Macromolecules **2003,** *36,* 549−552 **549**

Sectorization of a Lamellar Polymer Crystal Studied by Dynamic Monte Carlo Simulations

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Received November 20, 2002
Revised Manuscript Received December 20, 2002

1. Introduction. The morphology of polymer crystals is qualitatively different from that of crystals consisting of simple molecules.[1−4] This difference is primarily due to the difference between chain connectivity in polymers and assemblies of simple molecules. This affects the equilibrium crystal structure but even more the kinetics of crystal growth. This was already clear in the early days of polymer physics, when it was suggested that polymers do not form well-defined crystals, but rather crystallites that resemble "fringed micelles".[5] Following the experimental work of Keller et al. in the mid-1950s, the fringed-micelle picture was replaced by that of a chain-folded lamellar crystal.[6] On the basis of this picture, the classical Lauritzen−Hoffman (L−H) model was suggested for the mechanism of polymer crystal growth. This model assumes that the deposition of a single polymer stem initiates the growth of a single crystalline layer on a smooth substrate. This layer then spreads by reeling in and folding of polymer chains along the growth front.[7] The existence of lateral facets of single lamellar polymer crystallites is indicative of the existence of a (relatively) smooth growth front in polymer crystallization. To be more precise, one lamellar crystallite usually contains different sectors, and they are distinguished by a difference in the average orientation of regular chain folding, which is parallel to the smooth growth front.[8] Evidence for such sectorization comes from several experiments, most notably paraffin decoration techniques.[9]

Recent developments in computer simulations have made it possible to observe polymer crystal growth at a molecular level.[10−15] However, it turns out that it is computationally rather expensive to simulate the formation of a native (self-generated) smooth growth front. Smooth-front polymer crystal growth usually occurs at a small supercooling where the growth rate is low and the crystallite is large. Hence, simulations of this process tend to be lengthy and require large model systems. Therefore, we employed dynamic Monte Carlo simulations based on a relatively cheap lattice model.[16,17] Below, we show that this simple and physically transparent model allows us to simulate the spontaneous growth of single lamellae with well-defined faceted borders and sectorized chain-folding.

The remainder of this paper is organized as follows. After a brief description of the simulation method, we analyze the structural details of a single lamella that exhibits sectorization of chain folding. Then, we study the incorporation of individual chains into the smooth crystal growth front.

2. Simulation Techniques. We performed dynamic Monte Carlo simulations of a system of polymer chains living on a simple cubic lattice with periodic boundary conditions. A monomer can jump to any of its 26 neighboring lattice sites, provided that this site is not occupied by other monomers and that the move does not lead to an (unphysical) crossing of polymer chains. To maintain the chain connectivity, the single monomer jump is followed by partial sliding diffusion along the chain.[16] This microrelaxation method turns out to be quite efficient, as it combines some of the advantages of the bond-fluctuation model and the reptation scheme.

To generate a suitable initial condition, we equilibrated 40 chains, each containing 512 units at a volume fraction of about 1% which, for this length of chain, is in the semidilute regime but close to the threshold of coil overlapping. The total volume of the system is 128^3 lattice sites. We prepared the system by equilibration at high temperatures where we only included hard-core repulsions between the polymers. The result of this equilibration was to prepare a solution of weakly interpenetrating polymer coils. To induce crystallization, we should lower the temperature of the system. To this end, we switched on an attractive nearest-neighbor interaction between parallel polymer bonds (E_p). In addition, we increased the stiffness of the polymers by switching on an energy penalty (E_c) for the presence of noncollinear consecutive bonds in the polymer chains. From earlier work,[17] we know that both interactions favor the formation of polymer crystals. The ratio between the energy change in a Monte Carlo trial move and the thermal energy is given by

$$(cE_c + pE_p)/(k_BT) = (c + pE_p/E_c)E_c/(k_BT),$$

where c and p are the net changes in the number of noncollinear consecutive bonds and the number of nonparallel nearest neighbor bonds, respectively. The ratio $E_c/(k_BT)$ defines the (inverse) temperature of the system. We fixed the ratio E_p/E_c at a value of 1, which corresponds to semiflexible chains. Typical crystallization runs took 10 days on a Pentium 800 MHz processor. In what follows, time is expressed in Monte Carlo cycles, where one cycle corresponds to one trial move per chain unit.

In experimental polymer physics, growing a perfect single crystal is something of an art. In our simulations, we tried to borrow from the experience obtained in experiments to choose the crystallization conditions. At low crystallization temperatures, freezing happens spontaneously within the time window of our simulations. However, under these conditions, the crystal growth front appears rather irregular without distinguishable facets. In contrast, at higher temperatures, the incubation period for crystal nucleation was usually outside our time window. As our main interest in the present study is in growth, rather than nucleation, we speeded up crystallization at higher temperatures by introducing a small seed crystal. This seed was generated spontaneously in a short simulation (5×10^4 MC cycles) at a low temperature ($E_c/(k_BT) = 0.415$). We then increased the temperature of the system to a higher value ($E_c/(k_BT) = 0.305$). At this temperature, this small crystallite seems to be able to survive and acts as a "template" for

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10.1021/ma025853l CCC: $25.00

Figure 1. Snapshot of a single polymer crystallite viewed along the (001) direction. The snapshot was taken after 8.9 × 10^5 MC cycles at an inverse temperature $E_c/(k_BT) = 0.305$. The bonds connecting two units along the chain are drawn as solid cylinders. For the sake of clarity, dissolved chains are not shown.

subsequent crystallization. We performed our crystallization "experiment" at $E_c/(k_BT) = 0.305$ as this was the proper temperature where we observed a smooth growth front. At a slightly lower temperature, the crystallization front is irregular, whereas at a slightly higher temperature, it becomes rounded and has no distinct facets too. In the absence of faceting, no sectorization in the folding directions was observed. As more chains are incorporated into the crystal, the polymer concentration in solution decreases. This process would reduce the supersaturation. We compensated for this effect by mimicking the presence of a polymer reservoir: as soon as one chain was incorporated into the crystallite, a new disordered chain was automatically inserted into the simulation box at a position far away from the crystallite.

3. Results and Discussion. Figure 1 shows a single lamella grown from the semidilute solution. The thickness of lamella is about 12 repeat units. This snapshot was taken after 8.9 × 10^5 MC cycles. The snapshot shows the view along the stem direction ((001) direction). To make the fold surface better visible, we chose a large viewing angle. Most of the folds are sharp and regular, but short loops and cilia are also present. We can identify four sectors that originate from the center of the lamella where the seed is located. In each sector, the directions of the folds are, on average, parallel to the growth front. The shape delimited by four lateral growth fronts is almost square and the growth fronts resemble the {110} facets. During crystal growth, only the most slowly advancing surfaces survive. The observed predominance of {110} facets can be attributed to the fact that each layer-growth along (100) or (010) directions corresponds to an advance of one lattice unit while along (110) directions it advances only half a unit.

We find that the alignment of folds within a given sector is far from perfect. In this respect, our simulations do not conform to the idealized picture of chain-folding sectorization. We can calculate an order parameter that measures the alignment of folds: ($P = 2\langle\cos^2\theta\rangle - 1$) where θ measures the angle with the corresponding {110} facet. The average degree of ordering of the folds in the four sectors shown in Figure 1 is 0.17 ± 0.04. We find that the stacking of fold ends in successive crystal layers is also quite random. Such random stacking has been suggested to explain the (314) fold surface in solution-grown polyethylene single crystals.[18] However, occasionally, we observe short sequences of regular fold stacking. Parallel stacking is favored by the interaction between folds. The existence of such regions of regular fold stacking may be relevant for the experimental visualization of sectorization in lamellar crystals by surface decoration. This surface decoration exploits the fact that paraffin crystals may grow epitaxially on regions where the fold stacking has sufficient, but not necessarily complete, regularity.[9]

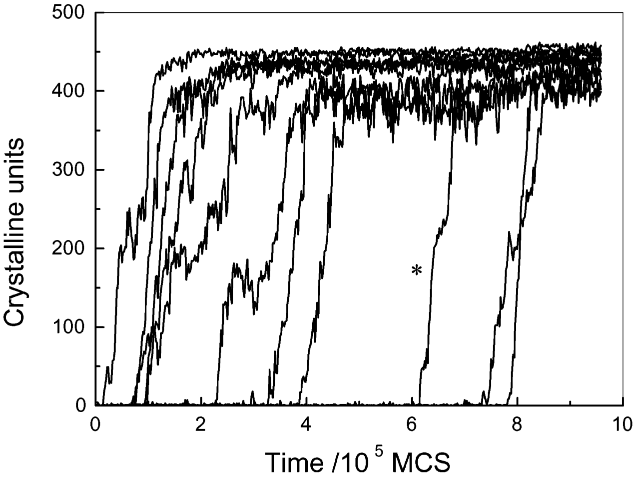

Figure 2. Crystallization history of individual chains (512-mers) at temperature $E_c/(k_BT) = 0.305$. Every trace corresponds to a separate chain incorporation. The bond units are considered to be crystalline if they are surrounded by five or more parallel bonds. Only the segments connecting the data points are drawn for clarity. As can be seen from the figure, the incorporations of chains are mainly successive but sometimes with long pauses.

As can be seen in Figure 1, the boundary between two sectors reveals an interesting folding pattern: two folding directions can be seen to overlap and form a cross. At present, it may still be difficult to verify this detailed prediction in experiments.

Next, we consider the process of crystal growth. As shown in Figure 2, chain molecules are incorporated sequentially into the crystal, one at a time. Moreover, the crystallization of individual chains may proceed in jumps, as is demonstrated in Figure 3a.

Similar intermittent behavior has also been observed in a numerical study of the growth of a polymer single crystal from a melt.[14] In that case, it appeared that during the initial deposition of polymer chains, the growth front has not yet reached its final thickness. As a consequence, the attachment of subsequent chain units is inhibited until the smoothness of the growth front is restored by a reorganization of the growth front. To test whether a similar phenomenon is responsible for the intermittent incorporation of monomers in a sectorized crystal, we performed an additional simulation in which an isolated chain was allowed to grow onto a large smooth substrate and form a single layer. As can be seen in Figure 3b, no intermittent behavior

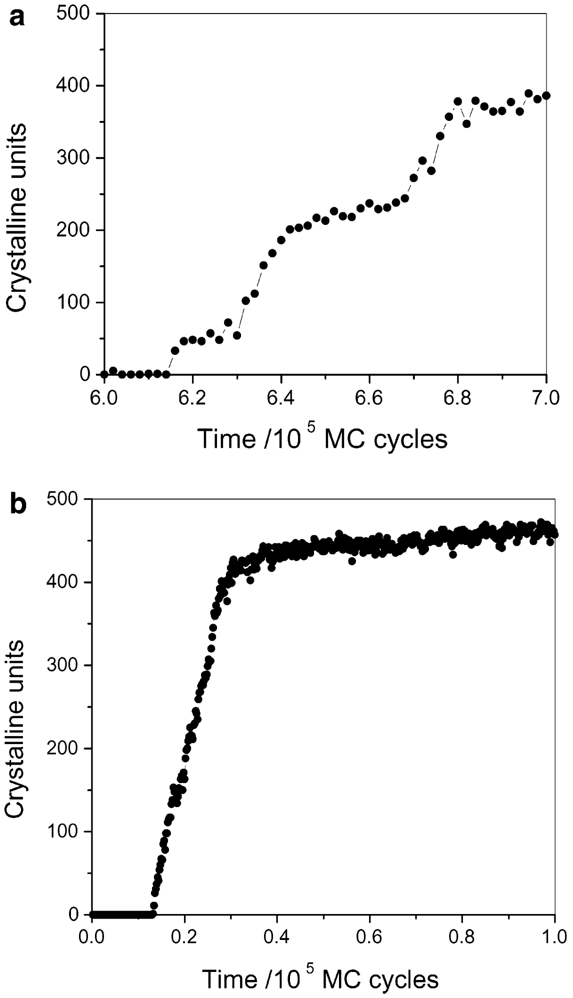

Figure 3. Crystallization curves of a single chain at temperature $E_c/(k_BT) = 0.305$: (a) a typical chain denoted with a star in Figure 2; (b) an isolated chain on a smooth substrate extending over the periodic boundary of the lattice.

occurs under this condition. This suggests that the limited sizes of smooth parts of the substrate are responsible for the pauses. The deposition of an imperfect crystal layer temporarily blocks the deposition of a subsequent layer. Indeed, our simulations showed that the growth front of the polymer crystallite is continually reorganizing. The annealing of an initially disordered growth front is illustrated in Figure 4. Once the growth front becomes smooth again, a new layer can grow on its top. This process is responsible for the last jump in Figure 3a. This final layer is, in fact, a continuation of the same chain molecule, a so-called “superfold”. Superfolding has been proposed to explain the results of infrared spectroscopy and small-angle/wide-angle neutron scattering experiments on solution-grown polyethylene single crystals.[19]

It is only due to the ability of the growth front to smoothen itself that sectorization of the lamellar crystal can be reproduced. The imperfect alignment of fold ends implies that the lateral smoothening is not always complete. At lower temperatures, the growth front cannot reorganize and remains rough. In contrast, at higher temperatures, a smooth growth front may not be stable and the facets could disappear.

4. Conclusions. We have simulated the formation of a single polymer crystallite grown from semidilute solution. In our simulations, we observed facets and a clear sectorization of chain folding. The structural details agree well with existing experimental results. In addition, we find that, at the boundary between two sectors, crossed folds may occur. We observed long pauses during the incorporation of individual chains. These pauses were attributed to the reorganization and smoothening of the growth front that is required to enable the nucleation of subsequent crystal layers and, a fortiori, the formation of the sectorized crystallite.

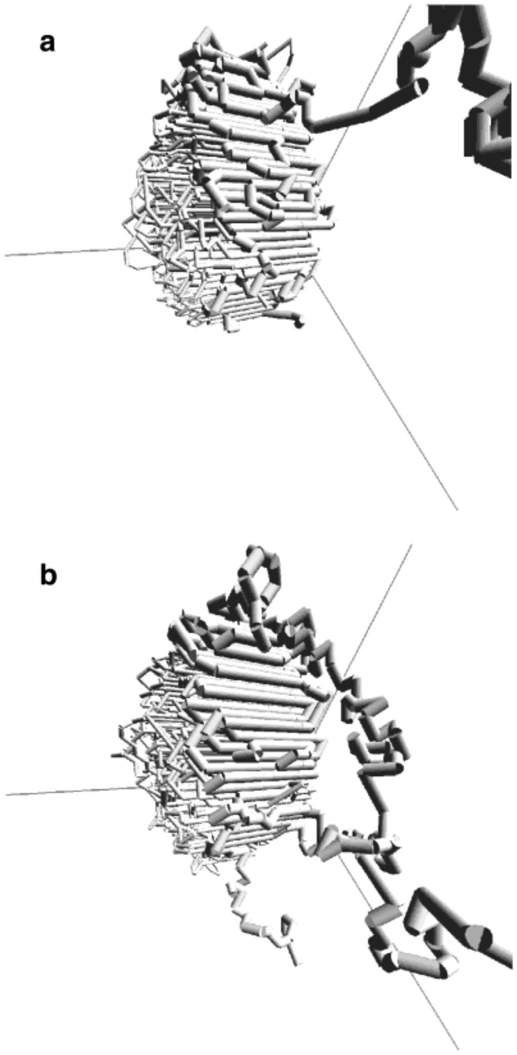

Figure 4. Snapshots of the chain crystallization shown in Figure 3a at (a) 6.72×10^5 and (b) 6.74×10^5 MC cycles. For the sake of clarity, the bonds belonging to the crystallizing chain are drawn with double thickness. Dissolved chains are not shown.

Acknowledgment. W.H. gratefully acknowledges financial support by DSM. We thank Prof. D. C. Bassett, Prof. B. Lotz, and Dr. M. Miller for stimulating comments. This work is part of the research program of the “Stichting voor Fundamenteel Onderzoek der Materie (FOM)”, which is financially supported by the “Nederlandse organisatie voor Wetenschappelijk Onderzoek (NWO)”.

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MA025853L