Polymeric Micelles: A Star Model

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ABSTRACT: A scaling theory is given for the structure of micelles formed by A–B diblock copolymers in a highly selective solvent. We consider micelles consisting of a small insoluble B core and an extended soluble A corona, i.e., the case $N_A \gg N_B$ (N_A and N_B are the polymerization degrees of the A and B blocks). The analysis is based on the Daoud–Cotton model for star polymers. It is found that the core radius scales as $N_B^{3/5}$ while the overall micelle radius scales as $N_B^{4/15}N_A^{3/5}$.

I. Introduction

Flexible diblock copolymers are the macromolecular counterpart of ordinary surfactants. In particular, both species form micelles in a selective solvent,[1] that is, a solvent which associates preferentially with one of the blocks. Current thermodynamic theories of polymeric micelle formation are based on a model proposed by de Gennes.[2] In this model as in others, we distinguish between two spherical, concentric, micellar regions: a central core, consisting solely of blocks immiscible in the solvent, and an outer corona, formed of soluble blocks swollen by the solvent. The central feature of this model is the assumption of *constant concentration* in each of the regions, i.e., the concentration is taken to be independent of r, the distance to the micelle center (Figure 1a). This assumption enables us to construct a Flory-type mean-field theory of micellar structure and to calculate all the micellar properties (core size, overall size, cmc, etc). Theoretical investigations along those lines were carried out by Noolandi et al.[3] and by Leibler et al.,[4] yielding results in good agreement with experimental data. However, as was already pointed out by de Gennes,[2] this model is best suited for micelles with thin and dense coronas. In micelles with an extended corona and a small core, coronal chains sample a larger volume the farther they are from the core boundary. For such systems, the assumption of constant concentration in the corona becomes untenable. Rather, the coronal monomer concentration must be a decreasing function of the distance from the micelle's center (Figure 1b). A possible way out of this difficulty entails a self-consistent calculation allowing for radial concentration variations. However, this approach is inherently complicated. Nevertheless, a simple micellar model incorporating all essential features may be constructed once we realize that micelles are structurely similar to colloidal particles coated by grafted chains, i.e., chains attached to a surface by a head group only. The colloidal particle corresponds to the micellar core while the grafted chains correspond to the corona. Colloidal particles coated by grafted chains are, in turn, similar to star polymers.[5,6] We are thus in a position to apply recent theoretical advances[5–7] with regard to star polymers to construct a "star model" of polymeric micelles. Specifically, we present a *scaling analysis of polymeric micelle structure based on their similarity to star polymers.* As it happens, early theories of polymeric micelle structure utilized the analogy between micelles and star polymers. This approach, attributed[1a] to Gallot et al.,[8] was used to interpret scattering data.[9] However, at the time, it was impossible to base thermodynamic theory on this model.

We consider a solution of monodispersed A–B diblock copolymers in a selective solvent S. The A–B copolymers consist each of N_A A monomers and N_B B monomers. S is a low molecular weight solvent such that isolated B coils in it are completely collapsed. On the other hand, S is a good solvent for the A coils. We focus on the case $N_B \ll N_A$ i.e., *the insoluble B block is much smaller than the A block.* for very incompatible B and S, this system has a very low critical micelle concentration (cmc). Well past the cmc most chains are aggregated into micelles. We discuss this regime, where micelle structure is determined essentially by the *free energy per chain of a single micelle.* For simplicity we assume the micelles to be *completely spherical* and *monodispersed*, consisting each of f A–B copolymers. As is customary with scaling analysis we ignore numerical prefactors.

II. The Model

As is commonly done we take each micelle to be made of two concentric spherical regions: an inner core consisting of close packed B monomers and an outer corona of A coils swollen by the solvent S. Our model is different in the description of the micellar corona. Rather than assuming a constant concentration in the corona, we allow the concentration to fall off with distance as it does in star polymers' "corona". We first review the essential features of the core and then proceed to present, in some detail, the proposed model for the corona.

Provided that the *temperature is higher than* T_g, the glass transition temperature, the core is essentially a melt of B chains. Accordingly we may assume ideal chain statistics. However, because the chain end (actually, the copolymer A–B junction) is constrained to the interface, packing constraints ($\phi_B \approx 1$) may require chain deformation. Because $\phi_B \approx 1$ we have $R_{core}^3 \approx fN_Ba^3$ where a is a typical monomer size, and thus

$$R_{core} \approx f^{1/3}N_B^{1/3}a \qquad \text{(II-1)}$$

On the basis of previous investigations[2–4] we expect $R_{core} > N_B^{1/2}a$ and thus a certain amount of chain stretching. It is common to assume that all B chains are uniformly stretched with an end-to-end distance equal to R_{core}. However, experience with small-chain micelles[10] indicates that such an assumption may lead to a serious overestimate of the average chain deformation. In such systems the radial distribution function of the terminal segments is very similar to that of an ideal grafted chain, i.e., it is undeformed except for effects due to the presence of a repulsive interface at the grafting site. This is due to the steep decrease in available volume on approach to the origin. For simplicity we make use of the uniform stretching assumption while keeping in mind the overestimate involved. We further assume a sharp interface between the core and the corona; i.e., the interface thickness is assumed to be negligible in comparison with R_{core}.

In the following we adapt the Daoud–Cotton (DC) treatment[7] of star polymers to treat micellar coronas. This approach rests on two observations: (1) The corona, like the micelle itself, has spherical symmetry. (2) One expects the monomer volume fraction in the corona, ϕ_A, to be a

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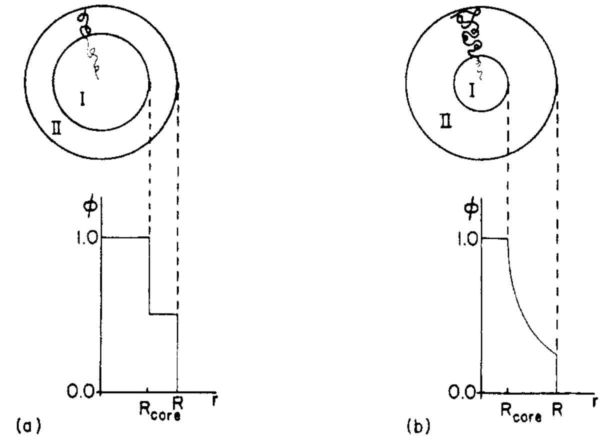

Figure 1. Model for A–B diblock copolymer micelle in a selective solvent which is a good solvent for A: schematic cross sections and plots of monomer volume fraction (ϕ) versus distance from the micelle center (r). Region I is a core consisting of a melt of B blocks ($\phi = \phi_B \approx 1$). Region II is a "corona" of A coils swollen by the solvent ($\phi = \phi_A < 1$). (a) The large core limit, $N_B \gg N_A$. (b) The small core limit, $N_B \ll N_A$.

decreasing function of r. This is due to the larger volume available to a coil the farther it is from the core surface. To obtain an explicit form for $\phi_A(r)$, we analyze coronal coil conformations in terms of "blobs": chain segments exhibiting single linear chain behavior. Blobs occupy regions of size ξ, which depends on the local monomer concentration. Following DC we now postulate that (1) ξ depends on r only: $\xi = \xi(r)$. This means that the concentration profile is self-similar and thus $\xi \sim r$. (2) In a spherical shell of radius r and thickness $\xi(r)$ there are f blobs. The second postulate determines the f dependence of ξ because it leads to $r^2\xi = f\xi^3$ and thus to

$$\xi \approx r/f^{1/2} \tag{II-2}$$

As S is assumed to be a good solvent for A coils, excluded volume effects are important within the blob and $\xi(r)$ is given by

$$\xi(r) \approx n^{3/5}(r)a \tag{II-3}$$

where $n(r)$ is the number of monomers in a blob located at a distance r. On comparing (II-2) and (II-1) we obtain an explicit form for $\phi_A(r)$

$$\phi_A(r) \approx \frac{fn(r)a^3}{r^2\xi(r)} \approx f^{2/3}(a/r)^{4/3} \tag{II-4}$$

This $\phi_A(r)$ replaces the $\phi_A(r)$ = constant assumption used in the current literature. Within this model $\phi_A(r)$ decays as $r^{-4/3}$ in the micellar coronas as in the swollen periphery of many-armed stars. To obtain the corona's thickness we use

$$a^3fN_A = \int_{R_{core}}^{R} \phi_A(r)\ \mathrm{d}r \approx f^{2/3}a^3(r/a)^{5/3}\Big|_{R_{core}}^{R} \tag{II-5}$$

Nor $N_A \gg N_B$, when the core is relatively small, we find

$$R \approx f^{1/5}{N_A}^{3/5}a \tag{II-6}$$

The micellar radius as given by (II-6) is identical with that of a star polymer with the same f. However, for a star polymer f is determined by the synthesis. In a micellar system f is self-adjusting: it has yet to be determined by minimizing the appropriate free energy.

In effect, a coronal coil is grafted to the narrow end of a truncated cone with nonadsorbing walls. The confinement free energy with respect to a free coil is roughly kT times the number of blobs in the coil.[11] To calculate the number of blobs in the corona, n_{blob}, we use the Witten–Pincus trick.[6] In a self-similar region, the blobs in a given shell are ω times larger than the blobs in the adjacent inner shell. As a result, the thickness of the region is given by a sum of a geometric series. Thus, given the region boundaries we may obtain the number of shells, n_s, in it. The total number of blobs in the region is given by $n_{blob} = fn_s$. For any shell, j, in a spherical self-similar region we have

$$\omega \equiv \frac{\xi_{j+1}}{\xi_j} = \frac{r_{j+1}}{r_j} \approx 1 + \frac{\xi_j}{r_j} \approx 1 + f^{-1/2} \tag{II-7}$$

The corona's thickness is thus given by

$$R - R_{core} \approx \xi(R_{core})(\omega + ... + \omega^{n_s-1}) \approx \xi(R_{core})\frac{\omega^{n_s} - 1}{\omega - 1} \tag{II-8}$$

Which yields

$$n_s \approx \frac{\ln\ (R/R_{core})}{\ln\ \omega} \approx f^{1/2} \ln\ (R/R_{core}) \tag{II-9}$$

The confinement free energy, ΔF_{con}, of the f coronal chains is then

$$\Delta F_{con}/kT \approx n_{blob} \approx fn_s \approx f^{3/2} \ln\ ({N_A}^{3/5}f^{-2/15}{N_B}^{-1/3}) \tag{II-10}$$

III. Scaling Laws for a Single Micelle

The total free energy of a micellar solution is indispensable for a complete discussion of the system:[4] relative stabilities, the fraction of nonaggregated chains, the determination of the cmc, etc. The total free energy includes the free energy of the micelles themselves as well as the mixing free energies of the micelles and of the free copolymer chains. However, for systems well past the cmc but before the onset of micelle–micelle interactions, micellar properties are determined by the free energy per chain of a single micelle. Since the DC approach is justified for $N_A \gg N_B$ *in the limit of large f* values, it is not strictly applicable in the vicinity of the cmc where f is small. We thus limit our discussion to the regime dominated by the free energy of a single micelle, i.e., $c \gg$ cmc and $c_{micelle} \ll c^*_{micelle}$, where c denotes the copolymer concentration, $c_{micelle}$ the micelle concentration, and $c^*_{micelle}$ the lowest $c_{micelle}$ for which micelle–micelle interactions are important.

We calculate the free energy of a micelle with respect to the free energy of f free, nonaggregated, copolymer chains. The solvent S is such that the B coil is completely collapsed while the A coil is swollen. Because the B coil is collapsed and $N_B \ll N_A$, we assume the interaction between the two blocks is negligible. Assuming, as we do, that the temperature is well below the Θ temperature for the B coil, we may approximate its free energy using the Flory-type mean-field approach.[12] The detailed assumptions concerning the reference state are not really important. The reference state's only essential feature is the extensitivity of its free energy in f. Accordingly, the choice of a reference state only determines the free energy per micellar chain up to an additive constant and has no effect on the minimum condition.

We approximate the free energy of a single micelle, $F_{micelle}$, as a sum of three contributions due to the core, the corona, and the interface between them.

$$F_{micelle} = F_{core} + F_{interface} + F_{corona} \tag{III-1}$$

F_{core} accounts for the change in the configurational entropy of the B chains on aggregation. Assuming that each core chain is stretched with an end-to-end distance of R_{core}, we obtain

$$F_{\text{core}}/kT \approx f\left(\frac{R_{\text{core}}}{N_{\text{B}}^{1/2}a}\right)^2 - (\text{term linear in } f) \approx f^{5/3}N_{\text{B}}^{-1/3} - (\text{term linear in } f) \quad \text{(III-2)}$$

Let us stress again that the uniform stretching approximation may lead to a serious overestimation of F_{core}. Recall that within our model, micellization is due to the system's tendency to lower its surface free energy: the decrease in the interfacial energy due to micellization is then roughly

$$F_{\text{interface}} \approx \gamma R_{\text{core}}^2 - (\text{term linear in } f) \approx \gamma a^2 f^{2/3} N_{\text{B}}^{2/3} - (\text{term linear in } f) \quad \text{(III-3)}$$

The A coil in the corona is effectively grafted to the narrow end of a truncated cone with nonadsorbing walls. The resulting confinement is associated with a loss of free energy reflected in the last term

$$F_{\text{corona}}/kT \approx f^{3/2} \quad \text{(III-4)}$$

F_{corona} is actually ΔF_{con} obtained in (II-10) except for a logarithmic factor which we have approximated as a constant. The reference state for ΔF_{con} is that of a free A coil. Interactions between the A and B blocks are thus neglected. This approximation is justified in the limit $N_{\text{A}} \gg N_{\text{B}}$ particularly as the B block is taken to be collapsed. Our expression for F_{micelle} does not account for certain entropic contributions due to the localization of the A–B joint at the core surface. Because of this constraint we consider both core and coronal coils as grafted to the core surface. Core chains are grafted to the inner surface, while coronal coils are considered as grafted to the exterior surface. However, we do not allow for the bond between the core and coronal coils at the grafting site, i.e., the A and B blocks are not independently grafted. This approximation is justified because the necessary correction term is essentially linear in f and has thus no effect on the minimum condition.

The free energy *per coronal chain*, in the limit of large f and for $N_{\text{A}} \gg N_{\text{B}}$ is then given by

$$F_{\text{micelle}}/kT \approx (\gamma a^2/kT)N_{\text{B}}^{2/3}f^{-1/3} + N_{\text{B}}^{-1/3}f^{2/3} + f^{1/2} + \text{constant} \quad \text{(III-5)}$$

Minimization with respect to f yields

$$f^{-1/2}[1 + (N_{\text{B}}^{-2}f)^{1/6}] \approx (\gamma a^2/kT)N_{\text{B}}^{2/3}f^{-4/3} \quad \text{(III-6)}$$

We assume and later verify that $fN_{\text{B}}^{-2} \ll 1$ thus justifying the approximation of the LHS by $f^{-1/2}$. Further justification is due to the fact that the fN_{B}^{-2} term on the LHS results from the uniform stretching approximation and is thus suspect as an overestimate. We obtain

$$f \approx N_{\text{B}}^{4/5} \quad \text{(III-7)}$$

On substituting (III-7) in (II-1) and in (II-6), we find

$$R_{\text{core}} \approx N_{\text{B}}^{3/5}a \quad \text{(III-8)}$$

and

$$R \approx N_{\text{B}}^{4/25}N_{\text{A}}^{3/5}a \quad \text{(III-9)}$$

Equations III-7–III-9 are our main result. Experimental values of R of styrene–butadiene diblock copolymer micelles in *n*-heptane[13] conform to scaling low, (III-9), within an accuracy of 10% (Table I). The agreement is satisfactory considering the nonnegligible core size in these experiments. It is instructive to compare our results with scaling relations obtained for highly incompatible systems in the opposite limit: $N_{\text{A}} \ll N_{\text{B}}$. One then finds[2]

$$f \approx N_{\text{B}} \quad \text{(III-10)}$$

and

$$R \approx R_{\text{core}} \approx N_{\text{B}}^{2/3}a \quad \text{(III-11)}$$

Table I
Experimental[13] Radius (R_{exp}) of Gyration of Styrene–Butadiene Diblock Copolymer Micelles in *n*-Heptane and the Corresponding $R_{\text{exp}}/N_{\text{B}}^{4/25}N_{\text{A}}^{3/5}$

N_{A}	N_{B}	R_{exp}, Å	$R_{\text{exp}}/N_{\text{B}}^{4/25}N_{\text{A}}^{3/5}$
1020	210	171 ± 4	1.138
1315	115	173 [illegible] 4	1.089
1720	120	195 ± 4	1.038

The micellar radius in the large core limit ($N_{\text{A}} \ll N_{\text{B}}$) is essentially equal to the core radius. In the opposite limit, of small core micelles ($N_{\text{A}} \gg N_{\text{B}}$), the core radius is negligible in comparison to R, the micelle overall radius. In both limits, micelle formation is driven by the system's tendency to lower its surface free energy. For large core micelles ($N_{\text{A}} \ll N_{\text{B}}$), this tendency is countered by the stretching of the ideal core chains and the resultant increase in free energy. In our case of small core micelles ($N_{\text{A}} \gg N_{\text{B}}$), micellar growth is checked by the increasing confinement free energy of the swollen coronal chains.

IV. Concluding Remarks

In this paper we have considered the structure of diblock copolymer micelles with a small core and an extended corona. Such micelles are structurally similar to star polymers. Specifically, one may then use the Daoud–Cotton model for star polymers to describe the micellar corona thus allowing for radial concentration variations. This last feature is essential to the proper description of micelles with cores which are small compared with the overall micelle size. Our main results are scaling laws relating the core size and the micelle size to the number of monomers in each of the blocks. The scaling relation for the overall micelle size is in reasonably good agreement with experimental data. However, we expect even better agreement for micelles with cores which are relatively smaller. Because this approach is valid only for high f values, it can only be used to describe micelle structure well past the cmc. It cannot be used to investigate the cmc itself.

The similarity between small core micelles and star polymers is also of interest from another point of view. The study of star polymers with high functionalities may be susceptible to spurious effects due to the complicated structure of their center. Dense chemical grafting of small colloidal particles by long chains results in starlike objects but may prove difficult for kinetic reasons. Diblock copolymer micelles seem to provide starlike systems, seemingly free from such flaws. One may then suggest that apart from their inherent interest, such micelles should be studied as model systems for star polymers.

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Communications to the Editor

Transformation of Native Cellulose Crystals Induced by Saturated Steam at High Temperatures

Cross-polarization/magic-angle spinning (CP/MAS) ^{13}C NMR spectroscopy has proved to be very useful in characterizing crystalline and noncrystalline regions of cellulose.[1-24] However, the origin of the fine multiplicities appearing in the crystalline resonance lines still remains a controversial problem. Two models[10,11,15] have been proposed, which indicate that all native celluloses are a mixture of two crystalline modifications although each modification is differently defined in the two models. In contrast to these proposals, we have recently found by using a computer-line-shape analysis[20] that relative intensities of the C1 and C4 triplets are not explained in terms of a linear combination of two crystalline modifications based on either model. Moreover, the crystalline spectra of native cellulose, which were successfully separated from the noncrystalline components by using the difference in ^{13}C spin-lattice relaxation times T_{1C}, are classified into two types, cotton-ramie type and bacterial-valonia type. Although these spectra were referred to as celluoses I_a and I_b, respectively, both spectra seem to be composites of different crystal forms in accord with previous proposals.[10,11,15] The main cause of the unsuccessful interpretation of the experimental spectra in terms of their models may be inappropriate identification of the spectrum of each pure crystal form.

For the purpose of solving the controversial problem of cellulose crystals, it is very important to obtain more information about cotton-ramie type and bacterial-valonia type crystals, which are also here referred to as celluloses I_a and I_b for convenience although such nomenclature may not be exact in crystallography.[25] In a previous paper[19] we reported that cellulose I_b was readily transformed into cellulose I_a when the sample was regenerated from cellulose triacetate which was prepared under a low swelling condition. Similar transformation from cellulose I_b to I_a was also recognized in the case of the regeneration from cellulose III_I.[21] In contrast to this peculiar transformation of cellulose I_b, cellulose I_a crystals stay almost unchanged during these processes. In an attempt to examine the interconversion between cellulose I_a and I_b in a more direct way, we have studied in this paper the possible transformation of the crystals induced by saturated steam at higher temperatures.

The cellulosic materials used are bacterial and valonia celluloses, the crystals of which are referred to as cellulose I_b, and cotton cellulose, which contains cellulose I_a crystals. After conventional purification, these samples were subjected to annealing by saturated steam at 230-280 °C for 30 min in an autoclave. In this case each sample was kept in the vapor phase by fixing it with glass fiber sheets and stainless steel nets without contact with the liquid phase. CP/MAS ^{13}C NMR measurements, at 50 MHz were performed on a JEOL JNM-FX200 spectrometer using a magnetic field of 4.7 T for the annealed samples in the hydrated state and using a MAS rotor with an O-ring seal.[13,26] The experimental conditions are almost the same as described in the previous papers.[19,20] The chemical shifts relative to tetramethylsilane (Me$_4$Si) were determined by assuming the crystalline peak of linear polyethylene to appear at 33.6 ppm.[27]

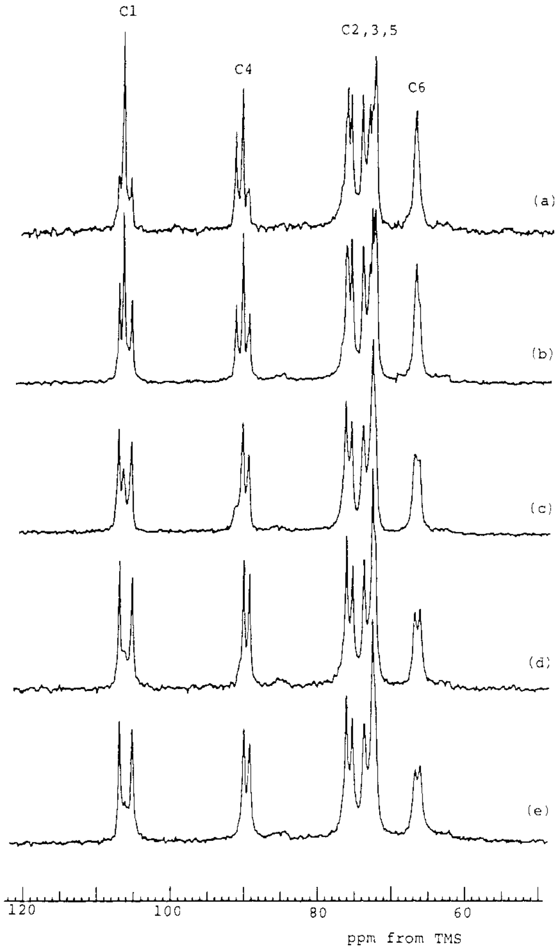

Figure 1. CP/MAS ^{13}C NMR spectra, 50 MHz, of valonia cellulose treated with steam at different temperatures: (a) original; (b) 230 °C; (c) 245 °C; (d) 260 °C; (e) 280 °C.

Figure 1 shows 50-MHz CP/MAS ^{13}C NMR spectra of

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