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Topological Constraints and Their Influence on the Properties of Synthetic Macromolecular Systems. 2. Micelle Formation of Triblock Copolymers

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ABSTRACT: A simple theory for micelles in triblock copolymer–homopolymer mixtures is formulated. The model is a straightforward extension of Leibler et al.'s treatment of micelles in diblock–homopolymer blends. It is shown that the reduction in entropy due to loop formation of the middle block can have a dramatic effect on the critical micelle concentration. In many cases, it will essentially prevent micelle formation, in agreement with recent experimental observations on triblock copolymer solutions.

1. Introduction

This paper is motivated by the recent observation in our laboratory[1] that triblocks of poly(2-vinylpyridine)–polystyrene–poly(2-vinylpyridine) do not form micelles in solvents that are thermodynamically good solvents for the middle block but poor solvents for the end blocks. Diblocks of poly(2-vinylpyridine)–polystyrene, on the other hand, readily form micelles in the same solvents. Furthermore, only the triblock with the smallest polystyrene block could be dissolved in methanol, which is a good solvent for the end blocks but a nonsolvent for the middle block, and did form micelles. All this indicates that micelle formation is more difficult for triblocks than for diblocks. A similar behavior was found many years ago by Tanaka et al.[2,3] for block copolymers of poly(methyl methacrylate) and polystyrene. They suggested that micelle formation for the triblocks in good solvents for the middle block did not occur because the two end blocks associate and are prevented from further association with other end blocks by the middle block forming a protective shield. In our opinion, this is not a very likely explanation, since if association of the two end blocks of the same triblock is thermodynamically favorable, the formation of a real micelle should even be more favorable. It seems more likely that the reduction in entropy due to backfolding of the middle block is the determining factor. Micelle formation of styrene–butadiene–styrene triblock polymers in selective solvents or solvent mixtures has been observed by various groups.[4-7] In all cases, a nonsolvent for the middle block was involved.

In recent years, considerable progress has been made in the theoretical understanding of micelle formation in mixtures of diblock polymers and homopolymers.[8-11]

In recent years, considerable progress has been made in the theoretical understanding of micelle formation in mixtures of diblock polymers and homopolymers.[8-11] Both Leibler et al.[9] and Noolandi et al.[10,11] developed a mean-field theory which, although different in details, essentially predicts the same behavior. Homopolymers are used as a solvent to justify the mean-field description and to minimize the number of interaction parameters involved. In the following, Leibler et al.'s[9] model will be extended to mixtures of triblock polymers and homopolymers, but it should be clear that Noolandi et al.'s[10,11] theory could just as well have been used as a starting point.

It is the purpose of this paper to show that the reduction in entropy due to loop formation of the middle block will make micelle formation for triblock polymers far more difficult than for the corresponding diblock polymers.

2. Theoretical Model

We consider a mixture of completely flexible triblock copolymers B–A–B, containing N A monomers and two end blocks of $N/2$ B monomers each, and homopolymers containing N_h A monomers. Furthermore, N_h is assumed to be smaller than N, and the interaction between A and B monomers, described by the Flory–Huggins parameter χ, is unfavorable. Micelles are assumed to be spherical with an inner core containing only B monomers and a corona containing A monomers belonging to the copolymers and the homopolymers. A schematic picture is given in Figure 1. The theoretical description follows closely Leibler et al.'s[9] formulation and we will therefore use their notation. In the following, a short description of the model will be given and the appropriate modifications will be introduced where necessary.

The free energy of a mixture of micelles and a "sea of solvent" containing "free" triblock copolymers and homopolymers has three main contributions: the free energy of a single micelle $\mathcal{F}$, the free energy of the "solvent" F_{mix}, and the entropy of mixing micelles and "solvent" S_m. The free energy of a single micelle will be considered first.

$\mathcal{F}$ contains essentially four different contributions: the free energy of the interface between the inner core and corona, $\mathcal{F}_s$, the free energy of mixing, $\mathcal{F}_m$, due to the homopolymers in the corona, the free energy of deformation, $\mathcal{F}_d$, and the free energy of the loop formation, $\mathcal{F}_l$, of the middle block. The first two terms are identical with the diblock case.

The surface free energy is given by

$$\mathcal{F}_s = 4\pi R_B^2 \gamma \tag{2.1}$$

where γ is the interfacial tension given by

$$\gamma = (kT/a^2)(\chi/6)^{1/2} \tag{2.2}$$

and a is the length per monomer. R_B is the radius of the inner core (Figure 1). The second contribution is given by

$$\mathcal{F}_m = \frac{4}{3}\pi \frac{(R^3 - R_B^3)}{a^3} kT \frac{1-\eta}{N_h} \ln (1-\eta) \tag{2.3}$$

where R is the radius of the micelle and η is the fraction of A monomers in the corona belonging to the copolymers. $1 - \eta$ is the fraction of A monomers in the corona belonging to the homopolymers. Equation 2.3 is the Flory–Huggins expression for the translational entropy of the homopolymers in the corona. There is no contribution from the block copolymers since they are attached to the interface, a situation which closely resembles swelling of networks.[12,13]

As far as the elastic free energy of deformation of the end blocks is concerned, there is no essential difference between a diblock and a triblock. The loop-forming middle block of length N will be treated as two separate linear

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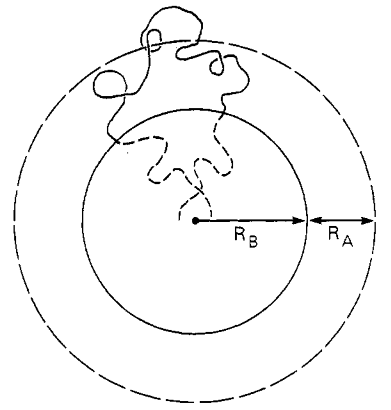

Figure 1. Schematic presentation of a spherical micelle consisting of B–A–B triblocks in a matrix of A homopolymers. The sphere with radius R_B is the inner core containing soley B monomers. The shell with size R_A is called the corona and contains a homogeneous mixture of A blocks and A homopolymers.

chains of length $N/2$. This approximation is supported by the fact that the mean square radius of gyration of a ring polymer of length N, given by $Na^2/12$,[14] is identical with the mean square radius of gyration of a linear chain with length $N/2$. Furthermore, as will become clear, the exact expression for the free energy of deformation is nearly irrelevant, as far as the influence of the reduction of entropy due to the backfolding of the middle block on the critical micelle concentration (cmc) is concerned. The above considerations lead to the following expression:

$$\mathcal{F}_d = \frac{3}{2}kT(2p) \times \left\{\frac{R_B^2}{(N/2)a^2} + \frac{(N/2)a^2}{R_B^2} + \frac{R_A^2}{(N/2)a^2} + \frac{(N/2)a^2}{R_A^2} - 4\right\} \quad (2.4)$$

where p is the number of block copolymers in the micelle. The factor 2 in front of p corresponds to the two end blocks and the approximative treatment of the middle block. This expression, similar to the one used by Leibler et al.[9] for diblocks, differs slightly from the corresponding expression used by Noolandi et al.,[10,11] because it neglects the localization of the copolymer joints to the interface between the inner core and corona.[13,15,16] For the present discussion, this difference is unimportant.

The most important contribution to consider is the reduction in entropy due to loop formation of the middle block. Long ago, Jacobson and Stockmayer[17] showed that the condition for the ends of a linear chain of length N to lie in the same plane corresponds to a factor proportional to $N^{-1/2}$ in the partition function. If the chain has to stay at one side of the plane, this factor reduces to $N^{-3/2}$.[18] It is well-known[17] that the cyclization probability is also proportional to $N^{-3/2}$. In all cases, the reduction in entropy is proportional to $\ln N$. We will therefore assume that the contribution to the free energy of the micelle due to backfolding of the middle block is of the form

$$\mathcal{F}_l = \frac{3}{2}kTp\beta \ln N \quad (2.5)$$

where β is probably 1, as long as excluded volume effects can be neglected. If excluded volume effects become important, which usually is the case when solvents are involved, β may even be larger than 1 (cf. ref 19).

The free energy of a single micelle, $\mathcal{F} = \mathcal{F}_s + \mathcal{F}_d + \mathcal{F}_m + \mathcal{F}_l$, can be expressed as a function of p and η if the system is assumed to be incompressible. Then the following relations hold:

$$4\pi R_B^3/3 = pNa^3 \quad (2.6a)$$

$$4\pi(R^3 - R_B^3)\eta/3 = pNa^3 \quad (2.6b)$$

and $\mathcal{F}$ is given by

$$\mathcal{F}/kT = A_1\chi^{1/2}p^{2/3}N^{2/3} + A_2(1 + C(\eta))p^{5/3}N^{-1/3} + A_3(1 + 1/C(\eta))p^{1/3}N^{1/3} + \alpha p\frac{1-\eta}{2\eta} \ln (1-\eta) - 12p + \frac{3}{2}p\beta \ln N \quad (2.7)$$

where $A_1 = (4\pi/6^{1/2})(3/4\pi)^{2/3}$, $A_2 = 6(3/4\pi)^{2/3}$, $A_3 = (3/2)(4\pi/3)^{2/3}$, $\alpha = 2N/N_h$, and $C(\eta)$ is defined by

$$C(\eta) = \left[\left(\frac{\eta+1}{\eta}\right)^{1/3} - 1\right]^2 \quad (2.8)$$

Let ζ denote the fraction of triblock copolymers aggregated in micelles, Ω the total number of A and B monomers in the system, and ϕ the concentration of copolymer monomers. The total number of micelles in the system N_m is then given by

$$N_m = \Omega\phi\zeta/(2pN) \quad (2.9)$$

and the free energy F of the total system becomes

$$F = \frac{\Omega\phi\zeta}{2pN}\mathcal{F} + F_{mix} - TS_m \quad (2.10)$$

To find F_{mix}, we note that there are $\alpha p(1-\eta)/\eta$ homopolymers and p copolymers per micelle. The volume occupied by "free" copolymers is $\phi(1-\zeta)\Omega a^3$ and the volume of the system not occupied by micelles is given by $(1 - \xi\phi\zeta)\Omega a^3$, where $\xi = (1+\eta)/2\eta$. Hence, the volume fraction of "free" copolymers, ϕ_1, relevant for F_{mix} is

$$\phi_1 = \phi(1-\zeta)/(1-\xi\phi\zeta) \quad (2.11)$$

and F_{mix} is given by the Flory–Huggins expression

$$F_{mix}/kT = \Omega(1-\xi\phi\zeta) \times \left\{\frac{\phi_1}{2N} \ln \phi_1 + \frac{1-\phi_1}{2N/\alpha} \ln (1-\phi_1) + \frac{1}{2}\chi\phi_1(1-\phi_1/2)\right\} \quad (2.12)$$

It differs from ref 4 by having $2N$ instead of N in the denominator of the first two terms.

Finally, S_m is given by the ideal entropy of mixing expression

$$S_m/k = -\Omega\left\{\frac{\phi\zeta}{2Np} \ln (\xi\phi\zeta) + \frac{1-\xi\phi\zeta}{2Np\xi} \ln (1-\xi\phi\zeta)\right\} \quad (2.13)$$

To obtain the critical micelle concentration eq 2.10 has to be minimized with respect to p,η, and ξ. This results in the following three equations:

$$f + \frac{1}{p} \ln \frac{\xi(\phi-\phi_1)}{1-\xi\phi} - \ln \phi_1 - \frac{N\chi}{2}(\xi\phi_1^2 - 2\phi_1 + 2) + \alpha(1-\xi) \ln (1-\phi_1) + (1-\alpha)(\xi\phi_1 - 1) = 0 \quad (2.14)$$

$$\frac{\partial f}{\partial p} - \frac{1}{p^2}\left\{\ln (\xi\phi\zeta) + \left(\frac{1}{\xi\phi\zeta} - 1\right) \ln (1-\xi\phi\zeta)\right\} = 0 \quad (2.15)$$

$$\frac{\partial f}{\partial \eta} + \frac{1}{2\eta^2}\{\alpha(1-2\phi_1) \ln (1-\phi_1) - (1-\alpha)\phi_1 + N\chi\phi_1^2/2\} + \frac{2 \ln (1-\xi\phi\zeta)}{\phi\zeta p(1+\eta)^2} = 0 \quad (2.16)$$

where $f = \mathcal{F}/pkT$. The most important difference compared to the diblock case is the extra term $^3/_2\beta \ln N$ in the

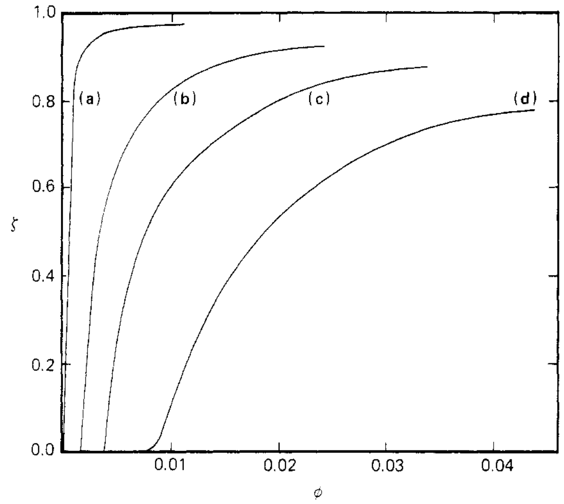

Figure 2. Fraction ζ of copolymer aggregated in micelles as a function of the overall copolymer concentration ϕ for four different values of the loop entropy parameter β. (a) $\beta = 0$; (b) $\beta = 0.3$; (c) $\beta = 0.4$; (d) $\beta = 0.5$.

expression for f. It is important to realize that both $\partial f/\partial p$ and $\partial f/\partial \eta$ are independent of β.

In the above considered case, the middle block of the copolymer and the homopolymer contain the same monomer A. As a consequence, the loop formation of the middle block occurs in the corona. However, it is clear that exactly the same equations would have been obtained for the opposite case, of homopolymers consisting of B monomers, where loop formation takes place inside the inner core.

3. Results and Discussion

In this final section, the discussion will center around the influence of β on the critical micelle concentration. As a typical example, we take $\chi = 0.1$, $N = 200$, and $\alpha = 10$. The influence of these parameters on the micelle formation is essentially equivalent to the diblock case and will not be considered again here. It was pointed out in ref 9 that eq 2.14 can be used to give a very simple estimate of the critical micelle concentration ϕ_c as long as $p \gg 1$ and $\phi_c \ll 1$. In this limit, the concentration of free copolymer is given by

$$\phi \simeq \exp\{-(\chi N - \alpha + 1 - f)\} \tag{3.1}$$

where the value of f to be used is determined by $\partial f/\partial p = \partial f/\partial \eta = 0$. Equation 3.1 predicts that ϕ_1 is indpendent of ϕ. Obviously, this can only hold for $\phi \geq \phi_1$ and $\phi \geq \phi_c$. It implies that the concentration of "free" copolymer is essentially constant above the critical micelle concentration. Hence, ϕ_1 is also a good approximation for the critical micelle concentration in this limiting case. However, as will become clear, the condition $\phi_c \ll 1$ is no longer satisfied for values of $\beta > 0.1$. The term $N\chi\phi_1$ in eq 2.14, in particular, cannot be neglected anymore. An improved approximation for ϕ_c is given by

$$\phi_c(\beta) \simeq e^{f(\beta)-N\chi+\alpha-1}/(1 - N\chi e^{f(\beta)-N\chi+\alpha-1}) \tag{3.2}$$

For $\beta = 0$, eq 3.1 is still very good and using the fact that

$$f(\beta) = f(0) + \tfrac{3}{2}\beta \ln N \tag{3.3}$$

we obtain

$$\phi_c(\beta) \simeq e^{(3/2)\beta \ln N}\phi_c(0)/(1 - N\chi e^{(3/2)\beta \ln N}\phi_c(0)) \tag{3.4}$$

In general, $\phi_c(\beta)$ can be obtained from eq 2.14–2.16 by a numerical iterative procedure only. The results are presented in Figure 2. Plotted is the fraction ζ of copolymers aggregated in micelles as a function of the overall block copolymer concentration ϕ for various values of β. From these curves, the critical micelle concentration can be obtained by using the onset approximation, well-known from glass transition temperature studies. In particular, $\phi_c(0)$ is found to be approximately 1.3×10^{-4}. The values for the number of copolymers per micelle, p, and the fraction of monomers in the corona belonging to the copolymer, η, are very insensitive to β. In all cases, $p \simeq 39$ and $\eta \simeq 0.19$, in complete agreement with Leibler et al.'s[9] results of $p \simeq 79$ and $\eta \simeq 0.19$. The factor 2 difference in p values reflects the fact that our description of the triblocks of length $2N$ closely resembles two diblocks of length N.

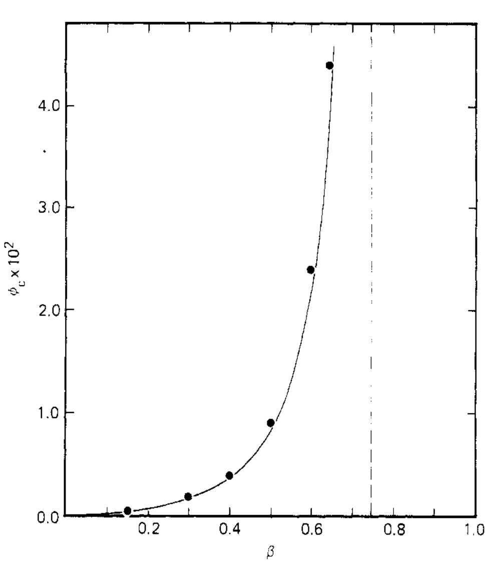

Figure 3. Critical micelle concentration ϕ_c as a function of the loop entropy parameter β. Full line, eq 3.4 with $\phi_c(0) = 3.4 \times 10^{-4}$; (●) full calculation.

Figure 3 shows $\phi_c(\beta)$ as a function of β obtained numerically. The dramatic influence of β is obvious. With the above-stated value of $\phi_c(0)$, $\phi_c(\beta)$ can be calculated from eq 3.4. The result is also presented in Figure 3 and the agreement between both results is very good. For the particular case considered, eq 3.4 predicts that $\phi_c(\beta) \rightarrow \infty$ for $\beta \rightarrow 0.749$. Since, as stated before, β is probably 1, this implies that for the given values of the parameters, micelle formation of triblocks is impossible. Micelle formation requires a larger value of χ. In that case, the cmc of a comparable diblock system will be much smaller than 10^{-4}.

Although the above discussion does, strictly speaking, only apply to high molecular weight solvents, it provides ample evidence for the large effect which backfolding can have. The cmc of various diblocks of poly(2-vinylpyridine)–polystyrene in toluene is of the order of 6×10^{-5}.[1] It seems reasonable to conclude that the experimental observation[1] that the corresponding triblock systems do not form micelles in toluene is due to the entropy loss accompanying backfolding of the middle block.

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Topological Constraints and Their Influence on the Properties of Synthetic Macromolecular Systems. 3. Triblock Copolymers Attached to a Surface

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ABSTRACT: Chain molecules with both ends strongly adsorbed to a surface are discussed as a model system for adsorption of triblock copolymers. Irreversible adsorption and absence of interaction between chain monomers and surface are assumed. Monte Carlo calculations are used to investigate the average conformation and the probability of knot formation for separate coils. A comparison is made with the probability of knot formation in ring polymers and scaling predictions. For overlapping coils scaling predicts that the layer thickness depends on the preparative stage due to the requirement of conservation of topological state, which leads to an additional excluded volume effect.

1. Introduction

Sterically stabilized colloidal suspensions are becoming increasingly important. Often polymers are used and various groups are currently investigating the forces between adsorbed layers of macromolecules.[1-8] Three essentially different systems can be distinguished, according to whether the adsorbed species are homopolymers, diblock copolymers, or triblock copolymers. To illustrate this, we will restrict ourselves to a discussion of the forces between layers adsorbed on mica involving polystyrene (PS) and poly(2-vinylpyridine) (PV2P). We will also assume that the polymer layer is irreversibly adsorbed.

The case of PS homopolymers adsorbed on mica and immersed in cyclohexane has been the subject of some controversy.[1,2,6,9,10] The force measured as a function of the distance between the micas contains a repulsive part followed by an attractive part for temperatures below and above the Θ-temperature (34.5 °C). Two explanations were put forward, a phase separation argument and a chain-bridging argument. Both may be present, but there are indications that bridging is the dominant factor.

Bridging can be avoided by using PS–PV2P diblock copolymers. The PV2P block adsorbs strongly on mica and if the surface is saturated, additional adsorption of PS will be negligible. In toluene, a good solvent for PS, the force is only repulsive with a steep uprise due to the onset of overlapping PS tails. This situation can be described well[8] by the Alexander–de Gennes theory[11,12] of terminally anchored chains. The overlapping coils force the PS chains away from the surface in a stretched conformation, leading to a flat concentration profile and a long-range repulsive force. Furthermore, the attractive part of the force reappears, but much smaller in magnitude than in the case of homopolymers, probably due to the absence of bridging.[8]

A third possibility is the use of PV2P–PS–PV2P triblock copolymers.[13] Again bridging is avoided. However, the repulsive layer now consists of loops instead of tails. In combination with the assumed irreversibility, this can have a significant effect since the topological constraints introduced in this way will lead to additional excluded volume effects.

There is another reason we are interested in triblock adsorption. In the dilute limit of separate coils, the situation closely resembles cyclization of linear polymers as described in a previous paper.[14] In particular, knots will again be present. Precisely how many is difficult to estimate off-hand, because the influence of the average monomer concentration inside the coil on the probability of knot formation is not well-known. That this is a problem of more than academic interest was pointed out by de Gennes recently.[15] In a short paper he suggested that the long-time memory effects in melts of crystallizable linear polymers may be related to tight knots. These might have been created during a previously conducted crystallization process accompanied by reeling in chains, containing a knot, from both ends. All these cases, ring polymers, loops, and unperturbed chains are characterized by different geometries and different average monomer concentrations.

The organization of this paper is as follows. In the next section a short description of the Monte Carlo method used to study the conformations and knot structure of ideal chain molecules attached with both ends to a plane will be given. Then in section 3 the results for the dilute limit of separate coils will be discussed. Finally, in section 4 the case of overlapping coils will be considered.

2. Monte Carlo Calculations

The Monte Carlo technique is used to create random walks which start and end at a flat surface and never cross the surface. As in the case of ring polymers we are con-

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