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Effect of molecular weight on the interpenetration of polymer chain-globules

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Summary

Molecular dynamics simulations were performed to investigate the influence of molecular weight on the interpenetration process of two initially isolated globule-chains. From molecular weight lower and higher than the critical molecular weight, the analysis of the simulation result indicate the duration of interpenetration has the relationship with chain length: $\tau \sim N^2$, which is different from that of the relaxation time in reptation model. It also shows that the interaction between chains measured by the mean force increases with the increment of chain length, and a turning point was found at the position corresponding to the critical molecular weight. Before the turning point, the mean force increases fast versus molecular weight, and after that the increase turns to be slow. Through correlating the simulation result with the experimental tensile strength of polymer films, it shows that the interpenetration of the chain segments with critical molecular weight is necessary for the formation of entanglement structure.

Introduction

Entanglement among chains, based on the idea that segments may slide past but not cut through each other due to long chain connectivity, has been considered as one of the fundamental structures in amorphous polymer materials, and this structure not only leads to the unique viscoelastic property, but also influences the temperature of glass transition [1,2], crystallization rate and temperature [3] and others. The “tube” model (or reptation theory) proposed by de Gennes [4] and Edwards et al [5] has simplified the complicated concept and gives a clearly entanglement structure image, and has been verified for a range of polymer systems. And recently, Kröger has proposed an algorithm to measure the degree of entanglements quantitatively [6]. While how this special structure generates microscopically is still not understood well, as experimentally it is difficult to observe the topological structure directly.

As entanglement structure of polymers arises from the inter-chain penetration, therefore, its formation is closely related to the interpenetration state among chains. The film formation from polystyrene latex particles by the interdiffusion of chains is a good example to understand this. Yoo et al [7] found that, when the penetration depth of adjacent latex particles reaches a distance around the radius of gyration of chain with the critical molecular weight, the tensile strength meets an elbow. Our recent work [8,9] has attempted to investigate the origin of entanglement from the view of interpenetration by means of Molecular dynamics (MD), and we found that the interpenetration process of two compact isolated polymer globule-chains in vacuum (as shown in Figure 1) is driven by conformational entropy, and the dynamic behavior of chains is different from that in bulk. So we think the investigation of inter-chain penetration is a convenient way to understand the onset of entanglement.

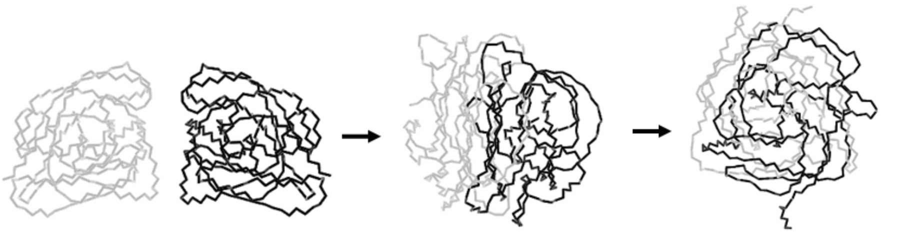

Figure 1. The schematic of the interpenetration process of two isolated compact chain globules.

For linear polymers, as long as the molecular weight of chain is more than a certain value, the influence of entanglement on material properties shows up. Experimentally, the appearance of plateau modulus for various species in the melt state is one expression of entanglement effect, and the corresponding molecular weight is termed entanglement molecular weight M_e; another particular importance characteristic of entanglement is the crossover of zero shear viscosity η_0 from $\eta_0 \sim M$(low molecular weight) to $\eta_0 \sim M^{3.4}$(high molecular weight) rheologically, and the crossover between the two regions is determined by critical molecular weight M_c. For M_e and M_c, different scaling laws have been reported by Kröger [10]. Generally, the relaxation time of chain with M_e is named entanglement time τ_e [11], and that for longer chain is called disentanglement time τ_d, which is comparative to the reptation time in "tube" model. Our effort is from the view of interpenetration among chains to investigate the onset of entanglement, so the study of the molecular weight dependence of inter-chain penetration is important to understand its relationship with entanglement, and it is the aim of the present work.

In this paper, following the previous work [8,9], the interpenetration of two isolated globule-chains with different molecular weight has been simulated by means of molecular dynamics. The two collapsed chains separate with the distance between the nearest edges about 5 Å initially, a little larger than the radius of van der Waals interaction of group CH_2. As our attention focuses on the inter-chain penetration process, so those unsuccessful cases that two chains depart away from each other are not included in our analysis. The molecular weight dependence of duration of interpenetration, as well as of the interactive mean force between chains, has been reported. The formation of entanglement and the interpenetration between chains has been connected.

Model and Details

The Cerius2 4.0 software was used in this work for building polymer structure, and performing energy minimization and molecular dynamics simulations. The linear polyethylene was used as model chain, where the CH_2 and CH_3 were approximated to united atoms. The potential energy function consists of bond length, bond angle, torsion and van der Waals interactions. The force field parameters came from Dreiding II [12], and the non-bonded cutoff distance was 9 Å. The canonical (constant NVT) Nose-Hoover method was adopted. The integration time step was 2 fs and the relaxation constant for the heat bath variable was 0.1 ps. The interval of recording the trajectory data is 1 ps. The simulation temperature was set at 600K, much higher than the melting point of PE, in order to get the system reach equilibrium stage as soon as possible. No external force was used and all simulations were carried out in vacuum.

In the present study, the model adopted is a two-chain system. After each chain collapsed into a compact globule from an all-trans backbone conformation by MD simulation in vacuum, such two globules apart from each other with the nearest edge distance of ~5Å were used as the initial structure in the simulation of the interpenetration process. Several cases of chain length were investigated, where the backbone of chain contains 50, 100, 200, 250, 300, 400, 500, and 600 CH_2 groups respectively and the corresponding simulation time for each is 1 ns, 5 ns, 10 ns, 10 ns, 12 ns, 14.8 ns, 23 ns, and 24 ns.

Results and Discussions

Duration of interpenetration

The first that our attention paid on is the time necessary for the uniform interpenetration. Before referring it, we mention the method used to characterize the degree of interpenetration — the intensity of first neighboring peak of the inter-chain radial distribution function (RDF), which has been successfully used in our previous work [8,9].

For a system containing two chains, each can be labeled as chain A and chain B respectively, the inter-chain RDF can be expressed as

$$G_{AB}(r) = \frac{N_{AB}(r)}{N_A N_B 4\pi r^2 dr} \qquad (\mathbf{1})$$

where N_A and N_B stand for the number of CH_2 groups in chain A and chain B, and $N_{AB}(r)$ denotes the total number of CH_2 pairs in which the two groups belong to different chains and are apart from a distance of $r \sim r+dr$. The inter-chain RDF describes the distribution of the probability that CH_2 in one chain finding another one in another chain apart with various distances, providing the statistical mixed information of systematic structure at atomistic level. Inter-chain RDF analysis shows that the first neighboring peak of the curve, which was located at about 5 Å, varies with the evolution of simulation time [8]. In bulk amorphous polymers, segments are closely packed with the typical inter-chain separation of CH_2 group for polyethylene being about 5 Å [13,14]. On this basis, the intensity of the first neighboring peak of inter-chain RDF can characterize the neighboring extent of different chains, i.e. the degree of interpenetration.

Figure 2 shows the intensity of the first neighboring peak of inter-chain RDF versus simulation time for the sample system that chains contain 250 CH_2 in backbone (each point is the average value of 100 recording data). It was found that when this parameter meets plateau, the interpenetration process has been completed more than

~85% [8], therefore, we consider that the dynamic penetration reaches approximately equilibrium stage, and call the time region "duration of interpenetration τ". Figure 2 shows that for the chain with 250 CH_2 in backbone, the duration of interpenetration τ is about 4400 ps. This quality for the cases of other various chain lengths was shown in Figure 3, which indicates that the longer the chains are, the more time their interpenetration needs to complete. In other words, the chains of lower molecular weight interpenetrate each other more easily. This is consistent with Arda and co-worker's study [15], in which the processes of the film formation by the inter-diffusion of latex particles for high and low molecular weight were monitored by using a UV-visible technique.

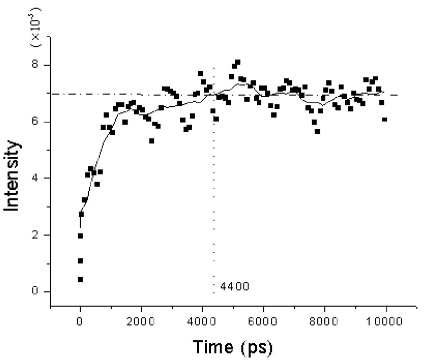

Figure 2. The intensity of the first neighboring peak of inter-chain RDF as a function of simulation time for the chains with 250 CH_2 in backbone.

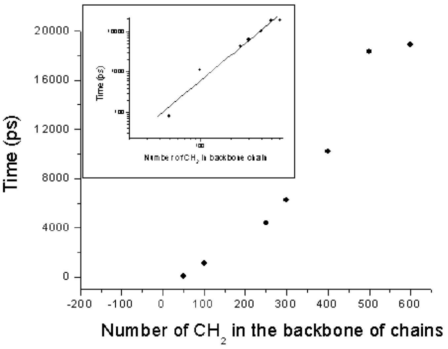

Figure 3. The duration of interpenetration time versus the length of polymer chains.

In Figure 3, the inserted shows the data again with both logarithmical axes. In this figure, the slope of the fitting line for the data is ~2.0. It means in the studied systems, the relation of chain length N and the duration of interpenetration τ, can be described as

$$\tau \sim N^2 \tag{2}$$

This power relation looks similar with that of the relaxation time versus N in Rouse model, but it covers the range of the molecular weight from 700 (50 CH_2 in backbone) to 8400 (600 CH_2 in backbone), through the critical molecular weight $M_c \approx 4000$. We also should note that, τ here is different from the relaxation time in reptation model (in that model, the relaxation time is proportion to the cube of chain length). As discussed in earlier work [9], the dynamic behavior of two globule-chains interpenetration was different from that of chains in bulk, because the two-chain system possesses higher surface energy and the end groups always float on the surface of the system, losing the capacity of leading chain reptating through other polymer chains. Therefore, the molecular weight dependence of the duration of interpenetration shows different power relation from that of the relaxation time in reptation model.

The mean force

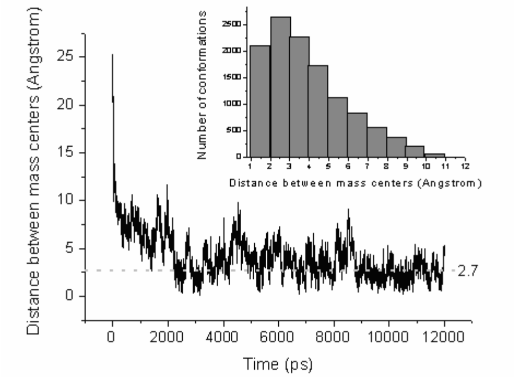

Figure 4. The variation of distance between mass centers of two globules with the simulation time for the chains with 300 CH_2 in backbone. The inserted is the number population of conformation pairs with the distance between mass centers.

Another property that we investigated is the mean force, which shows the interaction between the two chains and relates to free energy of system. As we know, in canonical ensemble, according to the thermodynamic first and second laws, the increment of Helmholtz free energy is related to the work made by the environment. In our case:

$$\Delta A = \Delta U - T\Delta S = -W \tag{3}$$

For minute change of the distance between two chains, the tension of the system can be obtained from the change of free energy

$$f = \left(\frac{\partial A}{\partial r}\right)_{T,V} \tag{4}$$

This measurement was also elaborated in our earlier work [8]. It displays inter-chain interaction and is consistent with the concept of the potential of mean force. When the two chains being apart from each other with a distance of r, one chain will apply a force on the other. This force is a sum of forces of every pair atoms between the two chains. Since with a certain distance one chain has thousands of conformations, each conformation would be applied a different force on another chain from another conformation. Therefore, for a distance of r, if the contribution of the ith pair of conformations is $f_i(r)$, the forces for all of the number of conformation pairs, say n, within the globule have an average value, which we call the mean force:

$$<f(r)> = \frac{1}{n}\sum_{i=1}^{i=n} f_i(r) \tag{5}$$

We have to obtain the mean force as a function of r. However, during the simulation, we cannot fix r between chains to get all the conformations from dynamics. As shown in Figure 4, the distance between mass centers fluctuates markedly with the simulation time. Then, for each interval distance of 1 Å, a number of pair conformations can be collected from the trajectory. Averaging the force and the distance of these conformation pairs, the statistic approximate value of mean force for the corresponding distance can be obtained. The inserted in Figure 4 shows the number population of conformation pairs for each interval distance. As the mean force indicates the tension between the two interacting chains, this quality is comparable to the macroscopic tensile strength of polymer materials. In the following, the mean force is discussed with the tensile strength in experiments.

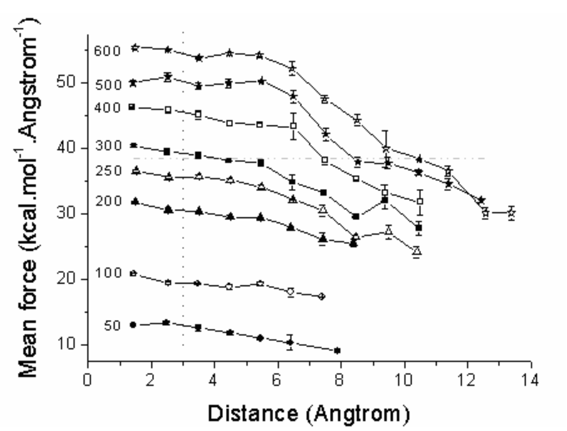

Figure 5. Mean force of two chains interaction versus the distance between mass centers.

Figure 5 shows the variation of the mean force with the distance between mass centers for the cases of chains of various lengths. For each case, with the distance between mass centers increasing, the mean force declines, in other words, the interaction between chains decreases. The measurement of distance between mass centers roughly indicates the degree of interpenetration between two chain-globules, as discussed in previous work [9]. Therefore, Figure 5 indicates that the higher degree of interpenetration is encountered, the larger interaction generates. It means if the chains have higher degree of penetration, it needs more force to drag them away from each other. Namely, the polymer materials with well interpenetration among chains have a larger mechanical strength. This result lets us view the chain entanglement through a new window. It is consistent with Shen et al's experimental work [16], where the atactic-polystyrene films cast from solution of different concentrations were prepared. The films obtained by this method contained different degrees of interpenetration corresponding to various initial concentrations. It was found the tensile strength of the films increases with the increment of solution concentration. In Yoo and co-workers' experiments [7,17] about the film formation from polystyrene latex particles, the relationship between the actual depth of particles penetration and the tensile strength buildup has been investigated via SANS, the results also showed that before the ultimate value was reached, the tensile strength increased with the depth of the interdiffusion of polymer chains among neighboring particles. Although comparing these experiments, our simulated systems are much smaller in length scale, we believe the results obtained here can provide some microscopic interpretation for the experiments.

Figure 5 also displays that the interaction between chains increases with molecular weight. The result can also be compared with the experiments [7,17], although one particle in these experiments might involve more than one chain: when the same depths of the inter-diffusion were reached, the tensile strength for chains with high molecular weight was larger than that for chains with low molecular weight. The data in Figure 5 also show the similar trend in the mean force.

The turning point

As mentioned in the above section, the mean force is approximately obtained by averaging the forces of the collected conformation pairs at various distances between mass centers. In Figure 4, it shows the distance between mass centers versus the simulation time for chains with 300 CH_2 in backbone, and the level line indicates that when the simulation reaches about equilibrium stage, the distance between the two mass centers fluctuates around 3 Å. The inserted figure, which shows the number population of conformation pairs versus the distance between mass centers, also indicates that the largest number is at about 3 Å. It means around 3 Å is of the two chains in a well-interpenetrating state and the mean force at this distance is most exact. For all cases of different molecular weights, the measurement of the distance between mass centers with simulation time displays the same characteristic: all of the cases show that when interpenetration reaches equilibrium, the distance of mass centers is about 3 Å. In principle, for the systems we investigated contain only two chains, they would penetrate uniformly in equilibrium, that is, the distance between mass centers should be zero thermodynamically. But in our study, the temperature 600K is much higher than the melting point, the chains move fast, so this distance, the scalar quantity, fluctuates around a balanced value, ~ 3 Å. Hence, we extract the data of the mean force at this particular distance from Figure 5 and show them renewedly in Figure 6.

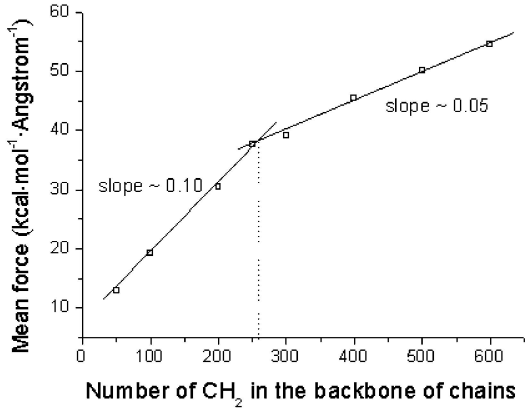

Figure 6. Molecular weight dependence of the mean force between two chain-globules at around 3 Å between mass centers.

Unexpectedly, it was found that the mean force displays a turning point with the increase of chain length. As shown in Figure 6, before the turning point or for low molecular weight, the slope equals about 0.10, and for high molecular weight or after the turning point, it turns to ~0.05. Crossover of the two lines (which are guides to eyes) occurs at around the position corresponding to critical molecular weight M_c (for polyethylene, M_c is about 4000, i.e. ~280 CH_2 in backbone [18]), and the corresponding mean force is ~38 kcal(mol·Å)$^{-1}$. This means that in such fully interpenetrated two-chain system, the interaction of the two chains depends on the molecular weight and shows up a rushed increase to meet the turning point. Since critical molecular weight is the characteristic quality for the generation of entanglements, so from the results here we believe that full interpenetration of chains with critical molecular weight is necessary to form entanglement structure, and that when the system has such strength, it possesses basic entanglement effect of polymers. In Yoo et al's experiments [7], the molecular weight of the polystyrene latex particles is much higher than the critical molecular weight. The measured tensile strength increases with the penetration depth of particles and an elbow appears around 45-50 Å, comparative to the radius of gyration of the polystyrene with critical molecular weight. It implies that when the molecular weight is beyond M_c, only the segments involved in the interpenetration are more than critical length, the system can possess enough strength to form entanglement structure. Combining the experimental results, we can conclude that in spite of the chain length, the interpenetration of the segments with the beyond critical molecular weight is the necessary structure for the onset of chain entanglement.

Obviously, polymer interface healing or polymer welding, especially the formation of film from the annealing of the latex particles, are closely related to the present study of the interpenetrating process of isolated globules. The results in this investigation will provide new insight into the origin of entanglement from the view of interpenetration among chains.

Conclusions

Influence of molecular weight on the interpenetration of two isolated globule-chains has been studied by means of molecular dynamics simulations. The results indicate that the duration of the interpenetration and chain length have the relationship $\tau \sim N^2$, different from that of the relaxation time in reptation model, which may be caused by different diffusion behavior of chains. The mean force has been calculated approximately to measure the interaction between chains. It increases with the increment of chain length and shows a turning point at the position corresponding to the critical molecular weight. The results have been compared with the related experimental data and it indicates that the interpenetration of the chain segments with critical molecular weight is necessary for the formation of entanglement structure.

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