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The effect of chain interpenetration on an ordering process in the early stage of polymer crystal nucleation

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Abstract

In the present study, the degree of chain interpenetration was considered as a structural attribute of the entanglements in polymer chain system. Inter-chain radial distribution function (RDF) was used to perform this measurement. We applied this method to a model system, in which an ordering process in the early stage of polymer crystal nucleation at the atomistic level was simulated by means of molecular dynamics (MD). Initial chain structures possessed different degrees of interpenetration and underwent the ordering process at 400 K. Obtained results indicated that at the nanosecond scale the degree of interpenetration impedes the ordering process remarkably, which agrees with the experimental observation at laboratory time scale. Such behavior among chains indicates that at the atomistic level a creeping polymer chain is able to recognize if the neighbor group on the 'tube' is from the same chain or other chains. This recognition manifests that the reptation time of a chain would be influenced by the 'tube' composition or the degree of interpenetration. It also showed that the degree of interpenetration changes little during the ordering process, which means that the motion of the chain segments is mainly predominated by the ordering process rather than further adjusting the entanglement extent under the conditions simulated.

Keywords: Molecular dynamics; Degree of interpenetration; Early stage of crystallization

1. Introduction

Entanglement among polymer chains, which derives from the long-chain topological connectivity, is a kind of the fundamental structure of polymer materials, and influences many properties [1–6]. The 'tube' model or reptation theory proposed by de Gennes [7] and Edwards [8] simplifies the complexity, gives a clear image of entanglement structure, and has been verified for a range of polymer systems. But as such detailed topological structure is difficult to be observed experimentally, the mechanism of its influence on material properties is still not well understood.

One of such unclear things is its effect on primary nuclei formation in polymer crystallization. Hoffman et al. nucleation theory [9,10], the mostly well known and adopted theory of the kinetics of polymer crystallization, introduced the reptation concept to consider the role of entanglements. Primary nuclei formation from the metastable undercooled state is still argued intensively [11], and the precise picture of nucleus formation remains unclear. Computer simulation methods can provide some insight into this subject. From the first work of Sundararajan's [12,13], to later works of Yang et al's. [14,15], Yamamoto's [16] and Muthukumar's [17–19], some desirable results have been obtained. However, none of these works related to the quantitative effect of chain entanglements on nucleus formation.

The effect of entanglements, which usually requires that polymer chains slide past but not through each other during motion, is mainly attributed to interpenetration among the chains. Although the interpenetration is not the entanglement itself, the interpenetration is logically a necessary condition for the system to demonstrate entanglement behavior, compared with compact single-chain globules without entanglement between chains. We propose that study of the degree of interpenetration may lead to a method for studying the extent of chain entanglements.

Our effort in recent studies [20,21] has been to seek a method to measure the degree of interpenetration by means of molecular dynamics (MD). We found that the inter-chain radial distribution function (RDF) is a good measure for it. Because of the limitation in the space and time scales, atomistic MD is

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presently difficult to use to simulate the nucleation process of bulk molten polymer. We think, in the early stage of the nucleation, there are many baby-nuclei in the system. The baby-nucleus occupies a domain of some nanometers size under a critical value. Chains in the domain suffer from an ordering process to become nuclear candidates in nanoseconds. If the size of the candidate is not beyond the critical value, and its activation energy is not enough to jump over the nucleation barrier, the ordered structure may melt again. Such ordering process occurring to a baby-nucleus in the early stage of the nucleation is just in a space and time scale, which can be simulated by atomistic MD.

In the present study, by characterizing the degree of interpenetration quantitatively through the inter-chain RDF, we investigated the influence of different interpenetration structures on the ordering process of the early stage of the nucleation. Using atomistic MD, we attempt to observe changes in the degree of entanglement from a new standpoint. Initial structures with different degrees of interpenetration were extracted from an interpenetration process of a few chain globules. The degree of order was measured by a bond orientation function. The influence of the degree of interpenetration on the ordering behavior during the process was then discussed.

2. Simulation method and model

In the present study, polyethylene (PE) with 600 CH_2 (CH_2 is approximated to united atom) in backbone, is used as the model chain. The force field parameters come from the Dreiding II force field [22]. The total potential energy E_{total} consists of four parts: (1) the bond-stretching energy E_{strech} for two adjacent united atoms, (2) the bond-bending energy E_{bend} among three adjacent united atoms, (3) the torsion energy E_{torsion} among four adjacent united atoms, and (4) the 12-6 Lennard-Jones potential E_{vwd} between two nonbonded atoms. This is expressed as

$$\begin{aligned} E_{\text{total}} &= E_{\text{bond}} + E_{\text{vwd}} \\ &= E_{\text{strech}} + E_{\text{bond}} + E_{\text{tersion}} + E_{\text{vwd}} \\ &= (1/2)K_b(R-R_0)^2 + (1/2)K_\theta(\theta-\theta_0)^2 \\ &\quad +(1/2)K_\phi(1-\text{d}\cos(3\phi))^2 + D_0[(\sigma/r)^{12} - 2(\sigma/r)^6] \end{aligned}$$

Where R is the bond length between two adjacent atoms, R_0 the equilibrium bond length, θ the bond angle between three adjacent atoms, θ_0 the equilibrium bond angle, ϕ the dihedral angle formed by four consecutive atoms, and r the distance between two nonbonded atoms. The cut off distance for the van der Waals interaction is 9 Å. The canonical Nose–Hoover molecular dynamics method is used in the simulations. The integration time step is set to 0.001 ps and the relaxation constant for the heat bath variable is 0.1 ps. All the simulations were performed in vacuum.

We here build two models, one containing two chains, the other containing six chains. In order to get polymer systems with various degrees of interpenetration, simulations of the interpenetration process for isolated chain-globules have been performed firstly. For the six-chain system, the simulation was performed for 18 ns at 1000 K and for the two-chain system, it was performed for 15 ns at 800 K (the temperature 1000 K and 800 K are much higher than the melt temperature T_m of PE in order to speed up the equilibrium period). The structures exacted from the trajectories with different degrees of interpenetration were separated into two groups, one with the higher (Group H) and the other with the lower (Group L) interpenetration. The degree of interpenetration was characterized through the inter-chain RDF, as discussed in detail in the following section.

3. Results and discussion

3.1. Acquirement of samples with different degrees of interpenetration

We have recently used the interchain RDF to measure the degree of interpenetration of polymer chain systems [20,21]. The interchain RDF shows the statistic probability of a group in one chain finding a group in another chain at various distances. The first peak intensity of the interchain RDF, which represents the population of a pair of groups from different chains as first neighbors, was used in monitoring changes in the interpenetration of chains. In the present study, we improved the expression of the degree of interpenetration as ζ

$$\zeta = \frac{G_{\text{AB}}(r_1)}{G_{\text{total}}(r_1)} \tag{1}$$

$$G_{\text{AB}}(r) = \frac{N_{\text{AB}}(r)}{N_{\text{T}}4\pi r^2 \text{d}r} \tag{2}$$

$$G_{\text{total}}(r) = \frac{N(r)}{N_{\text{T}}4\pi r^2 \text{d}r} \tag{3}$$

Here, r_1 means the distance corresponding to the first peak of inter-chain RDF. G_{AB} and G_{total} are the RDF between

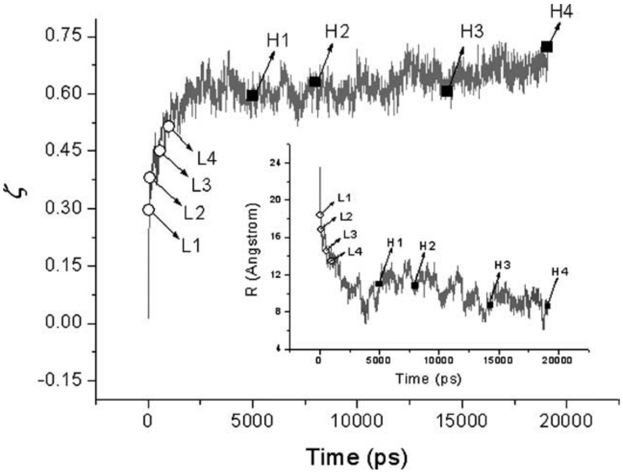

Fig. 1. The variation of the degree of interpenetration during the interpenetration process of six chain-globules. The insert is the average distance between chain mass centers versus simulation time. Hollow circles: Group L; solid squares: Group H.

different chains and the RDF of all chains, respectively. N_T stands for the total pairs of CH_2 in the system. $N_{AB}(r)$ is the number of the group pairs with one in chain A and the other in chain B separated by r. $N(r)$ is the number of the group pairs with the interval of r and not distinguishing whether the two groups are in the same chain or not.

Fig. 1 gives the variation of degree of interpenetration ζ during the interpenetration process for the six-chain system.

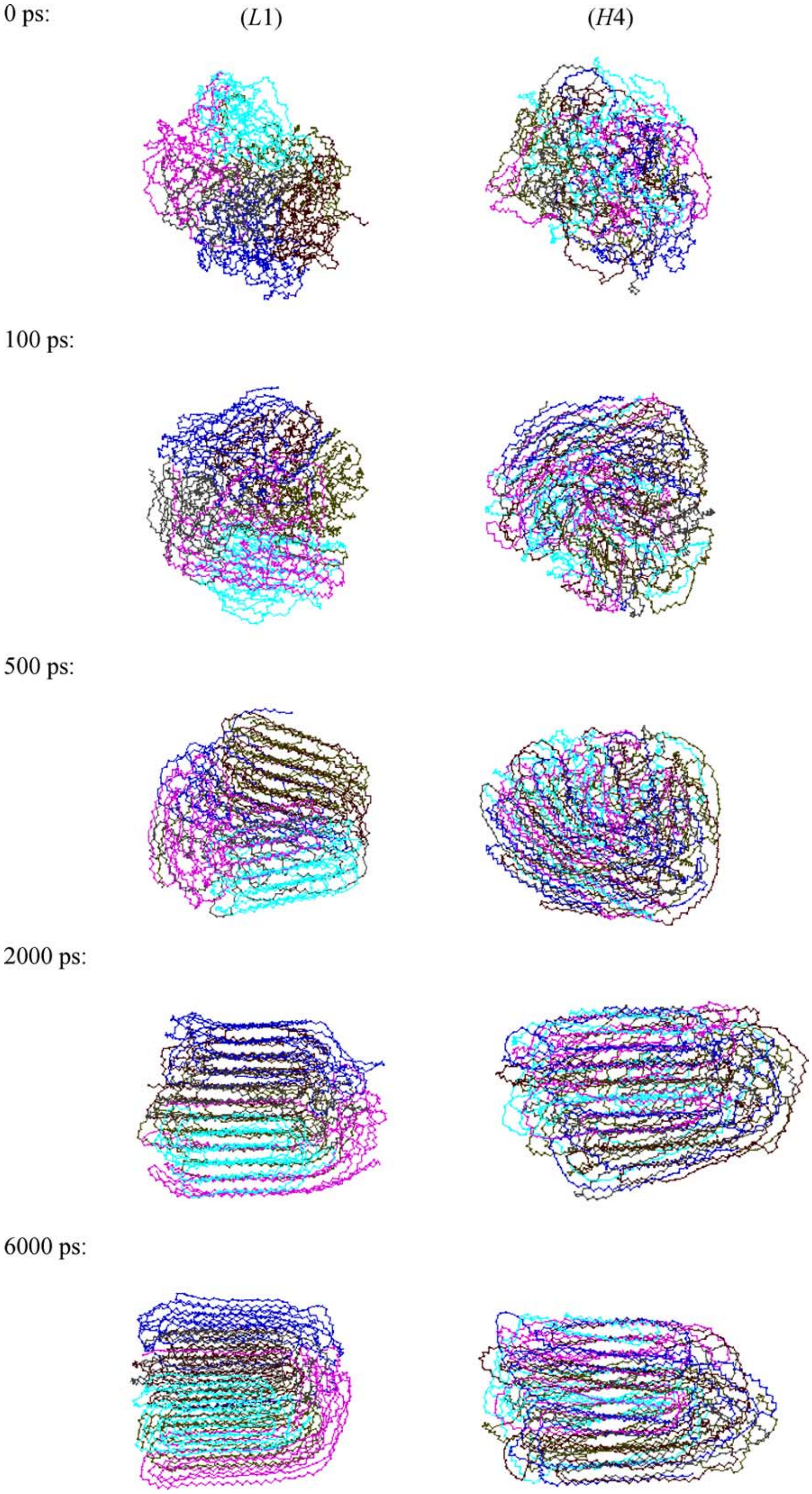

Fig. 2. The side view morphologies of the examples in two groups (Group L and Group H) during ordering process of six-chain system.

The inserted figure shows the mean distance variation of mass centers of each pair of chains with the simulation time. From the trajectory of the interpenetration process, eight structures have been extracted and divided into two groups: Group L with lower degrees of interpenetration (L1–L4), and Group H with the more completed and uniform interpenetration states (H1–H4), shown as the hollow and solid points, respectively, in Fig. 1. Here, it should be noted that for the structures extracted, as all the chains have been fusing into one approximate globule shape, there are differences only in the degree of interpenetration among chains, without considering the contribution of surface tension. Using the eight structures in two groups as the initial ones, the simulations have been performed at 400 K in 6 ns, respectively. For the two-chain system, we also selected two groups of structures, l1–l4 and h1–h4, as initial states and carried out the simulations in 8 ns under the same conditions.

3.2. The morphologies in the ordering process

In the absence of impurities or seed nuclei, the simulations concern the early stage of homogeneous primary nucleation. Fig. 2 shows two typical sequences of images depicting this event, one is the example from Group L (L1) and the other from Group H (H4) from six-chain system. The images indicate the process of chains going from random to order.

One interesting thing found here is that for both groups, several local order domains appear in the early stage, most of which are located at the surface and have different orientations of their domain directors, as seen in the morphologies at 100 ps in Fig. 2. These domains then merged into several larger ones by 500 ps, until finally they become one ordered region over the whole system (shown at about 2000 ps). The following stage is the cooperative readjustment of the segments. Comparing the two examples in Fig. 2, we found that the final lamellar structures of the former (L1) appear more perfect in orientation than those of the latter (H4). This obviously arises from the smaller interpenetration among chains in the initial structures.

Fig. 3 shows the top view of the final structures of the examples from the two groups in the ordering processes, ‘A’ from six-chain and ‘B’ from two-chain system. These images clearly indicate that when chains form a primary nucleus, the system with slight chain interpenetration at beginning, like the samples L1 and l3, still possess lower interpenetration. From the top view, one sees the ordered structures in direction of the chains, and different chains in different colors, the colors in L1 and in l3 appear in different domains. These look like morphology of phase separation when comparing with H4 and h4, which have their colors relatively even distributed, indicating that they are seriously interpenetrated chains, though they all become highly ordered.

3.3. The effect of the degree of interpenetration on the ordering process

The analysis of potential energy (Fig. 4(A)) and the fraction of trans conformation (Fig. 4(B)) evolution versus simulation time for the six-chain systems show that the potential energy of Group L is lower than those in Group H, and the fraction of trans-conformation is a little higher in the process. As

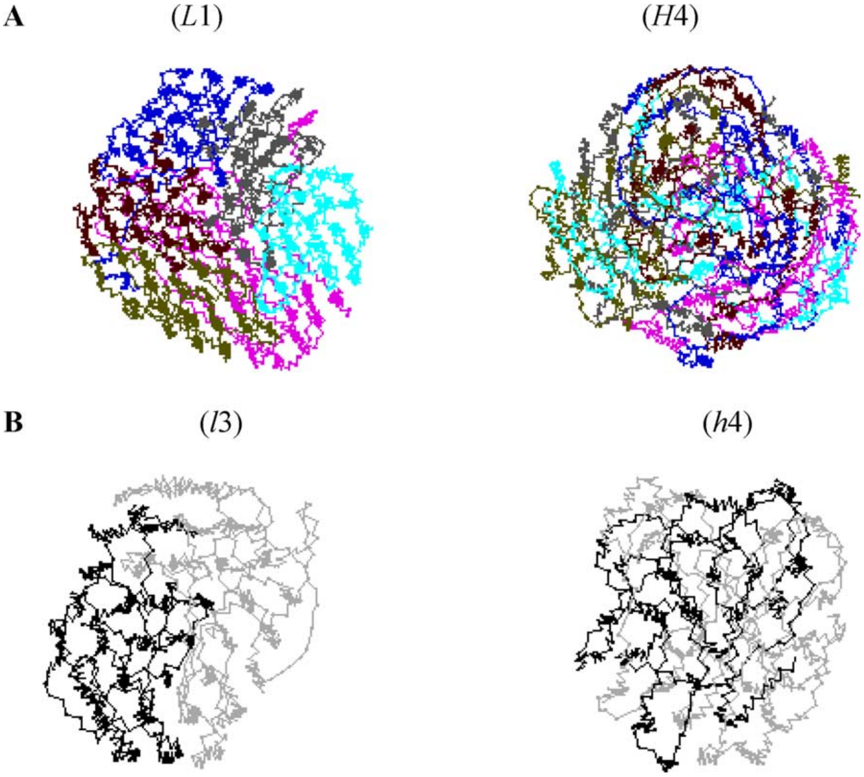

Fig. 3. The top view morphologies of the examples in two groups at the final moment. (A) Six-chain systems; (B) two-chain systems.

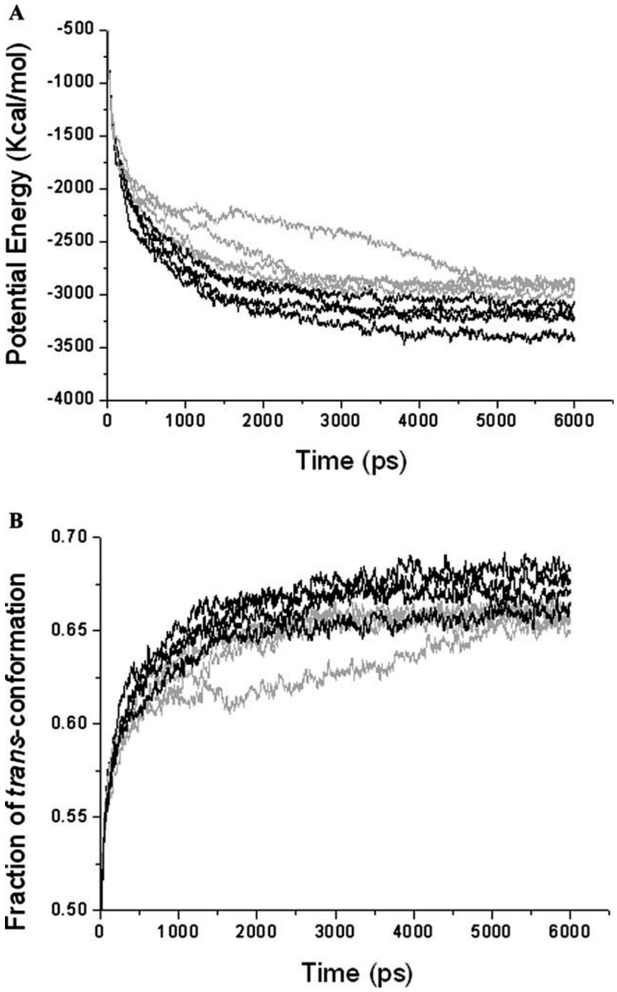

Fig. 4. (A) The potential energy as the function of simulation time. (B) The fraction of trans-conformation versus simulation time. Black lines: Group L; light gray lines: Group H.

mentioned above, what we studied here is an instantaneous ordering process in the early stage of the nucleation with a size too smaller to be a crystal. In this case, the degree of order can be expressed by chain segment orientation. The orientation is usually described by the order parameter P_2:

$$P_2 = \frac{\langle 3\cos^2(\varphi) - 1 \rangle}{2} = \frac{3}{2}\langle (\mathbf{e}_i \cdot \mathbf{e}_j)^2 \rangle - \frac{1}{2} \tag{4}$$

$$\mathbf{e}_i = \frac{(\mathbf{r}_{i+1} - \mathbf{r}_{i-1})}{|\mathbf{r}_{i+1} - \mathbf{r}_{i-1}|} \tag{5}$$

Where $\boldsymbol{e}_i$ is the orientation vector of the ith group along the chain backbone, $\boldsymbol{r}_{i-1}$ and $\boldsymbol{r}_{i+1}$ stand for the coordinate vector of the i-1th and the $i+1$th groups. By calculating the angles ϕ between various orientation vectors and performing the average over all the possible angle values, according to formula (5), the value of P_2 at any time can be obtained [17,23].

Fig. 5 shows the variation of P_2 with simulation time for the two group samples of the six-chain system, and it shows a similarity to the two-chain system. As shown in Fig. 5, P_2 of Group L with less entanglement shows a relatively more rapid increase in the ordering process than that of Group H. When the curves reach the plateau region, the values of P_2 of Group L are obviously higher than those of Group H. The data given in Fig. 5 demonstrate that entanglements, which are stored in the interpenetrated structures, hinder the sliding and diffusive motion of chain segments. It leads to less regular lamella. This causes the curves in Group H to be much lower than those in Group L, and to need more time to reach their plateaus.

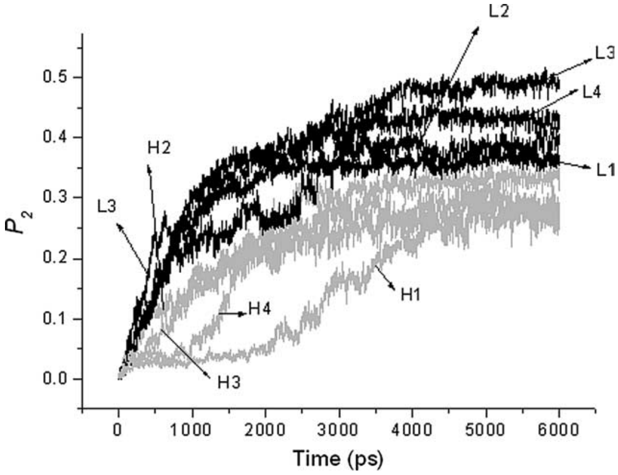

Fig. 5. The variation of P_2 during the orientation of chain segments. Black lines: Group L; light gray lines: Group H.

The results obtained here are much compatible with those studied in Bu et al. experiments [24,25]. Bu et al. showed that the crystallization behavior of single chain or pauci-chains is much faster than that of multiple-chain system like polymer bulk at low undercooling. These results give clear evidence that the interpenetration or the entanglement structure of polymer chains delays the ordering process and reduces the degree of order of systems. Our investigation shows that such a delay effect from the chain entanglement even works through a very wide time scale, from nanoseconds to seconds. To our knowledge, although it is so simple, no theory mentions such behavior, since the theories do not concern systems with different degrees of entanglement.

It is interesting that the chain motion is modulated by the degree of interpenetration. This indicates that the groups can recognize if its neighbor is from the same chain. What is the way where the chain can recognize each other? The answer should be in motion nature of polymer chains. In macroscopic time scale, reptation is the motion. In microscopic, say in picosecond, results obtained here and in the early studies [21,26] show that during chain dynamics the motion of each group along direction of the chain axis is much more stable than that in the perpendicular directions. This anisotropic motion stability indicates that movements of all groups in one chain are cooperative through the backbone bonds. Simulation of the ordering process here gives that such cooperativity is

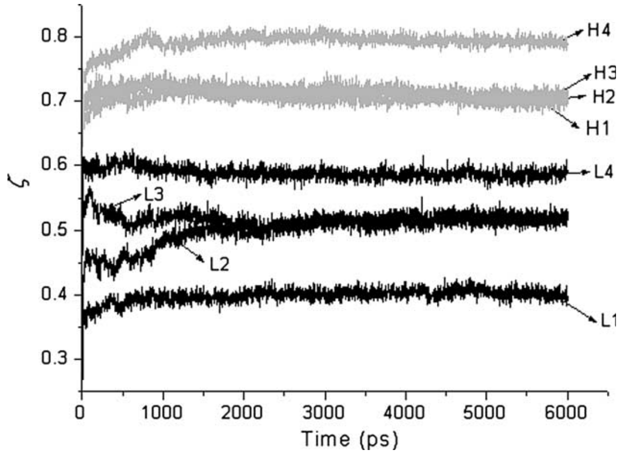

Fig. 6. The degree of interpenetration versus simulation time during the orientation of chain segments. Black lines: Group L; Light gray lines: Group H.

seriously blocked by the interpenetration or the entanglement among chains.

3.4. The degree of interpenetration during the ordering process

It is useful to monitor the variation of the degree of interpenetration during the ordering process. The present study provides such a chance.

Fig. 6 gives the variation of the parameter ζ of two group samples as a function of time for the six-chain model system. The curves show that for Group L, during the ordering process, the degree of interpenetration is still much less than that of the systems in Group H. All the curves reach plateau in a very short time, usually less than 1 ns, and their variation with time is very small.

We suggest that in such simulations there is a competition between two free energy driven processes: the chains orientation and the interpenetration. In our early work [12], we measured free energy evolution in the interpenetration process, and proved that it is a spontaneous process driven by conformational entropy. As is well known, the orientation process is also a spontaneous process driven by the enthalpy. This difference results in a competition.

If the interpenetration process were to dominate the whole process, Group L would increase their ζ in the process, and would ultimately cancel the difference Δζ between the two different groups. However, this was not observed. Under 1 ns, most of the curves in Fig. 6 increase to some extent, and a few decrease, and after 1 ns all the curves remain almost constant. On average, there is no evident change in ζ. This observation manifests that on the contrary the orientation process dominates the whole process under the conditions simulated, and the ordering and adjusting movement of chain segments occurs in situ.

Obviously, a temperature variation will trigger a different competition in the system. Such results will be published in the near future.

4. Conclusion

In the present study, we proposed a method to measure the degree of interpenetration among polymer chains. Since, the interpenetration is a necessary structural attribute for a system having the entanglement behavior, this measure was expected to gain insight into the structural nature of chain entanglement at atomistic level. The present study applied such a method to a model system, in which an ordering process in the early stage of the polymer crystal nucleation was studied.

Using atomistic level MD, initial structures with different degrees of chain interpenetration were prepared. The simulation of the ordering processes for these structures was performed at 400 K. The order parameter P_2 and degree of interpenetration ζ obtained during the simulation show that the degree of interpenetration influences the ordering process tremendously, even at the nanosecond scale when comparing with experimental observation at the laboratory time scale [25]. The results indicate that at the atomistic level the polymer chains are able to recognize each other. If we consider the chain motion here as the short scale portion of whole chain reptation, this infers that the reptation time of chains would be influenced by the degree of interpenetration.

The results obtained also show that the degree of interpenetration changes little during the ordering process. This means that the motion of chain segments is mainly predominated by the orientation process without further interpenetration or de-interpenetration under the conditions simulated.

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