



Molecular dynamics in fiber formation of polyethylene and large deformation of the fiber

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ABSTRACT

Fiber formation from highly stretched melt and mechanical deformation of the fiber are investigated by molecular dynamics simulations. Polyethylene molecules of moderate chain length comprising 513 united atoms are simulated under constant temperature and stress ($N\tau$) conditions. Rapid crystallization into fiber structures of alternating crystalline amorphous layers is observed, where emergence of very thin lamellae and their subsequent thickening are found to be the basic mechanism of the fiber formation. The incipient lamellae are also suggested to have an intermediate degree of order. Mechanical elongation of the fiber along its axis reveals initial elastic deformation and large reorientation of the crystalline chains, which is followed by specific yielding due to chain slips in the crystals. Further elongation of the fiber leads to the formation of crazes and microfibrils. On the other hand, the transverse deformation of the oriented sample exhibits much lower Young's modulus and larger plastic deformation. During the transverse deformation, the fiber texture is severely distorted giving rise to the pronounced melting and recrystallization (or breaking and reformation) of the crystalline textures, through which the oriented fiber accomplishes nearly complete 90° reorientation.

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1. Introduction

Polymer crystallization during flow or large deformation has long attracted constant attention due to its scientific and industrial interest. Of various flow fields and polymer systems, we here pick up melt crystallization of polyethylene by elongational flow. The so-called melt spinning is a basic process of fiber formation, and innumerable reports have already been given [1–6].

As to the molecular process of melt spinning, however, the underlying physics is rather complicated involving macroscopic elongational flow, microscopic chain extension and relaxation back to the random coil, and ordering into crystalline states. The stress-induced chain orientation will relax within a specific time scale depending on the stress state and temperature, while the highly stretched chains can easier find pathways to crystal formation than random coiled chains. Description of polymer crystallization from the highly deformed melt is still phenomenological and its molecular level understanding lags far behind that of crystallization under quiescent conditions [5,6].

Besides the mechanism of flow-induced crystallization, mechanical properties of the products, hereafter we simply call “fibers”, and their structural response to the applied stress are also

of great interest [7–11]. The fiber structure of alternating crystalline and amorphous layers is well-established, but its atomic-scale and large-scale structures have been great issues in polymer science. Especially the changes in large-scale structures under mechanical loads and the mechanism of fracture by large deformation have attracted many researchers. However, their atomic-scale descriptions are still in their infancy.

Molecular simulations with computers have been spreading rapidly in the studies of polymer crystallization [12–16]. The research interest expands from understanding fundamental molecular mechanism of chain folding to mesoscopic scale reproduction of the crystallization process, both aiming at solving age-old mysteries of polymer crystallization. Recent simulation works are growing further into studies of various types of self-organization in complex systems such as block-copolymers and nano-composites [17,18].

Despite its great potential to reveal complicated non-equilibrium processes, computer simulations of polymer crystallization during flow or large deformation did not receive proper attention except in a few recent reports [19–23]. Also attracting scare interest is the molecular simulations of mechanical deformation in crystalline polymers [24], and this is quite in contrast to the amorphous polymers for which mechanical properties and mechanism of brittle fracture with crazing are intensively investigated in these days. Fascinating complexity in the mechanical

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responses in crystalline polymers, with stacked crystalline and amorphous layers, is undoubtedly great challenge, and the molecular understanding will greatly contribute to the science and technology of polymers.

In this paper, we consider polyethylene (PE), a chemically simplest polymer. After describing our simulation model, method, and analysis in Section 2, we first consider uniaxial stretching of the melt and crystallization from the highly stretched melt in Section 3. Then in the next Section 4, we study two types of large deformation of the fiber obtained, one along the fiber axis and the other perpendicular to the fiber axis. The latter mode of deformation, which resembles the so-called sequential biaxial deformation, will be found much more complex than the former. The aim of the present paper is to show that the molecular simulations are very fruitful in understanding flow-induced crystallization and in exploring the molecular mechanisms of large deformation in crystalline polymers.

2. Molecular model, simulation procedures, and data analyses

We here study PE with a united atom model by combining all hydrogen atoms with carbons. The model is known not to reproduce accurate crystal structure of PE, especially its specific space group symmetry $Pnam$. However, we here focus not on the accurate crystal structure but on the molecular process of fiber formation and the subsequent large deformation where accurate crystal structure will have minor relevance.

We consider 21 PE molecules each comprising 513 CH_2 groups C_{513} . The Hamiltonian we adopted is from the conventional Rigby–Roe force field [25] consisting of the intramolecular energy terms, for the C–C bond-stretching U_{bond} , the bond-angle-bending U_{angle} , and the dihedral-angle rotation $U_{torsion}$,

$$U_{bond}(r) = k_b(r - r_0)^2/2 \quad (1)$$

$$U_{angle}(\theta) = k_\theta(\cos \theta - \cos \theta_0)^2/2 \quad (2)$$

$$U_{torsion}(\tau) = k \sum_{n=0}^5 a_n \cos^n \tau \quad (3)$$

where r_0 is the equilibrium bond length of 0.152 nm, θ_0 is the equilibrium bond-angle of 70.5° , and the torsion angle τ is measured from trans. The van der Waals interactions U_{vdW} between all atoms of different chains and between those of the same chain more than three bonds apart are expressed by the following equation:

$$U_{vdW}(r) = 4\varepsilon \left\{ \left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right\} + U_{cutoff} \quad (4)$$

where $\varepsilon = 0.5$ kJ/mol and $\sigma = 0.38$ nm, and the interactions are cut-off at a distance $r_c = 2.5\sigma$ without tail corrections. The numerical values of the parameters, though they are the same as Rigby and Roe's, are listed in Table 1 for convenience in reduced units described later.

We place 21 chains of PE within the parallelepiped having three sides of lengths (A , B , C) and angles (α , β , γ) which is periodically replicated along the X -, Y -, and Z -directions; the box region is simply called the MD cell. The temperature and pressure are controlled by combining the Nose–Hoover and the Parrinello–Rahman methods; most of the simulations are, however, done by assuming rectangular MD cells with $\alpha = \beta = \gamma = \pi/2$ [26]. For convenience, we here summarize the units of relevant variables:

Table 1
Values of the parameters used in the simulation.

Parameters	Values	Units
m	14	g/mol
ε	500	J/mol
σ	0.37	nm
r_0	0.4	σ
k_b	10,000	ε/σ^2
θ_0	70.5	degree
k_θ	1000	ε
k	18	ε
a_0	1.0	
a_1	1.31	
a_2	-1.414	
a_3	-0.3297	
a_4	2.828	
a_5	-3.3943	

unit length $\sigma = 0.38$ [nm], unit time $\tau = 2.01$ [ps], unit mass $m = 14$ [g/mol], unit energy $= 0.5$ [kJ/mol], unit temperature $T^* = \varepsilon/(k_B N_A) = 60$ [K], and unit pressure $P^* = \varepsilon/(N_A \sigma^3) = 15.1$ [MPa], where N_A and k_B are the Avogadro constant and the Boltzmann constant, respectively. Hereafter most of the physical quantities are expressed by these units. The parameters adopted for the temperature and the pressure control, Q and M respectively, are $Q = 20$ [$m\sigma^2$] and $M = 20$ [m], both of which are the same as we adopted in our previous simulations of crystallization in helical polymers [27]. All the simulations are done using the coarse-grained molecular dynamics program (COGNAC) in the open computational tool for advanced materials technology (OCTA) [28].

The initial melt sample was constructed within a cubic MD cell, and annealed at $T = 10$ for 1 ns under hydrostatic pressure $P = 1$. It was then cooled and annealed further for 4 ns at $T = 6$. The equilibrated melt within the initial MD cell of the size $A = B = C = 17$ was then stretched at $T = 6$ under the constant volume condition along a direction, here the Z -axis direction, by the rate,

$$dC/dt = \alpha C \quad (5)$$

where C is the MD cell dimension along the Z -axis and α was set to be 1.2×10^{-3} [$1/\tau$]; the MD cell size C is doubled in about 2 ns. During the elongation, the tension along the Z -axis τ_{zz} rapidly increased with the concomitant emergence of small compressive stress τ_{xx} and τ_{yy} along the transverse directions X and Y .

We then studied crystallization in highly stretched melt under constant temperature and stress, where the diagonal components of the stress tensor, hereafter abbreviated as τ_x , τ_y , and τ_z , were chosen close to the value generated during the melt drawing. Generally, the system rapidly crystallized into fiber structures of alternating crystal and amorphous layers within several nanoseconds. Though we carried out simulations at various temperatures and stress conditions, we will here discuss a few typical cases only.

At the next section, we study structural response of the fiber when it is subjected to uniaxial elongation along the fiber axis or perpendicular to it. During both types of uniaxial elongation, the MD cell sizes in the transverse directions were controlled to maintain constant lateral stress. Therefore the MD cell showed considerable shrink in the lateral directions, but the volume of the cell remained nearly constant until fracture occurred at larger deformation. A simulation study of the PE fiber deformation was already reported by Lee and Rutledge [24], where they prepared the fiber on their statistical mechanical model for the interfacial amorphous regions. Our investigations started from the fiber spontaneously generated by the MD simulation without assumptions as to the fiber structure.

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