



Strong influence of branching on the early stage of nucleation and crystal formation of fast cooled ultralong *n*-alkanes as revealed by computer simulation

Sara Sanmartín, Javier Ramos, Juan Francisco Vega*, Javier Martínez-Salazar

Biophym, Departamento de Física Macromolecular, Instituto de Estructura de la Materia (IEM), Consejo Superior de Investigaciones Científicas (CSIC), C/ Serrano 113 bis, 28006 Madrid, Spain

ARTICLE INFO

Article history:

Received 18 July 2013

Received in revised form 23 September 2013

Accepted 28 October 2013

Available online 9 November 2013

Keywords:

Polymer crystallization
Branched ultralong *n*-alkanes
Molecular dynamics
Homogeneous nucleation
Chain folding

ABSTRACT

Molecular dynamics simulations were performed on a series of ultralong *n*-alkanes in order to shed light on the early stage processes of the crystallization from the melt at high undercooling. The study contemplates a linear ($C_{191}H_{384}$) and two symmetrically branched [$C_{96}H_{193}CH(CH_3)C_{94}H_{189}$ and $C_{96}H_{193}CH(C_4H_9)C_{94}H_{189}$] ultralong *n*-alkane samples. These systems can be considered as good models for the study of the mechanism of polymer folding at the early stage of crystal formation. First of all, it is observed that the short branch provokes a delay of the nucleation as compared to the linear chain. Additionally this process is further delayed as the branch length increases. To follow the process we compute the time evolution of the structure factor $S(q)$ as the material is undercooled. It is obtained that both crystal thickness and chain packing are dramatically affected by the presence of the branches. The crystallinity, expressed as the mass ratio of the ordered structure to the total amount of material, also decreases as the length of the branch increases. The observed folding in the linear system is closer to the irregular model of folding at least for the early stages of crystal nucleation and formation. The length of the branch clearly determines its inclusion or not in the nuclei and consequently it disturbs in a different way the formation of the crystals.

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1. Introduction

Ultralong *n*-alkanes, in the range of 150–390 carbon atoms, are considered model materials for the study of polyethylene chain folding and crystallization process [1–3]. These materials, which can be linear or branched, are monodisperse and produce exceptionally final regular crystals. Since the first synthesis of linear ultralong *n*-alkanes (LLA) [1], Ungar and co-workers have comprehensively studied the crystalline structure of these materials focusing their interest on the nature of the folding chain [4]. In these LLAs the crystalline fold length takes values $l = L/n$, where L is the extended chain length and n an inte-

ger. Small-Angle X-ray Scattering (SAXS) and Raman LAM spectroscopy studies carried out on solution- and melt-crystallized samples have shown that *mature* crystals have fold lengths equal or very close to integer fractions (IF) of L [4–7]. In contrast, real-time SAXS experiments of *in situ* melt-crystallized material has revealed that the *primary* crystals, when grown below the folded-chain melting temperature, present a typical length which is a non-integer fraction (NIF) of L [5,7]. These primary crystals with an l -value between L and $L/2$ were found to subsequently transform to IF forms via either thickening (to the extended form) or thinning (to the once-folded form with $l = L/2$).

At the end of the 1990s branched long alkanes (BLAs) were synthesized by Brooke and co-workers [8], and then the effect of defects (branches) on the crystalline structure was also studied [9–13]. As in the case of LLAs, it seems

* Corresponding author. Tel.: +34 915 616 800; fax: +34 915 615 413.
E-mail address: jf.vega@csic.es (J.F. Vega).

that the primary crystals which are formed below the melting point of the folded chains are characterized by lamella with NIF of the period L . Following their formation, the NIF crystals transform to the once-folded or F2 form [10]. Surprisingly, this NIF/F2 transition is very fast in the BLAs, and considerably slower in the LLAs. Additionally, it has been also reported that the branches in the mature crystal are located at the fold surface. On the other hand, Basset and co-workers studied the kinetics and the morphological aspects of the crystallization of both LLAs and BLAs, demonstrating, on one side, the exclusion of the branches from the folds and, on the other, a low melting temperature and a reduction in the crystallization kinetics of the branched systems [11]. Similar results have been also obtained by Grasso and Titman [14]. These authors found a average size of 8 ± 2 carbon atoms for the folded segment in the LLA chain $C_{246}H_{494}$ in the F2 form at 293 K.

Computer simulation is nowadays a valuable complementary tool to experimental techniques at the molecular scale since it helps us to better understand the polymer crystallization process. For more details concerning computer modelling of polymer crystallization the authors recommend the recently published review by Yamamoto [15], which covers information published until 2008. Later on, the effect of short chain branches (SCB) on the crystallization process of ethylene/ α -olefin random copolymer models in dilute solution has been studied by us [16,17]. We showed that both methyl and butyl branches slow down the ordering processes of the chains. Furthermore, the longest branches provide a higher reduction in both crystallinity and thickness of the crystals. Large-scale Molecular Dynamics (MD) simulations at a Coarse-Grained (CG) level of both crystallization and melting processes have been performed by Luo and Sommer [18–21]. More recently, Rutledge's group has performed MD simulations of homogeneous crystal nucleation of C_{150} and C_{1000} chains. They characterized the formation and shape of the crystal nuclei as well as the crystal surface in terms of folds, loops and tails. They also calculated the free energy and its dependence with the temperature within the framework of classical nucleation theory [22].

In this work, we study the early stages of the crystallization from the melt for a LLA (C_{191}) and two BLLAs with methyl (MBLA or $C_{191}-C_1$) and butyl (BBLA or $C_{191}-C_4$) branches at high supercooling by MD simulations. These systems are shown in Fig. 1a. We explore the effect of the SCB on the formation of nuclei, packing of ordered segments and size of the crystals. Later, we discuss the folding and the inclusion/exclusion of the SCB from the ordered segments in these early stages of the growing structures.

2. Computational methods

2.1. Molecular dynamics details

All MD runs were performed with LAMMPS package [23]. The integration of the motion equations were performed through the velocity Verlet algorithm with a time

step of $\Delta t = 2$ fs. Simulations were performed on the isothermal-isobaric (NPT) ensemble. The Nose–Hoover thermostat and barostat were used to control the temperature and the pressure, respectively. Pressure was set up to 1 atm in all simulations. The structures were dumped every 20 ps for subsequent analysis using in-house codes. Molecular graphics have been generated using the VMD package [24].

2.2. System description and preparation of initial melt structures

The simulation boxes for the LLA, MBLA and BBLA involves 500 chains of $C_{191}H_{384}$, $C_{96}H_{193}CH(CH_3)C_{94}H_{189}$ and $C_{96}H_{193}CH(C_4H_9)C_{94}H_{189}$ united atoms, respectively (Fig. 1a). Let us recall that hydrogen atoms are not explicitly taking into account in our model. The initial structures for molecular dynamics have been prepared as follows. The generation and packing of the 500 alkane chains was initially performed using a modified recoil growth algorithm with periodic boundary conditions [25]. The initial melt density has been set to 0.740 g/cm^3 for all systems. Subsequently, the chains in the simulation box were minimized with fixed box length and then the box volume was relaxed by NPT MD during 6 ns at 600 K using the full potential described below.

2.3. Cooling temperature protocol

The temperature protocol is shown in Fig. 1b. The generated melts were cooled from 600 to 475 K by decreasing the temperature in steps of 25 K and equilibrated by 6 ns at the desired temperature, for a total of 36 ns. When a temperature of 450 K was reached, the polymer chains were found to undergo ordering in the three systems here studied. To insure isothermal crystallization conditions, the simulations were run for 120 ns at 450 K.

2.4. Force field

As usual, the total potential energy of a model long chain system, consists of a bonded and non-bonded terms. The bonded terms comprises bond stretch U_r , angle stretch U_θ and bond torsion U_ϕ and it can be described by the following equations and parameters:

$$U_r = k_b(r - r_0)^2 \quad (1)$$

where $k_b = 350 \text{ kcal}/(\text{mol } \text{Å}^2)$ and $r_0 = 1.53 \text{ Å}$ is the equilibrium bond length. The angle stretch term is given by:

$$U_\theta = k_\theta(\theta - \theta_0)^2 \quad (2)$$

where $k_\theta = 60 \text{ kcal}/(\text{mol rad}^2)$ and $\theta_0 = 109^\circ$ is the equilibrium angle bond. The torsion potential is given by:

$$U_\phi = \sum_{i=1}^3 k_i [1 - \cos(i\phi - \phi_i)] \quad (3)$$

where $k_1 = 0.81 \text{ kcal/mol}$, $k_2 = -0.43 \text{ kcal/mol}$, $k_3 = 1.62 \text{ kcal/mol}$, $\phi_1 = 0^\circ$, $\phi_2 = 180^\circ$ and $\phi_3 = 0^\circ$.

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