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Influence of chain stiffness on the micellization of block copolymers in a selective solvent as observed in Monte Carlo simulations

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The micellization in a selective solvent of a diblock copolymer with blocks of different stiffness is studied with Monte Carlo simulation on a cubic lattice. When the stiffness of the insoluble block increases, the critical micelle concentration (cmc) decreases and the averaged micelle size increases. On the other hand, an increase in the stiffness of the soluble block does not affect the micellization process to any appreciable extent. The decrease in the cmc when the stiffness of the insoluble block increases is interpreted as arising from the conformational contribution to the effective χ parameter. We interpret this contribution as being due to an increased number of heterocontacts between the insoluble block and the solvent molecules when the stiffness of the insoluble block increases.

I. INTRODUCTION

Recently Bates *et al.*¹ reported an influence of the flexibility of a chain on the phase separation of polymer blends and block copolymers. This influence is understood as arising from the contribution of conformational entropy to the effective χ parameter. Since the contribution is positive, a difference in the stiffness of two polymer chains will promote phase separation. This phenomena was first described by Flory,^{2,3} who demonstrated that a mixture of rods and coils will separate into two phases. Liu and Fredrickson⁴ have given a theoretical interpretation of the contribution to the effective χ parameter in a blend of chains with different stiffness.

We report here a similar influence of chain stiffness on the thermodynamic properties, but in a different situation. We performed a Monte Carlo simulation of the micellization of an *AB* diblock copolymer in a selective solvent. The equilibrium of free chains with the micellar phases was monitored. When the insoluble block becomes stiff, the equilibrium between the free chains and the micellar phase is shifted toward the micellar phase. The concentration of free chains in the system decreased. This effect is similar to an increase in the effective χ parameter for the interaction between the insoluble block and the solvent. However, an increase in the stiffness of the soluble block does not affect the equilibrium to any appreciable degree.

II. CHAINS IN WHICH BOTH BLOCKS ARE FLEXIBLE

We have recently developed a Monte Carlo simulation on a cubic lattice of the micellization of *AB* diblock copolymers in a selective solvent.⁵ The simulation uses nonintersecting chains and periodic boundary conditions in all three directions. Reptation and the extended Verdier–Stockmayer moves⁶ are used to convert one replica into another. Acceptance of new replicas is based on the Metropolis rules.⁷ In the previous work, the two blocks may be distinguished by

the energies of their pairwise interactions, but they were indistinguishable in their flexibility. There was no energetic distinction between two successive bonds that form angles of 90° and 180°. Angles of 0° were prohibited because the chain is self-avoiding. The simulation reveals the micellization behavior clearly, and the results can be compared favorably with theoretical prediction.⁸ Figure 1 presents the volume fraction of free chains as a function of the total concentration of a symmetric *A*₁₀*B*₁₀ diblock copolymer. The reduced pairwise interaction energy, ϵ , between a bead of *A* and either solvent (vacancy) or a bead of *B* is 0.45. All other pairwise interactions are zero. In the simulation, the solvent has the same energetic interaction as a segment of *B*. At low concentration the free copolymer concentration increases as the total volume fraction increases. Formation of micelles begins when the concentration reaches the vicinity of the critical micelle concentration (cmc). As a result, the volume fraction of free copolymer chains begins to decrease with further increases in the total concentration.

The cmc can be compared with the prediction from the theory of Leibler, Orland, and Wheeler.⁸ In Fig. 1 the solid line is the calculation according to Leibler's theory, using

$$\chi = \frac{\epsilon}{N_A} [(N_A - 1)(z - 2) + (z - 1)] = 1.845, \quad (1)$$

where N_A is the number of beads in the insoluble block and z is the coordination number. The diblock copolymer used in the simulation has $N_A = 10$, and z is six for a cubic lattice. Notice here the concentration of free chains is slightly different from the ϕ_f used by Leibler, Orland, and Wheeler. In the Leibler *et al.* model, ϕ_f is defined as the volume fraction of free chains outside the micellar domain, and ϕ_f increases slightly at concentrations above the cmc. Here we use the concentration of free chains over the total volume (denoted as ϕ'_f), and it decreases above the cmc. Using the same notation as employed by Leibler, Orland, and Wheeler, ϕ_f is related to ϕ'_f through

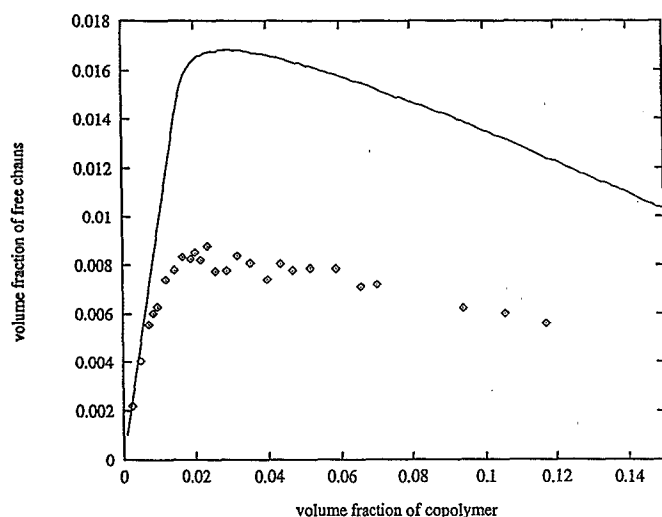


FIG. 1. The volume fraction of free chains as a function of the total concentration of the copolymer, obtained for $A_{10}B_{10}$, $\epsilon=0.45$. The bending energies are $\omega_A=\omega_B=0$. The solid line is the calculation according to the Leibler *et al.* theory.

$$\phi_f' = \frac{\phi_f}{1 - \xi\phi\zeta}, \quad (2)$$

where $(1 - \xi\phi\zeta)$ is the volume fraction occupied by the micelles.

The transition in the behavior of the concentration of free chains is similar in the Leibler *et al.* model and in the results from the simulation. However, the value of the concentration of free chains in the simulation is lower than the value according to the Leibler *et al.* model. This difference is due to a simplification in the model. In the Leibler *et al.* model, micelles of a single size are assumed to be in equilibrium with the free chains. In the simulation, micelles of various sizes exist in the system, as well as "premicelles" composed of two or three chains. Nevertheless the agreement in the cmc between the simulation and the Leibler *et al.* model is surprisingly good, considering the fact that the simulation is carried out on a cubic lattice while the theoretical model is based on a continuum. This agreement confirms that the simulation provides a useful description of the micellization of the block copolymer.

The averaged micelle size in the simulation can also be compared with the Leibler *et al.* theory, but with a less satisfactory result. The Leibler *et al.* theory predicts a micelle size ranging from 24 to 25 at concentrations above the cmc, but the simulation gives a weight average micelle size varying from 20 to 30. One of the paramount phenomena in the simulation is the polydispersity in the micelle size, which is ignored in the Leibler *et al.* theory.

III. CHAINS WITH BLOCKS OF DIFFERENT STIFFNESS

The simulation has been extended to incorporate a difference in conformational entropy between the two blocks. A reduced positive bending energy ω is assigned whenever two successive bonds form an angle of 90° . This energy will

TABLE I. $\langle r^2 \rangle / l^2$ for $A_{10}B_{10}$ at different ω .

ω	A block	B block	Entire chain
0.0	15.3	15.3	35.7
0.5	17.4	17.3	40.6
1.0	20.7	20.7	48.6
1.5	25.7	25.7	61.6
2.0	32.9	32.8	82.0
3.0	51.2	50.8	152
4.0	65.1	65.1	231
5.0	75.0	74.6	307
6.0	78.6	78.8	339
...
∞	91	91	361

make the chain adopt a stiffer conformation that favors a bond angle of 180° . We use ω_A and ω_B to denote the bending energy assigned to two bonds that meet at a bead of A, and two bonds that meet at a bead of B, respectively.

A slight problem is created in the simulation when one incorporates the bending energy. Reptation and the extended Verdier-Stockmayer relaxation are the motions of the chains that are adopted to equilibrate the system. In the limit where $\omega \rightarrow \infty$, the chain adopts a rodlike conformation. Then the above two motions will not be sufficient to equilibrate the system, because the rods can only slide parallel to the edge of the lattice. For this reason, we avoid the limit where the chain becomes so stiff that it essentially behaves as a rod. We only examine the behavior in the region where the chain can still be considered as flexible, but with slight differences in the stiffness of each block. A measure of the strength of the bending energy on the stiffness of the chain is to calculate a dimensionless mean square end-to-end distance, $\langle r^2 \rangle / l^2$, of a single chain as a function of the bending energy. Here l denotes the distance between bonded beads. In Table I, $\langle r^2 \rangle / l^2$ for a single $A_{10}B_{10}$ chain is presented as a function of $\omega = \omega_A = \omega_B$. In the simulations that will be reported here, ω_A and ω_B were varied from 0.0 to 1.0. This range changes $\langle r^2 \rangle / l^2$ of each block by 35%, as can be seen from Table I.

Figure 2 presents two sets of data, obtained with $\omega_A=0.0$ and 1.0 while $\omega_B=0.0$, $\epsilon=0.45$. The increase in ω_A produces a decrease in the cmc which is both reflected in the concentration at the transition as well as the concentration of free chains when the total concentration of the copolymer is above the cmc. The weight averaged micelle size is also increased, as shown in Fig. 3. The effect of the increase in ω_A (at constant ϵ) is similar to the effect of an increase in ϵ (at constant ω_A), or an increase in the effective χ parameter. Indeed when these results are compared with other simulations using varying ϵ and zero bending energies,⁹ they resemble the results obtained using $\epsilon=0.48$ and $\omega_A=\omega_B=0.0$.

The volume fraction of free chains is a sensitive measure of the equilibrium between the free chains and micelles. Thus we monitored the volume fraction of free chains for a system which has the total copolymer concentration of 0.05, while varying the ω_A or ω_B from 0.0 to 1.0 with increments of 0.1. Figure 4 presents the result. When the A block (insoluble block) becomes more stiff, one sees a continuous

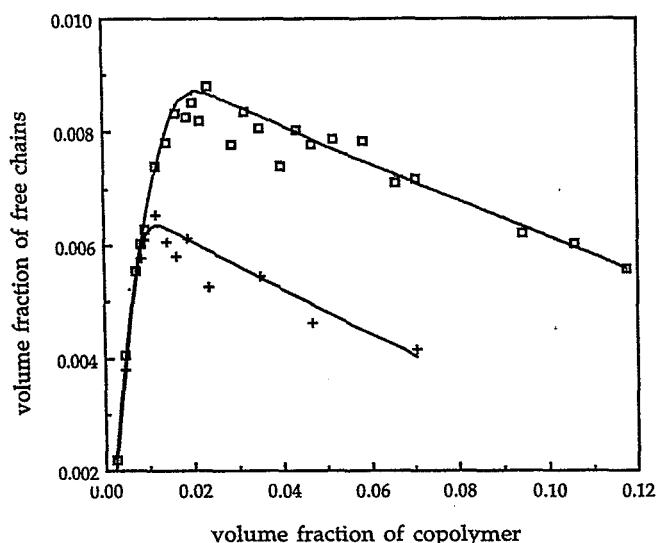


FIG. 2. The volume fraction of free chains as a function of the total concentration of the copolymer, obtained for $A_{10}B_{10}$, $\epsilon=0.45$, $\omega_B=0$, and (\square) $\omega_A=0$, ($+$) $\omega_A=1$. The curves are to guide the eye.

decrease in the volume fraction of free chains. However, when the soluble block becomes more stiff, the change in the volume fraction of free chains barely exceeds the scatter in the data. The weight averaged micelle size is less accurate when it is estimated in the simulation. Thus no conclusion is drawn about the influence on the size of the micelle when the stiffness of the soluble block is changed.

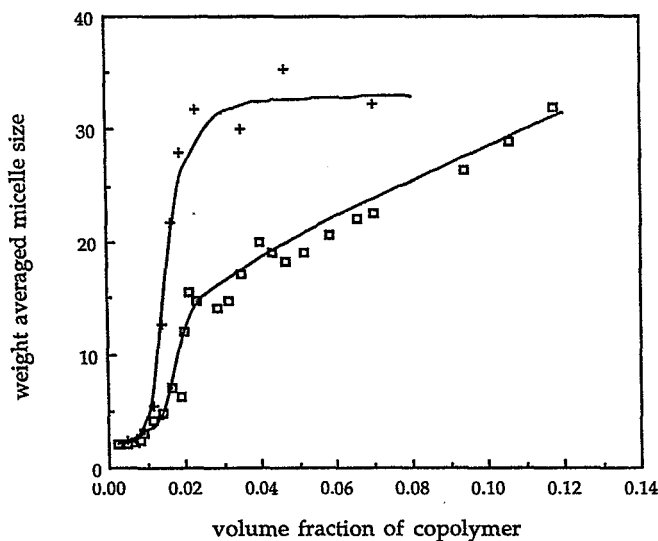


FIG. 3. Weight averaged micelle size as a function of the total concentration of the copolymer for the same systems as in Fig. 2. The curves are to guide the eye.

IV. DISCUSSION

The influence of the stiffness of the insoluble block on the cmc can be understood using the following intuitive argument. When the insoluble block becomes intrinsically more stiff, it makes more heterocontacts with the solvent if that chain is dispersed in the solvent as a single chain, because the stiffness of the chain prevents it from reducing the number of heterocontacts by self-interaction. Thus the free energy of the free chain is increased, and it shifts the equilibrium between free chains and micelles toward the formation of micelles.

Since the insoluble block has only ten beads in our simulation, one might wonder whether such an effect would be significant. A simulation with only one such block copolymer on the lattice was carried out to measure the number of heterocontacts between A segments and solvent when ω_A equals 0.0 and 1.0. The total number of $A-S$ contacts of one such chain is 34.5 ± 0.1 and 36.1 ± 0.1 , respectively. This change corresponds to a 4.6% increase in the total enthalpic interaction energy. If the original state with $\omega_A=0.0$ corresponds to an effective $\chi N=18.45$, then with a positive bending energy of $\omega_A=1.0$ the effective $\chi N=19.30$. This increase in χN gives the decrease in the cmc and concentration of the free chains that one would expect using the Leibler *et al.* model.

The above view may be extended to consider a blend of chains with different stiffness. When one species is intrinsically stiff, it will have a large radius of gyration, and have more interpenetrations and heterocontacts with the other kind of chain if they were homogeneously mixed. Thus one would expect an increase in the effective χ parameter, which would favor phase separation. We believe the contribution to the

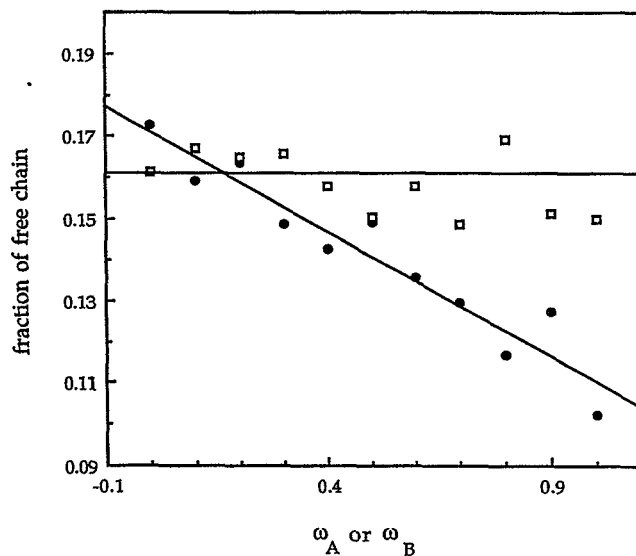


FIG. 4. The fraction of free chains as a function of bending energy applied to the (\bullet) A block, (\square) B block. The volume fraction of $A_{10}B_{10}$ is 0.05, and $\epsilon=0.45$. The lines are to guide the eye.

effective χ parameter due to the conformational difference in the chains is positive.

Liu and Fredrickson considered the conformational contribution to the effective χ parameter.⁴ They introduced a quadrupolar interaction parameter which favors the mutual alignment of segments. The contribution of the difference in chain stiffness to the effective χ parameter could be negative or positive, depending on the value of this quadrupolar interaction parameter. Only when this quadrupolar interaction is larger than $B/2$, will the contribution to the effective χ parameter be positive. Here B is a positive, nonzero parameter which is dependent on the stiffness of the chain. In our simulation, there is no such quadrupolar interaction, corresponding to $B=0$. Then according to their theory, one would expect a negative contribution to the effective χ parameter. This expectation is not confirmed by the simulation.

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