Polysoaps within the *p*-Cluster Model: Solutions and Brushes

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ABSTRACT: The *p*-cluster model, proposed by de Gennes for PEO, is applied to polysoaps and hydrophobically modified water soluble polymers incorporating numerous "stickers" joined by long spacer chains. The phase behavior is determined by three parameters, the critical micelle concentration of the unpolymerized amphiphiles, ϕ_{cmc}, their aggregation number, p_o, and the length of the spacer chains, n. The phase behavior of free chains is discussed in the limit of infinite polymerization degree, $N \rightarrow \infty$, which is applicable to polymer brushes of any N. When n is high enough, a layering, vertical phase separation may occur in brushes of associating polymers.

1. Introduction

Water-soluble, associating polymers are commonly utilized as viscosity modifiers and colloidal stabilizers in the formulation of waterborne suspensions.[1,2] Their efficacy in this role is traced to the formation of weak, reversible, physical gels. These break under shear but re-form once the shear stress is removed, thus leading to shear thinning behavior. Both the phase behavior of the associating polymers and the interfacial properties of the colloidal particles affect the formulation of these systems. A simple description of the phase and interfacial behavior of associating polymers is possible within the framework of the *p*-cluster model proposed by de Gennes.[3] In the following discussion, we utilize this model to describe two aspects of the behavior of associating polymers: the phase diagram of solutions of free polymers in water and the structure of brushes formed by terminally anchored chains. In the case of free chains, we focus, following de Gennes, on the limit of infinite degree of polymerization, $N \rightarrow \infty$. For specificity, the discussion is concerned with a particular class of associating polymers, *polysoaps*. These are flexible, water-soluble chains that incorporate, at intervals, a large number of covalently bound amphiphilic monomers.[4−6] The analysis is however applicable to a wider class of hydrophobically modified water-soluble polymers.

The *p*-cluster model was originally proposed in order to explain certain properties of aqueous solutions of poly(ethylene oxide), PEO.[3] It has since been invoked in the interpretation of the behavior of other neutral, water soluble polymers, in particular poly(*N*-isopropylacrylamide) (PNIPAM).[4−6] The model is not limited to water-soluble homopolymers. It may apply to associating heteropolymers in organic, nonpolar solvents as well as in aqueous media. The key ingredient of this model is the assumption that clusters of $p > 2$ monomers can form stable aggregates. The precise nature of the aggregates is not specified. They can be, for example, micelles or *p*-stranded helices. In this phenomenological model, the formation of the stable clusters gives rise to an attractive correction to the pth virial term in the free energy density. The model contains two phenomenological parameters, p, the aggregation number and ρ, the corresponding correction to the pth virial coefficient. The formation of stable clusters can lead to phase separation of free polymers in a good solvent, i.e., when the monomer−monomer interactions are repulsive. Furthermore, within this model the phase separation may assume two forms. The distinction between them is clearer in the limit of $N \rightarrow \infty$. In the familiar form of coexistence, the concentration of the dilute phase is zero. The "second type" of phase separation[3] involves two phases of finite concentration. In turn, the second type of phase separation gives rise to a vertical phase segregation within polymer brushes.[8] An inner dense phase, at the surface, coexists with a dilute outer phase. This, in turn, leads to qualitative modification of the interactions of brush-coated surfaces with other surfaces and with colloidal particles.[9] As we shall discuss, the applicability of this model to PEO and PNIPAM is problematic since the nature of the clusters is not established and both p and ρ are presently unknown. However, by construction, the *p*-cluster model can describe the behavior of polymers, polysoaps, incorporating amphiphilic monomers capable of self-assembly into micelles. In this case the clusters can be identified with the micelles formed by the polymerized amphiphiles (Figure 1). Furthermore it is possible to estimate p and ρ as well as their dependence on the molecular architecture. In the following we adapt the *p*-cluster model to the case of polysoaps comprising of m amphiphilic monomers joined by flexible water soluble spacers of length n; *i.e.*, $N \approx nm$. As we shall see, three molecular design parameters emerge. One is the length of the spacer chains, n. The nature of the amphiphilic monomers specifies p and the critical micelle concentration, CMC, of the free, unpolymerized amphiphile, ϕ_{cmc}. These three parameters determine ρ. The paper is organized as follows. The *p*-cluster model for homopolymers is briefly summarized in section II. Section III summarizes the structure of brushes within this model. The implementation of the model to polysoaps, copolymers incorporating amphiphilic comonomers, is discussed in section IV.

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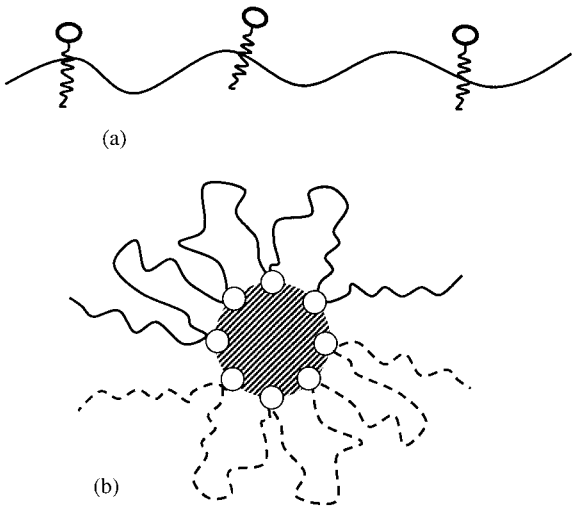

Figure 1. Polysoaps comprised of amphiphilic monomers joined by flexible, water-soluble spacer chains. The amphiphiles consist of an ionic headgroup and a hydrophobic tail (a). In water, the amphiphiles self-assemble into micelles. These play the role of clusters. When N is finite, the aggregates can incorporate amphiphiles that belong to different chains (b). These function as cross-links giving rise to a gel. This effect is not present in the case of $N \rightarrow \infty$.

2. The *p*-Cluster Model for Homopolymers

In the Flory−Huggins free energy, the chain aspect of the polymer molecules is described by the entropy term. The enthalpic contribution, as in the theory of regular solutions, reflects only binary interactions.[10] The *p*-cluster model is a generalization of the Flory−Huggins theory in that it allows for the enthalpy arising from multiple contacts.

It is helpful to begin with a brief summary of the Flory−Huggins description and the associated phase behavior. The interaction free energy per lattice site of a polymer solution is

$$\frac{F_{\text{int}}}{kT} = \frac{1}{\mathrm{N}}\phi \ln \phi + (1-\phi)\ln(1-\phi) + \chi\phi(1-\phi) \qquad (1)$$

Here k is the Boltzmann constant and ϕ is the monomer volume fraction. χ, the Flory parameter, allows for the mixing enthalpy. For a given polymer−solvent system, χ depends only on the temperature, T. In the good solvent regime, when $\chi < {}^1/_2$, the F_{int} vs ϕ plot is convex and the uniform polymer solution is thermodynamically stable (Figure 2). When $\chi > {}^1/_2$ the solvent is poor. For $\chi > \chi_c$ the plot is partially concave, leading to a coexistence involving a concentrated polymer solution and a very dilute one. A critical point occurs at (χ_c, ϕ_c) specified by $\chi_c = {}^1/_2 + 1/\sqrt{\mathrm{N}}$ and $\phi_c = 1/\sqrt{\mathrm{N}}$. In the coexistence regime the monomer volume fraction in the dilute phase is exponentially small *i.e.*, $\phi_d \sim \exp(-N^{2/3})$. The crossover between the two regimes occurs at the θ point, $\chi = {}^1/_2$. For small ϕ, F_{int} may be expanded in powers of ϕ leading to

$$\frac{F_{\text{int}}}{kT} = \frac{1}{N}\phi \ln \phi + \frac{1}{2}(1-2\chi)\phi^2 + \frac{1}{6}\phi^3 + \ldots \qquad (2)$$

where the second virial coefficient is $v = b^3(1-2\chi)$ and b is the size of the monomer. Within this model only the second virial coefficient may change sign. All higher order virial coefficients are positive. In other words, binary monomer−monomer interactions may be repulsive or attractive, depending on T, but higher order interactions are always repulsive.

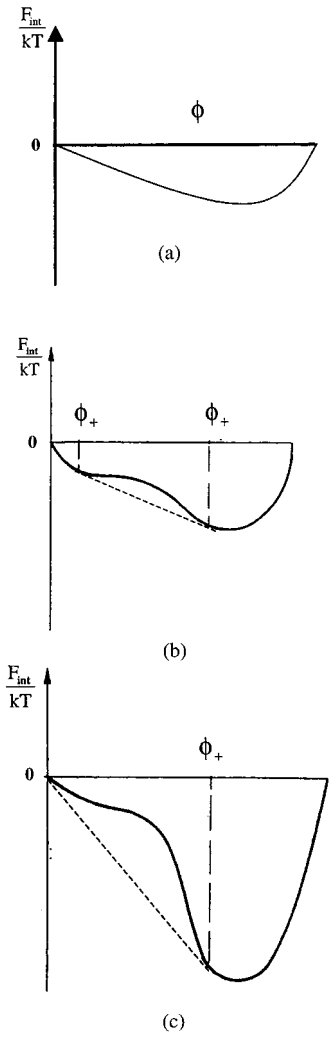

Figure 2. Plots of the interaction free energy, F_{int} vs the monomer volume fraction in the limit of $N \rightarrow \infty$. No phase separation occurs in case a, $\rho < \rho_c$. A second type of phase separation occurs when $\rho_c < \rho < \bar{\rho}$ (b) when $0 < \phi_- < \phi_+ < 1$. (c) When $\rho > \bar{\rho}$, the coexistence involves $\phi_- = 0$.

In the *p*-cluster model, monomer−monomer interactions are repulsive but a cluster of $p > 2$ monomers forms a stable aggregate.[3] Following de Gennes, we consider the corresponding free energy for the simple case obtained in the limit of $N \rightarrow \infty$ and an athermal good solvent, $\chi = 0$ or $v = b^3$

$$\frac{F_{\text{int}}}{kT} = (1-\phi)\ln(1-\phi) + \rho(T)(\phi - \phi^p) \qquad (3)$$

Here $-\rho(T)\phi^p$ allows for the free energy gain upon aggregation of p monomers. The ϕ^p factor reflects the probability of encounter between p uncorrelated monomers. At this point $\rho > 0$ is a purely phenomenological coefficient that may vary with T. As we shall see in section IV, it is the correction to the p virial term of the Flory−Huggins free energy due to the attractive interaction arising in clusters of p monomers and the mixing entropy that results from the formation of the *p*-clusters. Higher order correction terms reflecting, for example, micelle−micelle interactions are not included in the analysis, thus limiting its validity at the high ϕ range. The $\rho(T)\phi$ term ensures that F=0 for ϕ=0, as is required

from a mixing free energy. The model, does not specify either p or ρ.

It is important to note a useful experimental signature of the $-\rho(T)\phi^p$ term. In the presence of this term, we may utilize F_{int} as given by eq 1 provided χ is replaced by a ϕ-dependent, effective $\chi_{ef} = \chi - \rho\phi^p(1-\phi)^{-1}$. Thus, analysis of thermodynamic data in terms of such a modified eq 1 should reveal a ϕ-dependent χ_{ef}. In fact, the p-cluster model was partially motivated by the observation of such behavior for PEO.[11]

The $-\rho(T)\phi^p$ term gives rise to a qualitative modification of the phase diagram as obtained from the Flory–Huggins model. Phase separation can occur in a good solvent, that is, when the binary, monomer–monomer interactions are repulsive. Three regimes emerge. When $0 < \rho < \rho_c$, the uniform solution is stable for all ϕ. This is the counterpart of the "standard" good solvent regime. A critical point, specified by the condition $\partial^2 F_{int}/\partial f^2 = \partial^3 F_{int}/\partial f^3 = 0$, occurs at ($\phi_c$, ρ_c) as given by

$$\phi_c = \frac{p-2}{p-1} \quad \rho_c = p^{-1}\left(\frac{p-1}{p-2}\right)^{p-2} \tag{4}$$

For large p values, the range of interest in the case of polysoaps, these reduce to

$$\phi_c \approx 1 - \frac{1}{p} \quad \rho_c \approx \frac{e}{p} \tag{5}$$

Phase separation involving a dilute and concentrated phases, ϕ_- and ϕ_+, can occur when $\rho_c < \rho < \bar{\rho}$ (Figure 2). In this last range $\phi_- > 0$ and a uniform solution is stable only while $0 < \phi < \phi_-$. This second type of phase separation has no counterpart in the Flory–Huggins model where $\phi_- = 0$ when $N \to \infty$. For $\rho = \bar{\rho}$ it is possible to construct a common tangent to ϕ_+ and $\phi_- = 0$.[12] For large p this yields

$$\bar{\rho} \sim 1 - \exp(-p) \tag{6}$$

and the corresponding $\phi_+ = \bar{\phi} \approx 1$. Thus, for $\rho > \bar{\rho}$, the phase separation involves $\phi_- = 0$ coexisting with ϕ_+. Consequently, a uniform solution is thermodynamically instable for any $\phi > 0$. Within the p-cluster model this is analogue of the poor solvent regime in the Flory–Huggins model.

The simplicity of the p-cluster model is traceable to three primary assumptions. The introduction of each assumption exacts a price. First, the p-cluster model is a generalization of the Flory–Huggins approach. As such, it does not allow for the structure of the clusters. As we shall discuss in section IV, this can be important for high p values. Second, a single term, $-\rho\phi^p$, allows for the formation of the clusters. Cluster–cluster interactions are thus partially ignored.[13] These are likely to play a role in determining the high ϕ regions of the phase diagram. In addition, the p-cluster model does not allow for polydispersity in p. Yet, the qualitative features of the system should not be affected by this approximation. Third, the present discussion is confined to the $N \to \infty$ limit. This assumption calls for a number of comments: (i) F_{int} as obtained in the $N \to \infty$ limit applies to grafted chains of any N since their translational entropy is lost. (ii) The coexistence predicted for $\rho > \bar{\rho}$ in the $N \to \infty$ limit involves $\phi_- = 0$ while $\phi_- > 0$ is expected for finite N. (iii) For finite N it is important to distinguish between a sol phase, involving finite aggregates, and a gel phase, when an infinite, macroscopic network is formed. This distinction is lost in the $N \to \infty$ limit. This aspect, as well as the general theory of the phase behavior of associating polymers, was studied extensively by Tanaka.[14] A different view on this topic was recently proposed by Semenov and Rubinstein.[15]

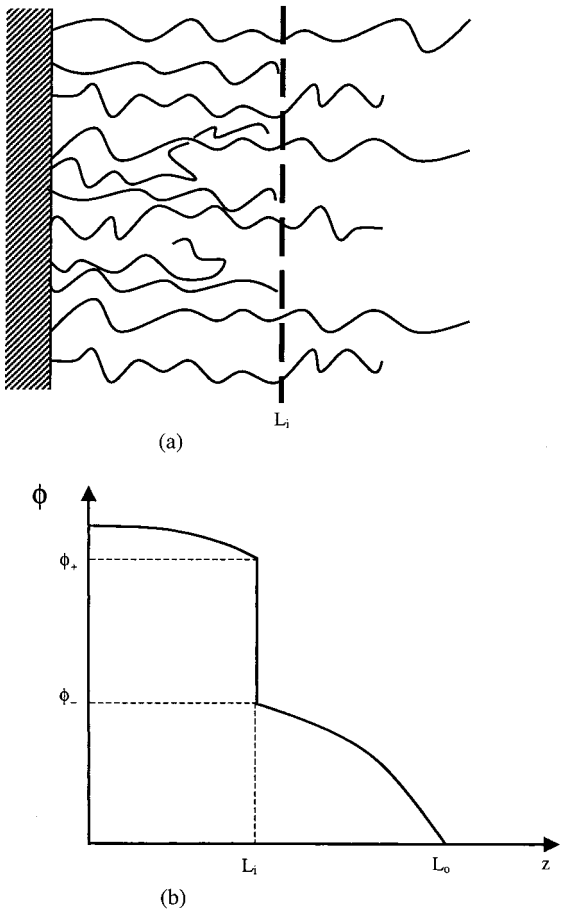

Figure 3. Schematic cross section (a) and a concentration profile of a brush exhibiting coexistence (b) due to a second type of phase transition.

It should be stressed that the $0 < \phi_- < \phi_+ \leq 1$ coexistence in the $N \to \infty$ limit can also result from qualitatively different molecular mechanisms. A variety of mechanisms involving solvation may give rise to similar behavior. These include, for example, interconversion between hydrophobic and hydrophilic states of the monomers, as was proposed for the case of PEO.[16] Another proposed mechanism invokes association of hydrophobic chains once the solubilizing hydrogen bonds are broken.[14]

3. Brush Structure within the *p*-Cluster Model

The unusual solution phase behavior predicted by the p-cluster model leads to corresponding effects on the structure of brushes. It is possible to distinguish between three regimes. No modification is expected while $\rho < \rho_c$. In this case the attraction due to p-clusters is too weak. When $\rho_c < \rho < \bar{\rho}$, the brush can undergo a vertical phase separation, along the normal to the grafting surface. This leads to a discontinuity in the concentration profile[8] (Figure 3). The onset of the coexistence is controlled by the grafting density, σ^{-1}, or, alternatively, by compression along the normal to the surface. Full collapse is expected whenever $\rho > \bar{\rho}$. The second scenario is distinctive to the p-cluster model and

to related models that allow for the second type of phase separation that is, $0 < \phi_- < \phi_+ \leq 0$ coexistence in the $N \rightarrow \infty$ limit.[9]

The essential physics is as follows. The chemical potential, μ, of the monomers within the brush is parabolic.[21−23] When the brush is semidilute and no coexistence occurs $\mu \sim \phi$ and the concentration profile is parabolic as well. This is the case while the monomer volume fraction at the surface, $\phi(0)$, is smaller than ϕ_-.[8,9] When $\phi(0) > \phi_-$, the concentration profile can no longer be parabolic. A discontinuity should occur at an intermediate altitude, $z = L_i$, where the ϕ_+ phase coexists with the ϕ_- phase. The onset of coexistence within the brush occurs at an area per chain σ_c, determined by $\phi(0) = \phi_-$. A dense collapsed brush is formed whenever $\rho > \bar{\rho}$.

The structure of polymer brushes within the *p*-cluster model was analyzed by Wagner et al.[8] using the self-consistent field (SCF) formalism.[22] It is possible to recover most of these results[9] by using a simple approximation introduced by Pincus[17,18] (Appendix I). In the equilibrium state, the brush is specified by $\mu[\phi(z)]/kT = \lambda - Bz^2$ where $B \approx 1/N^2b^2$. λ is determined by the constraint $Nb^3 = \sigma \int_0^{L_o} \phi \, dz$ together with the requirement that $\phi(L_o) = 0$ where L_o is the height of the unperturbed brush. Accordingly

$$\mu/kT = B(L_o^2 - z^2) \tag{7}$$

When $\mu \sim \phi$, this leads to the familiar parabolic concentration profile. Such is the case when $\rho < \rho_c$ or when $\rho_c < \rho < \bar{\rho}$ and σ^{-1} is low enough, $\sigma > \sigma_c$. In these situations $\phi(z) \approx B(L_o^2 - z^2)$ and $L_o \approx N(b^2/\sigma)^{1/3}b$ yielding

$$\phi_o(z) \approx \left(\frac{b^2}{\sigma}\right)^{2/3}\left(1 - \frac{z^2}{L_o^2}\right) \tag{8}$$

The onset of coexistence in the brush, when $\rho_c < \rho < \bar{\rho}$, is attained once $\phi_o(0) = \phi_-$. This, together with eq 8, leads to

$$\sigma_c/b^2 \approx \phi_-^{-3/2} \tag{9}$$

When σ decreases below σ_c a discontinuity appears in $\phi_o(z)$. Its appearance is signaled by multiple roots to eq 7. These, in turn, are due to the van der Waals loop traced by $\mu[\phi(z)]$ in the $\phi_- < \phi < \phi_+$ range. The coexistence within the brush is specified by two conditions. (i) The first is $\mu_{brush}(\phi_-) = \mu_{brush}(\phi_+)$ where $\mu_{brush} = \partial F_{brush}/\partial\phi$ is the local exchange chemical potential at z. This leads to $\mu(\phi_-) - Bz_-^2 = \mu(\phi_+) - Bz_+^2$. Note that μ_{brush} includes a term allowing for the extension penalty of the chains. At the "phase boundary", $z_- = z_+ = L_i$ and $\mu(\phi_-) = \mu(\phi_+)$. (ii) The second is $\pi_{brush}(\phi_-) = \pi_{brush}(\phi_-)$ where $\pi_{brush} = \phi^2[d(F_{brush}/\phi)/d\phi]$ is the local osmotic pressure. This condition reduces to $\pi(\phi_-) = \pi(\phi_-)$. Thus, while the coexistence in the brush involves the bulk monomer volume fractions, ϕ_- and ϕ_+, it occurs at a single altitude, L_i, specified by

$$\mu(\phi_\pm)/kT = B(L_o^2 - L_i^2) \tag{10}$$

Within this picture, the brush in the $\rho_c < \rho < \bar{\rho}$ range comprises two regions: An inner dense phase that extends up to L_i and an exterior, dilute phase that extends to $L_o > L_i$. The concentration within each phase is not constant because of the parabolic form of the chemical potential. This is in marked difference to the phase separation of free chains in the bulk. This picture is valid in the limit of $N \rightarrow \infty$. However, for finite chains it is necessary to allow for the depletion of the exterior layer: As σ decreases, the relative weight of the inner phase grows.[8] As a result, for finite N, the exterior region may be comprised of a fraction of monomer per chain.[9] Thus for $\sigma < \sigma_u$ the exterior region of the brush is effectively absent. To obtain a rough estimate σ_u one may argue that at σ_u all monomers are incorporated into an inner region of height $L_o/b \approx N(b^2/\sigma_u)^{1/3}$ and average monomer volume fraction $Nb^3/L_o\sigma_u \approx \phi_+$ thus leading to

$$\sigma_u/b^2 \approx \phi_+^{3/2} \tag{11}$$

Note that this criterion is somewhat arbitrary. A different estimate is possible.[9] In any case, the estimates are easier to justify when ϕ_+ is close to unity. When $\rho > \bar{\rho}$, the brush collapses and forms a uniform dense layer.

For $\rho_c < \rho < \bar{\rho}$, it is possible to control the phase coexistence in the brush by compression. If $\sigma > \sigma_c$, the onset of coexistence occurs at critical L_c determined by the requirement that $\phi(0) = \phi_-$. A weakly compressed brush, with $L < L_c$, is characterized by $\phi \approx \lambda - Bz^2$ and $\lambda \approx \sigma^{-2/3}(L_o/L + L^2/L_o^2)$ where $L_o/b \approx N(b^2/\sigma)^{1/3}$. When $\sigma \gg \sigma_c$, $L_c \ll L_o$ and the first terms in the expressions for ϕ and λ are dominant, thus leading to

$$L_c \approx \sigma^{-2/3} L_o/\phi_- \tag{12}$$

Upon further compression the dilute phase is eventually exhausted. This occurs for $L < L_u$ where L_u is determined by the condition $Nb^3/\sigma L_u \approx \phi_+$ leading to

$$L_u \approx Nb^3/\sigma\phi_+ \tag{13}$$

The immediate consequence of the phase coexistence in the $\rho_c < \rho < \bar{\rho}$ range is the associated discontinuity in the concentration profile of the brush. In addition, this vertical phase segregation can give rise to qualitative modification of the interaction between the brush coated surfaces and other surfaces. The compression of a "normal" brush by a nonadsorbing surface is associated with a purely repulsive force profile. The vertical coexistence scenario raises the possibility of a compression by a selective surface that is nonadsorbing to one phase but attractive to the other.[9] A particularly interesting case is expected when this surface is repulsive to the dilute phase but attractive to the denser one. In this situation compression beyond L_u will be associated with onset of the adhesive force when the two surfaces are separated. This scenario is suggestive of the recent results obtained by Sheth and Leckband[24] for the case of PEO brush compressed by a protein-coated surface. A similar behavior is expected for the compression of two brush-coated surfaces. In this case, compression to L_u should result in conversion of the two brushes to a ϕ_+ phase and to the appearance of an adhesive force.

4. The *p*-Cluster Model for Polysoaps

The generality of the *p*-cluster, as described above, is both a strength and a weakness. Because the description is independent of the underlying molecular mechanism, it reveals general features. On the other hand, for the

same reasons, it cannot provide expressions for p and for ρ. To obtain these it is necessary to consider a specific aggregation mechanism. It is convenient to discuss the case of polysoaps because the aggregation behavior of monomeric amphiphiles is well understood.[25,26] We consider a polymer that incorporates amphiphilic monomers that self-assemble into spherical micelles. The amphiphilic monomers are characterized by their experimentally measurable properties in the free, unpolymerized state: the aggregation number of the free micelles, p_o, and the critical micelle concentration (CMC), ϕ_{cmc}. In turn, ϕ_{cmc} is related to the free energy gain of an amphiphile incorporated into a micelle of aggregation number p_o, $\epsilon_{p_o}\, kT < 0$, as $\phi_{cmc} \approx \exp(\epsilon_{p_o})$. We initially assume that p and ϵ_p remain the same when the amphiphiles are polymerized i.e., $p \approx p_o$ and $\epsilon_p \approx \epsilon_{p_o}$. This actually is wrong since both p and ϵ_p depend on the length of the spacer chain n. However, this dependence arises because of the local organization of the spacers around the micelle and as such is beyond the scope of this Flory type theory. The necessary refinements will be discussed later.

Following de Gennes, we adopt the case of a flexible, nonassociating homopolymer in an athermal good solvent as a reference state. In the $N \rightarrow \infty$ limit the free energy per site is

$$\frac{F_{int}}{kT} = (1-\phi)\ln(1-\phi) \tag{14}$$

This free energy should be supplemented by an additional term, F_{pc}, allowing for the presence of amphiphilic comonomers and their self-assembly into p-clusters. Two contributions are involved. The first is the excess binding free energy of the self-assembled amphiphiles, $(\psi\phi/n)\epsilon_p$ where ψ is the fraction of associated amphiphiles and ϕ/n is the monomer volume fraction of amphiphilic monomers. The second contribution is due to the mixing entropy of micellized and nonmicellized amphiphiles. It arises because the micelles are labile and their dissociation and reassembly gives rise to distinguishable states. Care must be taken to avoid "double counting" of states that are already allowed for in eq 14. The combinatorial argument involved is described in Appendix II. Altogether

$$\frac{F_{pc}}{kT} = \Big[\psi\epsilon_p + (1-\psi)\ln(1-\psi) + \frac{\psi}{p}\ln\frac{\psi}{p} - \psi\Big(1-\frac{1}{p}\Big)\ln\frac{\phi}{n}\Big]\frac{\phi}{n} - \Big(1-\frac{1}{p}\Big)\Big(1-\psi\frac{\phi}{n}\Big)\ln\Big(1-\psi\frac{\phi}{n}\Big) \tag{15}$$

The fraction of aggregated amphiphiles in equilibrium is set by the condition $\partial F_{pc}/\partial\psi = 0$ leading to

$$p\ln(1-\psi)\frac{\phi}{n} - \ln\frac{\psi}{p}\frac{\phi}{n} - (p-1)\ln\Big(1-\psi\frac{\phi}{n}\Big) = p\epsilon_p \tag{16}$$

This yields the law of mass action (LMA) for the micellization reaction where $K = p\exp(-p\epsilon_p)$ is the equilibrium constant. The LMA action is most transparent when written as

$$\frac{\frac{\psi\phi}{pn}}{1-\psi\frac{\phi}{n}} = \left[\frac{(1-\psi)\frac{\phi}{n}}{1-\psi\frac{\phi}{n}}\right]^p K \tag{17}$$

The $1-\psi(\phi/n)$ is the "free volume", allowing for the excluded volume of the micelles. Since our interest focuses on the $\psi\phi$/n range it is however more convenient to express the LMA as

$$\frac{\psi}{(1-\psi)^p} = p\,\exp(-p\epsilon_p)\left(\frac{\frac{\phi}{n}}{1-\psi\frac{\phi}{n}}\right)^{p-1} \approx p\,\exp(-p\epsilon_p)\left(\frac{\phi}{n}\right)^{p-1} \tag{18}$$

Substitution of eq 16 into eq 15 yields the equilibrium free energy

$$\frac{F_{pc}}{kT} = \frac{\phi}{n}\ln(1-\psi) - \Big(1-\frac{1}{p}\Big)\ln\Big(1-\psi\frac{\phi}{n}\Big) \tag{19}$$

When the fraction of aggregated amphiphiles is low, $\psi \ll 1$, the logarithmic terms in eq 19 can be expanded in powers of ψ leading to

$$\frac{F_{pc}}{kT} \approx -\frac{\psi}{p}\frac{\phi}{n} + \frac{1}{2}\psi^2\Big(\frac{\phi}{n}\Big)^2\Big(1-\frac{1}{p}-\frac{n}{\phi}\Big) \tag{20}$$

In the limit considered, $\psi \ll 1$, eq 18 reduces to $\psi \approx p(\phi/n)^{p-1}\exp(-p\epsilon_p)$. Noting that $\phi_{cmc} \approx \exp(\epsilon_p)$ we may rewrite eq 20 as

$$\frac{F_{pc}}{kT} \approx -\left(\frac{\phi}{n\phi_{cmc}}\right)^p + \frac{p^2}{2}\left(1-\frac{1}{p}-\frac{n}{2\phi}\right)\left(\frac{\phi}{n\phi_{cmc}}\right)^{2p} \tag{21}$$

Comparing eq 21 to eq 3, we identify $-\rho\phi^p$ with the first term and the explicit expression for ρ is

$$\rho = \left(\frac{1}{n\phi_{cmc}}\right)^p \tag{22}$$

The second term in eq 21 allows for micelle−micelle interactions. The corresponding coefficient changes sign at $\phi_\theta/n = p/(p-1)$. It is positive for $\phi > \phi_\theta$, thus signifying the onset of repulsive interactions between the micelles. This affects ϕ_+, but the analysis of this point is beyond the scope of this work. As noted in the Introduction, ρ is determined by control parameters: n, ϕ_{cmc}, and p. At this stage it is helpful to consider the phase behavior predicted by the p-cluster model for the case of polysoaps as specified by eq 22, *i.e.*, $p \approx p_o$, $\epsilon_p \approx \epsilon_{p_o}$, and $\phi_{cmc} \approx \exp(\epsilon_{p_o})$. As was discussed in section II, three ranges are distinguishable within this model, $\rho < \rho_c$, $\rho_c < \rho < \bar{\rho}$ and $\rho > \bar{\rho}$. When the n dependence of p is overlooked, $p \approx p_o \gg 1$ and, as a result

$$\rho_c \approx e/p \quad \bar{\rho} \approx 1 \tag{23}$$

Combining eqs 22 and 23 leads to the following regimes in the limit of $N \rightarrow \infty$. No phase separation is expected while $n\phi_{cmc} > (p/e)^{1/p}$ when $\rho < \rho_c$. A "second type" of phase separation becomes possible when $n\phi_{cmc}$ decreases and $\rho = \rho_c$ is attained at

$$n\phi_{cmc} \approx (p/e)^{1/p} \tag{24}$$

In this regime segregation occurs when $\phi > \phi_- > 0$. $\rho = \bar{\rho}$ is attained once $n\phi_{cmc}$ decreases further and

$$n\phi_{cmc} = 1 \tag{25}$$

For $n\phi_{cmc} \leqslant 1$, phase separation involving $\phi_- = 0$ and $\phi_+ \approx 1$ is expected for all ϕ values.

These results suggest that the second type regime is difficult to attain for polysoaps. $(p/e)^{1/p}$ varies over a narrow range, between 1.14 and 1.00, thus making the required tuning of $n\phi_{cmc}$ difficult. Furthermore, the measured values of ϕ_{cmc} are very small thus making the attainment of eq 24 for reasonable n unlikely. p_o decreases with the number of carbons in the hydrophobic tail while ϕ_{cmc} increases. The most favorable situation for realizing the "second type" situation involves thus short alkyl chains. For the case of short hydrophobic tails incorporating six carbons,[26] $\phi_{cmc} \approx 10^{-2}$ while $p_o \approx 15$. This suggests that $n\phi_{cmc} \leqslant 1$ for the reasonable choice of $1 < n < 100$. Furthermore, this result leads to the conclusion that it is difficult to adjust the molecular architecture so as to obtain a second type of phase separation.

This conclusion is only valid when the n dependence of p and ϵ_p is neglected. Within this approximation, the structure of the micelles is ignored. In particular, it overlooks the role of the starlike structure formed by the spacer chains upon aggregation of the polymerized amphiphiles. The Flory−Huggins type approach, as utilized above, does not allow for such structures. Yet, it is clearly of interest to explore the consequences of local correlations of this type on the phase diagram. To this end, we will incorporate the results of the appropriate scaling arguments into the analysis as described above. Before we proceed, it is important to note that the two theories are based on different approximations, and the results of this exploration should be viewed with caution.

The starlike structure of the micellar corona gives rise to a free energy penalty that introduces an n dependence of p and ϵ_p. Two regimes emerge when[27] the n dependence is introduced. These are determined by a dimensionless parameter

$$\kappa \approx \frac{p_o^{1/2} \ln n}{\gamma a_o} \tag{26}$$

where γkT is the surface tension of the boundary between the hydrophobic core and the aqueous medium and a_o is the area per headgroup in micelles formed by the free, unpolymerized amphiphiles. κ measures the relative importance of the coronal penalty per aggregated surfactant in a spherical micelle, $kT\, p_o^{1/2} \ln n$, and the energy of an aggregated amphiphile in a free micelle, $\gamma kT a_o$. When $\kappa \ll 1$ the effect of the micellar corona is negligible and the analysis presented above is valid. In the opposite limit, when $\kappa \gg 1$, the aggregation number is significantly smaller

$$p \approx p_o \kappa^{-6/5} \approx p_o^{2/5} \left(\frac{\gamma a_o}{\ln n}\right)^{6/5} \tag{27}$$

and $\exp \epsilon_p$ is increased

$$\exp \epsilon_p \approx \phi_{cmc} \exp(\gamma a_o \kappa)^{2/5} \tag{28}$$

In this last regime, eq 22 should be modified. $\exp \epsilon_p$ as given by eq 28 should replace ϕ_{cmc} and p as given by eq 27 should replace p_o. The $\kappa \gg 1$ behavior facilitates the design of polysoaps exhibiting the second type of phase transition. In the case of SDS as amphiphile and $n \approx 60$, a rough estimate leads to $p \approx 4$ and $\exp \epsilon_p \approx 0.5$.[29] Note however that this is a rough estimate because the scaling analysis leading to eqs 27 and 28 involves undetermined numerical factors of order unity. In addition, utilizing these relations in the p-cluster theory introduces uncertainties because these results cannot be obtained within the framework of the Flory−Huggins theory. In this context, it is interesting to comment on an additional feature that emerges from the scaling analysis. The transfer free energy of the hydrophobic tail as a function of T often exhibits a minimum. This feature may give rise to cold and hot denaturation of the polymerized amphiphiles, *i.e.*, destabilization of the micelles upon cooling and heating. In such systems, the stability range shrinks as n increases.[28] This effect may lead to a reentrant phase behavior as a function of temperature.

5. Concluding Remarks

The p-cluster model proposed by de Gennes for PEO provides a simple, albeit approximate, description of a wide variety of associating polymers. In particular, it applies to polysoaps and hydrophobically modified water-soluble polymers incorporating many "stickers". In the limit of $N \rightarrow \infty$, this model predicts three possible regimes: complete solubility, a "second type" of phase separation involving two phases of finite concentration, and, finally, coexistence of a dense phase with the solvent. All regimes are expected when the backbone of the chain experiences good solvent conditions. In the $N \rightarrow \infty$ limit the distinction between the gel and sol states of the denser phases is lost, and the phase diagram obtained is incomplete. However, the resulting analysis is applicable to polymer brushes of terminally grafted chains. In this case, the second type of phase separation is associated with a vertical phase separation in the brush. This, in turn, qualitatively modifies the interaction between the brush and selective surfaces that attract one phase but repel the other. For the case of polysoaps, the phase behavior is determined by three parameters: the aggregation number of micelles formed by the free amphiphiles, p_o, their critical micelle concentration, ϕ_{cmc}, and the length of the spacer chain, n. The analysis suggests that the "second type" regime is attainable for amphiphilic monomers with $\phi_{cmc} \ll 1$ provided n is large enough.

Our discussion focused on the case of polysoaps incorporating amphiphilic comonomers. In this case, the micelles formed by the free surfactants provide a clear starting point for the description of the clusters. However, the picture considered in this article can be applied to a wider class of hydrophobically modified water soluble chains. This is possible when the amphiphilic monomer is identified as the hydrophobic graft together with a short segment of the hydrophilic backbone.

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6. Appendix 1. The Pincus Approximation

The Pincus approximation occupies the middle ground between the Alexander[19,20] model and the full SCF theory of the brush.[22] In this picture the chain ends are

distributed throughout the brush and the mean free energy per unit area is $\gamma = \int_0^L F_{\text{brush}}(z)\,dz$ where z is the altitude and the free energy density is

$$\frac{F_{\text{brush}}}{kT} \approx b^{-3}\left[F_{\text{int}} + \frac{z^2}{Na^2}\Psi(z) - \lambda\phi(z)\right] \qquad (29)$$

The first term is the interaction free energy as given by eq 3. For a brush, this free energy is valid for any N, since the chains lose their translational entropy upon grafting. The handling of the elastic free energy penalty is the core of the Pincus approximation. A chain having its end point at altitude z is assumed to be uniformly extended Gaussian spring with a free energy penalty $F_{\text{el}}/kT \approx z^2/Nb^2$. In marked distinction, in the full SCF theory the chain stretching varies along the chain. The end points are assumed to be distributed throughout the layer with a density $\Psi(z)$. The key assumption is that the local fraction of chain ends, $\Psi(z)$, is proportional to the local concentration and to the fraction of chain ends within the chain itself, $1/N$. In other words

$$\Psi(z) \approx \phi(z)/N \qquad (30)$$

Note that in this approximation the endpoint distribution is *assumed* rather than derived as is the case in the SCF theory.[22] Furthermore, $\Psi(z)$ is wrong for small altitudes. Nevertheless, this approximation yields the correct concentration profile because $F_{\text{el}} \sim z^2$ and the large z contribution, where this assumption is reasonable, dominates. Finally, λ is a Lagrange parameter fixing the number of monomers per chain, N. The equilibrium state of the brush is specified by $\delta\gamma/\delta\phi = \partial F_{\text{brush}}/\partial\phi = 0$ leading to $\mu[\phi(z)]/kT = \lambda - Bz^2$ where $B \approx 1/N^2b^2$. λ is determined by the constraint $Nb^3 = \sigma\int_0^{L_o}\phi\,dz$ together with the requirement that $\phi(L_o) = 0$ where L_o is the height of the unperturbed brush. Accordingly

$$\mu/kT = B(L_o^2 - z^2) \qquad (31)$$

7. Appendix 2. A Combinatorical Derivation of F_{pc}

The clustering, micellization, of the amphiphilic comonomers gives rise to an additional configurational entropy term which is not reflected in the Flory–Huggins free energy. The micelles can form and dissociate freely. This process can take place with little effect on the position of the monomers involved. The primary contribution is due to the different possible placements of the micelles and the dissociated amphiphiles. To obtain a rough estimate of the additional mixing entropy we proceed in two stages: (i) Obtain the number of distinct microscopic states due to the micellization of the free, unpolymerized, amphiphilic monomers, W_f. (ii) Estimate the number of redundant states, W_o, and eliminate them. Two types of redundancies are involved. Certain states are already accounted by the Flory–Huggins free energy. Other states are unphysical because the amphiphiles are actually incorporated into a chain. In the following we identify W_o with the number of microstates resulting from free placement of the amphiphilic monomers. The argument is formulated on a lattice for consistency with the Flory–Huggins model. We first ignore the effect of excluded volume interactions between the micelles. In essence this description is equivalent to the Boltzman gas model as used in ref. 18 to discuss the micellization of free amphiphiles. We then introduce a rough approximation for the excluded volume effect. As expected, the second approximation reduces to the ideal gas result when the micellar density is low. Nevertheless, it is of interest because it determines the coefficient that allows for micelle-micelle interactions.

Before we proceed it is convenient to introduce three symbols to be used only in writing W_f and W_o. The number of dissociated amphiphiles, $p = 1$, will be denoted by M_1. M_p is the number of amphiphiles incorporated into micelles of aggregation number p. The number of micelles is M_p/p. It is important to note that in the following a micelle corresponds to a volume filling cluster of p amphiphilic monomers. This scheme does not reflect the known structure of the micelles, *i.e.*, polar headgroups that straddle the interface between a hydrophobic core, formed by the hydrocarbon tails, and the aqueous medium. The effect of this approximation on the entropy is however small. The total number of lattice sites is M_s.

Within this ideal gas approximation, each amphiphile and each micelle can be placed in any of the N_s sites. The micelles and the amphiphiles are indistinguishable among themselves.

$$W_f = \frac{M_s^{M_1} M_s^{M_p/p}}{M_1!\left(\frac{M_p}{p}\right)!} \qquad (32)$$

This approximation is reasonable while ϕ/n and the fraction of micellized amphiphiles, ψ, are small. The incompressibility constraint is introduced by noting that the total number of amphiphilic monomers is $M_1 + M_p = (\phi/n)M_s$. The redundant states are due to the free placement of the amphiphiles.

$$W_o = \frac{M_s^{M_1+M_p}}{(M_1 + M_p)!} \qquad (33)$$

The additional entropy per "lattice site" due to the clustering is thus

$$\frac{S_{pc}}{k} = \frac{1}{M_s}\ln\frac{W_f}{W_o} = \frac{1}{M_s}\ln\frac{(M_1 + M_p)!}{M_1!\left(\frac{M_p}{p}\right)!}N_s^{M_p((1/p)-1)} \qquad (34)$$

Evaluation (eq 34) using the Stirling's approximation yields

$$\frac{S_{pc}}{k} = -\left[(1-\psi)\ln(1-\psi) + \frac{\psi}{p}\ln\frac{\psi}{p} - \psi\left(1-\frac{1}{p}\right)\ln\frac{\phi}{n} + \psi\left(1-\frac{1}{p}\right)\right]\frac{\phi}{n} \qquad (35)$$

where ψ denotes the fraction of micellized amphiphiles.

Different expressions for W_f and W_o are required in order to roughly allow for excluded volume effects. In this case $W_f = W_1/W_m$, where W_1 is the number of distinguishable placements of M_1 amphiphilic monomers once M/p micelles were already placed. W_m is the number of different ways of placing the M/p micelles. W_o is identified with the possible states of the fully dissociated amphiphilic monomers.

$$W_o = \frac{M_s!}{(M_1 + M_p)![M_s - (M_1 + M_p)]!} \quad (36)$$

In the estimate of W_1, the excluded volume of the micelles appears as a reduction in the total number of available sites. In particular

$$W_1 = \frac{(M_s - M_p)!}{M_1![M_s - (M_1 + M_p)]!} \quad (37)$$

The "available volume" is reduced from M_s to $M_s - M_p$. Notice that only the total micellar volume, M_p, is utilized. To estimate W_m we consider the number of distinguishable ways for sequential placement of the micelles. The first can be placed in any of the M_s sites. The second can only be placed in $M_s - p$ sites, the third in $M_s - 2p$ etc. Accordingly

$$W_m = \frac{\prod_{i=0}^{(M_p/p)-1}(M_s - ip)}{\left(\frac{M_p}{p}\right)!} = \frac{p^{M_p/p}\left(\frac{M_s}{p}\right)!}{\left(\frac{M_p}{p}\right)!\left(\frac{M_s}{p} - \frac{M_p}{p}\right)!} \quad (38)$$

In this case the individual micellar "volume", p, is taken into account. In both cases, the micellar shape is not reflected in the estimates. Neither are finer packing considerations taken into account, such as the excluded volume between two close micelles that are not in grazing contact. This rough approximation is reasonable provided $M_p/M_s = \psi\phi/n \ll 1$. Altogether

$$\frac{S_{pc}}{k} = \frac{1}{M_s}\ln\frac{W_1 W_m}{W_o} = \frac{1}{M_s}\ln\frac{p^{M_p/p}\left(\frac{M_s}{p}\right)!}{\left(\frac{M_p}{p}\right)!\left(\frac{M_s}{p} - \frac{M_p}{p}\right)!}\frac{(M_s - M_p)!}{M_1!}\frac{(M_1 + M_p)!}{M_s!} \quad (39)$$

Evaluation (eq 39) using the Stirling approximation yields

$$\frac{S_{pc}}{k} = \left(1 - \frac{1}{p}\right)\left[\psi\frac{\phi}{n}\ln\frac{\phi}{n} + \left(1 - \psi\frac{\phi}{n}\right)\ln\left(1 - \psi\frac{\phi}{n}\right)\right] - \frac{\phi}{n}\left[\frac{\psi}{p}\ln\frac{\psi}{p} + (1 - \psi)\ln(1 - \psi)\right] \quad (40)$$

As required, this expression reduces to eq 35 in the limit of $\psi \ll 1$. This expression for S_{pc} when combined with the micellization energy term yields the p-cluster correction term

$$\frac{F_{pc}}{kT} = \frac{\psi\phi}{n}\epsilon_p - \frac{S_{pc}}{k} \quad (41)$$

thus leading to eq 15.

8. Appendix 3. Micellar Structure

It is convenient to use a model of free, unpolymerized amphiphiles as a starting point for the discussion of micelles formed by the polymerized ones. For simplicity we focus on spherical micelles as formed in aqueous solutions of high ionic strength. The hydrocarbon tails form a dense, hydrophobic core in a melt like state. The charged headgroup straddle the interface of the core. A simple model for such micelles was proposed by Isralachvili et al.[25] The free energy per amphiphile in a micelle comprising p surfactants, $\epsilon_p kT$, is

$$\epsilon_p \approx \gamma a + \frac{K}{a} - \delta \quad (42)$$

where a is the area per headgroup. γkTa is the corresponding surface energy, KkT/a allows for the repulsion between the headgroups and $-\delta kT$ is the transfer free energy of the hydrophobic tail from water into the core. At equilibrium γa is comparable to K/a thus defining an equilibrium area per headgroup, $a_o \approx (K/\gamma)^{1/2}$. It is than possible to rewrite eq 42 as $\epsilon_p \approx \gamma a_o\,(a/a_o + a_o/a) - \delta$. At equilibrium

$$\epsilon_{p_o} \approx \gamma a_o - \delta \quad (43)$$

and $\phi_{cmc} \approx \exp\epsilon_p$. The micellar structure, as described above, is modified when the amphiphiles are polymerized.[6,27] In this situation, the micellization gives rise to a semidilute corona of soluble spacer chains. For simplicity, we consider a corona of loops formed by the spacer chains; *i.e.*, each loop in the corona consists of n monomers. When the corona is extended compared to the size of the micellar core, it assumes a starlike structure. The span of the corona is $H/b \approx p^{1/5}n^{3/5}$ and the corresponding free energy per amphiphile is $F_{corona}/kT \approx p^{1/2}\ln n$. The micellar structure is described by eq 42 supplemented by F_{corona}/kT. Introducing a dimensionless parameter $u = p/p_o \approx (a_o/a)^3$, the free energy per amphiphile becomes

$$\epsilon_p \approx \gamma a_o(u^{-1./3} + u^{1/3} + \kappa u^{1/2}) - \delta \quad (44)$$

where $\kappa \approx p^{1/2}\ln n/\gamma a_o$. Two regimes may now be distinguished. When $\kappa \ll 1$ the $u^{1/2}$ term is negligible, thus leading to $p \approx p_o$ and $\epsilon_{p_o} \approx \gamma a_o - \delta$. In the opposite case, $\kappa \gg 1$, the $\kappa u^{1/2}$ is comparable to $u^{-1./3}$, yielding $u \approx \kappa^{-6/5}$ or

$$p \approx p_o^{2/5}\left(\frac{\gamma a_o}{\ln n}\right)^{6/5} \quad (45)$$

In this case, the equilibrium value of ϵ_p is

$$\epsilon_p \approx \gamma a_o - \delta + \gamma a_o \kappa^{2/5} \quad (46)$$

and

$$\exp\epsilon_p \approx \phi_{cmc}\exp(\gamma a_o \kappa^{2/5}) \quad (47)$$

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$$p = \frac{-\bar{\phi}\ln(1-\bar{\phi})}{\bar{\phi} + (1-\bar{\phi})\ln(1-\bar{\phi})}$$

$\bar{\phi}$ approaches unity as p increase and for large p, $p \approx \ln(1 - \bar{\phi})$ thus leading to eq 6.
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