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Melting of Isochronously Decorated Single Crystals of Linear Polyethylene, As Monitored by Atomic Force Microscopy

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Linear polyethylene, LPE, crystallizes from dilute solutions in the form of single pyramidal crystals.[1−3] The latter collapse upon sedimentation and drying giving rise to flat crystalline lamellae.[4] It was observed early on that the lamellar thickness, L_B, varies with isothermal crystallization temperature, T_c, whereby higher T_c's yield a larger lamellar thickness.[5] The dependence of L_B on the crystallization temperature can be also studied in nonisothermal conditions. A series of $L_B(T_c)$ values can thus be obtained from a single crystallization experiment, in which the polymer solution is subject to a controlled stepwise variation of T_c. The crystal displays characteristic height corrugations oriented along the crystal growth faces,[6] which can be further used as intralamellar markers of the periodic T_c changes. The nonisothermal crystallization experiment must be performed in such a way as to avoid reorganization or even dissolution of thinner regions formed at the lowest T_c when brought to the higher or highest T_c. Complex temperature programs (e.g., thermal cycling) can be designed to address different issues of crystallization kinetics and thermodynamics. For example, the crystallization of dilute LPE solution carried out alternately at two temperatures T_{c1} and T_{c2} separated by a few degrees (the so-called "isochronous decoration" method) helps to determine the linear growth rates of a single crystal during all the growth process as a function of T_c and solution concentration.[7] The latter results were used to show that fractionation process occurs during solution crystallization of LPE even with a low degree of polydispersity.[8,9] The development of nondestructive surface analysis techniques and, in particular, the environmental atomic force microscopy, AFM, makes it possible to visualize the fine structural features of LPE single crystals and to study their temperature evolution in situ.[10−15] The unprecedented sensitivity of AFM to height differences opens the way to monitor the temperature-induced structural transformations in single crystals on the scale of the unit cell of PE.[13] In a previous paper,[15] the morphology and melting behavior of truncated LPE single crystals were studied. It was found that the thickness of (200) sectors is slightly smaller than that of (110) sectors, in agreement with literature data.[10] The fold surface energies, σ_e, in both sectors were calculated from their respective melting temperatures using the classical Gibbs−Thomson equation. Since the values of σ_e for the (110) and (200) sectors are very similar, it was suggested that in the (200) sector the orientation of chain folds is parallel to (110) and (−110) planes,[16] leading to a jagged growth front.

The present study deals with similar truncated LPE crystals obtained by isochronous decoration, i.e., grown alternately at two crystallization temperatures. The morphology of such crystals is more complex than that of the truncated crystals grown at one temperature only since they are made of both (110) and (200) sectors crystallized at two different temperatures. Their annealing and melting behavior is expected to be rather complex. The main question addressed in the present work is *whether the lamellar thickness of a single LPE crystal is the only parameter responsible for its melting behavior*. To investigate this issue, the crystallization temperatures T_{c1} and T_{c2} ($T_{c1} > T_{c2}$) are selected in such a way that the thickness of the (200) sector parts formed at T_{c1} exactly matches that of the (110) sector parts

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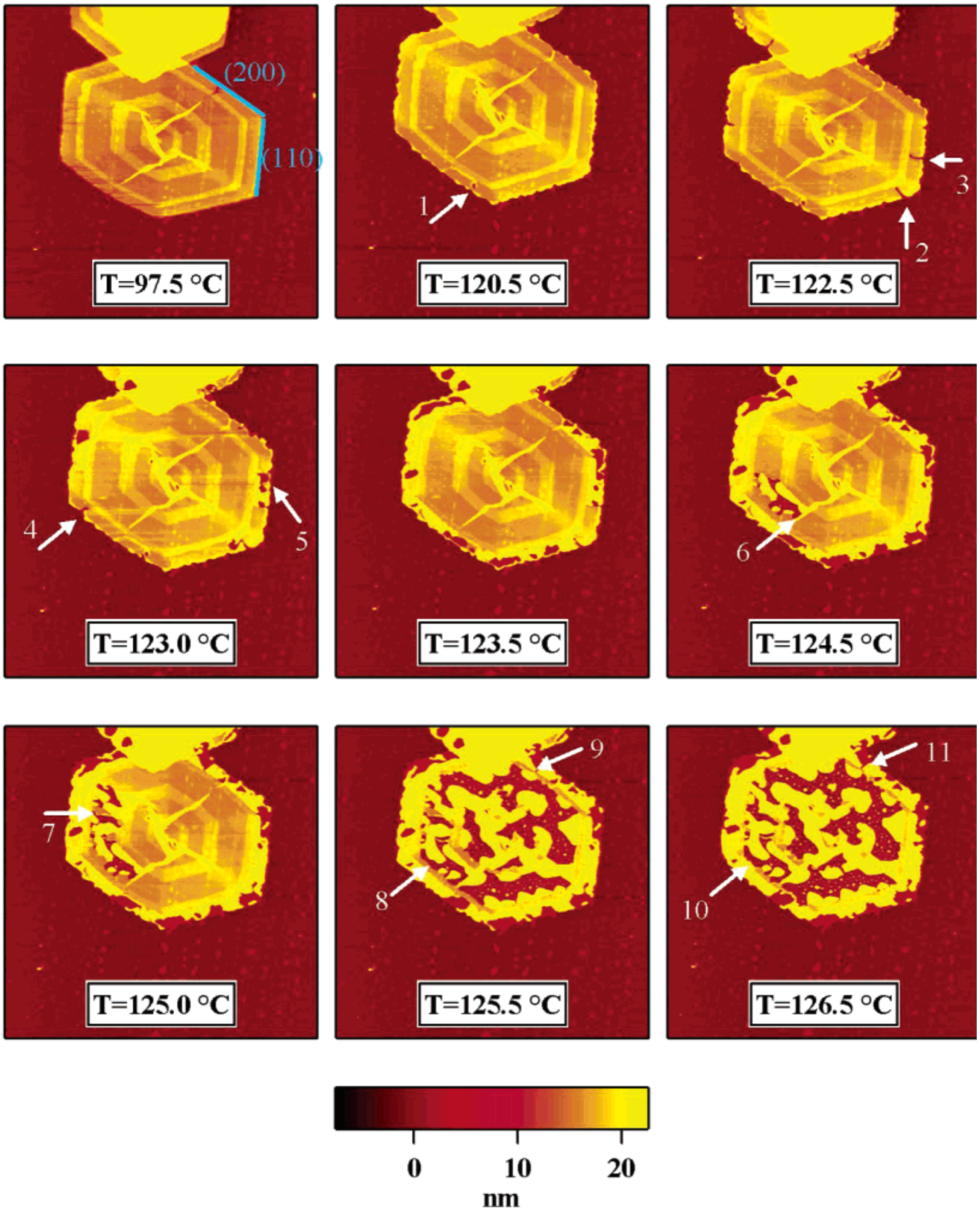

Figure 1. Tapping mode AFM images (13.0 × 13.0 μm^2) of a single LPE crystal prepared by alternate crystallization at $T_{c1} = 98$ and $T_{c2} = 95$ °C from *n*-octane. The crystal has four (110) sectors and two thinner (200) sectors. The most prominent feature of the crystal is a system of stripes of about 1.6 nm high running parallel to the crystal growth faces. Some morphological changes occurring upon thermal annealing of the crystal are numbered (see text).

formed at T_{c2}. The melting behavior of regions located in different parts of the crystal (e.g., center vs periphery or (110) vs (200) sector) but exhibiting equal thickness (iso-height regions) are compared. Since the surface energies in both crystal sectors are similar,[15] any difference in melting temperature of the iso-height regions would mean that the melting is not only affected by the crystal thickness and surface energy but also by other factors.

The LPE fraction having a molecular mass of $\langle M_w \rangle =$ 32 100 and a polydispersity index of $\langle M_w \rangle / \langle M_n \rangle = 1.15$ were purchased from N.I.S.T. (ref 1483). Single crystals were grown from solution by alternate isothermal crystallization at two temperatures, $T_{c1} = 98$ and $T_{c2} =$ 95 °C. LPE (0.01% w/w) was dissolved in boiling *n*-octane under a N_2 atmosphere. Self-seeding[17] was used to control the concentration of primary nuclei. After 30 min at the seeding temperature (107 °C), the solution was quickly transferred to the crystallization temperature T_{c1} for a time t_{c1}. The temperature was then rapidly dropped to T_{c2} and maintained for a time t_{c2}. The crystallization cycle was repeated between T_{c1} and T_{c2} several times. The times t_{c1} and t_{c2} were increased from one cycle to another to compensate the drop of the linear growth rate with concentration. After the crystallization was completed, the solution was slowly cooled to room temperature. For microscopic observations, a drop of the LPE single-crystal suspension was deposited on a clean Si wafer, and the solvent was allowed to evaporate.

The morphology and thermal behavior of single LPE crystals were characterized by AFM (Multimode AFM coupled to the Nanoscope III controller of Digital Instruments, Santa Barbara, CA) in Tapping Mode under dry Ar. The vertical sensitivity of the scanner was

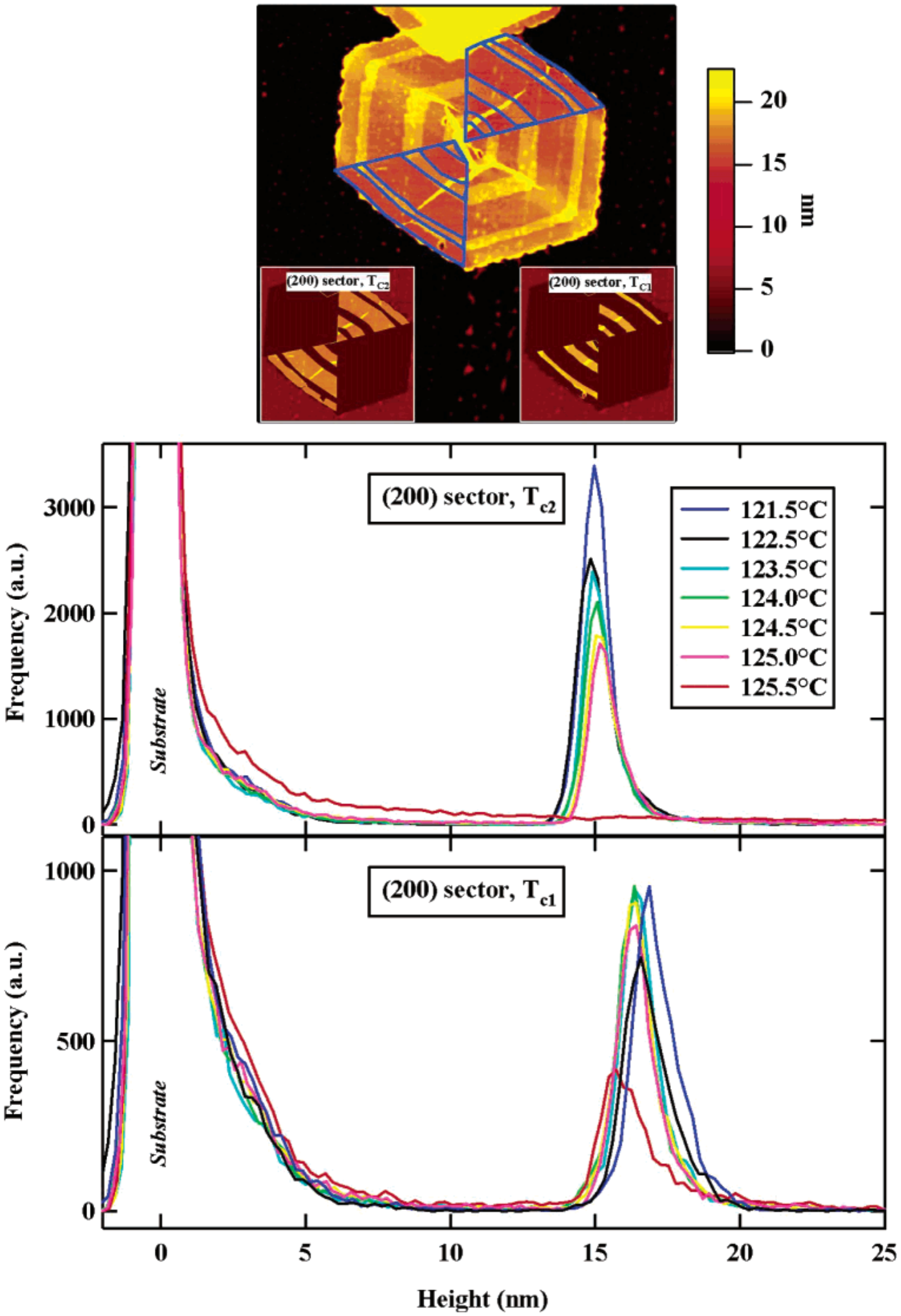

Figure 2. Height histogram analysis of AFM images, exemplified for (200) crystal sector. The top image shows the delimitation of regions formed at T_{c1} and T_{c2} in the (200) sectors. The resulting decomposed images (inserts) were used for computation of the height histograms (lower part). Note that the average lamellar thickness (height) remains constant during annealing. However, the area under the peak, which is proportional to the surface of the regions pertinent to the initial structure, decreases with temperature. For example, the regions formed at T_{c2} disappear completely at 125.5 °C.

calibrated with height standards (NTMDT, Russia) chosen according to the thickness of the studied objects. The AFM is equipped with a high-temperature heater accessory[18] that allows control of both the sample and tip temperature. The temperature of the sample was calibrated with phenacetin (mp 134.7 °C); the temperature of the cantilever was measured from its fundamental resonant frequency and adjusted by applying a voltage to a small resistive heater located inside the tip holder. Details of the AFM operation at high temperature have been described elsewhere.[19] Processing and analysis of AFM images—flattening, cross section, and histogram analysis—were performed with appropriate programs written in Igor Pro (Wavemetrics Ltd.). The image analysis routines are coupled to drawing tools, allowing operations on selected parts of the image.

Selected variable temperature AFM images of an isochronously decorated single LPE crystal measured between 97.5 and 126.5 °C are shown in Figure 1. They illustrate different stages of the crystal's morphological evolution during stepwise heating. The initial crystal has an almost hexagonal shape with two pairs of (110)

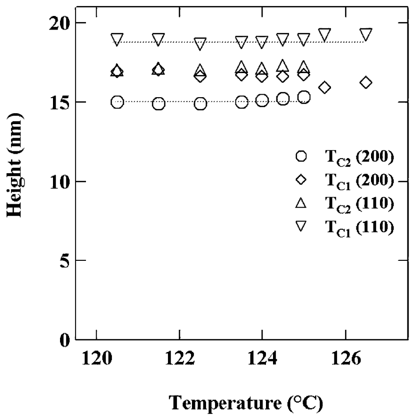

Figure 3. Temperature evolution of the average lamellar thickness of the regions formed at T_{c1} and T_{c2} in both sectors. The dotted lines indicate the upper and lower limits of lamellar thickness found in the crystal.

and one pair of slightly thinner (200) sectors. The orientation of the growth planes is indicated in the first image in Figure 1. The crystal displays the characteristic pattern originating from its complex genesis, i.e., a system of stripes about 1.6 nm high running parallel to the crystal growth faces. The color code of Figure 1 reveals a small height difference between (110) and (200) sectors and also between the regions formed at T_{c1} and T_{c2}. Note that the central pleat, which results from the collapse of the initially hollow 3D pyramidal crystal during sedimentation, is different from the one typically observed for isothermally grown single crystals: instead of lying parallel to the crystallographic *b*-axis, the central pleat developed four branches, two of which are oriented parallel to *b* and two others which are parallel to the *a*-axis. This unusual organization of the pleat, which is found typical for isochronously decorated crystals under study, will be of importance for the propagation of melting, as explained further.

The method and results of the AFM image analysis performed on different crystal regions are first exemplified for the (200) sector in Figure 2, which illustrates the partitioning of the crystal surface into regions according to the crystallization temperature. The image decomposition procedure was performed for both crystal sectors and all studied temperatures. The resulting height histograms corresponding to the regions formed at T_{c1} and T_{c2} are given in the middle and bottom plots of Figure 2. The area under the histogram peak, which is proportional to the surface of the corresponding region, decreases with temperature due to the progress of melting/reorganization. Eventually, the regions formed at T_{c2} disappear completely at 125.5 °C. However, the histogram peak positions are virtually unaffected by the annealing temperature (cf. Figure 3), indicating that some parts of the initial structure are present even at the highest annealing temperature.

The onset of crystal modification can be detected already at 120.5 °C, when the crystal edges become irregular and develop a brighter (i.e., higher) rim (Figure 1).[20] In addition, a hole is formed in the thinner outer frame of the (200) sector (Figure 1, arrow N1). Crystal defects[21] such as cracks running perpendicular to the (110) faces become visible at 122.5 °C (Figure 1, NN2,3). Interestingly, the propagation of cracks is stopped by the thicker stripes formed at T_{c1}. Raising the temperature to 123.0 °C induces a substantial reorganization of the regions adjacent to the cracks, which results in the appearance of thickened areas (brighter contrast). The reorganization affects the thin outer frame of both types of sectors (i.e., (200) and (110)) (Figure 1, NN4,5). Upon heating to 123.5 °C, the outer frame is largely reorganized. It exhibits thickened regions and holes left by migrating material. Close inspection of the crystal morphology at higher magnification reveals that the holes are surrounded by elevated rims, which means that melting/reorganization is paralleled by the thickening process, the extent of which remains however limited. In subsequent steps, along with the formation of a completely recrystallized outer frame contiguous to the last zone formed at T_{c2}, the reorganization of the inner thin regions starts from the (200) sector (Figure 1, N6), which is in line with previous results.[15] However, this process seems to be limited by one of the pleat branches, and the reorganizing front propagates toward the adjacent (110) sector (Figure 1, N7). As temperature increases, almost all inner regions formed at T_{c2} disappear, leaving patches of thicker material and holes. Some parts of the thicker frame formed at T_{c1} remain however intact in both (200) and (110) sectors up to 126.5 °C (Figure 1, N11). It is worth noting that the parts of this frame surrounded by recrystallized material survive heating to 126.5 °C (cf. N9 and N11 in Figure 1), while the isolated ones undergo melting (cf. N8 and N10 in Figure 1). The not-yet-reorganized regions remaining at 126.5 °C have different thickness (Figure 3) but display similar thermal stability: they melt simultaneously at 127.5 °C (image not shown). Importantly, most of the regions formed at T_{c1} in each of the crystal sectors become surrounded by thicker regions formed by reorganization of areas grown at T_{c2}. Such “protection” from reorganization via spatial confinement of thinner crystals by thicker ones indicates that crystal melting/reorganization cannot be considered as a purely thermodynamic event, as already observed by other authors.[22] The mobility of holes in single crystals close to their melting point was previously noticed in high-temperature AFM studies on ultralong alkanes.[14,23] Moreover, the coexistence of two reorganization mechanisms was found in a recent TEM work on the PE single-crystal mats.[22] Analyzing the interplay between these two mechanisms, Matsuda et al.[22] conclude that the low-temperature process consists of a solid-state rearrangement and can be characterized by certain kinetics, which is very different from melting being considered as a purely thermodynamic event. These and other findings are in general agreement with the picture of the so-called α_c relaxation associated with the onset of the PE chains mobility in the crystalline phase.[24−27]

In conclusion, the atomic force microscopy study of thermal behavior of truncated single crystal of LPE alternately crystallized from *n*-octane at $T_{c1} = 98$ and $T_{c2} = 95$ °C indicates that the morphological evolution during annealing of iso-height crystal regions is nonuniform. In particular, the crystal edges reorganize first, giving rise to thickened areas and holes. The melting of thin inner frames, i.e., the regions formed at T_{c2}, starts inside the (200) sector. Propagation of the melting is first hindered by the curved central pleat and then extends into the (110) sector. Melting−reorganization of the initially thinner parts formed at T_{c2} generates much thicker regions that frame the initially thick parts formed at the higher T_{c1}. The latter become therefore spatially confined by thickened material, which protects them from the propagation of crystal defects followed by crystal reorganization. The complexity of the thermal behavior of the isochronously decorated LPE crystal is consistent with earlier analyses mentioning the coexistence of thermodynamic and kinetic processes such as melting followed by recrystallization into thicker crystals and solid-state rearrangements occurring in the crystalline phase. It provides however a much more detailed picture of local reorganization and melting processes taking place for example at boundaries of growth sectors and/or transition zone between different lamellar thickness.

Further AFM studies on these crystals will deal with the rates of lamellar thickness variation when switching from T_{c1} to T_{c2} and vice versa. These studies are aimed at understanding the role of secondary nucleation in polymer crystallization.

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