphology of regions with almost parallel aligned edge-on lamellar crystals. These lamellae show a distinct blocklike submorphology, which is discussed in detail. The work demonstrates that controlled polymerization and crystallization using a surface science model catalyst on a flat surface offers an excellent approach for fundamental studies of polymer physics, e.g., the study of the origin of crystal formation.

Introduction

Recently, surface science model systems, in which the catalytically active phase is applied on a planar, conducting substrate, have attracted interest for spectroscopic and microscopic studies of supported catalysts.[1] To prove that such systems are realistic, it is essential to demonstrate that a model catalyst exhibits representative catalytic turnover. Magni and Somorjai successfully have modeled a Ziegler−Natta catalyst in a surface science environment and demonstrated its activity in the catalytic polymerization of ethylene and propylene at room temperature[2] with a turnover frequency of about 0.1−1 molecule (surface site)$^{-1}$ s^{-1}.[3]

A successful planar surface science system of the Phillips or $CrO_x/SiO_2/Si$ catalyst that forms linear high-density polyethylene (HDPE) has recently been introduced.[4,5] The molecular-level study of the physical and chemical properties of this catalyst is complicated by its complexity and its sensitivity to catalyst poisons in the ambient, e.g., acetylene, CO, CO_2, traces of alkali and water, respectively. Hence, removing impurities is crucial when working with a surface science model exposing 1 cm^2 of active surface only. Essential for polymer formation on this model system, a reactor was developed with a specially designed filter for the ethylene feed.[5]

Planar surface science catalysts offer attractive opportunities to investigate polymer formation and crystallization. In combination with a surface sensitive tool such as atomic force microscopy (AFM), new insights can be gained in the crystallization process and the correlated morphology. AFM studies have been aimed at visualization of polymer morphology, nanostructure, and molecular order and have been performed on a large number of polymer samples.[6,7]

In a previous investigation, the controlled formation of homogeneous polymer layers is shown, which are crystallized from the melt after the polymerization of ethylene on a planar Si substrate.[5] Especially, the linear dependence of the thickness of the polyethylene layer on the polymerization time has to be pointed out; e.g., a layer thickness of approximately 40 nm is formed for a polymerization time of 5 min. AFM micrographs reveal that these samples exhibit regions with edge-on lamellar crystals in almost parallel alignment, which show a distinct blocklike submorphology.

The purpose of this report is to demonstrate that the new preparation technique, polyethylene polymerization and crystallization on a planar model of the Phillips catalysts on a silicon (100) substrate, offers excellent opportunities for visualizing polymer morphology by AFM, e.g. the formation of crystals or the morphology of nascent, as-polymerized reactor powders, and for our understanding of polymer crystallization in general.

Experimental Section

The $CrO_x/SiO_2/Si$ model-catalyst was prepared as described in detail before.[4] Briefly, Si(100) silicon disks were calcinated at 750 °C for 24 h to obtain a flat, amorphous silica layer of approximately 90 nm thickness. The silicon wafers were then cleaned in a mixture of concentrated hydrogen peroxide and ammonia (30/70 vol %) at 70 °C. After being cleaned further in boiling water, the wafers were mounted on the spin-coating device and were covered with the impregnation solution, chromic acid in water, under nitrogen atmosphere. Upon spinning, most of the solution was ejected from the wafer, leaving behind a thin evaporation layer. As the thickness of this layer can be calculated for any given rotation speed (2800 rpm), temperature (20 °C), and solvent (water), the loading of the model catalyst can be controlled simply by varying the concentration of the dilute spin-coating solution.[8] The results reported in this study were obtained using a loading of 2 Cr/nm^2 on the Si-wafer and a polymerization time of 5 min.

For polymerization of ethylene, the model catalyst was inserted in a specifically designed reactor equipped with filters to purify the ethylene feed as described elsewhere.[5] After being dried at 200 °C in a vacuum, the catalyst was calcinated in flowing O_2/Ar at 550 °C for 30 min. After being cooled to 160 °C, the gas flow was stopped, and the O_2/Ar was exchanged to argon and subsequently to ethylene. Ethylene was polymerized in flow at 160 °C and atmospheric pressure. Pumping away the ethylene and changing to argon atmosphere stopped the reaction. The polyethylene formed on the catalyst surface is initially present as a molten film and first is cooled to 100 °C for 2 h (only for reasons of practice) before final cooling of the reactor to room temperature. A common chemical character-

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ization (M_w, M_w/M_n, NMR) could not be performed, because of the low amount of a few nanograms of polymerized PE, but for the given conditions, it is known that the Phillips catalysator polymerizes linear PE. Using a FT-IR spectrometer equipped with a Golden Gate single reflection attenuated total reflectance (ATR) accessory, we were able to collect infrared spectra (not shown) of an approximately 200 nm thick PE layer polymerized and crystallized on a Si-wafer. Comparison with spectra of linear and branched PE has shown no indication for branches; the methyl group concentration of our investigated samples is below the detection limit.

A Digital Instruments, Inc., (Santa Barbara, California) Dimension 3100 was used for AFM investigations in tapping mode of the morphology of the samples. Height and phase information yielded consistent results, with the better contrast in the phase mode. Images were recorded at room temperature, and only an additional contrast enhancement of the raw data was performed.

Results and Discussion

Figure 1 shows the surface morphology of a polyethylene layer with a thickness of approximately 40 nm polymerized on a planar Si-wafer. By use of AFM as an investigation method, the appearance of the general morphology is similar for the used imaging modes, for height and phase contrast. Stacked platelike agglomerations of edge-on lamellar crystals are present, which may be assigned to sheaflike structures related to spherulite precursors. The representative surface area with a size of $20 \times 20\ \mu m^2$ shows a height variation of 10 nm from dark to bright areas (Figure 1a), which indicates a closed and homogeneous PE layer of low roughness. In addition to height mode, the phase contrast image shows the same morphology in more detail of the lamellar architecture (Figure 1b). Regions with parallel aligned lamellar crystals are found which are surrounded, or guided, by pronounced edge-on lamellae with a length of several micrometers. A similar morphology has been observed in transmission electron microscopy studies on thin cast films of isotactic and syndiotactic polystyrene.[9,10]

More details of the morphology of lamellae agglomerations and their interaction with other regions can be studied at higher magnification. Using phase mode and a scan size of $4 \times 4\ \mu m^2$ several regions with almost parallel aligned edge-on lamellar crystals are clearly separated (Figure 2a). Because of the tip−sample interaction, the thickness of the lamellar crystals (∼30 nm) is the sum of both the thickness of the crystalline and of the amorphous phase and should be compared only with repeat periodicity data from small-angle X-ray scattering investigations. Next to edge-on lamellar crystals, some regions of Figure 2a exhibit of crystals with different shapes; here, accumulated crystals have a low aspect ratio of almost 1. The corresponding sketch (Figure 2b) indicates the main localization of these regions. The crystals with low aspect ratios are present, especially at the boundaries between two regions with parallel edge-on lamellae. In the height mode image (not shown), these boundary regions are always the lowest and least pronounced areas of the sample surface. Because of their location at the boundaries and their smaller size compared to the thickness of the edge-on lamellae, the formation of the crystals with low aspect ratios could be assigned to a secondary crystallization.[11−13] Diffraction or spectroscopic techniques could result in additional data related to orientation of the crystals relative to the substrate (edge-, end-, or flat-on).

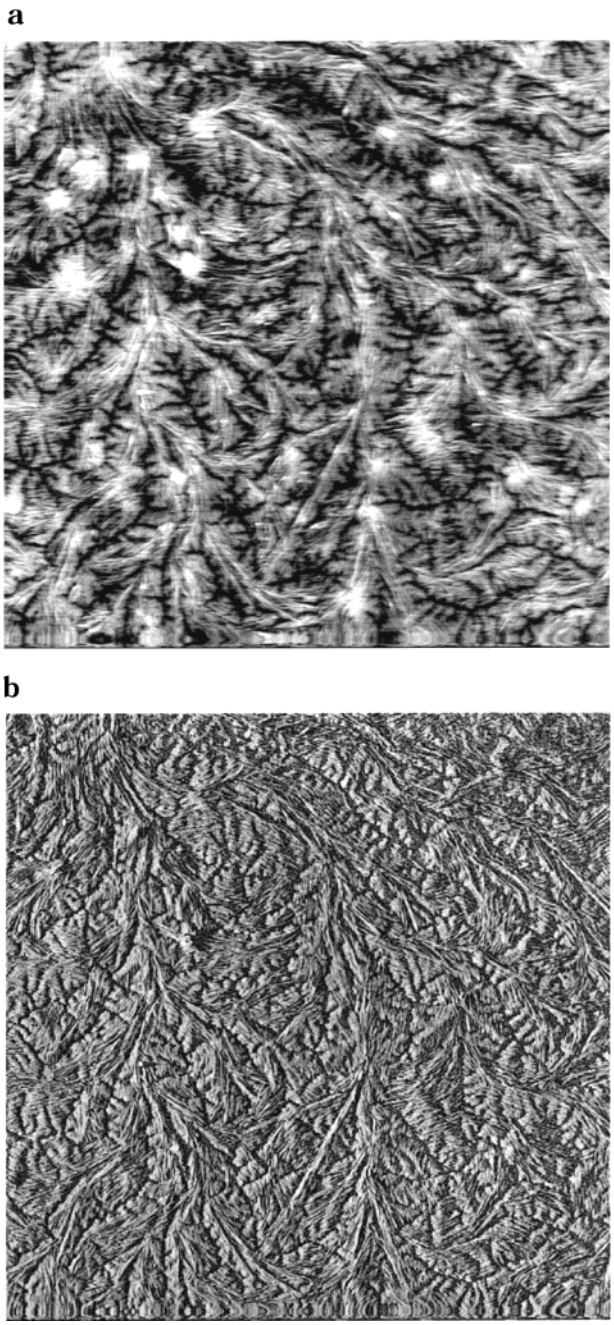

Figure 1. AFM images of the polyethylene surface morphology recorded in (a) height and (b) phase contrast. Scan size is $20 \times 20\ \mu m^2$, and height variation is 20 nm in Figure 1a.

Further increasing of the magnification results in more details of the architecture of the regions formed by edge-on lamellae and their boundaries. In addition to a more precise determination of the local lamellae thickness, the phase mode image with a scan size of $1 \times 1\ \mu m^2$ presents an uniform blocklike submorphology of the lamellae (Figure 2c), which is not visible in the height image (not shown). A similar blocklike morphology is observed for polyethylene copolymers[14,15] and syndiotactic polypropylene.[16] In tapping mode, the cantilever is excited into resonance oscillation with a piezoelectric driver. The oscillation amplitude is used as a feedback signal to measure topographic variations of the sample. In phase imaging, the phase lag of the cantilever oscillation, relative to the signal sent to the cantilever's piezo driver, is simultaneously monitored. The phase lag is very sensitive to variations in material

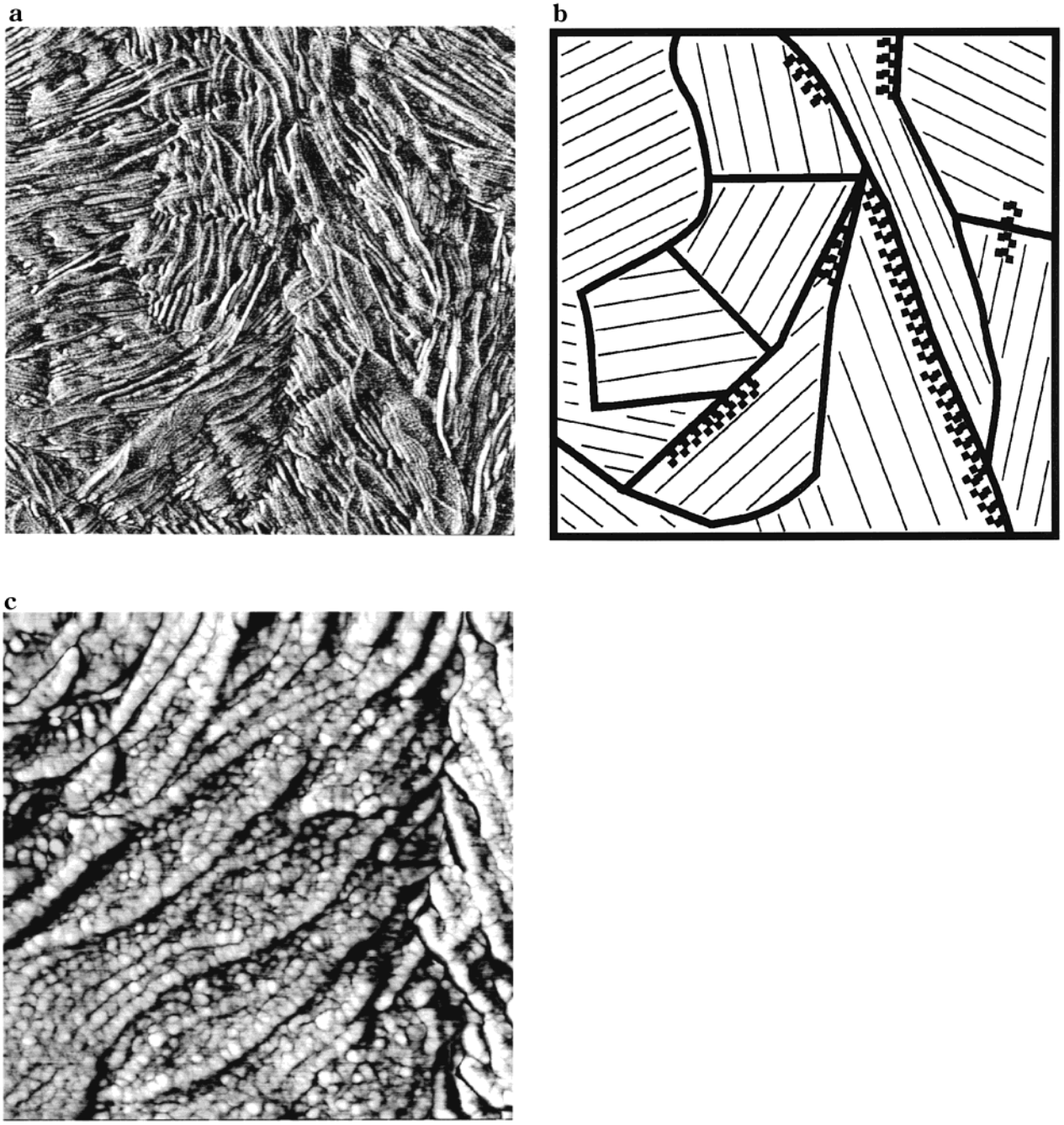

Figure 2. AFM images of the polyethylene surface morphology recorded in phase contrast. Scan size is (a) $4 \times 4\ \mu m^2$, (b) corresponding sketch indicating lamellae agglomerations with same growth direction and regions with crystals with low aspect ratio (dotted), and (c) $1 \times 1\ \mu m^2$.

properties such as adhesion and viscoelasticity; consequently, the phase imaging is useful for differentiating between component phases of semicrystalline polymers.[17] Therefore, in the phase contrast image, the visualization of the lamellae is caused by the different phase lag of the cantilever for the crystalline core and the amorphous layers, and additional phase lag variations inside the lamellar crystals contribute the image of the blocklike submorphology.

A phase image similar to the that observed in Figure 2c could be caused by small cracks at the surface, formed during cooling and possibly initiated by local surface tension during crystallization. We stress, however, that especially in the height images we did not find any indications for cracks at the surface of the investigated samples.

A set of two AFM images using height and phase contrast is presented in Figure 3. By use of a scan size of $400 \times 400\ nm^2$, the images show details similar to the lamellae submorphology. The lamellae are formed by blocks having a thickness-to-width ratio of approximately 3:2, e.g., a thickness of 32 nm and a width of 21 nm for the block marked in Figure 3b. The lamellar crystals are distinctly separated from other lamellae, whereas the block boundaries inside the crystal are less pronounced. For optimized scanning conditions, the height contrast yields additional information on the origin of the blocklike submorphology (Figure 3a). In addition to height variations on the order of 2 nm between the crystalline core of the lamellae and the surrounding amorphous layers, slight height variations between the blocks and the block/block interfaces are

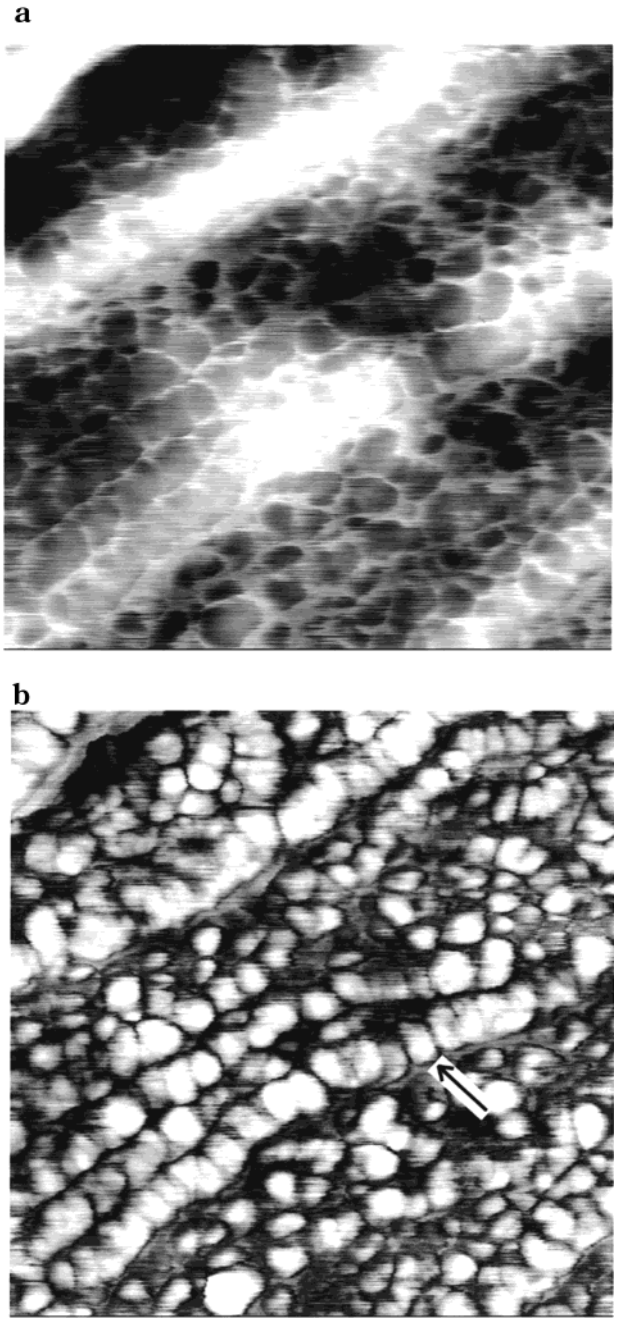

Figure 3. AFM images of the polyethylene surface morphology recorded in (a) height and (b) phase contrast. Scan size is 400 × 400 nm^2, height variation is 10 nm.

present in a single lamellar crystal. Interpretation of this result is hard. By starting from the experimental evidence that during the polymerization a molten PE film with homogeneous thickness is formed, application of a three phase model might be considered. Beside the crystalline core with high density (phase I) and the amorphous phase with relative low density (phase II), a less organized interphase of intermediate density is introduced (phase III).[18,19] Therefore, after crystallization of the polymer, the height variation between the lamellar core and the amorphous layers reflect only the final density differences of these two phases. Ultimately, the slight height differences between the grainy blocks and the block/block interfaces should be assigned to a less organized interphase with intermediate density. In addition, the phase contrast image (Figure 3b) reflects the same density variations because of its high sensitivity to material properties. The density difference between the crystalline core (I) and the interphase (III) could be caused by a higher defect density (incorporated short chain branches) in the interphase.

Conclusion

It is shown that the polymerization on defined and planar substrates offers interesting possibilities for investigations of the initial crystal formation and the morphology development in thin layers of semicrystalline polymers. Regions with parallel aligned edge-on lamellar crystals have been found, and details as a blocklike submorphology of the lamellae and the architecture of the interface between two blocks are described. We expect that this approach, polymerization and crystallization on flat substrates, in combination with further studies of the blocklike submorphology for different crystallization and annealing temperatures will significantly contribute to the present discussions on the origin of polymer crystallization soon. In addition, controlled polymerization on a flat surface at temperatures below the melting temperature of the polymer crystals offers an excellent preparation tool for fundamental investigations of the nascent, as-polymerized morphology of reactor powders.

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