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Molecular dynamics simulations of polymer crystallization under confinement: Entanglement effect

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ABSTRACT

We carried out molecular dynamics simulations to study the crystallization of polymer melts subjected to confinement between two parallel walls. Two types of walls, bare and grafted walls, are studied. The bare walls are slippery for chain motions, and the interactions between polymer chains and the walls are moreover chosen either attractive or repulsive. The crystallization in the case of bare walls generally consists of surface-induced processes close to the walls followed by homogeneous nucleation in both the boundary and middle regions. In the case of grafted walls, parts of polymer chains residing close to the walls are adhesive to the surfaces and become permanent graft points. We find that the surface-induced crystallization is increasingly suppressed with increasing grafting density. At high grafting densities, only crystallization in the middle regions is observed. We calculated the spatial distribution of entanglement lengths and related it to the crystallization behavior. The entanglement length close to the walls is found to decrease with increasing grafting density, as the adhesion points act as effective entanglement knots. In light of our recent results that less entangled polymer melts lead to faster crystallization and higher crystallization order, we now show that this conclusion stands also for the case of confined polymer melts. Our results suggest entanglements to be an universal factor towards the understanding of polymer crystallization under different situations, in particular at supercooling.

1. Introduction

The comprehensive understanding of polymer crystallization is an open question in polymer physics [1–3], even after several decades of intense researches. It is of great technological importance since more than sixty percent of industrial plastics are in semi-crystalline states and their functional properties are directly related to their structures. Due to its highly non-equilibrium nature, a common polymer crystallization process is complex and intimately related with transitions of metastable states [4]. Besides the classical Lauritzen-Hoffman (LH) theory [5–8], several models have been proposed to depict different aspects of the panorama of polymer crystallization, such as Sadler-Gilmer's entropic barrier theory [9,10], Olmsted's spinodal decomposition theory [11], and Strobl's multi-stage crystallization theory [12,13]. All these approaches are trying to answer the fundamental question on how polymer chains form folded crystalline structures from randomly coiled conformations, in particular at the early stages.

Recently, increasing focus was placed on the polymer crystallization under spatial confinement such as thin films under nanometer confinement or on substrates [14–26]. Generally, thin polymer films can be considered subjected to quasi one-dimensional confinement and they are the ideal objects to study the effects of confinement and interface. In experiments, the morphology, glass transition, crystallization kinetics, and other physical properties of thin films have been probed both in situ and real time with high resolution devices such as an atomic force microscopy [14,15,18,26,27], in contrast to the averaged properties obtained from bulk systems. In experiments, the orientations of crystalline chains ("edge-on" or "flat-on") have been observed dependent on film thickness as well as the interactions between polymers and substrate surfaces [15,28]. Tracz et al. found that crystallization at solid substrate is facilitated and leads to considerable thicker lamellae [29].

With the increasing power of modern computer systems,

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numerical simulation has become a powerful tool in many fields and also in the understanding of polymer crystallization. Computer simulations can be carried out to test theoretical model assumptions, to reproduce and predict experimental results, and to present underlying microscopic insights. Monte Carlo (MC) and Molecular Dynamics (MD) simulations have been successfully used to study polymer crystallization. Doye and Frenkel studied the mechanism of thickness selection in polymer crystals using lattice MC simulations [30]. Chen and Higgs simulated the growth of short *n*-alkanes in dilute solution using the bond fluctuation model [31]. Hu et al. studied nucleation and crystallization properties of polymers using a lattice model where crystallization is driven by local alignment of chain segments [32–34]. Sommer and Reiter established a kinetic MC algorithm for polymer crystallization in thin polymer films using polymer chains as elementary objects [14,35]. Fujiwara and Sato studied the crystallization of short *n*-alkanes by MD simulations [36,37]. Welch and Muthukumar investigated several aspects of the crystallization of model polyethylene-like polymers chains by MD and Langevin dynamics simulations [38,39]. Gee et al. used a polyethylene-like united atom model with increased bond stiffness and carried out large-scale MD simulations [40]. Yamamoto developed a coarse grained model and investigated the crystallization from polymer melt of a constrained system [41–43]. Meyer and Müller-Plathe developed a coarse grained model based on poly(vinyl alcohol) (PVA) using a multi-scale approach [44–46], which model is used also in our previous simulations [47–49]. Zerze et al. studied the nucleation formation of short polyethylene chains [50] by MD simulations and Yi et al. did similar MD simulations to study the nucleation of few longer polyethylene chains [51]. Yu et al. studied the crystallization of polymer drops and discussed the entanglement effect by MD simulations [52]. Karayiannis et al. studied the crystal nucleation and role of bond tangency by MD simulations, as well as the entanglement in polymer melts [53–58]. Ni et al. studied the effect of bond length fluctuations on crystal nucleation of hard bead chains [59,60]. All these simulations provided many insights for further understanding of polymer crystallization. Particularly for polymer crystallization under confinement conditions, Ma et al. studied the crystal orientations of “edge-on” and “flat-on” by MC simulations [61].

For long polymers, entanglements dominate many physical properties of the amorphous state and has also been recognized for decades that they should play a significant role in polymer crystallization kinetics, going back to Hoffman's argument of the effect of reptation to the crystallization kinetics [8,62,63]. Here it was argued that, polymer chains crystallize via folding near a prior crystalline surface and the reptation from entangled melts limits the folding rate and affects the lamellar thickness as well. In our recent simulation works, we studied the correlation between entanglements and crystallization structures [47–49]. We found that entanglement networks are largely conserved during crystallization, particularly in homogeneous crystallization. Also, we found that the initial entanglement length directly controls final crystalline lamellar thickness at super cooling, independently with the quench temperatures and therefor the growth kinetics. This provides a new approach to understand polymer crystallization via the concept of entanglement restriction and consistent with the indications of recent NMR experiments [64–66]. Entanglements can be affected by walls [67], therefore it is interesting to study the entanglement effect on polymer crystallization under confinement. Up to now, there were no such studies combining the observation of both effects under confinement, neither in experiments nor in simulations.

We emphasize that polymer crystallization is a non-equilibrium process and polymer melts are always in a non-equilibrium state as soon as being cooled. Nevertheless the free energy difference between the melt and the crystal phase is considered as the being responsible for the growth rate and the lamellar thickness. Besides the problem of definition of entropy in a non-equilibrium state the predictions require additional assumptions such as about nucleation barriers and further ad hoc concepts about the pathway chains take into the crystalline state. Moreover it is a challenge for computer simulations to calculate the free energy at various conditions. Our previous work suggests a completely different, nearly orthogonal approach to thermodynamic-kinetic based models in the literature, namely a direct relation between the state of entanglement and crystallization, which is independent of the equilibrium properties [48,49]. Specifically prepared non-equilibrium states of polymer melts were used in some recent experiments to study the effect of entanglements in melts on the following crystallization processes. The measurements indicated enhanced crystallization for reduced entanglement density [68–72].

If the entanglement density is the key to understanding polymer crystallization one should seek for scenarios where a change in the state of entanglement is expected but the thermodynamic properties of the polymer are unchanged. Here, solid surfaces seem particularly suited since it is know that the entanglement density is reduced close to substrates [67], and that the thermodynamical properties are only changed in the direct contact zone [73]. Therefore, we investigate in this work the crystallization behavior of dense entangled melts confined by smooth substrates under the variation of properties which would either change thermodynamic state, such as adsorption, or has considerable influence on the entanglement density, such as grafting chains at the substrate. The rest of this work is structured as follows.

Section 2 introduces the model and provides some technical details about the simulations. Section 3 presents the details of our analysis methods, such as those for the determination of the local entanglement length. In Sections 4–6 we present and discuss the results of our simulations, separately for three situations involving two types of walls: bare walls, grafted walls, and instantaneously removed bare walls. The entanglement state in melts and its effect on the crystallization behavior during cooling will be addressed. We present a brief discussion about the size effect in Section 7. The concluding Section 8 emphasizes entanglement restriction as a simple and universal concept to understand polymer crystallization, in particular at its early stages and for the case of homogeneous nucleation.

2. Model and simulation details

Same as in our previous work [47,48,74–76], we treat polymer chains by the bead-spring style Coarse Grained Polyvinylalcohol (CG-PVA) model proposed by Meyer and Müller-Plathe [45]. In the CG-PVA model, a coarse grained bead represents one monomeric unit of PVA and the beads within a polymer chain are connected by harmonic springs. The key point of the CG-PVA model is that it maps the torsional potential of atomistic backbones to an additional bending potential in a bead-spring model to eliminate high frequency oscillations and thus to speed up simulations. The bending potential had been systematically parameterized from all-atom simulations and stored in a tabular form. The nonbonded interactions are approximated by a Lennard-Jones-9-6 potential (LJ96). Furthermore, for the simulation of dense melts, it is sufficient to take only the repulsive part of the potential into account [77,78], with a compensation of higher effective pressure. These approximations are essential to speedup simulations of polymer crystallization as the crystallization process of polymers is very slow. Although these approximations lead to some quantitative shifts of energy and pressure, the qualitative behavior of the system