Polymer−Surfactant Interaction in Thermoreversible Gels

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ABSTRACT: The influence of low-molecular-weight surfactants on the sol/gel transition of hydrophobically modified water-soluble associating polymers is studied on the basis of the recent theory of thermoreversible gelation with multiple junctions. It is shown that the existence of a lower and an upper bound in the aggregation number of hydrophobes at the network junctions leads to nonmonotonic polymer gelation concentration as a function of the surfactant concentration. There is a certain surfactant concentration where gelation is most promoted, thereby exhibiting a peak in the viscosity and modulus. Relation between this peak concentration and the critical micelle concentration of the added surfactant is detailed. The fraction of surfactant molecules adsorbed into the network junctions is also shown to exhibit a peak near the enhanced gelation point. The number of elastically active network chains is calculated in the postgel regime as a function of the surfactant concentration and compared with the experimental data on the high-frequency storage modulus of HEUR/SDS systems.

I. Introduction

The interaction between polymers and surfactants has been a subject of great interest.[1,2] The problem was found initially in studies of proteins associated with natural lipids, and later in studies of their association with synthetic surfactants. More recently, interaction of water-soluble synthetic polymers such as poly(ethylene oxide) with ionic and nonionic surfactants[3−6] has attracted the interest of researchers because of the scientific and technological implications. Adding surfactants to polymer solutions with formation of a polymer/surfactant complex can substantially alter the physical properties of the starting polymers. The effect can be summarized in the following four categories:

(i) Conformational transition of polymers, such as coil−globule transition[7,8] and coil−rod transition.[9,10]

(ii) Expansion and shift of the phase separation region on the polymer/solvent phase plane.[11]

(iii) Formation of composite microphases.[12]

(iv) Shift of the sol/gel transition line[13−15] and modification of the rheological properties.[16−18]

When polymers carry a small fraction of hydrophobic groups, the effects are dramatically enhanced, as is seen in some of the above examples. Such polymers are often referred to as "associating polymers" because they show a tendency to self-assemble, leading to gelation in the extreme cases, caused by the aggregation of hydrophobes. The ability of surfactant binding is enhanced through the hydrophobic interaction between polymer hydrophobes and surfactant hydrophobes. Thus, typical model polymers such as hydrophobically ethoxylated urethane (HEUR), ethyl hydroxyethyl cellulose (EHEC), and hydroxypropyl methyl cellulose (HPMC) have recently been the focus of study. A profound influence of added surfactants on the rheological properties has been reported. For example, the plateau modulus of HEUR solution exhibits a peak when sodium dodecyl sulfate (SDS) is added at low polymer concentrations. The peak disappears at higher polymer concentrations.[16] It was also reported that the viscosity of HPMC/SDS solution exhibits a similar peak at low polymer concentrations.[17]

In this paper, we focus our interest on the influence of added surfactants on thermoreversible gelation of associating polymers. On the basis of our recent theory of thermoreversible gelation with multiple junctions,[19] we present a theoretical description of sol/gel transition in the polymer/surfactant mixtures. The structure of the mixed micelles at network junctions is analyzed. The amount of surfactant adsorbed into the network is calculated as a function of the temperature and concentration. The relationship between the peak in the modulus and the critical micelle concentration of the surfactant is clarified. In the postgel regime, topological properties such as path connectivity and the numbers of elastically effective chains and of dangling ends in the gel network are calculated and compared with the experimental data on the high-frequency storage modulus.

II. Mixture of Associating Polymers and Surfactants

To model the associating polymer−surfactant system, we consider a mixture of polymers and low-molecular-weight surfactant molecules in a solvent. Each polymer is assumed to carry a number f (≥ 2) of associative groups (hydrophobes in the case of HEUR) along its chain comprising r_f statistical units, and each surfactant molecule is modeled as a molecule carrying a single hydrophobe connected to the hydrophilic head of volume r_1 the volume measured relative to the polymer statistical unit) (see Figure 1). The hydrophobe on a surfactant molecule may generally be different from that on a polymer chain, but throughout this paper we assume for simplicity that they are exactly the same. The difference could be included easily, but only at the expense of more cumbersome notation, which does not seem worthwhile at the present stage of the study. The total number of statistical units on a polymer is then given by $n_f = r_f + fr_0$, and that on a surfactant molecule is $n_1 = r_1 + r_0$, where r_0 is the volume of the hydrophobe measured relative to that of a statistical unit. We then have a mixture of f molecules and $f = 1$ molecules in a solvent. This is a special case of the model solution treated in our previous study[19] on the associating

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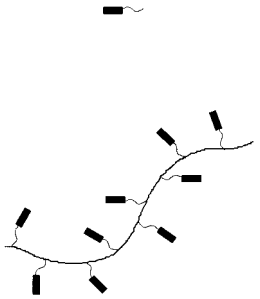

Figure 1. Mixture of associating polymers with f hydrophobes and low-molecular-weight surfactant molecules with a single hydrophobe.

polymers capable of forming networks with multiple cross-link junctions. We therefore start from the lattice theoretical free energy detailed in it.

Let us first describe some stoichiometric definitions. Let $N_i (i = 1, f)$ be the number of molecules of each species in the system of volume V. In a lattice theoretical picture, the volume is described by the total number $\Omega \equiv V/a^3$ of fictitious cells, each of which can accommodate only one statistical unit, where a is the size of the cell. The volume fraction of each species is then given by

$$\phi_i = n_i N_i/\Omega \quad (i = 1, f) \tag{2.1}$$

and the number of hydrophobes carried is

$$\psi_i = i\phi_i/n_i = i\nu_i \quad (i = 1, f) \tag{2.2}$$

where $\nu_i \equiv \phi_i/n_i$ is the number of molecules of the type i per lattice cell. Since the total number of hydrophobes in the solution is given by $\psi = \psi_1 + \psi_f$, the weight distribution w_i of associative groups on the species i is given by $w_i = \psi_i/\psi$. This distribution gives the number- and weight-average functionality as

$$1/f_n \equiv \sum w_i/i = (\nu_1 + \nu_f)/\psi \tag{2.3}$$

$$f_w \equiv \sum i w_i = (\nu_1 + f^2\nu_f)/\psi \tag{2.4}$$

In equilibrium, hydrophobes on the polymers and on the surfactants aggregate into micelles that work as cross-link junctions in various sizes of clusters and also in networks at high enough concentrations. The aggregation number differs from one micelle to another (see Figure 2). To specify the size of the junctions, we introduced the concept of *junction multiplicity* in the previous study.[19] The multiplicity k is defined by the number of chains combined together into a junction. It agrees with the aggregation number of the micelles in the case of associative hydrophobes. Thus, $k = 1$ indicates unassociated hydrophobes. Let p_k be the probability for a randomly chosen hydrophobe to belong to a junction of multiplicity k at a certain given temperature and polymer and surfactant concentrations. Then, $p_1 \equiv 1 - \alpha$ is the probability for a hydrophobe to remain unassociated, where α is the extent of reaction (or conversion) in the conventional meaning. It was shown in ref 19 that the probability p_k is given by

$$p_k = K_k \psi^{k-1} {p_1}^k \tag{2.5}$$

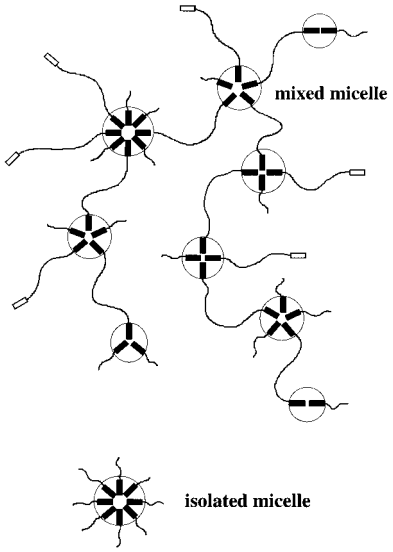

Figure 2. Mixed micelles at the network junctions and an isolated pure micelle consisting of surfactant molecules only. Active hydrophobes ($k = 1$) are shown as white squares.

with equilibrium reaction constant

$$K_k = [\lambda(T)]^{k-1}\gamma_k \tag{2.6}$$

where

$$\lambda(T) \equiv (\zeta - 1)\exp(-\beta\Delta g_0) \tag{2.7}$$

is the association constant (ζ being the lattice coordination number $\beta \equiv 1/k_B T$, and Δg_0 the free energy change for binding a hydrophobe into a micelle). The factor γ_k comes from the surface term in the free energy of a micelle of the multiplicity k.

III. Sol/Gel Transition

From the normalization condition $\sum p_k = 1$, we find that the total concentration ψ of the hydrophobes should satisfy the relation

$$\lambda(T)\psi = zu(z) \tag{3.1}$$

where the function $u(z)$ to be used to characterize micellar junctions is defined by

$$u(z) \equiv \sum_{k=1}^{\infty} \gamma_k z^{k-1} \tag{3.2}$$

The parameter z that appeared in this relation is defined by

$$z \equiv \lambda(T)\psi p_1 = \lambda(T)\psi(1 - \alpha) \tag{3.3}$$

and gives the (reduced) concentration of the hydrophobes that remain unassociated in the solution. These two equations lead to a relation

$$u(z) = 1/(1 - \alpha) \tag{3.4}$$

that expresses the junction function in terms of the conversion. If we use the (reduced) volume fraction $c_f \equiv \lambda(T)f\phi_f/n_f$ instead of ψ_f for polymers and $c_1 \equiv \lambda(T)\phi_1/$

n_1 for surfactants, then relation 3.1 can be transformed into

$$c_f(1 + \eta) = zu(z) \tag{3.5}$$

where

$$\eta \equiv c_1/c_f \tag{3.6}$$

is the ratio of the surfactant concentration to the polymer concentration. Solving this relation with respect to z, we find z, and hence the conversion α, as a function of a given temperature and concentration. By using the relative concentration η, we can write the weight distribution w_i as

$$w_1 = \eta/(1 + \eta) \quad \text{(for surfactant)},$$
$$w_f = 1/(1 + \eta) \quad \text{(for polymer)} \tag{3.7}$$

Now the theory of polycondensation with multiple junctions (Fukui−Yamabe[20] and also ref 19) gives

$$D_w = R/(1/f_w + 1/\mu_w - 1) \tag{3.8}$$

for the weight-average cluster size in the pregel regime. Here,

$$R \equiv \sum_{i=1,f} n_i w_i/i = (n_1\eta + n_f/f)/(1 + \eta) \tag{3.9}$$

is the average number of statistical units per hydrophobe, and

$$\mu_w \equiv \sum_{k\geq 1} kp_k = 1 + zu'(z)/u(z) \tag{3.10}$$

is the weight-average micellar size of the junctions. As the concentration is increased, the weight-average cluster size increases and eventually becomes infinite at a concentration at which the condition

$$(f_w - 1)(\mu_w - 1) = 1 \tag{3.11}$$

is satisfied. This is the sol-to-gel transition point. For our polymer/surfactant system, this sol/gel transition condition is explicitly given by

$$(f - 1)zu'(z)/(1 + \eta)u(z) = 1 \tag{3.12}$$

Combining this condition with relation 3.5 and eliminating the parameter z, we find the sol/gel transition curve on the temperature−concentration plane. In what follows, we calculate (reduced) polymer concentration c_f^* at gelation as a function of the (reduced) surfactant concentration c_1. The temperature appears only through the association constant $\lambda(T)$. In the more complex case where the binding free energy of surfactant into the micelles is different from that of a polymer hydrophobe, we have to introduce another association constant, and hence simple scaling by a single temperature shift factor does not hold.

To see how the sol/gel transition concentration shifts upon adding surfactant molecules, we have to specify the multiplicity of the junctions in more detail. At this stage, we have to stress the importance of both the lower and upper limits in the multiplicity allowed in order to describe the nonmonotonic behavior of the observed modulus and viscosity. We therefore introduce a model function

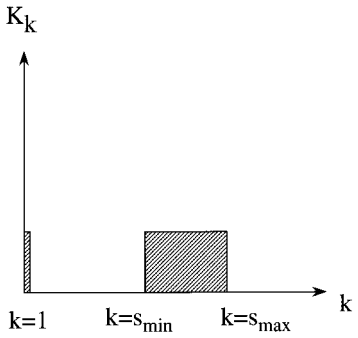

Figure 3. Reaction constant that allows multiplicity lying between a lower bound, s_{min}, and an upper bound, s_{max}.

$$u(z) = 1 + \sum_{k=s_{min}}^{s_{max}} z^{k-1} = 1 + (x^{s_{min}} - x^{s_{max}})/(1 - x) \tag{3.13}$$

where s_{min} is the minimum multiplicity and s_{max} is the maximum multiplicity allowed (see Figure 3). We have neglected any possible contribution to the free energy from the micellar surface and set all $\gamma_k = 1$ for $s_{min} \leq k \leq s_{max}$. Small micelles whose aggregation numbers are less than s_{min} and large micelles with aggregation numbers more than s_{max} are assumed to be unstable and to dissociate. This is a natural assumption. In fact, low-molecular-weight surfactant molecules are known to form micelles of a very narrow size spectrum. The upper and lower bounds here are determined by the geometrical suitability of the hydrophobes for spatial packing, flexibility of polymer chains, and other factors. When polymer concentration is low and the number of hydrophobes is not enough to form junctions, addition of surfactants combines the unassociated hydrophobes until their aggregation number exceeds s_{min} and stabilizes them. In this situation, the surfactant works as a cross-linking agent. To the contrary, when the polymer concentration is large and many junctions are already formed, some of the polymer hydrophobes in the junctions are replaced by surfactant hydrophobes and lead to the dissociation of network junctions. Figure 4 shows how junctions are formed and destroyed by added surfactants in the special case where the multiplicity is fixed at $s_{min} = s_{max} = 5$. From these considerations, we expect that there is no surfactant-mediated process if no minimum multiplicity exists, i.e., if $s_{min} = 2$. In such a special case, hydrophobes form stable junctions no matter how small their aggregation number may be. The addition of surfactants, therefore, simply destroys the already existing junctions.

To demonstrate these ideas, we calculate, by solving eqs 3.5 and 3.12, the concentration of polymers at the sol/gel transition point as a function of the concentration of the added surfactant. Figure 5 shows the result for the telechelic ($f = 2$) polymers. Both polymer and surfactant concentrations are expressed in terms of the reduced concentration, the number of hydrophobes (per lattice cell) times the association constant. To see the effect of the minimum multiplicity, s_{min} is varied from curve to curve, while the maximum multiplicity is fixed at $s_{max} = 8$. It is clear that the sol/gel concentration c_f^* monotonically increases with the surfactant concentration for $s_{min} = 2$ (no lower bound); i.e., gelation is blocked

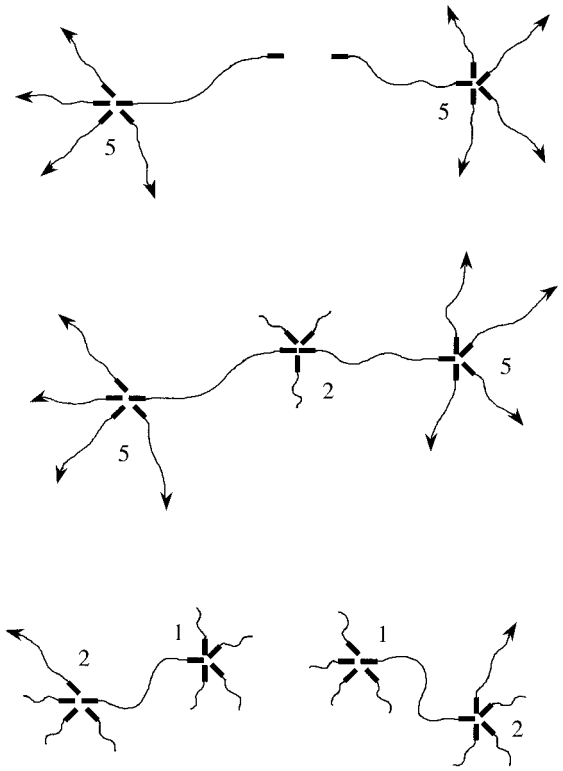

Figure 4. Formation of a junction with the help of surfactant molecules (surfactant-mediated association) and destruction of a junction by excess surfactant molecules. The allowed multiplicity is fixed at $s = 5$. Figures near the junctions indicate their branching numbers. Average branching number is $(5 + 5)/2 = 5$ (top figure), $(5 + 5 + 2)/3 = 4$ (middle figure), and $(2 + 2 + 1 + 1)/4 = 1.5$ (bottom figure). It monotonically decreases with surfactant concentration.

by the surfactant. But if there is a gap between $k = 1$ (unassociated) and $k = s_{min}$, a minimum in c_f* starts to appear. At this surfactant concentration, gelation is most promoted, as can be seen for $s_{min} \geq 3$. The surfactant concentration at which c_f* becomes minimum (hereafter referred to as surfactant-mediated gelation point, SMG) increases as the gap becomes larger.

To see the effect of the minimum multiplicity in more detail, we show in Figure 6a the special case where there is no upper bound i.e., $s_{max} = \infty$. The minimum s_{min} is varied from curve to curve. Specifically, when $s_{min} = 2$, where all multiplicities are stable, there is no effect of added surfactant. But appearance of the dip in c_f* shifting to higher c_1 is clearly seen as s_{min} is increased. Figure 6b shows the opposite case, where the gelation concentration c_f* monotonically increases with c_1 irrespective of the maximum multiplicity if there is no gap. The minimum multiplicity is fixed at $s_{min} = 2$, while the maximum multiplicity s_{max} is varied from curve to curve.

IV. Distribution Function of Clusters

In thermal equilibrium, the solution has a distribution of clusters with a population distribution fixed by the equilibrium conditions. Following the notation in Fukui–Yamabe[20] (and ref 19), we define a cluster of the type (**j**;**l**) to consist of l_i primary molecules of functionality i ($i = 1, 2, 3, ...$) and j_k junctions of multiplicity k ($k = 1, 2, 3, ...$). For our polymer/surfactant mixture, i takes either 1 (surfactant) or f (polymer), so that the bold

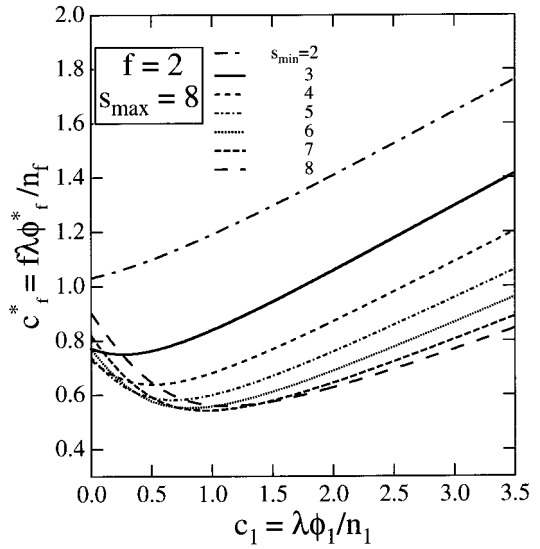

Figure 5. Polymer concentration at sol/gel transition as a function of the concentration of added surfactant. The concentration is measured in terms of the number density $f\phi/n$ of the hydrophobes times the association constant $\lambda(T)$ for each species. Minimum multiplicity s_{min} is varied from curve to curve under a fixed maximum multiplicity, s_{max}. While the sol/gel concentration monotonically increases with surfactant concentration for $s_{min} = 2$ (i.e., there is no lower bound in the multiplicity), there appears a minimum at a certain surfactant concentration for $s_{min} \geq 3$ (i.e., if there is a gap below the minimum allowed multiplicity). In the latter case, gelation is promoted by the surfactant molecules and referred to as surfactant-mediated gelation (SMG) in the text.

letter **l** means $\mathbf{l} \equiv \{l_1, l_f\}$. The junction indexes take the form $\mathbf{j} \equiv \{j_1, j_{s_{min}}, ..., j_{s_{max}}\}$. Note that $k = 1$ indicates unreacted functional groups. Specifically, an unassociated polymer is indicated by $\mathbf{j}_{0f} \equiv \{f,0,0,...\}$ and $\mathbf{l}_{0f} \equiv \{0,1\}$, while an unassociated surfactant molecule is indicated by $\mathbf{j}_{01} \equiv \{1,0,0,...\}$ and $\mathbf{l}_{01} \equiv \{1,0\}$.

Let $l \equiv \sum l_i = l_1 + l_f$ be the total number of primary molecules in a cluster. Then, the following two independent algebraic conservation conditions hold, provided there are no cyclic structures:

$$l = l_1 + l_f = \sum (k - 1) j_k + 1 \tag{4.1}$$

$$\sum j_k = (f - 1) l_f + 1 \tag{4.2}$$

One of these relations can be replaced by the useful identity

$$\sum k j_k = l_1 + f l_f \tag{4.3}$$

Starting from the free energy studied in ref 19 and posing the multiple equilibrium conditions to the cluster formation, we find the most probable cluster distribution function. It is written for our polymer/surfactant mixture as

$$\lambda(T)\nu(\mathbf{j};\mathbf{l}) = (\sum j_k - 1)!(l_1 + l_f - 1)! \left[\prod_{k \geq 1} \left(\frac{\gamma_k^{j_k}}{j_k!}\right)\right] \left(\frac{x_1^{l_1}}{l_1!}\right) \left(\frac{x_f^{l_f}}{l_f!}\right) \tag{4.4}$$

where

$$x_i \equiv i\lambda(T)\nu(\mathbf{j}_{0i};\mathbf{l}_{0i}) \qquad \text{for } i = 1, f \tag{4.5}$$

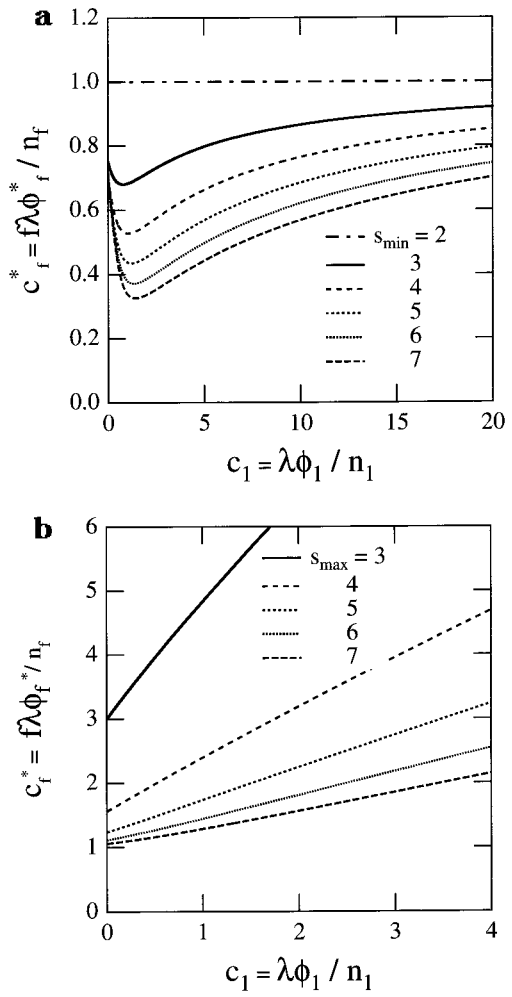

Figure 6. (a) Effect of the minimum multiplicity on the sol/gel transition, shown by varying s_{min} under no upper bound ($s_{max} = \infty$). The minimum grows as the forbidden lower gap becomes wider. (b) Effect of the maximum multiplicity on the sol/gel transition, shown by varying s_{max} under no lower bound ($s_{min} = 2$). The sol/gel concentration monotonically increases with the surfactant concentration. It is clear that no SMG takes place if there is no lower bound in the multiplicity.

are the reduced concentration of the unassociated molecules.

V. Adsorption of Surfactants into the Polymer Network

It is known that surfactant molecules form micelles above a certain concentration. The concentration at which micelles start to appear is referred to as the critical micelle concentration (cmc). To see how the cmc is affected by the presence of associating polymers, let us consider the surfactant molecules that are not associated to any polymers. The clusters composed purely of surfactant molecules are indicated by $l_f = 0$, so that we have $\mathbf{l} = \{l_1,0\}$. There is a single junction of the multiplicity $k = l_1$ in such a pure surfactant cluster. We then have $j_k = 1$ for $k = l_1$ and other $j_k = 0$. The distribution function becomes

$$\lambda\nu(\mathbf{j};\mathbf{l}) = \gamma_{l_1}(x_1)^{l_1}/l_1 \tag{5.1}$$

The total number density of the pure surfactant micelles

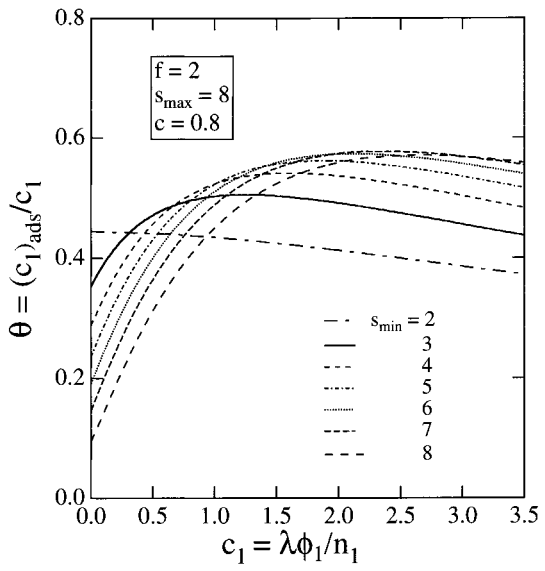

Figure 7. Relative concentration of surfactant molecules adsorbed into polymer junctions. It shows a broad maximum near the surfactant concentration at which gelation is most promoted, except for the case of $s_{min} = 2$. The polymer concentration is fixed at $c_f = 0.8$.

(including unassociated molecules) is then given by

$$\lambda\nu_1^{iso} \equiv \lambda\sum_{l_1\geq 1}\nu(\mathbf{j};\mathbf{l}) = \int_0^{x_1} u(x)\,dx \tag{5.2}$$

while the total volume fraction of the pure surfactant micelles is given by

$$\lambda\phi_1^{iso}/n_1 \equiv \lambda\sum_{l_1\geq 1} l_1\nu(\mathbf{j};\mathbf{l}) = x_1 u(x_1) \tag{5.3}$$

where function $u(x)$ is defined by (3.13). Since

$$x_1 = c_1(1-\alpha) = c_1/u(z) \tag{5.4}$$

by definition, we find

$$\lambda\phi_1^{iso}/n_1 = x_1 u(x_1) = c_1 u(x_1)/u(z) \tag{5.5}$$

and hence

$$\phi_1^{iso} = [u(x_1)/u(z)]\phi_1 \tag{5.6}$$

From this result, we find that the surfactant molecules adsorbed into the junctions made up of polymer hydrophobes is given by

$$\phi_1^{ads} = [1 - u(x_1)/u(z)]\phi_1 \tag{5.7}$$

Figure 7 shows the fraction $\theta = \phi_1^{ads}/\phi_1 = c_1^{ads}/c_1$ of the adsorbed surfactant molecules relative to the total amount as a function of the total surfactant concentration. The maximum multiplicity is fixed at 8, while the minimum multiplicity is varied from curve to curve. The polymer concentration is fixed at $c_f = 0.8$, at which polymers are in the postgel regime for $s_{min} = 3$, 4, 5, 6, but in the pregel regime for $s_{min} = 2$, 7, and 8, as can be seen from Figure 5. The ratio θ changes continuously across the sol/gel transition point and takes a maximum value at the surfactant concentration where gelation is

most promoted, except for the case of $s_{min} = 2$, with no gap in the aggregation number.

VI. Cmc of the Surfactant Molecules

From the distribution function (eq 5.1) of pure surfactant micelles, we can estimate the critical micelle concentration (cmc) of the surfactant. Here we define cmc as the surfactant concentration at which micelles consisting of only surfactant molecules start to appear. In what follows, therefore, we refer to this concentration as critical pure micelle concentration (cpmc). One conventional criterion for cmc is to find the concentration at which the osmotic pressure changes its slope most rapidly.[21] This criterion is almost equivalent to the condition that the weight density of the surfactant molecules expressed as a function of that of the isolated (unassociated) molecules ceases to have its inverse function.[21] In our present particular model, the contribution to the osmotic pressure from the surfactant molecules that are separated from polymers is proportional to eq 5.2 at low concentrations, and their weight density is given by eq 5.3. If we try to solve eq 5.3 for x_1 as a function of ϕ_1^{iso}, we will fail to find the solution whenever

$$\mathrm{d}(xu(x))/\mathrm{d}x = u(x) + xu'(x) = 0 \qquad (6.1)$$

holds. This equation is an algebraic equation for x and has its roots on the complex x-plane. These roots are branch points of the inverse function. When the concentration x_1 of the unassociated surfactant passes near the root that lies closest to the real x-axis, the osmotic pressure (eq 5.2) due to surfactant molecules changes its slope most rapidly.

To study the relative position of cpmc and SMG concentration, we consider a special multiplicity model in which junction multiplicity is fixed at a single value, $s_{min} = s_{max} \equiv s$. The function $u(x)$ in this fixed multiplicity model takes the form $u(x) = 1 + x^{s-1}$ by definition and leads to a set of equations

$$\lambda\nu_1^{iso} = x_1 + x_1^s/s \qquad (6.2)$$

$$\lambda\phi_1^{iso}/n_1 = x_1 + x_1^s \qquad (6.3)$$

Equation 6.1 now gives the roots

$$x_k = s^{-1/(s-1)} \exp[2\pi i(k + 1/2)/(s - 1)], \quad k = 0, 1, 2, ..., s - 2 \qquad (6.4)$$

lying on a circle of radius $r \equiv 1/s^{1/(s-1)}$ on the complex x-plane. Now, setting $x_1 = r$ in eq 5.4, we find cpmc by

$$c_1/(1 + z^{s-1}) = r \qquad (6.5)$$

where the parameter z is expressed in terms of c_f and c_1 by solving eq 3.1, now taking the form

$$c_f + c_1 = z(1 + z^{s-1}) \qquad (6.6)$$

Figure 8 shows the result. Solid lines show the sol/gel concentration (vertical axis) as a function of the surfactant concentration (horizontal axis), and broken lines show cpmc (horizontal axis) as a function of polymer concentration (vertical axis). The multiplicity is changed from $s = 3$ to $s = 8$. There is an intersection between the solid and broken lines for each given multiplicity. This is a special point where the sol/gel transition and cpmc take place simultaneously. We call this special point the micellization gelation point (MGP). For instance, this point for $s = 8$ is located at a surfactant concentration nearly twice as large as the SMG concentration. To see the situation more clearly, we draw these two lines on the ternary phase plane. Figure 9 shows the sol/gel transition line (solid line) and the cpmc line (broken line) on the triangular plane of the polymer/surfactant/water system. SMG and MGP are indicated by the black and white circles. Their relative position may change if we allow a difference in the binding free energy for the polymer hydrophobe and for the surfactant hydrophobe into the micelles.

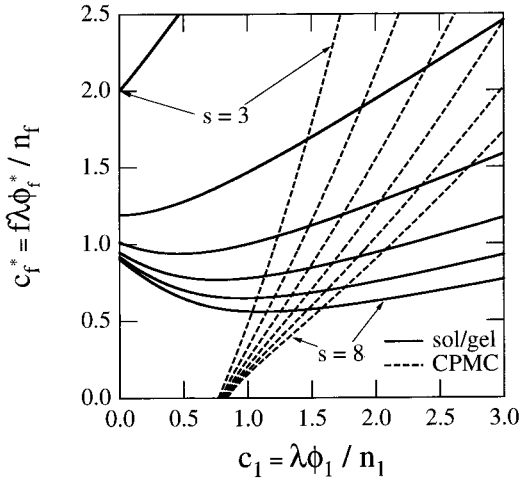

Figure 8. Sol/gel concentration (solid lines) and the critical pure micelle concentration (cpmc) (broken lines) plotted on the polymer/surfactant concentration plane. The multiplicity is fixed at $s_{min} = s_{max} = 8$ for simplicity. For $s = 8$, for instance, the cpmc is approximately twice as large as the SMG.

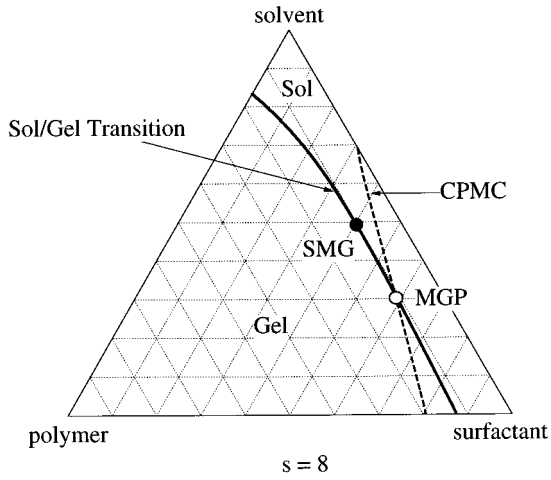

Figure 9. Sol/gel transition line and the cpmc line drawn on the ternary phase plane of polymer/surfactant/solvent system. The minimum gelation point is indicated by a black circle. The white circle shows a special point at which gelation and micellization simultaneously take place.

VII. Structure of the Network

Let us proceed to the study of the network structure. In general, a junction connecting polymers involves mixed micelles consisting of both polymer hydrophobes

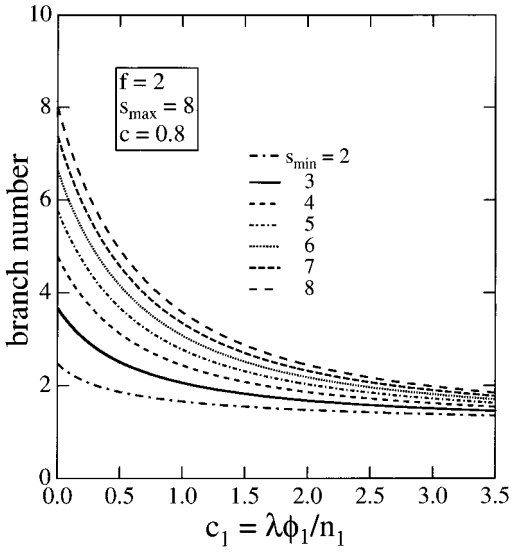

Figure 10. Average branch number of the network junctions as a function of the concentration of added surfactant. In all cases, including $s_{min} = 2$, the branch number monotonically decreases with the surfactant concentration.

and surfactant molecules. Let us first count the average total number, J, of the junctions in the solution. We have to exclude unassociated hydrophobes and the micelles formed by surfactant only. It is therefore given by

$$J = \sum_{\mathbf{j},\mathbf{l}}(\sum_{k\geq 2} j_k)\nu(\mathbf{j};\mathbf{l}) - \sum_{\mathbf{j},\mathbf{l}(l_f=0)}(\sum_{k\geq 2} j_k)\nu(\mathbf{j};\mathbf{l}) \qquad (7.1)$$

Since the total number of associated hydrophobes carried by the polymers is given by $(f\phi_f/n_f)\alpha$, the average number, Φ, of the chains combined in a single junction is estimated to be

$$\Phi = (f\phi_f/n_f)\alpha/J \qquad (7.2)$$

We call this the average branching number. From the relation

$$\sum_{\mathbf{j},\mathbf{l}}(\sum_{k\geq 2} j_k)\nu(\mathbf{j};\mathbf{l}) = \psi \sum_{k=s_{min}}^{s_{max}} \frac{p_k}{k} = \frac{1}{\lambda}\int_0^z (u(x) - 1)\, dx \qquad (7.3)$$

and

$$\sum_{\mathbf{j},\mathbf{l}(l_f=0)}(\sum_{k\geq 2} j_k)\nu(\mathbf{j};\mathbf{l}) = \sum_{k=s_{min}}^{s_{max}} \gamma_k \frac{{x_1}^k}{k} = \frac{1}{\lambda}\int_0^{x_1} (u(x) - 1)\, dx \qquad (7.4)$$

we find

$$\lambda(T)J = \int_{x_1}^z (u(x) - 1)\, dx \qquad (7.5)$$

As was demonstrated in Figure 4, the average branching number decreases with surfactant concentration even if new junctions are formed with the help of the surfactant molecules. Figure 10 shows a more general result. The average branching number Φ calculated by the above equations is plotted against the concentration of the added surfactant. The minimum multiplicity is

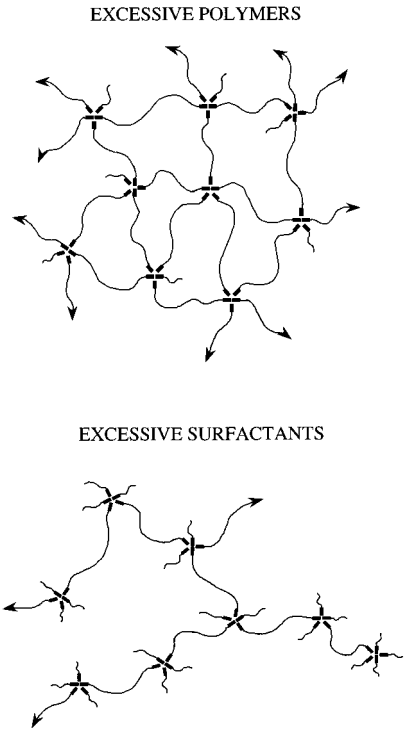

Figure 11. Structure of the polymer network under excessive polymers (top) and excessive surfactant (bottom). The network changes from a multiplly bound tight structure to a loosely bound one with small branch number.

changed from curve to curve, while the maximum multiplicity is fixed at 8. The polymer concentration is fixed at $c_f = 0.8$ where networks are well developed. Each curve starts from a value between s_{min} and s_{max} and monotonically decreases to the limiting value of 1 at high surfactant concentrations, where all polymer hydrophobes are separately trapped into the surfactant micelles. Figure 11 illustrates how the polymer network changes with surfactant concentration. At small surfactant concentrations, the network chains are tightly connected to each other by the junctions. In the presence of excess surfactant molecules, however, many junctions are dissociated, resulting in a loosely bound structure with junctions of small branching numbers.

VIII. High-Frequency Elastic Modulus

Having described structural changes in the networks with increase of the surfactant concentration, we now proceed to the study of the dynamic mechanical moduli. In the experiment on HEUR/SDS system,[16] addition of surfatant resulted in several effects. The moduli are no longer described by the simple Maxwell element with a single relaxation time, but a shoulder appears on the loss modulus at higher frequencies. Furthermore, the high-frequency plateau in the storage modulus reveals a nonmonotonic dependence on the SDS concentration. At low polymer concentration, it initially rises to a peak and then decreases monotonically, falling eventually to zero at higher SDS concentration. With an increase in the polymer concentration, the height of the peak decreases, and its position shifts to lower SDS concentration. Above a certain polymer concentration, the peak disappears. Finally, the average rheological relaxation time also shows a peak for all polymer concentrations measured.

To see these observations from a theoretical point of view, let us first count the number of polymer chains in the network that contribute to the mechanical moduli. A chain in the network can be classified into two main categories: an elastically effective chain and a dangling chain. An elastically effective chain is a chain whose ends are both connected to different network junctions. A dangling chain is a chain that belongs to a group dangling from the network. Stress is transmitted only through the elastically effective chains. The criterion to judge whether a chain is effective or ineffective is, however, not unique. Several candidates have been examined in the theoretical review on rubber elasticity.[22,23] Here, as in our previous study, we employ the most precise criterion proposed by Scanlan[24] and Case.[25] The Scanlan−Case criterion assumes that those chains whose ends are both connected to the junctions that carry at least three paths leading to the network matrix are elastically effective. A junction with one path to the gel unites a group of subchains dangling from the network matrix whose conformations are not affected by an applied stress. A junction with two paths to the gel merely extends the length of an effective subchain.

To see this in more detail, let us specify the junction type.[26,27] A junction of multiplicity k that is connected to the gel network through i paths is referred to as an (i,k) junction. Let $\mu_{i,k}$ be the number of junctions specified by the type (i,k) for $k = 1, 2, 3, 4, ...$, and for $0 \le i \le 2k$. The total number of junctions with multiplicity k in a unit volume is given by

$$\mu_k = \sum_{i=0}^{2k} \mu_{i,k} = (\sum_{i=1,f} i\nu_i)(p_k/k) \tag{8.1}$$

where ν_i is the number of primary molecules of species i in a unit volume. Repeating the combinatorial analysis by Pearson and Graessley,[25] we count the number of different ways to combine k functional groups on the separated molecules into a junction of the type (i,k) and find that $\mu_{i,k}$ for our polymer-surfactant mixture is given by

$$\mu_{i,k} = (\sum_{i=1,f} i\nu_i)p_k \sum_{0\le m\le i/2} \frac{(k-1)!}{(k-i+m)!(i-2m)!m!} \times (\zeta_0)^{k-i+m}(\zeta_1)^{i-2m}(\zeta_2)^m \tag{8.2}$$

where ζ_j $(j = 0, 1, 2)$ is the probability that a randomly chosen unassociated functional group be connected to the gel network matrix through j paths.

To calculate the number of effective chains by the use of the Scanlan−Case criterion, let us consider the connectivity ζ_j of a functional group to the gel network. As was done in our preceeding paper,[27] we introduce the probability v that a randomly selected functional group either is unreacted or is a part of the sol fraction.[27] It is a function of the temperature and the concentration of the polymers and surfactant molecules for the given associative interaction. Then the probability ζ_j $(j = 0, 1, 2)$ can be written in terms of v. The only difference from the pure polymer case is that the paths along a surfactant molecule are blocked by the dead end because it has only a single associative group. Thus, for the mixture we find

$$\zeta_0 = \sum_{i=1,f} \frac{w_i}{i} \sum_{m=1}^{i} v^{m-1}v^{i-m} = w_1 + w_f v^{f-1} \tag{8.3a}$$

$$\zeta_2 = \sum_{i=1,f} \frac{w_i}{i} \sum_{m=1}^{i} (1 - v^{m-1})(1 - v^{i-m}) = 2w_f[(1 - v^f)/f(1 - v) - v^{f-1}] \tag{8.3b}$$

$$\zeta_1 = 1 - \zeta_0 - \zeta_2 = w_f\left[1 + v^{f-1} - \frac{2(1 - v^f)}{f(1 - v)}\right] \tag{8.3c}$$

As in ref 27, let us introduce a function defined by

$$v(x) \equiv \sum_{k\ge 1} p_k x^{k-1} \tag{8.4}$$

where the probability p_k for an associated hydrophobe to be a member of a k junction is given by eq 2.5. Separating the unassociated term $(k = 1)$ from the others, this can also be written as

$$v(x) = 1 - \alpha + \alpha\theta(x) \tag{8.5}$$

where

$$\theta(z) \equiv \sum_{k\ge 2} (p_k/\alpha)x^{k-1} \tag{8.6}$$

At $x = \zeta_0$, this function gives the probability that a randomly chosen associative group is either unassociated or associated with the other groups that are connected only to the sol part. The sol fraction in the postgel regime of the solution is then given by

$$S = \zeta_0 v(\zeta_0) \tag{8.7}$$

This must be the same as

$$S = \sum_i w_i v(\zeta_0)^i \tag{8.8}$$

since a chain of the species i belongs to the sol if all functional groups it carries are connected to the sol. We thus find that the path connectivity ζ_0 is one of the roots of the equation

$$x = \sum_i w_i v(x)^{i-1} \tag{8.9}$$

that is smaller than unity.

On substituting p_k given by eq 2.5 into the definition 8.4, we find

$$v(x) = u(xz)/u(z) \tag{8.10}$$

Therefore, specifically for our polymer/surfactant system, ζ_0 should satisfy the equation

$$x = \{\eta + [u(xz)/u(z)]^{f-1}\}/(1 + \eta) \tag{8.11}$$

Let us summarize our procedure. From the relation 3.1, we find z as a function of the polymer concentration c_f and the concentration ratio η. Upon substitution of the result into eq 8.11, we obtain the probability ζ_0 for a randomly chosen unassociated group not to be connected to the gel network.

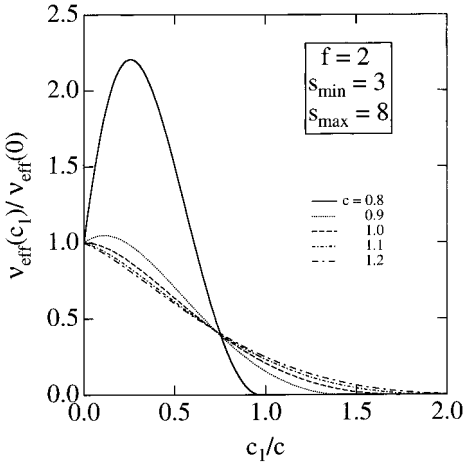

Figure 12. Number of elastically effective chains plotted against the ratio of the surfactant concentration and the polymer concentration. The polymer concentration is varied from curve to curve. At low polymer concentrations, the number of effective chains, and hence the high-frequency modulus, shows a peak at SMG surfactant concentration and then decreases. But at higher polymer concentration, it monotonically decreases. The effective chains disappear at a high surfactant concentration, at which solution turns into sol. Note that all curves cross at a single point.

We now employ the aforementioned criterion of Scanlan−Case[24,25] to decide whether a subchain connected to two junctions of the type (i,k) and (i',k') at its ends is elastically effective or not. The criterion says that only subchains connected at both ends to junctions with at least three paths to the gel are elastically effective. We thus have $i,i' \geq 3$ for an effective chain. We may call the junctions with $i \geq 3$ elastically effective junctions. An effective subchain is then defined as a chain that is connected to two effective junctions at its both ends. We thus find from eq 8.2

$$\mu_{\text{eff}} = \sum_{k=2}^{\infty}\sum_{i=3}^{2k}\mu_{i,k} = (\sum_{i=1,f} i\nu_i)\alpha\Big[\int_{\zeta_0}^{1}\theta(x)\,dx - (\zeta_1 + \zeta_2)\theta(\zeta_0) - \frac{1}{2}(\zeta_1)^2\theta'(\zeta_0)\Big] \quad (8.12)$$

for the number of elastically effective junctions in a unit volume, and

$$\nu_{\text{eff}} = \frac{1}{2}\sum_{k=2}^{\infty}\sum_{i=3}^{2k} i\mu_{i,k} = \frac{1}{2}(\sum_{i=1,f} i\nu_i)\alpha[(\zeta_1 + 2\zeta_2)(1 - \theta(\zeta_0)) - (\zeta_1)^2\theta'(\zeta_0)] \quad (8.13)$$

for the number of elastically effective chains, where $\theta'(x)$ is the derivative of $\theta(x)$.

Figure 12 shows the number, $\nu_{\text{eff}}(c_1)$, of elastically effective chains plotted against the surfactant concentration c_1. The number is normalized by the value $\nu_{\text{eff}}(0)$ in the absence of the surfactant. This ratio, therefore, gives the relative strength $G_\infty(c_1)/G_\infty(0)$ of the high-frequency plateau value in the storage modulus. Polymers are assumed to carry two functional groups ($f = 2$). The allowed multiplicity of a junction ranges from 3 to 8. The polymer concentration is changed from curve to curve. As expected, the curves for low polymer concentrations first rise to a peak and then monotonically decreases to zero, where the gel network is broken into sol by the surfactant. For the larger polymer concentrations, however, the curves do not show any peak, because junctions are well developed without surfactant molecules for these polymer concentrations, and the added surfactant merely destroys the junctions.

These calculations reproduce, at least qualitatively, the experimental data on such an HEUR/SDS as that reported by Annable *et al.* (Figure 3 in ref 16). In our theory, all curves cross each other at a certain surfactant concentration, whereas the experimental data reveal the same tendency, only for relatively higher polymer concentrations. The maximum in the modulus is caused by the existence of a forbidden gap in the multiplicity of the network junctions.

IX. Conclusion and Discussion

We have studied interaction of associating polymers with surfactants, thereby stressing how sol/gel transition is shifted and how the structure and mechanical properties of the network are modified. It was shown that the observed nonmonotonic change in rheological behavior with added surfactants is explained by the existence of a lower and an upper bound in the multiplicity of junctions. We assumed throughout this paper that the free energy for binding a surfactant molecule into a junction is exactly the same as that for binding an associative group on a polymer chain. This assumption can ideally be applied to, for instance, the interaction between a poly(ethylene oxide) polymer chain, modified by shoft alkyl chains, and nonionic amphiphiles poly(ethylene glycol) monoethers (C_mE_n), carrying alkyl chains of the same length. For the solutions in which the two binding free energies are different, we have to introduce another association constant, $\mu(T)$, for the surfactant binding. The reduced surfactant concentration, $c_1 \equiv \lambda(T)\phi_1/n_1$, should be replaced by $c_1 \equiv \mu(T)\phi_1/n_1$ in all calculations. A variety of phenomena are expected, depending upon the relative strength of these two association constants. For example, cpmc might occur before the gelation concentration reaches the minimum when μ is smaller than λ. A detailed study will be reported in a forthcoming paper.

We also stressed that there is a special point on the polymer/surfactant/water ternary phase plane where gelation and critical (pure) micelle concentration simultaneously take place. In a preceeding study[19] we showed that the osmotic compressibility reveals singularity across the sol/gel transition line due to the loss of the translational entropy of the macroscopic cluster. Gelation can, therefore, be regarded as a thermodynamic phase transition in Ehrenfest's sense. On the other hand, the derivative of the osmotic pressure abruptly falls at the cmc, although it shows no true analytical singularity. This confluent point is, therefore, to some extent similar to a higher order critical point where two different phase transition lines cross each other. The implication of new critical phenomena around this point is to be studied.

Another important problem with the polymer/surfactant system is modification of the phase separation region. Most water-soluble associating polymers undergo phase separation on heating, exhibiting a lower critical solution point. Such LCST behavior is caused by hydration of water molecules onto the polymer chains.[29] If dehydration is a necessary prerequisite of surfactant binding, addition of surfactant will make polymers less miscible in water, and hence enlarge the phase separation region, being accompanied by the shift

of LCST to lower temperature. In fact, such an enhanced LCST behavior was recently reported for the mixture of hydrophobically endcapped poly(ethylene oxide) and nonionic surfactant $C_{12}E_8$.[11] A similar tendency was reported also for the EHEC/SDS system.[15] The latter is a very complex system where both hydrogen-bonding and hydrophobic interactions compete. Construction of the complete phase diagrams on a ternary phase plane will have to await further work.

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