



Crystallization of polyethylene: A molecular dynamics simulation study of the nucleation and growth mechanisms



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ABSTRACT

We have performed molecular dynamics simulations to study the mechanism of crystallization from an undercooled polyethylene (C500) melt. We observe that crystal nucleation is initiated by the alignment of chain segments, which is followed by straightening of the chains and densification. Growth proceeds via alignment of segments, which are in the vicinity of the growth front, with the chains in the crystalline lamella. Once chains are attached, the lamella thickens by sliding of the segments along the long axis of the chain from the amorphous regions into the crystalline regions. We do not observe the formation of any folded precursors.

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1. Introduction

Semicrystalline polymers are widely used in industrial applications because of their mechanical properties. These properties depend on the morphology of the semicrystalline state, i.e. on the distribution of crystallites sizes and shapes, which is in turn caused by the crystallization process [1]. In the last seven decades a large amount of work has been done to understand the crystallization of polymers but still there are a number of question which are either unanswered or controversially answered [2,3]. A wide range of experimental techniques have been used to study the crystallization process of polymers under quiescent conditions [4–13] and under the influence of external fields [14–21] but the molecular level mechanisms of nucleation and growth have not yet been fully identified experimentally as they are difficult to resolve both, in space and time.

From the point of view of theory it is challenging to model the crystallization process, because relaxation of the polymer melt occurs on several time and length scales which makes it difficult to use quasi-equilibrium approaches. In such cases, computer simulations are powerful tools to unveil the molecular level

mechanisms. In the last one and a half decades, many computer simulation studies of crystallization of polymers have been carried out [1,22–52]. In very few of these studies [31,32,36], the molecular mechanism of crystal growth has been addressed. However, nucleation in short chain alkanes has been simulated [22–27,29,30] and a scenario for the nucleation mechanism has been identified.

There are two recent simulation studies [31,36] in which the growth mechanism has been addressed and the results do not agree with each other. As the systems were of different chemical composition (one was polyethylene the other PVA) agreement was not necessarily expected, but one might have hoped to find a generally applicable picture. At the same time neither of the simulation results is consistent with the classical theories on polymer crystallization presented by Lauritzen and Hoffman (LH) [53] and Sadler and Gilmer (SD) [54].

In this article, we present a detailed analysis of the formation of crystal nuclei and revisit the molecular mechanism of crystal growth from the melt in polyethylene. We find yet another crystallization mechanism.

2. Method

2.1. Model & order parameters

We have used a united atom model for polyethylene in which the chains consist of monomers that represent CH_2 and CH_3 groups

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[41,55]. The system parameters were the same as in ref. [56], apart from the Lennard-Jones cutoff radius, which we set to $r_c^J = 2.5\sigma$, where σ is the length scale given by the Lennard Jones interaction. We have used the ESPResSo package [57] to run the simulations and implemented the dihedral-cosine potential which was not present in the package by default.

In order to differentiate crystallites from the melt, we used several order parameters (we have previously applied the same approach to a melt of shorter chain alkanes [30,58], thus we only briefly summarize it here. For details we refer the reader to ref. [30]). For the purpose of the analysis we split the polyethylene chains (C500) into segments of 15 monomers and computed the radius of gyration R_g and the nematic order parameter S_2 of those segments that were involved in the formation of the critical nucleus.

In order to measure the local alignment of the chain segments, we computed the crystallinity order parameter. Monomers within a distance of $r_c = 1.4\sigma$ were considered as neighbours. We assigned a vector to every monomer i pointing from monomer $i - 1$ to $i + 1$. Two neighbours i and j were considered as “aligned” if the assigned vectors to these monomers were almost parallel ($\theta_{ij} \leq 10^\circ$). For a monomer to be considered “crystalline”, it had to have at least 12 aligned neighbours. We obtained this value by sampling the probability distributions of the number of aligned neighbours in the bulk crystal and the bulk liquid.

2.2. Simulation details

We have performed molecular dynamics simulations of a system consisting of 200 chains of polyethylene (C500). The system was equilibrated at 500 K which is well above the melting temperature of polyethylene. We set the density to 0.89 g/cm^3 and performed all molecular dynamics simulations under constant volume and constant temperature conditions. We used an integration time step of 0.006τ , where $\tau = \sqrt{\frac{k_B T}{m\sigma^2}}$, m is the mass of a monomer, k_B is Boltzmann’s constant and T is the temperature in Kelvin.

After equilibrating the system at 500 K, we quenched it to 280 K to observe the nucleation event and then heated it to 320 K to observe the growth process. We used the DPD thermostat [59] and the friction coefficient γ for the thermostat was $1.0\tau^{-1}$.

3. Results and discussions

3.1. Nucleation mechanism

To explore the nucleation mechanism, we identified the nucleation time t_0 (The time at which critical nucleus is formed.) and the monomers which participated in the formation of critical nucleus. We traced the structural and orientational properties of these monomers backward in time until they could not be distinguished from the melt monomers anymore. We analysed the formation of five nuclei in terms of the average radius of gyration R_g of all chain segments that were part of the nucleus at t_0 , the nematic order parameter S_2 of these chain segments, the local density in terms of the volume V of the Voronoi cell associated to each monomer that is part of the nucleus and the crystallinity order parameter defined above.

In Fig. 1 we show the relative variations of these quantities with respect to the values they had at $-170\Delta t$, where $\Delta t = 100,000\tau$. When we advance from the supercooled melt towards the formation of the critical nucleus at t_0 , we observe first an increase in the global orientational order S_2 , then an increase in the radius of gyration of the segments, and finally the local density increases and the crystal structure is formed. The mechanism we observed here is the same as

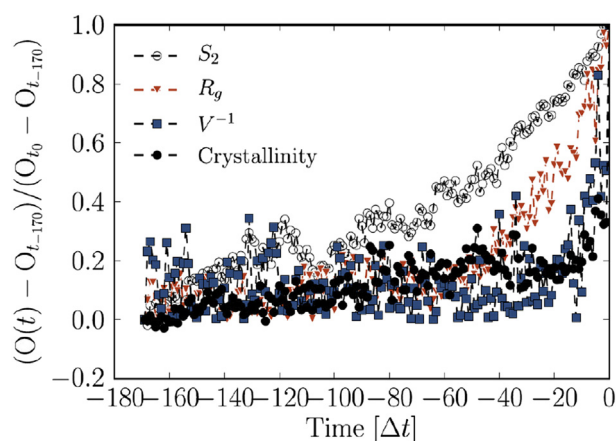


Fig. 1. Relative variation of several observables (O) from the melt to the formation of a critical nucleus, computed for those monomers that are part of the nucleus at the nucleation time $t = t_0$: orientational order S_2 (black, open circles), radius of gyration R_g (red, triangles), the local density in terms of the inverse of the Voronoi cell volume V (blue, squares) and the crystallinity order parameter (black, closed circles). The curves are averaged for the evolution of the five largest clusters progressing backward in time from the nucleation time $t = t_0$ in steps $\Delta t = 100,000\tau$ to $t = -170\Delta t$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the one we have found in short polymer chains [30,58]. We conclude that, at 280 K the undercooling is so strong that nucleation is a local event which does not depend on the chain length.

Snapshots of the critical nucleus are shown in Fig. 2. In the top view (Fig. 2 (b)) one sees that the stems are arranged hexagonally. In Fig. 2(c) we show the complete chain if more than one stems are formed by the chain, otherwise we only show the segment associated to these monomers. Several chains participate in the nucleation event with more than one stem.

3.2. Growth mechanism

To study the growth mechanism, we picked a configuration at

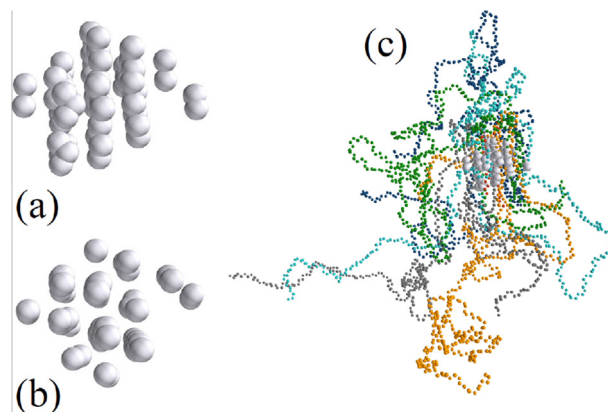


Fig. 2. Snapshots of the critical nucleus. (a): Only those monomers which are forming the critical nucleus at time t_0 . (b): Top view of monomers which are forming the critical nucleus at time t_0 . (c): Gray monomers: monomers that form the critical nucleus at t_0 . Red monomers: segments of chains that participate with a single stem in the formation of the critical nucleus. Blue, green, cyan, battleship gray and orange monomers: chains which fold back and participate in the formation of the critical nucleus with more than one stem. For the case of folded chains we show complete chains instead of segments so that folds and tails can be identified. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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