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Conformational Analysis in ABA Triblock Melts by Monte Carlo Simulation

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Introduction

It is well-known that block copolymers form spatially ordered microscopic structures under proper conditions owing to the self-assembly driven by the incompatibility between chemically linked blocks.[1,2] This tendency of self-assembly can be used for developing materials having specific properties related to its microstructure depending on the thermodynamics or the processing conditions. An example is provided by thermoplastic elastomers. One can design a thermally reversible microstructure consisting of domains of hard blocks in an elastic rubbery matrix, which leads to specific mechanical performance of the material.

Triblock copolymers of type ABA are one of the molecular species which can be applied for that purpose. Because of its molecular architecture, a triblock copolymer in the microscopically ordered structure is energetically favored to adopt one of two conformations. One is the “bridge” conformation connecting two different A-phases, and the other is the “loop” conformation where both A-blocks of the copolymer are in the same phase. These conformations play an important role in relation to mechanical properties. If block B is designed as the rubbery part, the bridge conformations form a network of connected domains consisting of hard A-blocks. For this reason, there has been considerable interest in the chain conformations of triblock copolymers with respect to the preferred conformation, “bridge” vs “loop”. In the strong segregation regime (SSR) the Alexander−de Gennes treatment, which assumes that all ends are located in the midplanes of the separated domains,[3,4] predicts that the free energies of loop and bridge conformations are identical so that there is no preference between these two conformations. However, a more sophisticated self-consistent calculation without the assumption of the Alexander−de Gennes treatment has demonstrated that the free energy of a loop conformation is lower than that of a bridge conformation.[5] A theoretical approach on the chain conformations in the weak segreagation regime (WSR) where existing theories assume that polymer chains behave as an ideal coil[6] has not been reported, and it becomes even more complicated, if possible.

In this paper, a brief report of a computer simulation study for the issue of “loop” vs “bridge” conformation in the weak segregation limit is presented. To address this, a dense system consisting of symmetric triblock copolymers, $A_{f/2}B_f\,A_{f/2}$ is simulated using the Monte Carlo method.

Model and Simulation

Symmetric triblock copolymer chains, A−B−A of $N = 32$ monomers consisting of $A_8B_{16}A_8$, are generated on a 40 × 40 × 40 cubic lattice with a volume fraction of polymer, $\phi_p = 0.8$. As usual in the lattice simulation, the interaction energy between monomers is modeled to be nearest-neighbor interaction. The interaction energy between monomer i and j, ϵ_{ij}, was taken to be $\epsilon_{AB} = \epsilon$ and $\epsilon_{AA} = \epsilon_{BB} = 0$, whereas the interaction with voids was assumed to be null so that the void acts as a neutral good solvent. The conformations of the polymer chains are self-avoiding and mutually avoiding walks to ensure excluded-volume effects.

The configurational space is sampled according to the dynamic Monte Carlo (MC) method using the Metropolis importance sampling[7] and slithering snake algorithm.[8] Here, it should be pointed out that the dynamics of slithering snake algorithm differs from the tube model known to be realistic for a dense system although it resembles some features of the latter model. In the tube model, the chain motion consists of two parts. One is the motion along the shortest path of the tube that is often called “primitive path”, and the other is a wriggling motion around the primitive path within the tube. In the slithering snake algorithm, on the other hand, such wriggling motion is absent so that the chain moves only along the primitive path. The dynamics of slithering snake algorithm is thus much faster than any other Rouse-type lattice dynamics. Using the advantage of this fast dynamics, the systems are equilibrated as follow. First, as an initial state, fully stretched polymer chains are relaxed under athermal condition. Starting from the athermal state, the temperature of the system was lowered very slowly with a small increment of $\Delta(N\epsilon/k_BT) = 0.1$. At each step with an increment of $\Delta(N\epsilon/k_BT)$, the system is allowed to equilibrate for 5×10^4 Monte Carlo steps (MCS). Therefore, as the temperature is lowered, the final configuration at the higher temperature was always used as a starting configuration to obtain a new configuration at a lower temperature. In this way of the equilibration based on a “very slow cooling”,[9,10] it is possible to produce a well-defined lamellar structure at low temperature as shown in Figure 1. For a reliable procedure of time average of conformational quantity from simulated configurations, the relaxation time of a conformational quantity should be estimated since the samples generated by the dynamic MC are correlated. The relaxation time of observable A can be numerically calculated from the correlation function of time series of observable $A(t)$ of m samples,[11,12]

$$\tau = \sum_{t=1}^{m} \rho(t) \tag{1}$$

$$\rho(t) = \frac{\overline{A(k)\,A(k+t)} - \overline{A(t)}^2}{\overline{A(t)^2} - \overline{A(t)}^2} \tag{2}$$

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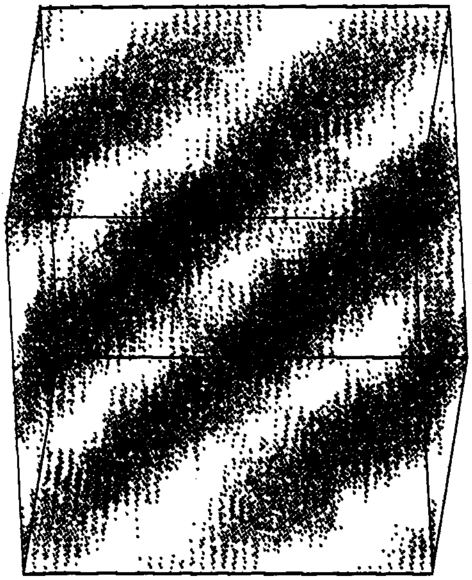

Figure 1. Snapshot of lamellar structure obtained at $N\epsilon' = 20$.

where

$$\overline{A(t)} = \frac{1}{m}\sum_{t=1}^{m} A(t), \quad \overline{A(t)^2} = \frac{1}{m}\sum_{t=1}^{m} A(t)^2 \tag{3}$$

$$\overline{A(k)\,A(k+t)} = \frac{1}{m-t}\sum_{k=1}^{m-t} A(k)\,A(k+t) \tag{4}$$

The number of observations, m, should be sufficiently large so that the correlation function $\rho(t)$ decays from unity to zero within the time series of m samples. As a choice of the observable $A(t)$ for a conformational relaxation time, τ_{conf}, the radius of gyration was used. After the system is equilibrated, the conformational quantity of interest was measured typically for $100\tau_{\mathrm{conf}}$ MCS and averaged over the time span by using the subblock-average method.[12]

Results and Discussion

To find the microphase separation temperature (MST) of the triblock copolymer system, the structure factor $S(q)$ of the system was calculated. Figure 2 shows the spherically averaged structure factor plotted against the absolute value of the scattering vector $\mathbf{q}$ for different values of the interaction parameter ϵ' $(=\epsilon/k_BT)$. At above $N\epsilon' = 10$, the shape of the structure factor becomes sharply peaked, which indicates that the system undergoes microphase separation. By calculating the structure factor as a function of ϵ', the location of the MST can be found by measuring the width at the half-maximum where the intensity of structure factor equals to the half of the maximum intensity. As the alternative, the MST can be also found by calculating the relaxation time of the dominant wave vector $\mathbf{Q}$,[13] as shown in Figure 3 where the width at the half-maximum intensity, W_h, and the relaxation time of $\mathbf{Q}$, $\tau_{\mathbf{Q}}$, are plotted as a function of $N\epsilon'$. The relaxation time $\tau_{\mathbf{Q}}$ is estimated by using eqs 1−4 with the time-dependent observable $\mathbf{Q}(t)$. Consistently, both curves of W_h and $\tau_{\mathbf{Q}}$ show an abrupt decrease (W_h) or increase ($\tau_{\mathbf{Q}}$) at $N\epsilon' = 10.5-11$, indicating that the system enters a critical region. From Figures 2 and 3, it is realized that the MST in this system is located at $N\epsilon' = 10.5-11$. In the following, the conformational behavior at $N\epsilon' = 0$ (above MST), 10 (near but above MST), and 20 (below MST) will be compared with each other.

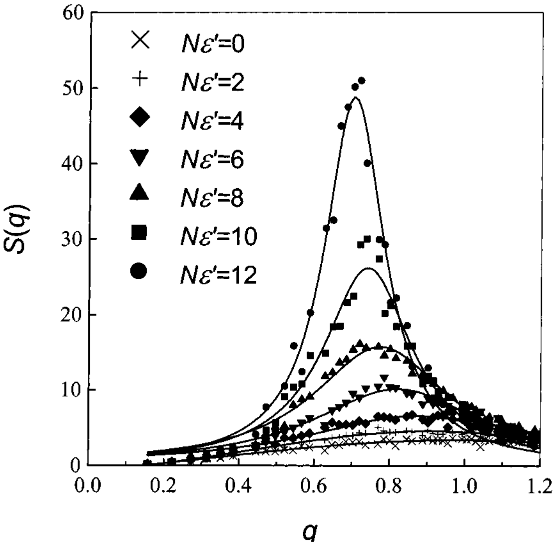

Figure 2. Structure factor $S(q)$ as a function of the absolute value of the scattering vector $\mathbf{q}$ for different values of $N\epsilon'$.

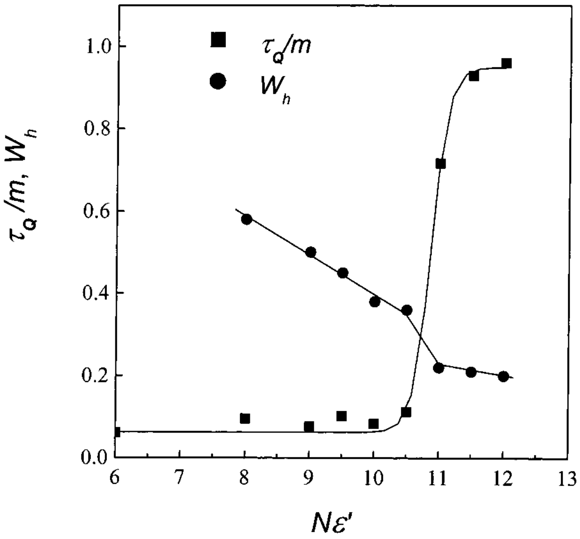

Figure 3. Normalized relaxation time of the dominant wave vector, $\tau_{\mathbf{Q}}/m$, and the width of the half-maximum intensity, W_h, as a function of $N\epsilon'$.

An interesting conformational quantity with respect to “loop” and “bridge” conformations of triblock copolymers is obtained by calculating the angle between the vectors from the center of mass of block B to the centers of mass of each A block. Denoting the position vector of the centers of mass of these blocks as $\mathbf{r}_A$, $\mathbf{r}_B$, and $\mathbf{r}_{A'}$, the quantity of interest is given as

$$\cos\phi = \frac{(\mathbf{r}_A - \mathbf{r}_B)\cdot(\mathbf{r}_{A'} - \mathbf{r}_B)}{|\mathbf{r}_A - \mathbf{r}_B||\mathbf{r}_{A'} - \mathbf{r}_B|} \tag{5}$$

Using this quantity, the distribution of $\cos\phi$, $P(\cos\phi)$, for the three cases of $N\epsilon' = 0$, 10, and 20 were calculated, and the results are shown in parts a, b, and c of Figure 4, respectively. Each distribution was obtained from 16×10^5 copolymer chains, and the increment of $\cos\phi$ in the histogram is 0.05. For chains satisfying random

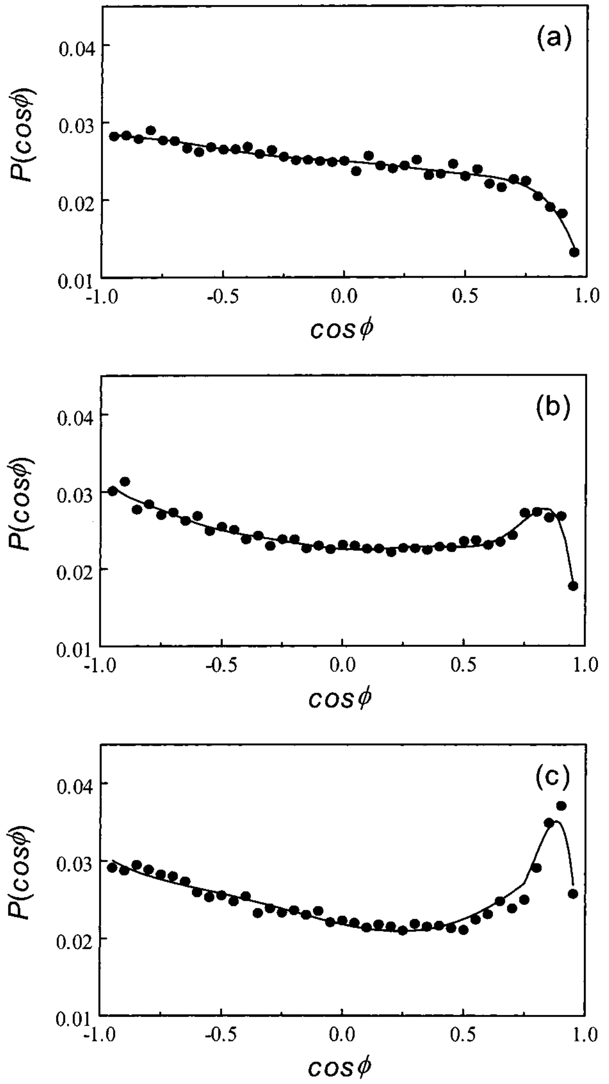

Figure 4. Distribution of cos ϕ for different values of $N\epsilon'$: (a) $N\epsilon' = 0$, (b) $N\epsilon' = 10$, (c) $N\epsilon' = 20$.

walk statistics, the angle ϕ can take any value so that $P(\cos \phi)$ is the uniform distribution. However, because of the self-avoiding constraint in this simulation, even for athermal case, $N\epsilon' = 0$ (Figure 4a), the distribution shows a slight slope and rapidly decays at cos $\phi \approx 1.0$; i.e., if the positions of the centers of mass of two ending blocks, $\mathbf{r}_A$ and $\mathbf{r}_{A'}$, become close, the probability having such positions becomes very low due to the self-avoiding constraint.

For the case of $N\epsilon' = 10$ (Figure 4b), the distribution shows a slight increase near cos $\phi \approx -1.0$ and cos $\phi \approx 0.9$ as a result of favorable "interchain" and "intrachain" interactions between monomers of two A blocks, which possibly form transient clusters near but above MST. The "loose string" shape of the distribution for this case suggests that polymer coils in the triblock copolymer system may take preferably either a loop or bridge conformation even above MST.

In Figure 4c, which shows the case of $N\epsilon' = 20$ corresponding to below MST, the value of $P(\cos \phi)$ at cos $\phi \approx 0.9$ is significantly increased as compared to the cases of $N\epsilon' = 0$ and $N\epsilon' = 10$, which implies that the loop conformations become dominant among all the conformations including the bridge conformations (cos $\phi \approx -1.0$). The smaller value of $P(\cos \phi)$ at cos $\phi \approx -1.0$ might be due to the elastic energy penalty arising from stretching of middle B blocks for the bridge conformations.

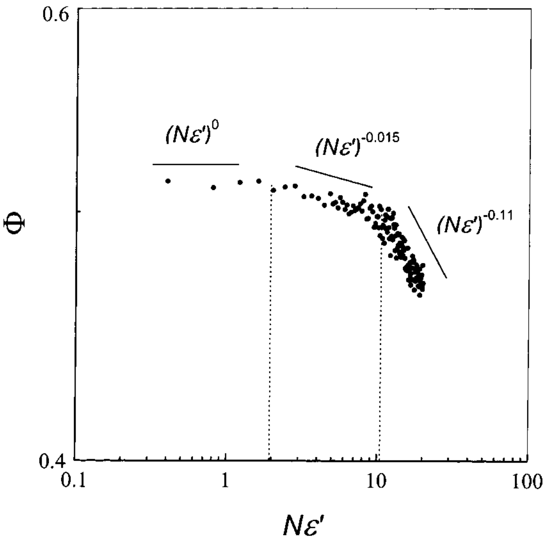

Figure 5. A log–log plot of the fraction of bridging chains, Φ_{br}, against $N\epsilon'$. The solid lines for each regime are obtained from the linear regression in the log–log plot.

In the strong segregation regime, Halperin and Zhulina calculated the free energy of B-layer in a lamellar phase consisting of ABA triblock copolymers by using a self-consistent-field analysis.[14] In their theory, the B-layer between two A-phases is essentially comprised of three regions: a center region where only bridging chains are present and two boundary regions where both bridging and nonbridging chains are present. Within this picture of B-layer consisting of three regions, chains in the central region are uniformly stretched whereas the stretching of chains in the boundary regions is not uniform. According to this model, the elastic free energy in the B-layer can be described by the sum of elasticity in each region. Using self-consistent calculation that gives the distribution of the end monomers in the boundary regions, the resulting free energy can then be expressed as a function of the fraction of bridging chains, Φ, and minimizing the free energy with respect to Φ gives the following scaling law:

$$\Phi \sim (N\chi)^{-1/9} \tag{6}$$

where χ is the Flory interaction parameter which is assumed to be linearly proportional to ϵ' in the simulation. Figure 5 shows the dependence of Φ on $N\epsilon'$ in the temperature regime between $N\epsilon' = 0$ and $N\epsilon' = 20$. The fraction of bridging chain is measured by using the distribution of cos ϕ:

$$\Phi \cong \int_{-1}^{0} P(u)\, \mathrm{d}u \tag{7}$$

where $u \equiv \cos \phi$. In Figure 5, three distinctive regimes are identified in terms of the power law, $\Phi \sim (N\epsilon')^{\nu}$. The regimes divided here, however, are merely a guide to explain some important features of the conformational behavior, and the best description for this curve is possibly a smooth function. In the first regime up to $N\epsilon' \cong 2$, no significant change in Φ is observed, and hence the power law is given with $\nu = 0$ in this regime. Of course, the terminology of "bridging" between different A-domains in the disordered state is inappropriate in the strict sense, since there are no segregated domains in the disordered state. More correctly, the bridging chain in this regime simply means an extended chain. From $N\epsilon' \cong 2$ to the point near the MST, $N\epsilon' \cong 10$, the fraction of bridging chains (extended chains) slightly decreases, and the power law is given with $\nu = -0.015$ for this regime. As observed in Figure 3b, this result indirectly supports the existence of transient clusters consisting of A-monomers near but above MST. In the third regime where the systems are microscopically demixed, the power law excellently agrees with the theoretical result in eq 6, having the exponent $\nu = -0.110 \cong -{}^1/_9$. This is somewhat remarkable since the simulation result is obtained in the weak segregation regime whereas the scaling law of eq 6 predicts the behavior in the limit of strong segregation where the condition of $N\chi \gg 1$ should be satisfied. A possible explanation for this unexpected agreement can be given as follows. In the theory, the free energy takes the form consisting four different contributions:

$$F = F_{\mathrm{sur}} + F_{\mathrm{el}}^{(\mathrm{c})} + F_{\mathrm{el}}^{(\mathrm{b})} + F_{\mathrm{mix}} \tag{8}$$

where the interfacial contribution F_{sur} is inversely proportional to the period of lamellar structure, and $F_{\mathrm{el}}^{(\mathrm{c})}$ and $F_{\mathrm{el}}^{(\mathrm{b})}$ are the elastic contributions in the central and boundary regions, respectively, and the last term F_{mix} is the free energy of mixing between the bridging and nonbridging chains. When the system approaches the weak segregation regime, the first three terms become inaccurate while the form of $\Phi \ln \Phi + (1 - \Phi) \ln(1 - \Phi)$ for F_{mix} is relatively a good approximation over the entire regime. Since the interfacial and the elastic terms are opposed to each other with respect to the variation of the period, the errors from the both terms in WSR where the period is smaller and the chains are less stretched are somehow compensated for each other. Therefore, it is very possible that the prediction of eq 6 is still good in WSR although each term described for SSR becomes inaccurate in WSR. This kind of cancellation quite often occurs in many theoretical approaches such as Flory's derivation for the swelling of polymer chain in a good solvent.[15] However, a more rigorous theoretical analysis is required to ensure the finding observed in this simulation study. The finding presented here may provide a clue linking between two limiting regimes with respect to the conformational behavior of a triblock copolymer melt.

Concluding Remarks

In this paper, the conformational behavior in the melt of a symmetric triblock copolymer is briefly reported with respect to "loop" and "bridge" conformations. Although the angle ϕ in eq 5 for identifying "loop" and "bridge" is a conformational quantity of copolymer itself rather than a quantity representing the pathway along the chain from domain to domain, we strongly believe that the measurement of ϕ is more reliable method in identifying two conformations than counting them directly from the simulation, since the microscopically ordered structures obtained from simulation or experiment usually have many structural defects and flections so that the identity of a conformation is rather ambiguous. Furthermore, measuring the angle ϕ that is proportional to the elastic energy is in accordance with theoretical treatment since in the theory the elasticity is the only tool to distinguish the identity of conformations.

One of our primary results shows that the loop conformation becomes preferred to the bridge conformation as the unfavorable interaction becomes stronger even above MST. Although our finding of $\nu = -0.015$ for the second regime in Figure 5 may not be universal due to the use of relatively short chain in our simulation, the main point in this regime is that the copolymer chains already have a conformational preference even in the disordered state. Similar behavior has been observed in a diblock copolymer melt, where the chain conformations of diblock copolymers already become dumbbell-like above MST.[13] In the third regime corresponding to below MST, the fraction of bridging chain is found to be proportional to $(N\epsilon')^{-0.11}$, which is consistent with the theoretical prediction in the strong segregation limit.

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