
Electronic Supplementary Information

Molecular Simulation of Polymer Crystallization under Chain and Space Confinements

Yongqiang Ming[a], Zhiping Zhou[a], Tongfan Hao[b*], Yijing Nie[a*]

[a] *Research School of Polymeric Materials, School of Materials Science and Engineering,*
Jiangsu University, 301 Xuefu Road, Zhenjiang 212013, China

[b] *Institute of Green Chemistry and Chemical Technology, School of Chemistry and Chemical*
Engineering, Jiangsu University, 301 Xuefu Road, Zhenjiang 212013, China

1. Acceptance probability of the new state.

The acceptance probability p of the new state is as follows:

$$p=\min\{1, \exp(-\Delta E/kT)\}, \qquad \Delta E=E_2-E_1$$

here E_1 represents the total energy of molecular configuration before motion, and E_2 represents the total energy of new molecular configuration after motion. Then, the difference of E_1 and E_2 is calculated to judge whether the motion is accepted or not. If the total energy of the new configuration is lower than that of the original configuration, the motion is accepted. On the contrary, if the total energy of the new configuration is higher than that of the original configuration, it is necessary to calculate the Boltzmann factor $\exp(-\Delta E/kT)$ and generate a random number at the same time. If the random number is greater than the calculated Boltzmann factor, the motion is rejected; if the random number is less than the calculated Boltzmann factor, the motion is accepted.

2. Energy parameters used in this work.

Three energy parameters, E_c, E_p and E_b, are introduced in the simulation. E_c is the energy change caused by non-collinear connection of two consecutive bonds along the chain, reflecting chain semi-flexibility. E_p is the energy change owing to the nonparallel arrangement of two adjacent bonds, corresponding to the driving force for

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[*] Corresponding author. E-mail address: haotf@ujs.edu.cn, nieyijing@ujs.edu.cn.

polymer crystallization. E_b is the energy change caused by the existence of monomer-nanocylinder pairs, which reflects the interaction between different components. When investigating the effect of free chain contents and nanocylinder sizes, E_b is not introduced into the systems, so the energy criterion of Metropolis sampling in the simulation is as follows:

$$\Delta E=cE_c+pE_p$$

where c is the net number of non-collinear connection pairs of continuous bonds and p is the net number of nonparallel packed pairs of bonds. When investigating the effect of interface interactions, the energy criterion of Metropolis sampling is as follows:

$$\Delta E=cE_c+pE_p+bE_b$$

where b is the net number of pair contacts between monomers and nanocylinder interfaces. The value of E_b/E_c is set to 0, -0.5, -1.0, -1.5 and -2.0 to study the effects of interface interaction on the crystallization of confined polymer system and the value of E_p/E_c is set to 1 to make chains have a proper flexibility at crystallization temperature. The negative value of E_b/E_c represents the attraction between the monomers and nanocylinder interfaces.

3. Unconfined systems.

In order to compare with the crystallization behavior of confined polymer system, the crystallization behavior of two groups of unconfined polymer system is simulated. The molecular chains are directly put into the simulation box to study the crystallization behavior of unconfined polymer system. In order to compare with the crystallization behavior of confined polymer systems (D=8 and D=12), the simulation boxes of the two groups of unconfined systems are set at 128 × 8 × 8 and 128 × 12 × 12 lattice points. The number and length of molecular chains in the two groups of unconfined systems are the same as those in the corresponding confined systems. The evolution of the crystallinity as a function of MC time for unconfined polymer systems is shown in Fig. S1. The curve (a) and (b) show the change of crystallinity with MC time of the unconfined system in the simulation box with 128 × 8 × 8 and 128 × 12 × 12 lattice points, respectively. It can be seen that there is an obvious nucleation induction period in the unconfined polymer system.

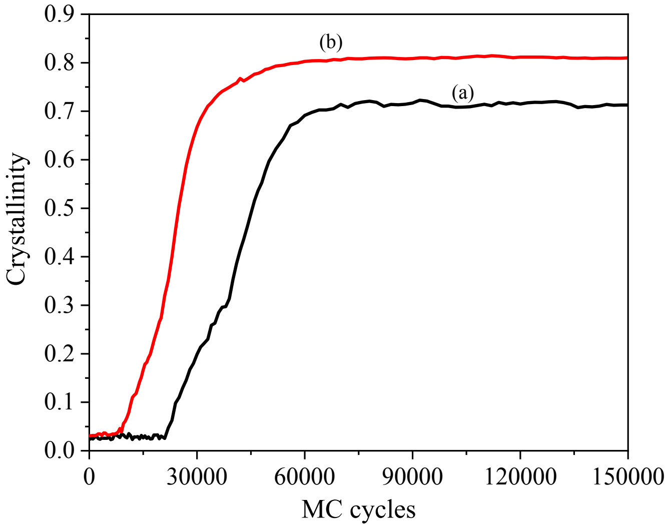

Fig. S1. Evolution of the crystallinity as a function of MC time for unconfined polymer systems in the simulation box with 128 × 8 × 8 (a) and 128 × 12 × 12 (b) lattice points, respectively.

4. Definition of orientational order parameter.

The orientational order parameter (P) is defined as following:

$$P = (3 < cos^2\theta > - 1)/2$$

where θ is the angle of crystal bonds relative to the long axis (i.e. X-axis) of the nanocylinder, and < > represents the average value of all corresponding crystal segments. When the value of P is -0.5, crystal rods are perpendicular to the long axis of the nanocylinder; when the value of P is 1, crystal rods are parallel to the long axis of the nanocylinder; when the value of P is 0, crystal rods have a random orientation.