

Biased hooking for primitive chain network simulations of block copolymers

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Abstract

Primitive chain network model for block copolymers is used here to simulate molecular dynamics in the entangled state with acceptable computational cost. It was found that i) the hooking procedure rearranging the topology of the entangled network is critical for the equilibrium structure of the system, and ii) simulations accounting for the different chemistry, *i.e.*, with a biased hooking probability based on interaction parameter χ for selection of the hooked partner, generates a reasonable phase diagram.

1. Introduction

Though several simulation methods for block-copolymers have been developed and have achieved remarkable success, the dynamics of block copolymers in the entangled state has not been simulated so far. General molecular dynamics schemes including those with coarse-grained potentials (Murat *et al.*, 1999; Aoyagi *et al.*, 2002) are useful for glassy systems where local motions of the chains are dominant. However, long time phenomena due to the global chain motion cannot be addressed due to huge calculation costs. Simulations based on density functional methods (Fredrickson *et al.*, 2002; Shima *et al.*, 2003; Uneyama and Doi, 2005) and coarse-grained particle dynamics (Groot *et al.*, 1999) are powerful tools to predict the equilibrium phase structure as well as the phase separation kinetics for unentangled copolymers. However, workable methods for the entangled situation have not yet been developed.

For entangled polymers, sliplink based simulations (Hua and Schieber, 1998; Masubuchi *et al.*, 2001; 2004; 2006; Doi and Takimoto, 2003; Schieber *et al.*, 2003; Likhtman, 2005) are promising because of their higher level of coarse graining, which allows simulation of the global chain dynamics with acceptable computational cost. In particular the primitive chain network model (Masubuchi *et al.*, 2001; 2004; 2006) has been applied not only to linear polymers but also to branched polymers and polymer blends. Differently from other sliplink models, the primitive chain network model has real space assignment of the entangled network.

In this paper, the primitive chain network model was

examined for what concerns the network rearrangement procedure to be used for entangled block copolymers. In the model, the polymer chains are dispersed in space and represented by sequentially connected springs that stand for chain segments between consecutive entanglements. Chains are linked to one another by sliplinks representing binary entanglements. The chain dynamics is described by i) the 3-dimensional motion of the entanglement nodes, ii) the 1-dimensional transport of monomers along the chain path and iii) creation and destruction of the sliplinks at chain ends. Modifications of the basic model to be adopted for the case of block copolymers, on both the entanglement node motion and the monomer transport, have been recently proposed by Masubuchi *et al.* (2006). In this study, however, a detailed investigation on the effects of the procedure for creation and destruction of sliplinks was performed. Indeed, the topological rearrangement of the network significantly affects the global chain motion, and hence the equilibrium structure of the system.

2. Model and simulation

2.1. Kinetic equations

Although a detailed description of the primitive chain network model can be found in earlier studies (Masubuchi *et al.*, 2001; 2004; 2006), the model used in this work will be presented with all relevant equations so as to eliminate possible confusion among the various versions published during model development.

For motion of the entanglement nodes and for monomer transport along the chain, the physicochemical forces included in the kinetic equations are: friction force, elastic force, field force induced by the chemical potential gradient and random force representing thermal agitation. The

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equation of motion of the entanglement nodes (sliplinks) for blends and copolymers is written as

$$(\zeta_\alpha + \zeta_\beta)(\dot{\mathbf{R}} - \mathbf{k} \cdot \mathbf{R}) = 3kT \left[\frac{1}{b_\alpha^2} \left(\frac{\mathbf{r}_i - \mathbf{r}_{i-1}}{n_i - n_{i-1}} \right) + \frac{1}{b_\beta^2} \left(\frac{\mathbf{r}_j - \mathbf{r}_{j-1}}{n_j - n_{j-1}} \right) \right] - \nabla(n_{0\alpha}\mu_\alpha + n_{0\beta}\mu_\beta) + \mathbf{F} \quad (1)$$

Here \mathbf{R} is position of the sliplink, \mathbf{k} is the velocity gradient tensor, ζ is the friction coefficient of the segments linked by the sliplink, kT is thermal energy, b is monomer length, \mathbf{r} and n are end-to-end vector and monomer number of the segment, respectively, n_0 is the equilibrium mean value of n , μ is chemical potential and \mathbf{F} is the random force obeying the fluctuation dissipation theorem. Suffices α and β indicate types of monomers in the two entangled chain segments, *i.e.*, the two segments connected by a sliplink. The first term on the right hand side of Equation (1) (representing the elastic force) is modified if a block boundary exists on the segment i as

$$\mathbf{F}_i^{el} = \frac{3kT\mathbf{r}_i}{b_\alpha^2 n_{i\alpha} + b_\beta^2 n_{i\beta}} \quad (2)$$

The second term on the right hand side of Equation (1) stands for osmotic force due to surrounding polymers that are not directly entangled with the test chain. Hence the chemical potential is derived from the following free energy (the same of that for binary polymer blends)

$$F = F_{mix} + F_{vol} \quad (3)$$

$$F_{mix}/kT = \chi \phi_\alpha \phi_\beta \quad (4)$$

$$F_{vol}/kT = \begin{cases} \varepsilon \left(\frac{\phi}{\langle \phi \rangle} - 1 \right)^2 & \text{for } \phi > \langle \phi \rangle \\ 0 & \text{for } \phi \leq \langle \phi \rangle \end{cases} \quad (5)$$

where ϕ is the monomer volume fraction, χ is the Flory interaction parameter, and ε is a phenomenological modulus for incompressibility (Masubuchi *et al.*, 2004; 2006).

The 1-dimensional monomer transport along the chain is described by a rate equation for monomer exchange through a sliplink, which is written as:

$$\zeta_\alpha \frac{\dot{n}}{\rho} = \frac{3kT}{b_\alpha^2} \left(\frac{r_i - r_{i-1}}{n_i - n_{i-1}} \right) - n_{0\alpha} \nabla \mu_\alpha + f \quad (6)$$

where ρ is the average monomer density in the two segments given by

$$\rho = \frac{1}{2} \left[\left(\frac{n}{r} \right)_i + \left(\frac{n}{r} \right)_{i-1} \right] \quad (7)$$

Finally, the third term in Equation (6) is a 1-dimensional random force.

2.2. Network rearrangement

In addition to the motion of the sliplink and the transport

of monomers mentioned above, the polymer dynamics in this model is described by creation and destruction of the sliplink at chain ends. The sliplink creation and destruction introduce a change of topology of the network, and hence generate global motion and diffusion of the chains. In polymer blends and copolymers, such global motions are crucial both for phase separation kinetics and phase structure.

Creation and destruction of sliplinks are triggered by number of monomers at chain ends. If the monomer number in an end segment becomes lower than a certain minimum as a result of the monomer transport along the chain, it is assumed that the chain end undergoes disentanglement, *i.e.*, the sliplink at the end segment is destroyed. On the contrary, when the monomer number exceeds a certain maximum, the chain end hooks a partner segment from the surroundings, in a range of $a = b\sqrt{n_0}$, creating a new sliplink on the end segment. The number ‘‘window’’ employed in this study is

$$0.5n_0 < n < 1.5n_0 \quad (8)$$

The detailed algorithm for hooking and unhooking can be found in our earlier publications (Masubuchi *et al.*, 2001).

It should be emphasized that the adopted hooking rules have some effects on dynamics and miscibility, since the global chain motion is affected by the topological rearrangement. In earlier studies (Masubuchi *et al.*, 2001; 2004) the selection of the partner to be hooked was performed in a random manner and results on rheology of homo-polymers and phase diagram of blends were consistent with data. On the other hand, a modified procedure to select the hooking partner has been recently proposed for block-copolymers (Masubuchi *et al.*, 2006), whereby the hooking partner is accepted with a biased probability written as

$$p = \exp(-\chi n_0) \quad (9)$$

Here n_0 is the average between $n_{0\alpha}$ and $n_{0\beta}$. Note that for the case of homo-polymers Equation (9) becomes $p = 1.0$ since $\chi = 0$ and hence the biased probability proposed here reverts back to random hooking in homo-polymers.

The main purpose of this study is the investigation of the effects of the biased hooking on the equilibrium structures and phase diagram. We shall compare the results with and without the biased hooking rule described by Equation (9) after giving some detail on the simulations.

2.3. Simulations

Linear diblock copolymers with a total monomer number of $N = 20n_0$ were considered. For simplicity, the two chemicals composing the copolymers have the same characteristics, *i.e.*, b , n_0 and ζ are the same. The parameter ε in F_{vol} was always set to 0.5 according to the fact that the results for homo-polymers and blends are consistent with

established results when $\varepsilon < 1.0$. We chose a as the unit length, kT as the unit energy and $a^2 \zeta / 6kT$ as the unit time. Periodic boundary conditions were used, with a simulation box of 12^3 . The number density of the segments was fixed at 10.

3. Results and discussion

Fig. 1 shows snapshots with the random and the biased hooking for block ratio $\phi = 0.1$ and $\chi n_0 = 4.0$, after equilibration for 10,000 time units. It is apparent that the random hooking leads to a homogeneous state, while the

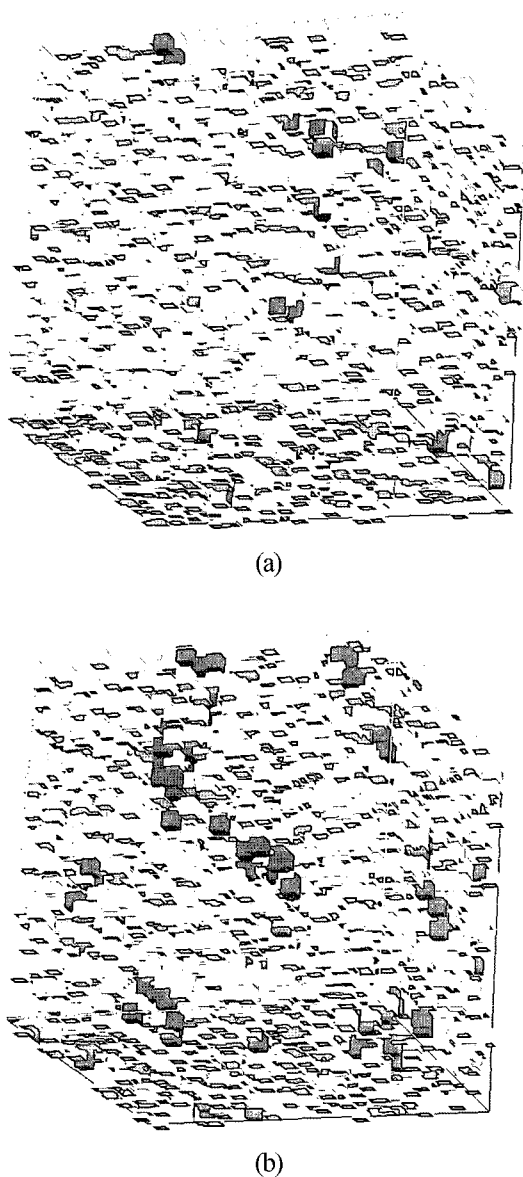


Fig. 1. Snapshot of linear block-copolymers with total monomer number of $20n_0$, block ratio $\phi = 0.1$ and $\chi n_0 = 4.0$, after 10,000 time units with (a) the random and (b) the biased hooking, respectively.

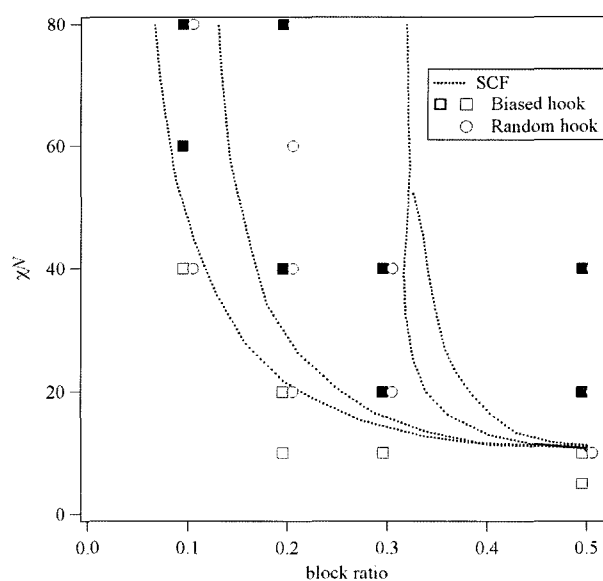


Fig. 2. Phase diagram of linear block-copolymers with total monomer number of $20n_0$. Squares and circles stand for the biased and the random hooking, respectively. Closed and hatched symbols represent immiscible state, while open symbols correspond to miscible state. Prediction by SCF calculation (Matsen and Bates, 1996) is also shown for comparison.

biased hooking generates a microphase separation. In Fig. 2, it clearly appears that the phase diagram obtained with random hooking is not consistent with self-consistent field calculations (Matsen and Bates, 1996) that have been established to predict reliable free energy. On the other hand, results obtained with the biased hooking mechanism are certainly more satisfactory.

We finally notice that random hooking, though certainly inadequate in the case of block copolymers, gives reasonable phase diagrams in the case of blends (Masubuchi *et al.*, 2004). A possible reason for these results is that the phase separated structures in copolymers and blends typically have largely different length scales. Indeed, in a phase separated blend, the characteristic length scale of the structure is typically much larger than the hooking range $a = b\sqrt{n_0}$, hence the effect of hooking is expected to be rather limited. On the other hand, for the case of copolymers, the characteristic size of the microphase structures is close to the hooking length scale a . Hence, random hooking (which favors miscibility) and biased hooking (which favors separation) can induce different equilibrium structures.

4. Conclusions

A biased hooking mechanism in the primitive chain network model was examined for entangled block copolymers and reasonable equilibrium phase diagrams were obtained,

showing microphase separation effects. The hooking mechanism is expected to affect the phase separation kinetics of copolymers (and probably of blends, too). Further investigation and quantitative comparison with experiments are in progress and the results will be reported elsewhere.

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