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Surfactant-Induced Lyotropic Behavior of Flexible Polymer Solutions

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ABSTRACT: A theoretical analysis is presented to describe the stiffening of flexible, linear polymer chains due to complexation with oligomeric surfactants. These surfactants might be functionalized protonic acids or possess other types of end groups that exhibit strong, specific interactions with the flexible polymer backbone. We consider the enhancement of the persistence length due to steric interactions between the bound surfactant tails and investigate the possibility of lyotropic behavior at finite polymer concentration. The results are discussed in the context of recent experiments by Cao and Smith, who reported liquid crystallinity in solutions of polyaniline complexed with camphorsulfonic acid.

I. Introduction

In a recent study, Cao and Smith[1] reported the observation of liquid crystalline order in polyaniline (PANI) solutions that were fully protonated with a functionalized acid, camphorsulfonic acid (CSA), and dissolved in *m*-cresol. This exciting finding opens a new path to processing PANI and may facilitate the manufacture of highly oriented conducting fibers. Moreover, the general scheme of complexing a conducting polymer with a functionalized acid (i.e., surfactant) that renders the complex both soluble in simple organic solvents *and* conducting could have far-reaching technological implications.[2]

Conjugated polymers in their doped, conducting form are somewhat rigid due to electronic delocalization,[3] but are generally not known to exhibit lyotropic behavior. Cao and Smith thus attributed the observation of liquid crystallinity in the PANI/CSA system to a combination of electronic stiffening and *steric stiffening* due to crowding of the associated CSA counterions. If the latter mechanism is indeed responsible for the lyotropic behavior, then one could envision using strongly associating surfactants to induce liquid crystallinity in solutions of even very flexible, nonconjugated polymers. Since processing from an orientationally ordered phase is capable of imparting a high degree of chain alignment and greatly enhanced mechanical, electrical, and optical properties, such a scheme could lead to powerful new processing methods for a wide variety of polymeric materials.

In the present paper we investigate the possibility that steric stiffening due to complexation with oligomeric surfactants can, acting alone, induce lyotropic behavior in flexible polymer solutions. This investigation involves several steps, the first of which is to quantify the enhancement of the persistence length of a chain for a particular aggregation number, i.e., number of associated surfactants. The second step is to carry out an analysis of the association equilibria in solution in order to determine how this aggregation number depends on the concentrations, molecular weights, and chemical natures of the species present. Finally, we combine these results with a theory of the isotropic–nematic transition for a semiflexible polymer solution to assess the conditions under which lyotropic behavior is to be expected.

Some of the individual steps just outlined are not particularly novel to the present study. Indeed, several related calculations have been previously described in the literature.[4] In particular, Birshtein et al.[5] and Aime[6] have studied the conformational properties of comblike macromolecules with permanently affixed side branches. Moreover, Wang and Safran[7] have investigated association phenomena and structure of cylindrical micelles formed from polymeric surfactants. Nevertheless, we believe that the application addressed in the present paper, stimulated by the pioneering experimental studies of Cao and Smith, is unique in its scientific merit and may be of practical utility.

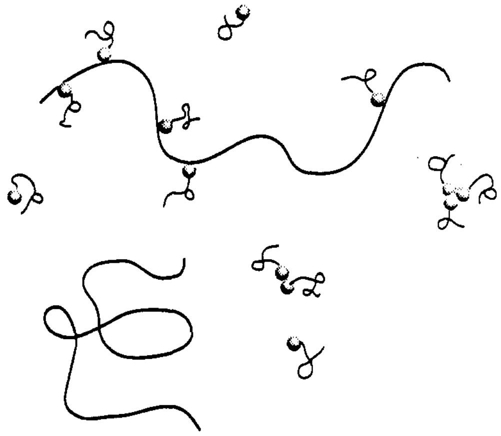

Figure 1. Model polymer/surfactant solution studied in the present paper. Flexible polymers of degree of polymer N and surfactants of degree of polymerization M ($N \gg M \gg 1$) are dispersed in a solvent that is athermal for the polymer backbone and the surfactant tails. The surfactant head groups (denoted by a solid dot) are capable of complexing with backbone monomers of the chain or possibility with each other, forming micelles.

Our model polymer/surfactant solution is a very simple and highly idealized one that, nevertheless, permits a rather detailed analysis. As shown in Figure 1, we consider flexible polymer chains of degree of polymerization N, dispersed in a good solvent along with oligomeric surfactant molecules of degree of polymerization M. The situation of primary interest is that of $N \gg M \gg 1$, for which universal scaling predictions can be deduced. To minimize the number of dimensionless parameters, we image that all monomers and solvent molecules occupy the same volume, denoted by a^3, and that the thermodynamic quality of the solvent for the tails of the surfactant and the polymer backbone is the same (athermal). One end monomer of each surfactant is taken to be a functional group, e.g., an acid, that has a strong affinity for complexation with backbone sites along the flexible chains. These binding sites are assumed to be uniformly distributed on the polymer backbones and we do not explicitly

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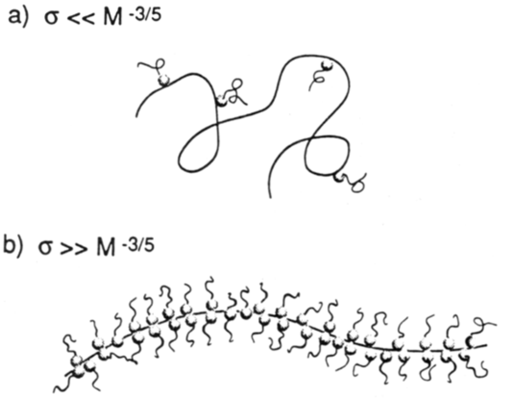

Figure 2. (a) Aggregates formed by polymer complexed with surfactant in the low-coverage limit, $\sigma \ll M^{-3/5}$. Macroscopically, each polymer remains in a coiled, swollen configuration. (b) "Bottle-brush" aggregates formed by polymer complexed with surfactant in the high-coverage limit, $\sigma \gg M^{-3/5}$. A transformation to a wormlike configuration with persistence length λ occurs. If λ exceeds the polymer contour length Na, then the global configuration is rodlike; if λ is significantly less than Na, the aggregate adopts a highly extended, coiled configuration.

allow for saturation; i.e., there are a continuum of potential sites along each chain. Nevertheless, as will be discussed in sections III and IV, it is possible to treat cases where full saturation is achieved. We denote the binding energy of a surfactant end group to a backbone site by $k_BT\epsilon$.

II. Surfactant-Induced Rigidity

As suggested by Figure 1, the model polymer/surfactant solution just described is capable of various types of self-assembly. Of primary interest is the complexation of surfactant molecules to the flexible polymer backbones, but the surfactant molecules can also aggregate together to form micelles with a distribution of shapes and sizes. In the present section we focus exclusively on the polymer/surfactant complexes and the rigidity imparted to the polymer backbone by the association event. Specificially, we consider a single polymer molecule with a fixed number of bound surfactant molecules.

A particularly convenient measure of the aggregation number for a polymer/surfactant complex is a dimensionless parameter σ, defined as the number of bound surfactant molecules per backbone monomer of the polymer. The number of surfactants per chain is thus σN and the volume fraction of the complex constituted by the surfactants is $\sigma M/(1+\sigma M)$. In section III we consider the thermodynamic and structural parameters that establish the average value of σ for a particular solution; in the present section we imagine σ to be known.

Depending on the value of σ, the complex can adopt either very flexible (coillike) or extended (rodlike) configurations. As depicted in Figure 2a, the coillike configuration is expected for relatively low aggregation numbers satisfying $\sigma \ll M^{-3/5}$. This corresponds to an average spacing of bound surfactants along the backbone that exceeds the Flory radius of the surfactants:

$$R_M \sim aM^{3/5} \tag{1}$$

For such low aggregation numbers, the configurational statistics of the surfactant tails are essentially unperturbed by attachment to the chain. Moreover, the enhancement in rigidity of the polymer backbone, discussed in section II.A, is small.

At larger values of σ, i.e., $\sigma \gg M^{-3/5}$, the bound surfactant tails must stretch out normal to the polymer backbone to avoid contacts with other tails. The resulting structure, resembling a "bottle-brush", is shown in Figure 2b. As will become apparent in section II.B, this polymer/surfactant complex can be quite rigid, possibly leading to lyotropic behavior as the concentration of complex is increased.

A. Low-Coverage Limit, $\sigma \ll M^{-3/5}$. When the surfactants are spaced an average distance along the chain that exceeds R_M, a simple Flory theory suffices to estimate the coil expansion due to complexation. The surfactant tails can be assumed to adopt coil configurations unperturbed from those of a free surfactant molecule; hence, they are modeled as spheres of radius R_M attached randomly along the polymer backbone. It follows that the overall size of the coiled complex, R, can be determined from the following free energy expression:[8]

$$\beta F = \frac{R^2}{Na^2} + a^3\frac{N^2}{R^3} + {R_M}^3\frac{(\sigma N)^2}{R^3} \tag{2}$$

where $\beta = 1/k_BT$. The first term on the right-hand side of this equation describes the elastic energy (configurational entropy) of chain deformation to a radius R, while the second and third terms are virial contributions to the free energy. The second term describes the excluded volume associated with the N backbone monomers, each of volume a^3. The third term, in contrast, describes the excluded volume of the σN bound surfactant coils, each of volume ${R_M}^3$.

Equation 2 is easily minimized with respect to R in order to determine the equilibrium dimensions of the complex. At very small aggregation numbers, $\sigma \ll M^{-9/10}$, the backbone excluded volume dominates the surfactant excluded volume and the flexible polymer coil is unperturbed by the complexed surfactant:

$$R \sim R_N = aN^{3/5}, \quad \sigma \ll M^{-9/10} \tag{3}$$

In this equation, R_N is the Flory radius of the polymer with no bound surfactant.

At larger aggregation numbers, $M^{-9/10} \ll \sigma \ll M^{-3/5}$, the surfactant excluded volume dominates that of the backbone and the complex size is determined by balancing the first and third terms of eq 2. This leads to

$$R \sim a\sigma^{2/5}M^{9/25}N^{3/5}, \qquad M^{-9/10} \ll \sigma \ll M^{-3/5} \tag{4}$$

It is convenient to reexpress this result in terms of a swelling ratio, α,

$$\alpha \equiv R/R_N \sim \sigma^{2/5}\, M^{9/25} \tag{5}$$

which gives the ratio of the polymer/surfactant complex size to that of the uncomplexed polymer. Equation 5 smoothly crosses over to the $\alpha = 1$ behavior predicted in eq 3 as σ approaches the lower bound of $M^{-9/10}$. For larger σ, eq 5 predicts a modest increase in the dimension of the coiled complex as the converage is increased or the surfactant tails are lengthened.

B. High-Coverage Limit, $\sigma \gg M^{-3/5}$. When σ is increased beyond the point that the surfactant tails begin to interact, $\sigma \sim M^{-3/5}$, the configuration of the complex gradually changes from that of a coil toward a more extended rod (Figure 2b). We do not attempt to describe this crossover, but instead focus on the rodlike state characteristic of $\sigma \gg M^{-3/5}$. In most situations of interest, namely, $1 > \sigma \gg M^{-3/5}$, the complex will be best described not strictly as a rod but as a semiflexible rod, i.e., a wormlike chain,[9] with a persistence length that may not exceed the overall chain contour length Na. Of particular importance to the present study is how this persistence length depends on the coverage σ and the surfactant molecular weight M.

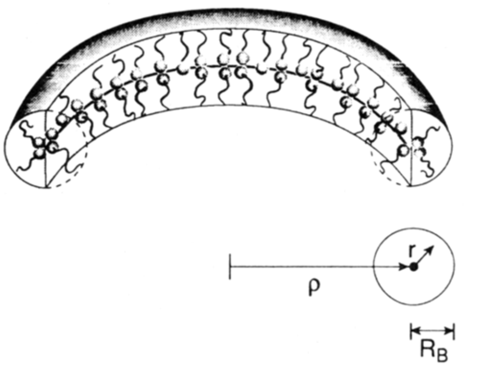

Figure 3. Toroidal configuration of the dense aggregate used to calculate the persistence length, λ. As detailed in the appendix, the linear aggregate of contour length $Na = 2\pi\rho$ is bent to form a torus of principal radius ρ. The cross-sectional radius is denoted R_B.

To calculate the persistance length of the bottle-brush structure shown in Figure 2b, we follow an approach similar to that used to calculate the elastic constants of deformed monolayers and bilayers in surfactant and block copolymer systems.[10,11] Namely, we bend the structure gently with a radius of curvature ρ that greatly exceeds the radius of the bottle-brush, R_B, and then calculate the change in the free energy per unit length from that of the undeformed structure. This free energy change is invariant to the sign of the curvature, so the leading term is second order in R_B/ρ. The persistence length is simply identified as the coefficient of this quadratic term in the free energy.

In the appendix we provide the details of the calculation just outlined. As illustrated in Figure 3, it proves convenient to bend the polymer/surfactant complex uniformly, i.e., into a torus of principal radius ρ. The evaluation of the free energy then amounts to an extension of the method developed for star polymers by Daoud and Cotton[4,12,13] to a toroidal geometry. For a rigid cylindrical aggregate ($1/\rho = 0$), the Daoud–Cotton method was recently employed by Wang and Safran[7] to compute the aggregated structure and free energy. In the present notation, these authors find that the linear aggregate has a radius that scales as

$$R_{B0} \sim a\sigma^{1/4}M^{3/4} \tag{6}$$

which indicates that the surfactant tails are significantly extended in the present high-coverage regime. It is of interest to note that R_{B0} crosses smoothly to the Flory radius R_M as $\sigma \to M^{-3/5}$. For the free energy per unit length of the rodlike aggregate, Wang and Safran find the scaling result

$$\beta\mathcal{F} \sim a^{-1}\sigma^{13/8}M^{3/8} \tag{7}$$

which exceeds k_BT per backbone monomer of the complex when $\sigma > M^{-3/13}$.

As discussed in the appendix, there are modifications of the Daoud–Cotton approach that are required to analyze the toroidal geometry. In particular, on bending the linear aggregate, there is a slight redistribution of surfactant tails from the inner half to the outer half of the torus. This redistribution must be self-consistently calculated, along with a slight curvature-dependent shift in the radius of the polymer/surfactant complex from R_{B0}. For the purpose of presenting the results of these calculations, it is convenient to introduce a dimensionless curvature c, defined as the ratio of the radius of the *linear* aggregate to the large radius of the torus:

$$c = R_{B0}/\rho \tag{8}$$

Expressed in terms of this curvature, the leading correction to the radius of the aggregate is given by

$$R_B = R_{B0}\left[1 + \frac{6}{245\pi^2}c^2 + O(c^4)\right] \tag{9}$$

Thus, the complex increases slightly in diameter on bending. (Note that we insist that the cross-section of the aggregate remains circular.) Similarly, we demonstrate in the appendix that the fraction of surfactant tails that occupy the inner half-torus, p, is given for weak curvature by

$$p = \frac{1}{2}\left[1 - \frac{8}{7\pi}c + O(c^3)\right] \tag{10}$$

The fraction of tails occupying the outer half-torus, $1-p$, is thus larger than 1/2. Finally, the free energy per unit contour length of the gently curved aggregate is given by

$$\beta\mathcal{F} \sim a^{-1}\sigma^{13/8}M^{3/8}\left[1 + \frac{113}{490\pi^2}c^2 + O(c^4)\right] \tag{11}$$

There are several points to be made with regard to eq 11. First of all, we note that eq 7 is recovered in the limit of vanishing curvature. Secondly, the equation shows that the $O(c^2)$ coefficient is *positive*, implying that the linear aggregate resists bending. This rules out a weak curvature instability of the polymer/surfactant complex to some sort of curve or helical shape, although higher order terms in eq 11 would be required to rule out a large-c instability, e.g., a first-order phase transition. In should be noted that Halperin, Tirrell, and Lodge[4] had previously suggested the possibility of such a bending instability. Next, we can use eq 11 to derive an expression for the persistence length, λ, of the complex at high coverage. If the semiflexible aggregate is viewed as a wormlike chain,[9] it follows that the free energy change on bending per unit contour length is related to λ by the simple scaling relation

$$\beta\Delta\mathcal{F} \sim \lambda/\rho^2 \tag{12}$$

Comparison of eqs 11 and 12 leads to an explicit expression for the persistence length

$$\lambda \sim a\sigma^{17/8}M^{15/8} \tag{13}$$

The polymer/surfactant complex appears rodlike when viewed on scales comparable to that given by eq 13 and coillike when viewed on much larger scales (provided the contour length Na greatly exceeds λ). The overall dimension of the aggregate, which is a self-avoiding random walk with steps of length λ, thus scales as

$$R \sim \lambda(Na/\lambda)^{3/5} \sim a\sigma^{17/20}M^{3/4}N^{3/5} \tag{14}$$

Finally, we again express this result in terms of a swelling ratio,

$$\alpha \equiv R/R_N \sim \sigma^{17/20}M^{3/4} \tag{15}$$

Comparison of eqs 5 and 15 indicates that the global coil dimensions increase much more rapidly with aggregation number or surfactant molecular weight in the high-coverage limit than in the low-coverage regime.

It is important to emphasize that the above calculations mandate a *locally* rodlike structure of the complex at high coverage. In particular, it follows from eqs 6 and 13 that the ratio of length to diameter of the persistent segments of the backbone scales as $\lambda/R_{B0} \sim \sigma^{15/8}M^{9/8}$, which greatly exceeds unity for $\sigma \gg M^{-3/5}$. This prediction contradicts an earlier study by Birshtein et al.,[5] who reported that

λ/R_{B0} remains $O(1)$ for a range of solvent conditions and grafting densities. As we shall see in section IV, a large aspect ratio is crucial for the onset of lyotropic behavior at higher polymer concentration.

III. Association Equilibria

Having established the dimensions and rigidity of a polymer/surfactant complex at a particular aggregation number σN, we now turn to consider the thermodynamic factors that control the mean value of σ. To keep the analysis simple, we initially ignore the formation of micelles by the association of surfactant molecules and restrict attention to aggregates formed by the complexation of surfactant molecules with polymer. We will return to consider the consequences of this restriction at a later point.

In general, at thermodynamic equilibrium, there will exist a distribution of molecular aggregates built up from a polymer molecule and one or more surfactant molecules, as well as free (not complexed) surfactant molecules and free polymers. We use the integer index n to denote the aggregation number (number of surfactants that are bound to a polymer) of a particular polymer/surfactant complex. Furthermore, the volume fraction of the solution occupied by complexes with aggregation number n is denoted by ϕ_n; ϕ_0 is thus the volume fraction of free polymer. The volume fraction of free surfactant is denoted ϕ_f. It follows that the volume fraction of solvent, ϕ_A, is given by

$$\phi_A = 1 - \phi_f - \sum_{n=0}^{\infty} \phi_n \tag{16}$$

If we assume an athermal solution and neglect interaggregate interations, then it is possible to use standard methods[14] to derive a law of mass action for ϕ_n:

$$\phi_n = \frac{\phi_p \phi_f^{\,n} \exp(-\beta\Delta_n)}{N \sum_{n=0}^{\infty} \phi_f^{\,n} (N + nM)^{-1} \exp(-\beta\Delta_n)} \tag{17}$$

In this expression, ϕ_p is the volume fraction of polymer in the solution (in all forms). The quantity Δ_n is defined by

$$\Delta_n \equiv \mu_n{}^\circ + k_B T - n(\mu_f{}^\circ + k_B T) \tag{18}$$

where $\mu_n{}^\circ$ is the free energy of formation of a complex with aggregation number n and $\mu_f{}^\circ$ is the reference chemical potential of a free surfactant molecule.

The total volume fraction of surfactant in solution, ϕ_s, a quantity under experimental control, can be expressed as the sum of ϕ_f and the volume fraction constituted by the bound surfactants. This can be expressed as

$$\phi_s = \phi_f + \phi_p M \frac{\langle n \rangle}{N} \tag{19}$$

where $\langle n \rangle$ is a mean aggregation number defined by

$$\langle n \rangle = \frac{\sum_{n=0}^{\infty} n \phi_f^{\,n} (N + nM)^{-1} \exp(-\beta\Delta_n)}{\sum_{n=0}^{\infty} \phi_f^{\,n} (N + nM)^{-1} \exp(-\beta\Delta_n)} \tag{20}$$

In order to compute $\langle n \rangle$, it is necessary to have an explicit expression for Δ_n. From the definition given in eq 18, it is apparent that we require the free energy of formation of an n-aggregate. This quantity can be expressed as a sum of two terms; the first is simply the energy gain associated with the binding of n surfactant heads to the backbone, i.e., $-nk_BT\epsilon$. The second contribution to $\mu_n{}^\circ$ corresponds to the configurational entropy loss of the surfactant tails in forming the aggregate. This contribution, however, is related to the free energy expressions developed in the previous two sections. Since we shall be primarily concerned with the high-coverage regime, for which lyotropic behavior may be achieved, we restrict consideration to cases of $\sigma \gg M^{-3/5}$ in the following. We can thus use Na times the expression for the free energy per unit contour length given in eq 7 in order to estimate the entropic contribution to $\mu_n{}^\circ$. It follows that at high coverage, Δ_n can be approximated by

$$\beta\Delta_n \approx 1 - n - n\epsilon + dNM^{3/8}(n/N)^{13/8} \tag{21}$$

where d is an undetermined $O(1)$ constant. We note that in writing the final term in eq 21, which derived from eq 7, we have replaced σ by the ratio n/N.

Our next step is to develop an approximation for the right-hand side of eq 20. Because the summands in the numerator and denominator of this expression are strongly peaked around a particular (large) value of n, denoted n^*, for the situations of interest in the present paper, we make use of the maximum term method to approximate the sums. By dropping subdominant terms in n (at high coverage), we find the following result for the mean aggregation number:

$$\langle n \rangle \approx n^* \approx [8/(13d)]^{8/5} N M^{-3/5} (1 + \epsilon + \ln \phi_f)^{8/5} \tag{22}$$

Within this approximation of a single species of aggregate, we reintroduce the dimensionless coverage $\sigma = \langle n \rangle / N$ and eliminate the volume fraction of free surfactant from eq 22 by use of eq 19. This step yields the following self-consistent equation for σ:

$$\sigma = [8/(13d)]^{8/5} M^{-3/5} [1 + \epsilon + \ln(\phi_s - \phi_p \sigma M)]^{8/5} \tag{23}$$

Equations 23 is the principal result of this section. The solution of this equation for σ gives the mean coverage of the polymers by surfactant molecules as a function of surfactant molecular weight, M, and the surfactant and polymer volume fractions, ϕ_s and ϕ_p. For the assumption of high coverage ($\sigma > M^{-3/5}$) to be met and, as we shall see in the next section, the possibility of liquid crystalline order, it is clear that the expression inside the square brackets of eq 23 must exceed unity. This condition can be met in one of two ways. First of all, the binding energy of the surfactant heads to the polymer backbone can be chosen to be larger than the thermal energy k_BT, i.e., $\epsilon > 1$. Because σ varies as $\epsilon^{8/5}$ for large ϵ according to eq 23, this is a particularly effective means of increasing the coverage and (cf. eq 13) the stiffness of the aggregates. Much less effective is to increase the concentration of surfactant in the solution. According to eq 23, this shifts the chemical equilibrium toward higher coverage aggregates, but only in a weak logarithmic fashion. Thus, we conclude that for all practical purposes dense bottle-brush-like aggregates will only be formed if the surfactants are strongly binding, $\epsilon > 1$.

At this point, we should comment on our earlier neglect of micelle formation between free surfactant molecules in the solution. The effect of such micellization will be primarily to limit the chemical potential of free surfactant in the solution, hence further diminishing the argument of the logarithm in eq 23. However, as discussed above, it is necessary to rely on the condition $\epsilon > 1$ for the development of dense aggregates, so any weak reduction in the logarithmic term due to micellization is largely irrelevant.

Finally, we should discuss the question of saturation of binding sites along the polymer chains. Our analysis of the chemical equilibrium that is set up between the various types of polymer/surfactant aggregates in solution leads to a unique coverage σ that reflects a balance of enthalpic and entropic forces. In certain polymer/surfactant systems, however, it may not be this balance of chemical forces that determines the coverage. For example, in cases of polymers that have a finite number of binding sites, these sites can become saturated with surfactant, limiting σ to a value given by the ratio of the number of binding sites per chain to the degree of polymerization, N. Such was the case in the PANI/CSA system studied by Cao and Smith,[1] where saturation was observed at a molar ratio of 0.5:1 CSA to phenyl–N repeat units of PANI. This molar ratio corresponds to complete protonation of the available binding sites; further increase in the ratio of CSA to phenyl–N units was found to be ineffective at changing the stiffness of the PANI/CSA complex and thus (by inference) the mean aggregation number. In more general circumstances, we expect that the condition $\sigma \gg M^{-3/5}$ leading to the bottle-brush configuration should be easy to achieve for strongly binding surfactants, regardless of whether the coverage is established by chemical equilibria or by a limited number of binding sites.

IV. Analysis of Lyotropic Behavior

Having studied the geometrical properties of polymer/surfactant complexes at a prescribed coverage and established how σ is determined, we are now in a position to investigate the conditions under which liquid crystalline phases are to be expected. Again, neglecting interaggregate interactions other than volume exclusion, we turn to the classical theory of lyotropic phase behavior developed by Onsager.[15] Onsager showed that for hard rods of diameter D and length $L \gg D$ a transition from an isotropic phase to a nematic phase occurs when the volume fraction of rods, ϕ, exceeds a critical value given by

$$\phi_i \approx 3.34(D/L) \qquad (24)$$

This threshold concentration is actually the lower boundary of a biphasic region in which an isotropic phase of volume fraction ϕ_i coexists with a nematic liquid crystalline phase of rod volume fraction $\phi_a \approx 1.343\phi_i$.

In order to apply eq 24 to the situation at hand, namely, the nematic ordering of bottle-brush aggregates, we replace ϕ_i in eq 24 with the volume fraction of aggregates, ϕ_n. In the maximum term approximation, this volume fraction follows from eq 17 as

$$\phi_n \approx \phi_p(1 + \sigma M) \simeq \phi_p\sigma M \qquad (25)$$

where we have assumed high coverage, $\sigma M \gg M^{2/5} \gg 1$. Furthermore, it was demonstrated in section II.B that the linear aggregate can be viewed as a cylinder of radius R_{B0} given by eq 6; hence we make the replacement of R_{B0} for $D/2$ in eq 24. Finally, we must address the fact that Onsager's theory is strictly applicable only to rigid rods in the limit of high aspect ratio, whereas the polymer/surfactant complexes were found in section II.B to be semiflexible with persistence length λ given by eq 13 and contour length Na. (Note, however, that at sufficiently high coverage it is possible that $\lambda > Na$, rendering the complex rodlike.) As discussed by Khokhlov and Semenov,[16] Onsager's theory can still be applied successfully to solutions of semiflexible chains, provided that the rod length L in eq 24 is replaced by the persistance length, λ, and provided that the aspect ratio of the locally rodlike sections of the complex is large, $\lambda/D \gg 1$. Thus, in applying eq 24, we replace L by the expression for λ given in eq 13.

With the above replacements, it follows that a transition from an isotropic phase to a nematic phase is expected in our polymer/surfactant solution when the polymer volume fraction exceeds a value that scales as

$$\phi_p \sim \sigma^{-23/8}M^{-17/8} \qquad (26)$$

This volume fraction is generally very small; indeed it is of order $M^{-2/5}$ at the lower limit of the high-coverage regime, $\sigma \sim M^{-3/5}$, and decreases strongly with σ at higher coverages. If σ is controlled by the chemical equilibria described in section III, then it follows that we can replace σ in eq 26 by the expression given in eq 23. For the purpose of this replacement, we note that for polymer concentrations not greatly exceeding eq 26 it is permissible to neglect $\phi_p\sigma M$ relative to ϕ_s in the argument of the logarithm in eq 23. Therefore, for the case of backbone binding sites that are not fully saturated with surfactant, the isotopic–nematic transition is expected at a volume fraction of polymer that scales as

$$\phi_p \sim M^{-2/5}[1 + \epsilon + \ln \phi_s]^{-23/5} \qquad (27)$$

This can be a very small volume fraction if an excess of surfactant is present and the binding energy $k_BT\epsilon$ is a significant multiple of k_BT.

Finally, we comment on how the results just presented should be modified if the coverage is so high that the persistence length λ exceeds the contour length of the polymers, Na. According to eq 13, this situation occurs when $1 > \sigma > N^{8/17}M^{-15/17}$. If this condition is met, then the analysis based on eq 24 still applies, however with the exception that L is to be replaced by Na. The steps outlined above then lead to the following prediction for the isotropic–nematic boundary (in place of eq 26):

$$\phi_p \sim \sigma^{-3/4}M^{-1/4}N^{-1} \qquad (28)$$

It should be noted that eq 28 smoothly crosses over to eq 26 for $\sigma \sim N^{8/17}M^{-15/17}$, but predicts a large value of ϕ_p as the coverage exceeds this crossover value. In the case of nonsaturated binding sites and $\sigma > N^{8/17}M^{-15/17}$, we can combine eqs 23 and 28 to obtain the following high-coverage replacement for eq 27:

$$\phi_p \sim M^{1/5}N^{-1}[1 + \epsilon + \ln \phi_s]^{-6/5} \qquad (29)$$

V. Conclusions

We have shown in the present paper that surfactants which bind strongly to specific sites along the backbones of flexible polymers are capable of imparting a high degree of rigidity to the polymers. In particular, for situations in which a dense coating of the polymers by surfactant is achieved, the individual polymers are transformed into wormlike objects whose persistence lengths can greatly exceed their diameters. At a volume fraction of polymer that is a strongly decreasing function of the surfactant coverage, an isotropic to nematic phase transition is possible in which the rigid wormlike aggregates sustain spontaneous orientational order.

The coverages necessary to achieve such lyotropic behavior should be easily attained in the laboratory. According to eq 23, the threshold value required for the number of bound surfactants per backbone monomer, $\sigma \sim M^{-3/5}$, is already achieved for binding energies of order k_BT or less. If surfactants, e.g., functionalized acids, are chosen that bind much more strongly to the polymer backbones, i.e., $\epsilon \sim 5$–10, then the high coverages required for liquid crystallinity should be easily attained. An interesting feature of our prediction, eq 27, for the polymer volume fraction at the isotropic/nematic boundary is that the amount of polymer required *decreases* as either the surfactant binding energy $k_BT\epsilon$ is increased *or* the surfactant molecular weight M is increased. The latter prediction is particularly interesting because the coverage decreases with M according to eq 23 due to conformational restrictions on the surfactant tails in the dense aggregate. Nevertheless, the ratio of the persistence length of the aggregate to the radius of the aggregate grows sufficiently rapidly with M to compensate for any decrease in σ. At higher coverages, i.e., $1 > \sigma > N^{8/17}M^{-15/17}$, the average persistence length of the complex exceeds the contour length of the backbone polymer and the aggregate is essentially a rigid rod. In such instances, the isotropic–nematic threshold becomes N-dependent; cf. eqs 28 and 29.

Cao and Smith[1] have shown that liquid crystallinity can indeed be achieved in polyaniline solutions with camphorsulfonic acid as a surfactant. The origin of nematic order is somewhat obscured in this case because of the fact that the protonation of PANI produces an electronic stiffening of the backbone. Nevertheless, the fact that lyotropic behavior is not observed for PANI complexed with sulfuric acid (effectively a much smaller M) suggests that the steric stiffening mechanism investigated in the present paper is operative in the PANI/CSA system. Our calculations, moreover, suggest that even very flexible nonconjugated polymers could be made to exhibit nematic order by the proper choice of surfactant. This opens up the exciting possibility of new processing schemes for flexible polymers that exploit intermediate liquid crystalline phases. Such schemes are known to produce polymeric materials with exceptional chain alignment and thus enhanced mechanical, electrical, and/or optical properties. One possibility might be to use surfactants as a preprocessing tool for the purpose of inducing macroscopic alignment and then strip them off at a later stage to improve chain packing.

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Appendix A: Free Energy of Toroidal Aggregate

In this appendix we extend the Daoud–Cotton method[12] to calculate the free energy and structure of a gently-curved toroidal aggregate in the high-coverage regime, $\sigma \gg M^{-3/5}$. As shown in Figure 3, we assume that the aggregate can be bent into a torus of large radius ρ and with a circular cross-section of radius R_B.

For the purpose of implementing the Daoud–Cotton method, it is useful to consider the regions enclosed by the inner half-torus and outer half-torus separately. We denote the fraction of chains that occupy the inner half-torus by p. The surface area of a shell at radius r (see Figure 3) of the inner half-torus is given by

$$S_i(r) = 2\pi r(\pi\rho - 2r) \tag{A1}$$

while that of the outer half-torus is

$$S_o(r) = 2\pi r(\pi\rho + 2r) \tag{A2}$$

In the Daoud–Cotton model,[12] each chain of the aggregate is imagined to traverse a radial string of blobs with the blob diameter varying with r in a manner to densely fill the aggregated out to a radius R_B. The space-filling constraint on the inside half-torus leads to a blob size $\xi_i(r)$ at radius r that satisfies[8]

$$\xi_i^2(r)p(\rho\sigma/a) = S_i(r) \tag{A3}$$

where $\rho\sigma/a \sim N\sigma$ is the total number of surfactants in the aggregate. Similarly, for the outer half-torus

$$\xi_o^2(r)(1-p)(\rho\sigma/a) = S_o(r) \tag{A4}$$

The number density of surfactant monomers at radius r inside the inner half-torus is given by

$$q_i(r) = \xi_i^{-4/3}a^{-5/3} \tag{A5}$$

An analogous expression can be written for the outer half-torus.

Next, we derive two conservation equations for the number of surfactant monomers in the inner and outer half-tori. By noting that the differential volume elements for these two regions are given by

$$\mathrm{d}V_i = S_i(r)\,\mathrm{d}r \tag{A6}$$

$$\mathrm{d}V_o = S_o(r)\,\mathrm{d}r \tag{A7}$$

the conservation equations follow as

$$pM(\rho\sigma/a) = \int_0^{R_B}\mathrm{d}r\; S_i(r)\; q_i(r) \tag{A8}$$

$$(1-p)M(\rho\sigma/a) = \int_0^{R_B}\mathrm{d}r\; S_o(r)\; q_o(r) \tag{A9}$$

It proves convenient to scale all lengths in the equations by the radius of the linear aggregate, R_{B0}, given by eq 6, or from eqs A8 and A9 in the limit that $1/\rho \to 0$. In particular, we define a dimensionless curvature c and a dimensionless radius R by the relations

$$c = R_{B0}/\rho \tag{A10}$$

$$R = R_B/R_{B0} \tag{A11}$$

Furthermore, it is useful to define a quantity δ by the expression

$$p = (1-\delta)/2 \tag{A12}$$

where we expect $\delta \ll 1$ for $c \ll 1$. With these rescalings and definitions, eqs A8 and A9 can be rewritten as

$$(1-\delta)^{1/3} = R^{4/3}\left(1 - \frac{8}{21\pi}Rc - \frac{8}{45\pi^2}R^2c^2\right) \tag{A13}$$

$$(1+\delta)^{1/3} = R^{4/3}\left(1 + \frac{8}{21\pi}Rc - \frac{8}{45\pi^2}R^2c^2\right) \tag{A14}$$

where we have kept terms on the right-hand side up to $O(c^2)$.

Our next step is to assume weak curvature expansions for δ and R of the form

$$\delta = A_1c + A_2c^2 + O(c^3) \tag{A15}$$

$$R = 1 + B_1c + B_2c^2 + O(c^3) \tag{A16}$$

and determine the coefficients A_i and B_i by substitution into eqs A13 and A14. This leads to the explicit results

$$A_1 = 8/(7\pi) \tag{A17}$$

$$A_2 = B_1 = 0 \tag{A18}$$

$$B_2 = 6/(245\pi^2) \tag{A19}$$

which corresponds to eqs 9 and 10 in the text.

Next we turn to the computation of the free energy of the gently curved aggregate. By the usual scaling assignment of k_BT of free energy per excluded volume blob, the total free energy can be written

$$\beta F = \int_0^{R_B} \mathrm{d}r\, [S_i(r)\, \xi_i^{-3}(r) + S_o(r)\, \xi_o^{-3}(r)] \tag{A20}$$

By working out the integrals in eq A20 to $O(c^2)$ and substituting the expressions A15 and A16 to eliminate δ and $R = R_B/R_{B0}$, it follows that the free energy is given by

$$\beta F \sim (\rho\sigma/a)^{3/2} c^{1/2} \left[1 + \frac{113}{490\pi^2} c^2 + O(c^4)\right] \tag{A21}$$

Finally, division of this result by the contour length of the toroidal aggregate, $2\pi\rho = Na$, yields the free energy expression given in eq 11 of the text.

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