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STRUCTURE AND EVOLUTION OF ORDERED DOMAINS IN DEEPLY QUENCHED POLYETHYLENE MELT

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Introduction

Solidification of polymeric materials, a complex process in which the entangled polymer melt becomes a composite of amorphous and crystalline domains, strongly depends on how the melt is cooled below its crystallization temperature. If cooling is at moderate rates, the most common and well understood mechanism is via nucleation and growth of spherulites, but special cases exist where crystallization is preceded by a pre-transition state induced by density fluctuations. Such multi-step crystallization scenarios are suggested by many experiments¹⁻⁴, and recent theoretical⁵ and simulation⁶ work. Via energetic and geometric analyses, we have examined the structure of mesomorphic domains and the dynamics of their formation and evolution, including atomic scale details of molecular addition to ordered domains, as well as particle dynamics in the system, including high mobility jumps in the ordered domains at wavelengths matching the monomer spacing.

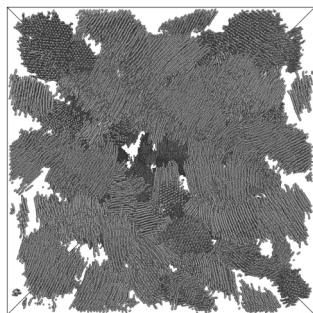
Computational Methods

The MD simulations of the polymer melt were carried out on bulk amorphous ensemble of non-polar linear polymer. All polymers were represented as united-atoms (UA). The simplified UA model affords the investigation of much larger polymer ensembles, thus reducing finite size effects. The polymer melt is composed of 5,832 768-bead polymer chains (4,478,976 united-atoms; $M_w = 10,752$ g/mol). The force field parameters consist of both valence (stretch, bending, and torsion terms) and nonbonded potential terms (van der Waals and Coulomb). All valence degrees of freedom were explicitly treated and unimpeded. Simulations were performed in an isobaric-isothermal statistical-mechanical ensemble (NPT). The PE melt ensemble was simulated at 600 K, where the periodic box was allowed to relax under NPT conditions. The volume equilibration process was carried out for a minimum duration of 5 ns. Following this step, the system was cooled in NPT runs in increments of 50 K and equilibrated for 5 ns at each incremental temperature down to 450 K, at which time a spontaneous crystallization is observed. The total simulation time at $T = 450$ K is 100 ns.

Results and Discussion

The first step in our analysis is to isolate ordered domains that are shown in Figure 1. We compute all chord vectors (line segment connecting the midpoints of two adjacent bonds on polymer chain) and stems which are consecutive trans sequences of chord vectors. Ordered domains are identified as clusters of well-aligned stems. The details of this algorithm will be available in the future publication.

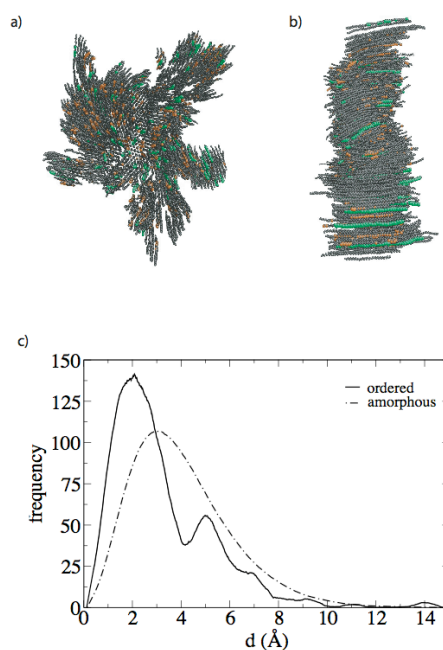
Figure 1. 100 largest domains at $t = 100$ ns isolated via clustering algorithm.



One of the most interesting results found in these simulations is a large monomer's displacement inside ordered domains. We compute displacements for each interval between observations, $\Delta r_i(\Delta t)$, for all monomers in the system. Figure 2 a) shows a domain isolated at 100 ns with monomers colored according

to their displacements (orange and green monomers are in the sets with the 5% smallest and largest displacements, respectively). Entire stems move in concert due to the constraints imposed by the domain structure, in a process related to "chain sliding diffusion" suggested by Hikosaka.⁷ Figure 2 b) shows the same domain as in Figure 2a but rotated so that axial direction is parallel to the side of the page. These two figures also illustrate the heterogeneous nature of dynamics inside ordered domain which is not intuitive since we think of ordered domains as a regions of low mobility, e.g. in a perfect crystal molecules vibrate around their equilibrium position but usually face large barriers to permanent displacement from equilibrium. Such heterogeneity is a general feature of domains at all times. Furthermore, mobility is uncorrelated with position inside the domain, whereas one might expect stems near the surface of a domain to exhibit higher mobility. Note that entire stems move in concert due to the constraints imposed by the domain structure, in a process related to "chain sliding diffusion" suggested by Hikosaka.⁷ Figure 2 c) demonstrates discrete nature of monomer displacements that is similar to monomer spacing.

Figure 2. Domain (~60,000 monomers) isolated from the melt at 100 ns and plotted such that its director D points out-of-the paper. b) Same domain rotated by 90°. c) Distribution of ordered monomers' displacement along the direction of domain.



Conclusions

We performed extensive molecular dynamics simulations of PE melts under deep quench that have the ability to probe at experimental time and length scales. These simulations provide additional insight into the structure and dynamics of polymer ordering after initial domain formation.

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