



Polymer communication

Primary nucleation of polyethylene: Embryogenesis from a semidilute solution



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ABSTRACT

Using “realistic” molecular dynamics simulation extended up to 100 ns, we have investigated the evolution of cluster size, intrachain vs. interchain potential energies and pair correlations of polyethylene (PE) in a semidilute (ca. 28 wt%) 1,2,4-trichlorobenzene solution at 300 K. Results indicate that the embryonic development begins with the aggregation of *trans*-rich sequences of characteristic length $l_o \approx 2$ nm, forming clusters of short stems. This is immediately followed by reorganization/thickening via intracluster axial translation and reeling-in of segments from the surrounding matrix in dynamic competition with neighboring embryos. Up to this stage, the embryonic clusters are loosely packed, retaining largely the conformer populations in the solution state but with *gauche* conformers enriched in the loose fold loops. After reaching a critical size with $l^* \approx 4$ nm, the intracluster order starts to significantly improve via a “solidification” process with sigmoidal decreases of valence and nonbonding energies, while axial diffusion dramatically slows down and intracluster torsions become fully adjusted to *trans* conformation by annihilation of *gauche* conformers. In these “solidified” embryos, although molecular packing remains deviated from the orthorhombic structure (as reflected in significant differences in pair correlations) while reminiscent of the mesomorphic “rotator” or hexagonal phase, the decrease in potential energy is already significant (corresponding to about half of the heat of crystallization) as the *intrachain* valence contribution is fully realized.

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1. Introduction

Primary nucleation of polymer crystals is poorly understood due to difficulties in studying embryos of limited size and transient lifetime. Previous studies of primary nucleation focused mainly on incipient crystals, with traditional wisdom extended from atomic crystals that the starting nuclei are natively similar to bulk crystals, only being much smaller in size and hence with significant surface effects [1]. More recently, with supporting evidences from small- and wide-angle X-ray scattering (SAXS/WAXS), Fourier-transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), electron microscopy, and molecular dynamics (MD) simulation, gradually emerged is an alternative picture of primary nucleation through bundling of extended chain segments (where the molecular packing within the bundle remains mesomorphic) into nanometer-sized embryos [2–8]. This lies much in line with

the “bundle” theory proposed by Allegra and Meille [9,10], in which the mesomorphic structure is assumed to comprise hexagonal arrays of extended stems. It is also reminiscent of Strobl’s “block” picture, where crystal *growth* is proposed to involve repeated scenarios of the *secondary* nucleation of mesomorphic blocks at the growth front that sequentially reorganize into matured/coalesced blocks of crystalline order [11]. Detailed evolution of chain conformation and molecular packing in the mesomorphic phase, however, remains to be clarified.

Qualitative differences in chain conformation between the mesomorphic embryos and the amorphous matrix upon cold crystallization of poly(dimethyl siloxane) have been indicated by Lund et al. [12] from a combination of DSC, broadband dielectric spectroscopy, and wide/small-angle neutron scattering results. This is consistent with the observation by Konishi et al. [13] on the presence of a relatively narrow “mesophase” contribution superimposed on the broad amorphous halo in the WAXS profile of ice-quenched isotactic polypropylene, which suggests that the distribution of molecular spacing in the mesomorphic state is different from that in the amorphous matrix. On the basis of parallel WAXS and FTIR results for a racemic blend of poly(L-lactide) and poly(D-

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lactide), we have further identified the correspondence between the mesomorphic peak in WAXS and the presence of long-lived precursors comprising loosely paired $3_2/3_1$ helices prior to the emergence of β_c crystals upon slow cooling from equilibrated melt state [14].

More quantitatively, Hikosaka et al. [15] showed that the primary nucleation rate I of polyethylene (PE) crystals under fixed supercooling scales with number-average molecular mass (M_n) according to $I \sim M_n^{-\eta}$ where the exponent $\eta = 2.3$ for folded-chain orthorhombic crystals and $\eta = 1.0$ for the extended-chain hexagonal (or “rotator”) phase. As the two values of η coincide with diffusion exponents for entangled vs. unentangled chains [16], Hikosaka et al. [15] conjectured that the nucleation process is kinetically controlled by the axial diffusion of polymer chains within the embryos. For linear alkanes, this rotator phase has been experimentally identified during the nucleation stage even for alkanes not exhibiting an equilibrium rotator phase [17,18]. Through theoretically treating crystal–melt interface as grafted brushes of loops in a self-consistent pressure field, Milner [19] showed recently that the rotator phase should indeed be favored in primary nucleation of PE crystals. Via a combination of analytical/numerical calculations and all-atom MD simulations for movement of soliton-like defects, Milner and Wenzel [20] further demonstrated low-barrier characteristics for axial motion in the rotator phase as compared to the orthorhombic phase of much restricted mobility. All these results appear to support the view that the rotator phase serves as mesomorphic precursor prior to full development of orthorhombic nuclei.

Pushing towards improved understanding of the dynamic evolution process in primary nucleation of PE crystals, here we show through MD simulation of a semi-dilute (28 wt%) solution of PE in trichlorobenzene (TCB) up to 100 ns that the nucleation process comprises 3 stages. These include (1) aggregation of short stems, (2) extension of stems via intracluster axial translation of segments and reeling-in of further segments from the surrounding matrix, and (3) solidification of the bundle structure with concomitant step decreases of valence and nonbonding energies, beyond which axial segmental diffusion becomes dramatically slow. During the first two stages, conformer populations remain largely unchanged, meaning that unfavorable *gauche* conformers are mainly concentrated in the loose fold-loops. Only during the solidification stage are the inner-domain torsions fully adjusted to *trans* conformation by annihilation of *gauche* conformers. The evolution process observed lends credibility and further insights to various molecular models previously proposed in the literature. The conservation of conformer populations in the earlier two stages of nucleation and the dominant annihilation (instead of excretion through chain ends) of *gauche* conformers only in the solidification stage may bear significance in the interpretation of the spinodal-like features in the cold-crystallization of polymers.

2. System and method

With periodic boundary conditions, the semi-dilute (ca. 28 wt%) PE/TCB solution system comprised a 1000-mer PE chain and 400 TCB molecules. For initial system generation and MD simulation, the DREIDING force field with a hydrogen-implicit parameters (in the C-32 form of the DREIDING force field) was adopted for each methylene group and the hydrogen atoms in PE chain were removed for decreased atom number to speed up the simulation while keeping the backbone torsion behavior unaltered, as the latter plays a key role in chain folding. The partial charge of TCB atoms was calculated by Gasteiger method whereas the partial charge in the PE chain was set to 0. The cut-off distance was set to 1.25 nm for non-bonding interactions.

To build the initial state, the random PE chain was stochastically generated from the rotational isomeric state (RIS) model in a segment-by-segment manner in the 3D simulation box, taking into account interactions with all atoms already positioned. The solvent molecules were then randomly placed. The initial system was set to a relative large box, i.e., 0.600 g mL^{-1} in density, for easier setup of the system. The density was stepwise increased to 1.000 g mL^{-1} by gradually decreasing box size. To eliminate strains and stresses during system generation, geometry optimization followed by an MD pre-run of 500 ps (in time steps of 2 fs) at 300 K in the isobaric-isothermal (NPT) ensemble were applied, yielding converged density of ca. 1.252 g mL^{-1} with <1% fluctuations in temperature. Nose and Berendsen methods were adopted for thermo- and barostat purposes, respectively. With this NPT ensemble, a specific long-term MD run in time steps of 2 fs at 300 K was performed up to $t = 100$ ns. Commercial package *Accelrys*[®] *Materials Studio* was used for initial system generation (*Amorphous Cell*) and MD simulation engine (*Forcite*). In the semidilute condition, the initial polymer chain may randomly pass through the boundary several times and result in several periodic images within the simulation box. In view of the large ratio between the box size and the Kuhn length of PE, these periodic images were considered as effectively different chains. Further details are given in the Electronic [Supplementary Information \(ESI\)](#) where the capability of the united-atom DREIDING force field to sustain orthorhombic packing of PE chains was specifically checked via an MD test run up to 60 ns (cf. Section [S2 in ESI](#)). To check for chain-length effects, MD simulation at 300 K for three shorter chains (each 333-mer in length) in 400 TCB molecules (i.e., 28 wt%) was also made. Results (cf. Section [S3](#)) indicate embryonic evolution behavior very similar to the single long-chain (1000-mer) case. A further MD simulation run using the Andersen barostat was also performed to check effects from the choice of barostat; results (cf. Section [S1](#)) indicated generally consistent potential energy values but the extension stage was significantly prolonged, without entering the solidification stage up to $t = 130$ ns.

3. Results and discussion

3.1. Embryogenesis

Given in [Fig. 1](#) are evolution profiles of the selected potential energy components and the embryonic size for the 28 wt% PE/TCB system at 300 K. There are 3 stages according to the evolution of the non-bonding energy between PE segments and that of chain-solvent interactions (cf. the lower two curves in [Fig. 1](#)). In the first stage (up to $t \approx 17$ ns), intersegment nonbonding interactions decreased quickly (at the sacrifice of polymer-solvent interactions) upon aggregation of some extended stems to form embryos of characteristic axial length $l_0 \approx 2.2$ nm (As an operational definition of “stem”, we considered only extended segmental sequences with torsion angles within the range of $180^\circ \pm 30^\circ$; segments of torsion angles outside this range such as those in the fold loops were excluded.) This is followed by the extension stage spanning from $t \approx 17$ –55 ns where more segments were reeled-in from the surrounding bulk solution via axial translation and extension of stems up to axial length $l^* \approx 3.6$ nm.

Correspondingly, there were only minor changes in both the intersegment nonbonding energy and in the polymer-solvent interactions, consistent with the observation that the aggregated domains were only loosely packed. After reaching the critical size $l^* \approx 3.6$ nm, the loosely packed embryo started to reorganize without further changes in the axial length, resulting in clearly decreased valence energy and also moderate decreases in

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