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Microphase separation in ABA triblock copolymer-based model conetworks in the bulk: Effect of loop formation

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Abstract

This work estimates the free energy and domain size and predicts the phase diagram of microphase-separated model polymer conetworks, consisting of end-linked ABA triblock copolymers with cross-link points of relatively low functionality, in the strong segregation limit (highly incompatible A and B). Considering the case when these conetworks were prepared in the disordered state, their microphase separation is accompanied by extensive loop formation, with the fraction of loops depending on the morphology. The free energy of these conetworks is approximated using the expressions for linear block copolymers, modified to take into account the presence of loops whose free energy is estimated in two different approaches. The domain sizes in the conetwork system are found to be larger than those of the same morphologies in the linear system because of the reduction of the retractive force due to loop formation in the former system. The conetwork phase diagram is very sensitive to the expression used to describe the energy for loop formation.

Keywords: Polymer model conetworks; Microphase separation; Loop formation

1. Introduction

During the past 20 years, microphase separated linear block copolymers in the bulk attracted much attention from the polymer science community [1,2]. There are now available extensive experimental investigations [3] and a complete theoretical framework [4] for the morphologies and domain sizes for linear AB and ABA triblock copolymers. There is also an increased understanding for segmented star copolymers in the bulk, both experimental [5,6] and theoretical [7]. In contrast, there are very few studies on the microphase separation of segmented conetworks, either experimental [8–19] or theoretical [20,21].

We are interested in a particular segmented model [22] conetwork system, comprising elastic chains based on monodispersed ABA triblock copolymers, end-linked at cross-linking nodules of precise functionality (exact number of arms emanating from the cross-link) [15–17]. Although we have already described theoretically such a system both in the swollen state [23,24] and in the bulk [25], in this study we re-examine the system in the bulk, aiming to explicitly incorporate in the description unique features resulting from the fact that cross-linking takes place in the disordered state.

2. Features of the cross-linked system

In this section, we describe the features of the cross-linked system at hand and point out the similarities and differences relative to linear block copolymer systems. We consider model (ideal) conetworks (no entanglements, dangling chains or loops upon synthesis) based on end-linked ABA triblock copolymers in the bulk in the strong segregation limit (leading to well-defined boundaries between the domains), forming spherical, cylindrical or lamellar morphologies, i.e. the same geometries as those encountered in ordered linear block copolymers. Thus, the interfacial free energy expressions used for the linear block copolymer systems can also be applied for the model copolymer network system.

Assuming a low functionality, f, at the core, e.g. $f=4$, the A blocks in the conetwork would have a similar conformation to those of the linear diblock copolymers, and they could be described by the same free energy expression. If the core functionality were high, e.g. $f=20$, realizable in several

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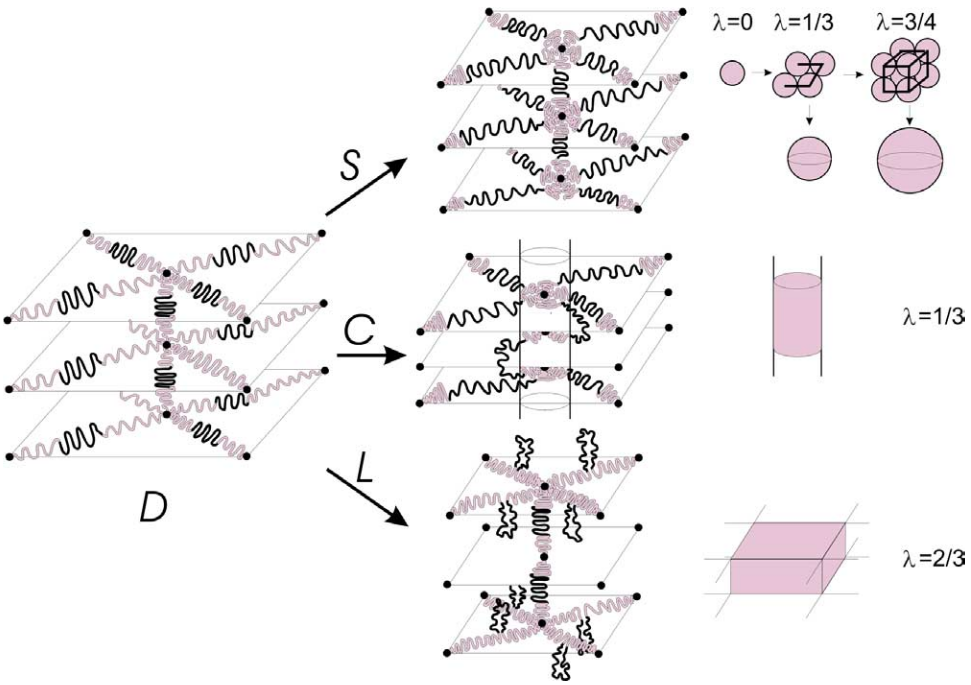

Fig. 1. Microphase separation of an ABA triblock copolymer model conetwork system into spherical (S), cylindrical (C), and lamellar (L) morphologies. The conetwork in the disordered (D) state, illustrated on the left, has no loops. The loop fractions for cylinders and lamellae shown in the middle column of the figure are 1/3 and 2/3, respectively, and are the values dictated by geometry. No loops are formed in the spherical morphology on the top of the middle column of the figure; however, the one- and three-dimensional fusion of cross-links, corresponding to spheres with loop fractions of 1/3 and 3/4, is also possible and is depicted on the top of the right-hand-side column of the figure.

experimental systems [15–17,26,27], there would be crowding in the core and differentiation in the conformation of the various chains, i.e. different A blocks would display different degrees of stretching, depending on their location in the core.

The main difference between the cross-linked and the linear system originates from the fact that the networks at hand were prepared in the disordered state. Although these networks are assumed to be loop-free upon synthesis, the presence of the cross-links, holding together f chains, would lead to the formation of loops upon microphase separation. In particular, as two cross-links, connected by the same chain, assemble during microphase separation, the interconnecting chain becomes a loop, as is schematically illustrated in Fig. 1.

In cylinders, the self-assembly of the cross-links is one-dimensional (the cores are aligned to give a cylinder), rendering loops 1/3 of the B blocks and leaving the remaining 2/3 as bridges. In lamellae, the cross-link self-assembly is two-dimensional (the cores are assembled in a plane to give a lamellar sheet), resulting in fractions of 2/3 and 1/3 for loops and bridges, respectively. The situation can be more complicated in the case of spheres, in which the absence of core aggregation is also a possibility. However, because of the low f value assumed, core aggregation would be strongly favored. In the analysis that follows, two cases for sphere aggregation are considered; one-dimensional, presenting the same fraction of loops as in cylinders, 1/3, and three-dimensional cubic, exhibiting a high loop fraction, 3/4.

3. Total free energy

The arguments provided in Section 2 secure that the interfacial free energy and the elastic free energy in microphase A of the conetwork system can be given by the same expressions as for the linear case. The free energy in microphase B of the conetwork system comprises two parts, that for bridges and that for loops. The (elastic) bridge component (per chain) for the network system is assumed to be the same as the corresponding for the linear system. The elastic loop component is set equal to zero because the loop ends are close to each other, allowing the chain in the main body of the loop to relax to a low-energy, unstretched conformation. However, there is a configurational entropy loss upon loop formation (due to the approach of the loop ends) and a corresponding increase in the free energy [28–31], which must be included in the total free energy. Given the above and following the formalism of Matsen and Bates for microphase separation in linear block copolymer systems [32], the total free energy per half chain of the conetwork is:

$$\begin{aligned}\frac{G^{\text{ordered}}}{fk_{\text{B}}T} &= \frac{G^{\text{A}}_{\text{elastic}}}{fk_{\text{B}}T} + \frac{G^{\text{B}}_{\text{elastic-bridge}}}{fk_{\text{B}}T} + \frac{G^{\text{B}}_{\text{loop}}}{fk_{\text{B}}T} + \frac{G^{\text{A}}_{\text{interfacial}}}{fk_{\text{B}}T} \\ &= \alpha^{\text{A}}\left(\frac{R}{aN^{1/2}}\right)^2 + (1-\lambda)\alpha^{\text{B}}\left(\frac{R}{aN^{1/2}}\right)^2 \\ &\quad + \frac{\lambda}{4}\ln[2\pi(1-\phi_{\text{A}})\chi N] + \beta(\chi N)^{1/2}\left(\frac{R}{aN^{1/2}}\right)^{-1} \qquad (1)\end{aligned}$$

Table 1
Expressions for the coefficients for the elastic free energies and the interfacial free energy for the various morphologies

Morphology	α^{A}	α^{B}	β
Lamellar	$\frac{\pi^2}{8}\phi_{\mathrm{A}}$	$\frac{\pi^2}{8}(1-\phi_{\mathrm{A}})$	$\frac{1}{6^{1/2}}$
Cylindrical	$\frac{\pi^2}{16}$	$\frac{\pi^2}{16}\frac{(1-\phi_{\mathrm{A}}^{1/2})^3(3+\phi_{\mathrm{A}}^{1/2})}{(1-\phi_{\mathrm{A}})^2}$	$\frac{2}{6^{1/2}}\phi_{\mathrm{A}}^{1/2}$
Spherical	$\frac{3\pi^2}{80}\frac{1}{\phi_{\mathrm{A}}^{1/3}}$	$\frac{3\pi^2}{80}\frac{(1-\phi_{\mathrm{A}}^{1/3})^3(6+3\phi_{\mathrm{A}}^{1/3}+\phi_{\mathrm{A}}^{2/3})}{(1-\phi_{\mathrm{A}})^2}$	$\frac{3}{6^{1/2}}\phi_{\mathrm{A}}^{2/3}$

where k_{B} is Boltzmann's constant, T is the absolute temperature, a is the statistical segment length, N is the total number of segments in one-half of the ABA chain, R is a measure of the domain size (that of microphase A), χ is Flory–Huggins interaction (incompatibility) parameter between the unlike segments A and B, α^{A}, α^{B} and β are coefficients listed in Table 1 [32,33] that depend on the polymer composition ϕ_{A} and the geometry of the microstructure, and λ is the fraction of loops formed by the B blocks, which is equal to 1/3 and 2/3 for cylinders and lamellae, respectively, and may acquire the values of 0, 1/3 or 3/4 for spheres. Because of the low fraction of loops observed in the linear ABA triblock copolymer system [34], a λ-value of 0 is appropriate for all morphologies formed by the uncross-linked system.

Taking into account the fact that our analysis is concerned with only one-half of the ABA triblock copolymer chain, the constant in the loop free energy term in Eq. (1) is 1/4 rather than the 1/2 presented in the relevant literature [30,31]. This loop free energy increases with the logarithm of the loop size, which is $2(1-\phi_{\mathrm{A}})N=2N_{\mathrm{B}}$ ($2N_{\mathrm{B}}$ is the degree of polymerization of the whole block B) [28–31]. However, even the most accurate forms of these free energy expressions [30,31] seem to have limitations, as evidenced by the discrepancies between theoretically predicted and experimentally measured critical micellization concentrations (cmcs) of flower-like micelles [30], which may arise from the failure of the theory to account for chain stiffness, especially for the shorter chains. Chain stiffness is expected to cause the loop free energy to decrease as the loop size increases, i.e. to produce the opposite dependence to the one displayed in Eq. (1). For this reason, two separate analyses follow in the manuscript: one where the loop free energy is as given in Eq. (1), and another where this energy is set equal to zero (qualitatively corresponding to the case when the loop entropy and the chain stiffness balance each other).

The free energy of the conetwork in the disordered state is given by the enthalpy of mixing the A and B segments. This energy per one-half ABA chain of the conetwork is:

$$\frac{G^{\text{disordered}}}{fk_{\mathrm{B}}T}=\frac{\Delta H_{\text{mixing}}^{\mathrm{AB}}}{fk_{\mathrm{B}}T}=\phi_{\mathrm{A}}(1-\phi_{\mathrm{A}})(\chi N) \tag{2}$$

4. Results and discussion

Minimization of Eq. (1) without the loop term with respect to R leads to the following expression for the (minimized) total free energy for the conetwork in the ordered state:

$$\frac{G^{\text{ordered}}}{fk_{\mathrm{B}}T}\bigg|_{\min}=\frac{3}{2}\{2[\alpha^{\mathrm{A}}+(1-\lambda)\alpha^{\mathrm{B}}]\beta^2(\chi N)\}^{1/3} \tag{3a}$$

This conetwork free energy minimum ($\lambda>0$) is lower than that of the linear system ($\lambda=0$) because of the reduction of the retractive force due to loop formation in the conetwork system. In the presence of the loop term, Eq. (1) is minimized to:

$$\frac{G^{\text{ordered}}}{fk_{\mathrm{B}}T}\bigg|_{\min}=\frac{3}{2}\{2[\alpha^{\mathrm{A}}+(1-\lambda)\alpha^{\mathrm{B}}]\beta^2(\chi N)\}^{1/3}+\frac{\lambda}{4}\ln[2\pi(1-\phi_{\mathrm{A}})\chi N] \tag{3b}$$

Thus, with the loop term, the minimum total free energy of the conetwork system is increased by an amount exactly equal to the loop free energy. The reason for this is the independence of the loop term in Eq. (1) on the domain size R. Compared to the linear block copolymer system, the conetwork total free energy minimum will be lower when the entropic penalty for loop formation is lower than the reduction in the retractive energy.

To provide an impression for the relative magnitude of the several free energy components, Fig. 2 plots the total free energy and its components as a function of the (normalized) domain size for the lamellar morphology and for the following parameter values: $N=200$, $\chi=0.5$ and $\phi_{\mathrm{A}}=0.4$.

The figure clearly shows that the loop free energy is of the same order of magnitude as the elastic free energy components but is independent of domain size. This independence of the loop free energy on domain size is also the reason why the conetwork domain size at the free energy minimum is given by the same expression, whether the loop free energy term is included or not:

$$R=a\left\{\frac{\beta}{2[\alpha^{\mathrm{A}}+(1-\lambda)\alpha^{\mathrm{B}}]}\right\}^{1/3}\chi^{1/6}N^{2/3} \tag{4}$$

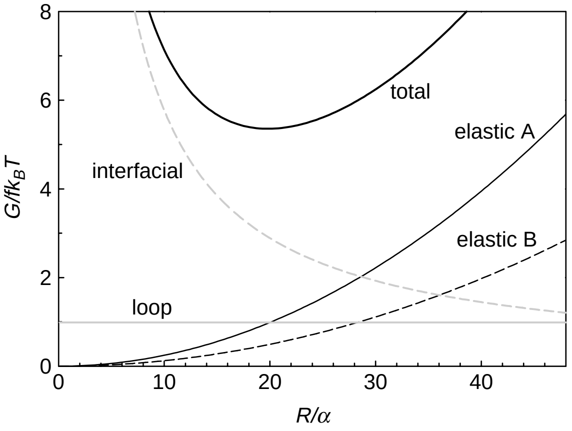

Fig. 2. Domain size dependence of the free energy components and of the total free energy for the lamellar morphology for the set of values $N=200$, $\chi=0.5$ and $\phi_{\mathrm{A}}=0.4$. Although independent of domain size, the loop free energy is of the same order of magnitude as the elastic free energy components.

Compared to the linear block copolymer system ($\lambda=0$ always), Eq. (4) suggests that the cross-linked block copolymer system ($\lambda \geq 0$) exhibits a greater domain size because of the reduction of the retractive force due to loop formation.

Fig. 3 depicts simplified phase diagrams, assuming strong segregation (large incompatibility) between the A and B units, derived from Eqs. (2) and (3a) for the conetwork system with zero loop free energy and for the three different values of loop fraction in spheres (a) $\lambda=0$, (b) $\lambda=1/3$, and (c) $\lambda=3/4$, as well as (d) for the linear block copolymer system. As expected, the value of the loop fraction is critical for the appearance of spheres on the phase diagram. Higher fractions of loops lead to lower free energies for the spheres. Thus, examining Fig. 3(a) through (c), no spheres appear in Fig. 3(a) in which the loop fraction in spheres is zero (only cylinders cover the area on the left of lamellae), all three morphologies are encountered in Fig. 3(b) in which the value of sphere loop fraction is intermediate, and spheres spread at the expense of cylinders in Fig. 3(c) where the highest value of loop fraction in spheres is examined. Although the lowest free energy for spheres is

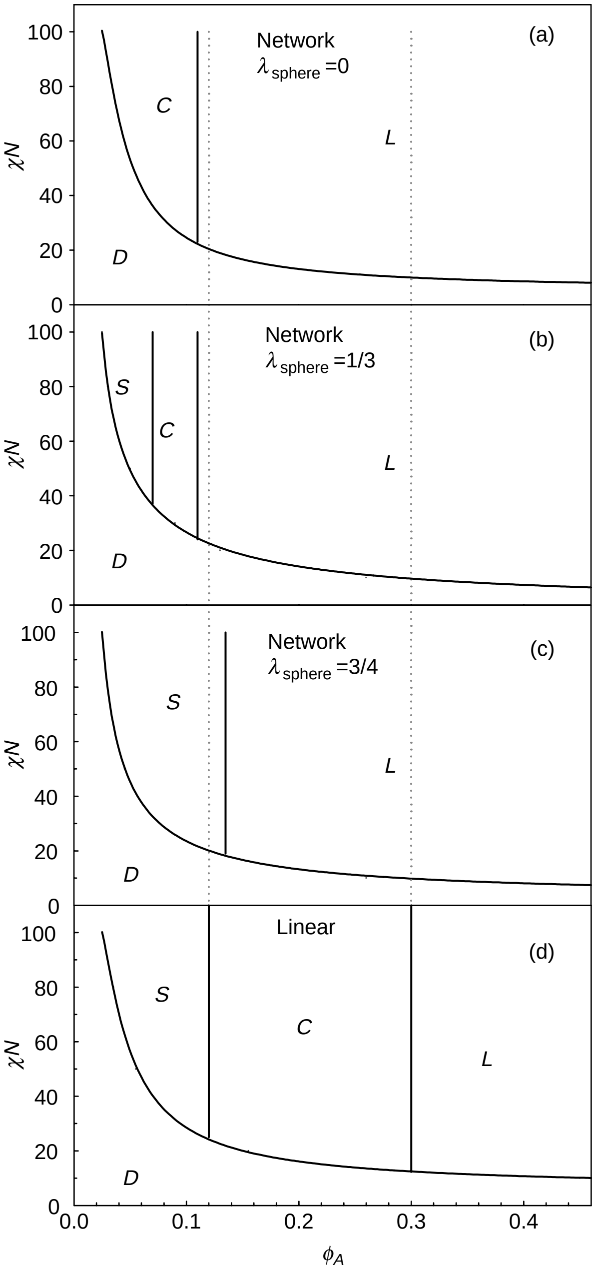

Fig. 3. Phase diagrams in the strong segregation limit for ABA triblock copolymer model conetworks without the free energy penalty for loop formation for three different loop fractions in spheres, (a) $\lambda=0$, (b) $\lambda=1/3$, and (c) $\lambda=3/4$, as well as (d) for linear block copolymers. D, S, C and L stand for the disordered, spherical, cylindrical and lamellar states/morphologies, respectively.

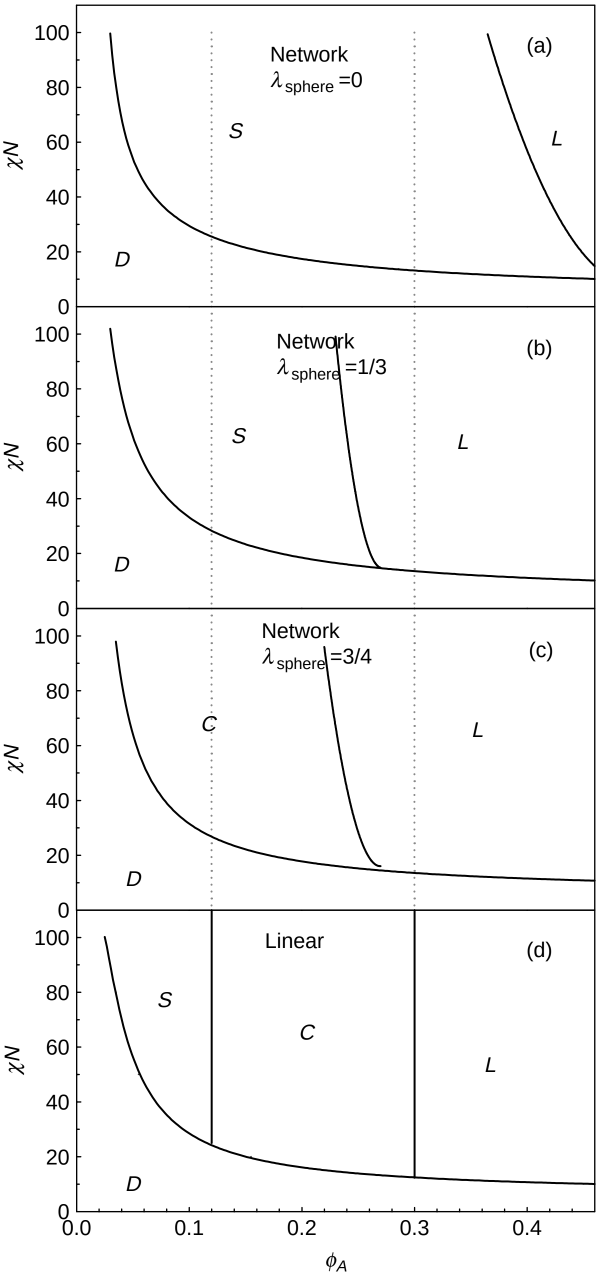

Fig. 4. Phase diagrams in the strong segregation limit for ABA triblock copolymer model conetworks with the free energy penalty for loop formation for three different loop fractions in spheres, (a) $\lambda=0$, (b) $\lambda=1/3$, and (c) $\lambda=3/4$, as well as (d) for linear block copolymers. D, S, C and L stand for the disordered, spherical, cylindrical and lamellar states/morphologies, respectively.

realized when the spheres have their highest loop fraction, this high loop fraction might not be accessible in an experimental system due to the presence of entanglements or insufficient annealing.

Fig. 3(d) is the (simplified) classical phase diagram of diblock copolymers in the strong segregation limit. The ϕ_A values in this diagram, at which the sphere-to-cylinder and cylinder-to-lamella morphological transitions occur, are extrapolated to the conetwork phase diagrams above it. Compared to the linear block copolymer phase diagrams, in all conetwork diagrams the lamellar region is expanded at the expense of the cylindrical (or even the spherical) region because the retractive force reduction is greater in lamellae than in cylinders due to the more extensive loop formation in the former morphology.

Fig. 4 shows the corresponding phase diagrams, derived from Eqs. (2) and (3b), for the conetwork system, accounting here for the loop formation free energy. Compared to Fig. 3, the area covered by the morphologies associated with high loop fractions is greatly reduced in Fig. 4 because the corresponding free energy penalty for loop formation is now included. In particular, in Fig. 4(a) the loop-free sperical morphology is spread over most of the phase diagram, whereas, from the loop-forming morphologies, the cylindrical one is totally absent and the lamellar one occupies only a small area on the top-right corner of the diagram. In Fig. 4(b), the lamellar morpholgy expands at the expense of the spherical morphology that has now been assigned a 1/3 loop fraction, and, finally, in Fig. 4(c), cylinders replace spheres whose loop fraction here has been increased to 3/4.

Examining Figs. 3 and 4 together, loop formation seems to be a very important morphology determining factor. Within a certain figure, an increase in the sphere loop fraction greatly influences the phase diagrams, illustrating the effect of the reduction of the retractive energy. At constant sphere loop fraction, the inclusion of the entropic penalty for loop formation leads to an even greater alteration of the phase diagrams, suggesting that knowledge of the exact functional form of the loop formation free energy is necessary for the accurate prediction of these morphology diagrams.

5. Conclusions

The microphase separation behavior of perfect conetworks, composed of end-linked ABA triblock copolymers, in the strong segregation limit was investigated. These conetworks, prepared loop-free in the disordered state, microphase separate by core–core approach and simultaneous extensive loop formation. This formation of loops is the main feature distinguishing this conetwork system from the linear non-cross-linked system, and resulting in greater domain sizes and morphology shifts in the cross-linked system.

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