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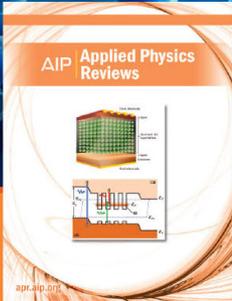
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Polymer gels with associating side chains and their interaction with surfactants

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Conformational behaviour of hydrophobically modified (HM) polymer gels in solutions of nonionic surfactants is studied theoretically. A HM gel contains hydrophobic side chains (stickers) grafted to its subchains. Hydrophobic stickers are capable to aggregate into joint micelles with surfactant molecules. Micelles containing more than one sticker serve as additional physical cross-links of the network, and their formation causes gel shrinking. In the proposed theoretical model, the interior of the gel/surfactant complex is treated as an array of densely packed spherical polymer brushes consisting of gel subchains tethered to the surface of the spherical sticker/surfactant micelles. Effect of stickers length and grafting density, surfactant concentration and hydrophobicity on gel swelling as well as on hydrophobic association inside it is analyzed. It is shown that increasing surfactant concentration can result in a gel collapse, which is caused by surfactant-induced hydrophobic aggregation of stickers, and a successive gel reswelling. The latter should be attributed to a growing fraction of surfactants in joint aggregates and, hence, increasing number of micelles containing only one sticker and not participating in gel physical cross-linking. In polyelectrolyte (PE) gels hydrophobic aggregation is opposed by osmotic pressure of mobile counterions, so that at some critical ionization degree hydrophobic association is completely suppressed. Hydrophobic modification of polymers is shown to open new ways for controlling gel responsiveness. In particular, it is discussed that incorporation of photosensitive groups into gel subchains and/or surfactant tail could give a possibility to vary the gel volume by light. Since hydrophobic aggregation regularities in gels and solutions are common, we hope our findings will be useful for design of polymer based self-healing materials as well. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4948730>]

I. INTRODUCTION

Polymers with incorporated hydrophobic segments (so-called hydrophobically modified (HM) polymers) demonstrate a more complex behavior as compared to non-modified ones. This should be attributed to the reversible formation of hydrophobic aggregates (domains) and their clusters in aqueous solutions because insoluble groups tend to avoid water. HM polymers are known to be highly sensitive to low molecular weight hydrophobic molecules, such as surfactants and hydrocarbons, by virtue of ability of these substances to incorporate into existing aggregates and change their morphology and structure. These systems are promising for the design of drug delivery systems^{1,2} and self-healing materials³⁻⁶ due to reversibility of formation of hydrophobic aggregates playing a role of physical cross-links in polymer systems.

In HM polymer solutions, where chains are not initially connected by covalent bonds, formation of hydrophobic domains under alternations of environmental conditions (e.g., surfactant or salt concentrations, temperature) is accompanied by changes of viscosity⁷⁻⁹ and solution gelation.^{7,10,11} Appearance and reorganization of aggregates inside polymer gels can affect the gel volume.¹²⁻¹⁶ Measurements

of shear storage and loss moduli,⁷ fluorescence of probe pyrene molecules,^{8,9,13,17} and NMR spectra¹³ are exploited for indication of hydrophobic aggregation in both gels and solutions.

Hydrophobic blocks can be either built in the main polymer chain of linear and branched polymers^{10,11,18} or grafted to the backbones as linear side chains (so-called stickers).^{7,8,12,13} Small-angle neutron scattering (SANS) was applied to study the structure of hydrophobic associates in polyelectrolyte gels modified by hydrocarbon stickers containing 8 or 12 C atoms.^{19,20} Stickers form micellar-like aggregates (domains) with size ranging within 1–3 nm, i.e., of the order of hydrocarbon side chain contour length. Crowding of these aggregates, inducing formation of hydrophobic clusters and microphase separation, takes place at low degree of gel ionization. It was found that clusters in annealed PEs are twice the size of those in gels with quenched charges unable to migrate along the gel subchains.²⁰ Increasing grafting density and length of stickers also favours formation of larger clusters because of a lower repulsion of hydrophilic backbones surrounding the hydrophobic domain.

Surfactant effect on the behavior of HM polymer solution/gel is found to depend on the existence of hydrophobic domains in the absence of surfactant. Surfactant molecules can either penetrate into already existing aggregates altering their structure or induce hydrophobic aggregation with

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mixed surfactant/sticker micelle formation. The first process described by so-called critical incorporation concentration (CIC)¹⁸ was shown to be non-cooperative, while micellization in initially non-aggregated system is highly cooperative and can result in jump-like changes in the system behavior.

Whereas phase behavior of solutions of HM linear polymers with associating groups^{21–25} and conformations of single polysoap molecules^{26–29} have been studied in detail, there is no theoretical model considering swelling of polymer networks with hydrophobic side chains in surfactant solutions. In the present article, we develop a theoretical approach to describe hydrophobic association inside these networks and to study their interaction with surfactants. Theoretical results are compared with existing experimental data.

II. THEORETICAL MODEL

Let us consider a polymer gel containing a small fraction of short hydrophobic side chains (stickers) immersed in the solution of nonionic surfactant (Fig. 1). Surfactant molecules are distributed between the gel and the outer solution, the equilibrium values of the surfactant concentrations inside and outside the network are determined by the equality of the surfactant chemical potentials. We suppose that in a general case surfactant molecules can form mixed micelles with stickers within the gel and pure surfactant micelles in the outer solution.

Let us denote by V_{tot} the total volume of the system. Polymer network consists of $\nu_0 = N/m$ flexible subchains, N and m being the total number of statistical segments in the gel and in a subchain, respectively. The length of the statistical segment is denoted by a , and its volume equals a^3 owing to the chain flexibility. Let σ be the average number of units between the nearest-neighbour stickers, N/σ be the total number of stickers in the gel, and p be the fraction of stickers involved in a micelle formation from their total amount.

The system contains $S = S_g + S_s$ surfactant molecules, where $S_g = gS$ and $S_s = (1 - g)S$ are the numbers of surfactants inside and outside the gel, respectively. Similarly, $S_m = qS_g$ is the number of surfactant molecules involved in hydrophobic aggregates inside the gel, while $S_g - S_m = (1 - q)S_g$ molecules move freely in the network interior. For simplicity, we neglect the dependence of the micelle aggregation number M on the aggregate composition²⁶ (i.e., the ratio of stickers and low-molecular-weight surfactants) as well

as environmental conditions³⁰ and suppose M to be fixed. Hydrophobic interactions are driving force of surfactants and stickers aggregation, ΔF_{surf} and ΔF_{st} are the absolute values of free energy gains from aggregation per surfactant and sticker, respectively. The absolute values of these free energy gains are ever positive, $\Delta F_{surf} > 0$ and $\Delta F_{st} > 0$, though hydrophobic association is favourable and diminishes the free energy; these designations are adopted for convenience. Below all free energies are given in $k_B T$ units, k_B is the Boltzmann constant and T is the absolute temperature. Micellization can take place in the outer solution as well at surfactant concentrations exceeding CMC. The fraction of aggregated surfactants outside the gel is denoted by d .

The equilibrium state of the system is defined by the fraction of stickers p enclosed in the micelles, the fraction of surfactants g inside the gel, the fraction of aggregated surfactants q inside the gel, and that in the outer solution, d . To describe changes in the gel volume under variation of the system parameters, it is useful to introduce dimensionless swelling ratio $\alpha = (V_{gel}/V_0)^{1/3}$, where $V_0 = a^3 N m^{1/2}$ is the volume of the unperturbed network of Gaussian subchains without aggregated stickers.

The free energy

In order to construct the free energy function, it is necessary to reveal the internal structure of the gel and hydrophobic aggregates in it. Since the total numbers of surfactant molecules and stickers involved in micelles are S_m and Np/σ , respectively, one can express the average fraction of stickers in a micelle as

$$\beta = \frac{Np/\sigma}{S_m + Np/\sigma}. \quad (1)$$

Then the average number of stickers in a micelle is equal to βM . We suppose it is favourable for stickers to be uniformly distributed throughout all micelles in order to minimize steric repulsion of network backbone units.

The number of elastically active subchains and their average length \bar{m} inside the gel change under sticker association since a micelle containing two or more stickers acts as a physical cross-link, similar to a multiplet in the ionomer state of polyelectrolytes.^{31,32} Each aggregated sticker gives rise to one new gel subchain regardless of the functionality of the cross-linking micelle (i.e., the number of stickers in the

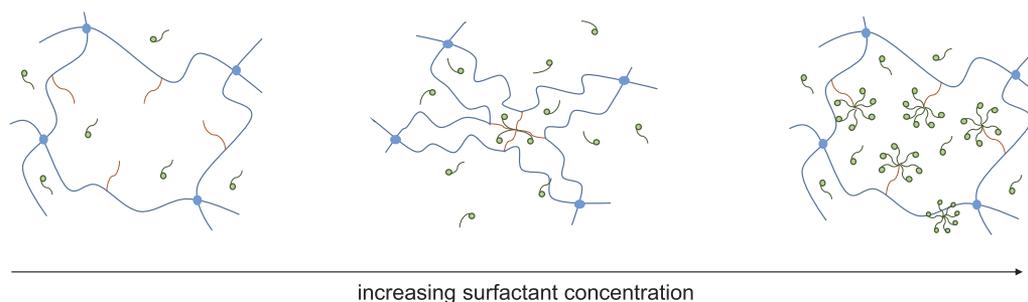


FIG. 1. Schematic representation of polymer gel with associating side chains at different surfactant concentrations.

micelle) except for the micelles containing only one sticker. Thus, depending on the value of βM , the fraction of stickers γ giving rise to new cross-links is defined as

$$\gamma = \begin{cases} 0, & \beta M \leq 1, \\ \beta M - 1, & 1 < \beta M < 2, \\ 1, & \beta M \geq 2, \end{cases} \quad (2)$$

and the average length of the polymer subchains reads

$$\tilde{m} = \frac{m}{1 + \frac{mP}{\sigma}\gamma}. \quad (3)$$

At $\beta M > 1$ each micelle can be treated as a core of polymer brush with $f = \beta M$ tethered chains, each of length \tilde{m} (see Fig. 2). Since here and below we use scaling arguments, it seems to be of low importance whether subchain is a bridge between two different micelles or a loop with both stickers confined in the same core.³³ Assuming for simplicity the volume of the sticker ba^3 equal to the volume of the surfactant tail, we can estimate the micelle core radius as $R_{core}/a \sim (bM)^{1/3}$. Here dimensionless b can be treated as the number of statistical segments in each sticker or in the surfactant tail. The height of the brush under Θ -solvent conditions is defined by the balance between triple volume interactions and chain elasticity, $R_{corona}/a \sim \tilde{m}^{1/2}f^{1/4}$. In a good solvent the brush swelling is defined by the interplay of the pair contacts between monomer units and the free energy of chain elongation, $R_{corona}/a \sim \tilde{m}^{3/5}f^{1/5}\tau^{1/5}$, with $\tau = (T - \Theta)/\Theta > 0$ being temperature deviation from the Θ -point.³⁴ In order to unify both these cases, the following interpolating formula is used:

$$R_{corona}/a \sim \tilde{m}^{1/2}f^{1/4}(1 + \tilde{m}^{1/10}f^{-1/20}\tau^{1/5}). \quad (4)$$

At $\beta M < 1$ each network junction point can be treated as a brush with the number f of the corona chains being of the order of unity, and the relationship $f = \beta M$ is used for any value of β . Note that at $f = 1$ one gets from Eq. (4) the correct estimate for the length of the network subchain $R_{corona}/a \sim \tilde{m}^{1/2}(1 + \tilde{m}^{1/10}\tau^{1/5})$.

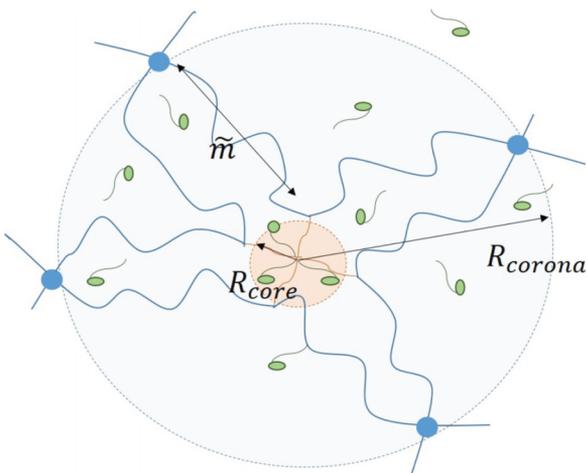


FIG. 2. Gel interior is treated as an array of spherical polymer brushes with core and corona radii R_{core} and R_{corona} , respectively.

At $\beta M > 2$ the total number of spherical brushes in the gel is $N_{br} = (Np/\sigma + S_m)/M$, while at $\beta M < 1$ their number equals to the number of gel junction points, $N_{br} = N/m$. These results are unified by the analytical interpolating formula

$$N_{br} = \frac{Np/\sigma + S_m}{M}\gamma + \frac{N}{m}(1 - \gamma), \quad (5)$$

providing continuous dependence of N_{br} on β . The total gel volume is proportional to the volume of a single brush and their total number, $V_{gel} \sim N_{br}R_{corona}^3$.

The total free energy of the system in $k_B T$ units reads

$$F = F_{brush} + F_{out} + F_{in} + F_m. \quad (6)$$

The first term F_{brush} in Eq. (6) takes into account both the energy of volume interactions of gel monomer units and the elastic energy of gel subchains deformation. It is calculated as an energy of spherical polymer brushes and in the limit of star-like brushes, $R_{corona} \gg R_{core}$, reads³⁴

$$F_{brush} = N_{br}f^{3/2} \ln \left(1 + \frac{R_{corona}}{R_{core}} \right). \quad (7)$$

The next two terms in Eq. (6) account for the translational entropy of surfactants outside and inside the gel, respectively,

$$F_{out} = (S - S_g - S_d) \ln \left(\frac{S - S_g - S_d}{kV_0 - V_{gel}} \right) + S_d \ln \left(\frac{1}{ba^3} \right), \quad (8)$$

$$F_{in} = (S_g - S_m) \ln \left(\frac{S_g - S_m}{V_{gel}} \right) + S_m \ln \left(\frac{1}{ba^3} \right). \quad (9)$$

Here k is the dimensionless ratio between the total volume of the solution and the initial volume of the gel, $k = V_{tot}/V_0$. The value of k influences surfactant exchange between the gel interior and the outer solution. The second terms in contributions F_{out} and F_{in} correspond to the translational motion of aggregated surfactant molecules within the micelles. For simplicity, we omit combinatorial terms responsible for selecting S_m and S_d aggregating surfactants out of their total number.^{21,25} Theory of micellization considering this combinatorial contribution (Refs. 21 and 35) gives the same result for the CMC as that neglecting it (Ref. 36).

Finally, the last contribution F_m in Eq. (6) is the free energy gain due to micelle formation

$$F_m = -\frac{Np}{\sigma}\Delta F_{st} - (S_m + S_d)\Delta F_{surf}, \quad (10)$$

with $S_d = d(1 - g)S$. Total free energy function $F_{tot}(p, g, q, d)$ should be minimized with respect to all four variables. In the following calculations $m = 1000$, $\tau = 0.1$, $b = 5$ and $M = 40$ are fixed. Chosen value of M is characteristic aggregation number of low-molecular-weight surfactants. Though the assumption about independence of mixed micelle aggregation number M on the micelle composition is not fulfilled in real systems, it violates primarily in the region of high stickers content and might result in slightly inaccurate values of the collapsed gel volume as well as surfactant concentration provoking collapse, but our essential findings should be valid notwithstanding this assumption.

III. RESULTS AND DISCUSSION

A. Neutral polymer network in the solution of nonionic surfactant

Dependences of equilibrium system parameters on the average dimensionless surfactant concentration $C_{all} = Sa^3/V_{tot}$ in the whole system volume V_{tot} are plotted in Fig. 3. Two curves correspond to different ratios k between the initial network volume and the total volume of the solution. At $k = 3000$ the outer solution can be treated as infinite, while in the case of $k = 15$ volumes of the swollen gel

and the outer solution are of the same order of magnitude. The dimensionless CMC in the outer solution calculated as $CMC = \exp(-\Delta F_{surf} - 1)$, see Refs. 35 and 36, is denoted by black arrows.

Increasing surfactant concentration leads to consequent network shrinking and reswelling (Fig. 3(a)). The first transition should be attributed to an intensive aggregation of both low-molecular-weight surfactants and stickers within the gel (Fig. 3(d)) resulting in formation of mixed cross-linking micelles. A shortening of the network subchains causes a decrease of the gel swelling ratio. Collapse of the gel occurs in

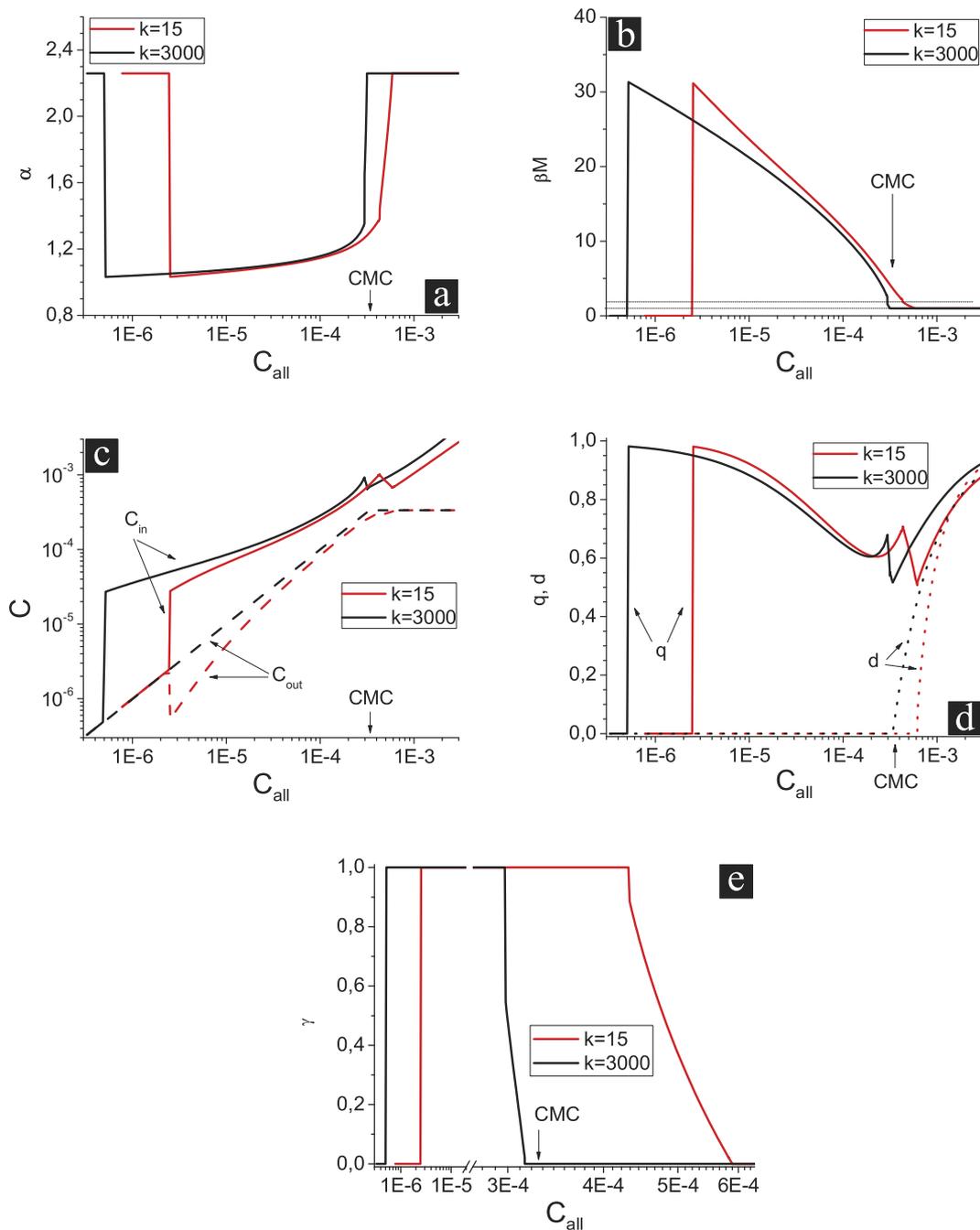


FIG. 3. Dependences of the gel parameters on the average surfactant concentration at two different values of $k = 15$ and $k = 3000$: (a) gel swelling ratio α ; (b) number of stickers in one micelle βM ; (c) inner C_{in} and outer C_{out} surfactant concentrations; (d) fractions q and d of surfactant molecules involved in micelle formation inside and outside the gel, respectively; (e) fraction γ of stickers giving rise to gel physical cross-links. Other parameters: $\sigma = 300$, energy gains $\Delta F_{st} = 15$ and $\Delta F_{surf} = 7$ here and below are given in $k_B T$ units, $CMC = 3.35 \cdot 10^{-4}$.

a jump-like fashion. In the case of infinite solution ($k = 3000$), surfactant concentration in the outer solution practically does not change in the course of surfactant sorption by the gel due to the large volume of the solution. However, when solution and gel volumes are of the same order of magnitude ($k = 15$), the surfactant redistribution upon gel collapse accompanied by abrupt formation of hydrophobic associates inside the gel provokes a sharp drop in C_{out} (Fig. 3(c)). Indeed, the volume of the swollen gel equals $V_{gel}/V_0 = \alpha^3 \approx 11.4$ at $k = 15$ and exceeds that of the rest part of the system, $(V_{tot} - V_{gel})/V_0 = 3.6$. Since entropy penalty of surfactant absorption by the gel grows as the volume of the outer solution (i.e., k) decreases, collapse (as well as reswelling) point shifts toward a higher average surfactant concentration C_{all} in the system.

Further addition of surfactant induces changes in a composition of mixed micelles. The more the number of surfactant molecules, the less the number of stickers within one micelle (Fig. 3(b)). This tendency causes slight swelling of a collapsed gel even at $C_{all} < CMC$. In the vicinity of CMC an intensive incorporation of low-molecular weight surfactant into the micelles results in a decrease of the number of stickers in one micelle, and the gel undergoes reswelling as βM reaches unity and mixed micelles cease to serve as gel physical cross-links. The gel reswelling takes place in the vicinity of the CMC and occurs as a sequence of three steps:

- (i) smooth gel swelling caused by gradual micelles reorganization and accompanied by reduction of stickers content in each micelle, in this region $\beta M > 2$ and $\gamma = 1$;
- (ii) jump-like transition with a moderate amplitude;
- (iii) consequent continuous though kept swelling with an amplitude exceeding that of the first and second steps due to disruption of physical cross-links and increasing number of micelles with a single sticker, $\beta M < 2$ and $\gamma < 1$.

It is important to stress that sharp bends and kinks near the CMC in Figs. 3(c) and 3(d) are manifestation of hydrophobic associates reorganization and of steep gel swelling rather than inaccuracy of calculations or numerical errors. Steps (ii) and

(iii) which can be clearly distinguished in Fig. 3(e) where the enlarged scale plot of the gel reswelling region is shown. At concentrations well above CMC, gel volume equals to one realized in the absence of surfactant because there are no stickers acting as network cross-links despite all of them belong to the mixed micelles, $\beta M \leq 1$.

The surfactant hydrophobicity in our model is governed by the parameter ΔF_{surf} . Its effect on the gel behavior is demonstrated in Fig. 4. Increasing ΔF_{surf} makes micelle formation more favourable owing to the strengthening of hydrophobic interactions, so that both shrinking and reswelling regions shift to lower surfactant concentrations. Swelling ratios of the gel for different ΔF_{surf} are close to each other at very low surfactant concentration, when sticker association have not been set in yet, as well as at rather high values of C_{all} , when low content of stickers in mixed aggregates (less than one per micelle) does not enable them to additionally bind network subchains. In the collapsed state of the gel at the same surfactant concentration C_{all} the gel density is lower in the presence of more hydrophobic surfactant ($\Delta F_{surf} = 9$). It should be attributed to a higher incorporation rate of this surfactant into hydrophobic aggregates and a consequent decrease of the number of stickers per micelle.

One can see in Fig. 4 that in a certain range of surfactant concentration, for instance, near $C_{all} = 10^{-6}$, the gel volume dramatically depends on the surfactant hydrophobicity, and even moderate changes in ΔF_{surf} provide drastic changes of the gel state. If one would take photosensitive surfactant containing, e.g., azo-group in the molecule tail, the gel collapse may be induced by solution irradiation with visible light since more hydrophobic trans-form of surfactant would provide formation of mixed micelles. Reversible gel swelling can be achieved by irradiation with UV-light switching surfactant to the less hydrophobic cis-form, the difference between the trans- and cis-form surfactant hydrophobicity being of the order of a few $k_B T$.³⁵ This approach has already been applied to a solution of HM polymer with photosensitive surfactant to control its viscosity by irradiation.³⁷ Reverse switching, i.e., swelling stimulated by visible light, can also be realized at higher surfactant concentrations, $C_{all} \approx 10^{-4}$. Another opportunity to supply gel with photo-responsibility, even in

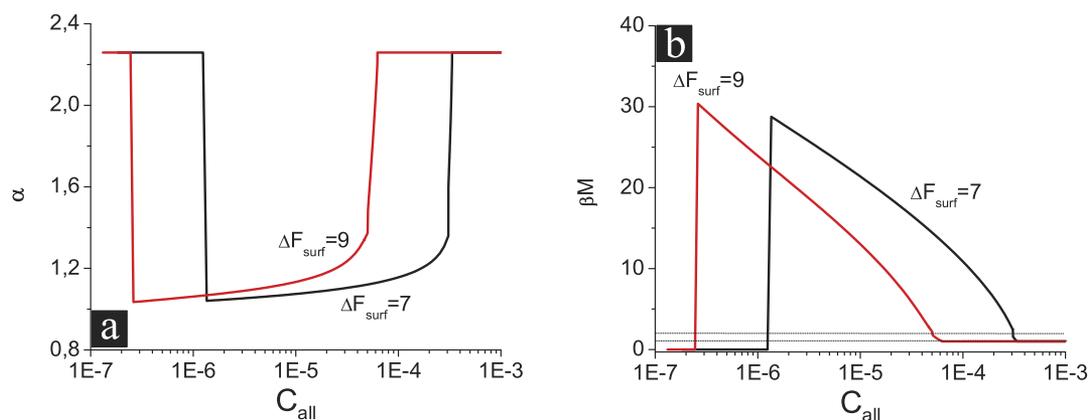


FIG. 4. Effect of surfactant hydrophobicity ($\Delta F_{surf} = 7$ and $\Delta F_{surf} = 9$) on the swelling of the network (a) and hydrophobic aggregation (b); $\sigma = 300$, $k = 200$, $\Delta F_{st} = 15$.

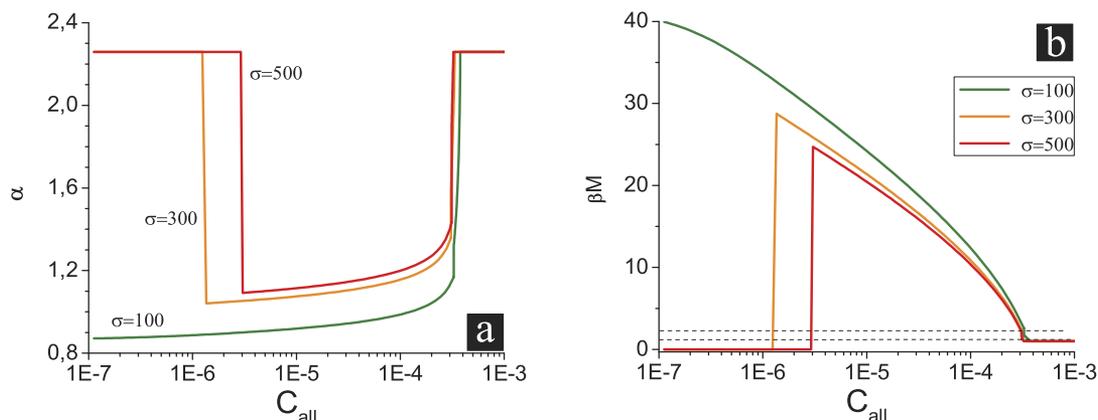


FIG. 5. Effect of the sticker grafting density ($\sigma = 100, 300,$ and 500) on the swelling of the network (a) and hydrophobic aggregation (b); $k = 200$, $\Delta F_{st} = 15$, $\Delta F_{surf} = 7$.

the absence of surfactant, is to incorporate photosensitive groups into stickers (see Fig. 6).

It is interesting to analyze the effect of the sticker grafting density on the system behavior because it influences not only the effectiveness of the surfactant absorption but also the conformational state of the gel in the absence of any surfactant. It is clearly seen in Fig. 5 that the gel swelling depends on σ even at surfactant concentration tending to zero. At relatively low grafting densities ($\sigma = 500$ and $\sigma = 300$) the hydrophobic side chains do not aggregate at $C_{all} = 0$ and the network swells in a good solvent, its degree of swelling does not depend on σ . However, at high content of stickers (the case of $\sigma = 100$) the free energy gain from their association exceeds the entropy loss, which decreases with increasing grafting density, and the most part of stickers assembles into micelles even in the absence of surfactant, i.e., at $C_{all} = 0$. Fig. 5(b) represents the number of stickers βM per one micelle vs C_{all} . Since $\beta M = 40$ at C_{all} tending to zero, the average corona block length in a brush equals $\bar{m} = m\sigma/(m + \sigma) \approx \sigma$. In the collapsed state, the gel with the highest sticker grafting density occupies the smallest volume due to the largest content of stickers in the mixed micelles and the shortest length of brush subchains.

The existence of hydrophobic aggregates in the gel interior at $C_{all} = 0$ defines the cooperativity of surfactant binding. If micelles consisting of stickers are present inside the network in the absence of surfactant ($\sigma = 100$), the surfactant sorption is non-cooperative, in accordance with Colby and co-workers.¹⁸ In this case the surfactant molecules continuously incorporate within the existing hydrophobic aggregates. On the contrary, at a smaller content of hydrophobic side chains, when the initial gel is swollen, an addition of surfactant causes highly cooperative association of both surfactants and stickers into mixed micelles resulting in the jump-like gel collapse. Reswelling of the network takes place in the vicinity of the surfactant CMC at any values of σ . It is a consequence of a change in the micelle composition upon surfactant addition resulting in increasing fraction of micelles with single sticker (Fig. 5(b)).

Similarly to growing sticker grafting density, increasing sticker hydrophobicity (i.e., sticker length or solvent quality for sticker) leads to a shift of the collapse transition to lower values of C_{all} (see Fig. 6). In contrast to σ , the value of ΔF_{st} affects the critical association concentration and, thus, the position of the collapse point rather than the gel conformations in the collapsed state. Indeed, at the same values of σ the

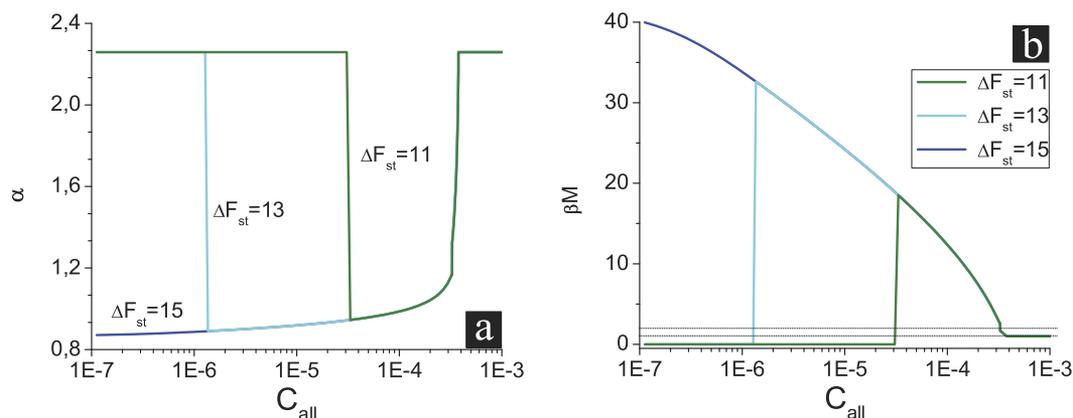


FIG. 6. Effect of the sticker hydrophobicity ($\Delta F_{st} = 11, 13$ and 15) on the swelling of the network (a) and hydrophobic aggregation (b); $k = 200$, $\sigma = 100$, $\Delta F_{surf} = 7$.

fraction of stickers incorporated into micelles in the collapsed gel state is close to unity and virtually does not depend on the sticker hydrophobicity. Hence, the gel swelling ratio is independent of ΔF_{st} as well.

B. Polyelectrolyte network in the solution of nonionic surfactant

We assume now that a small fraction i ($i \ll 1$) of monomer units of HM polymer gel is ionized and, thus, Ni counterions are held inside the network to satisfy the electroneutrality condition. Let us analyze the effect of gel ionization on its interaction with non-ionic surfactant.

We can describe the structure of the gel/surfactant complex within the similar model, namely, representing it as an array of spherical brushes grafted to the mixed surfactant/sticker micelles. However, polyelectrolyte brushes rather than neutral ones should be considered now.^{38–41} Brush thickness, defined by the balance between counterion osmotic pressure and chain elasticity (so-called osmotic brush regime), is given by⁴¹

$$R_{corona}/a \sim i^{1/2} \tilde{m} \quad (11)$$

and the free energy is defined by Eq. (7). These formulae are valid in the case of slightly charged brush chains when correlation free energy between charges is negligible in comparison with the counterion translational entropy.⁴²

In order to unify both neutral and polyelectrolyte gels under Θ -solvent conditions, the following interpolating formula is used:

$$\frac{R_{corona}}{a} \sim \tilde{m}^{1/2} f^{1/4} \left(1 + \left(\frac{i}{i_{thr}} \right)^{1/2} - \left(\frac{i}{i + i_{thr}} \right)^{1/2} \right), \quad (12)$$

with the threshold fraction of ionic units equal to $i_{thr} = M/\tilde{m}$. At low content of ionic groups, $i \ll i_{thr}$, we pass to the case of a neutral brush³⁴

$$R_{corona}/a \sim \tilde{m}^{1/2} f^{1/4}, \quad (13)$$

$$F_{brush} = N_{br} f^{3/2} \ln \left(1 + \frac{\tilde{m}^{1/2} f^{1/4}}{R_{core}/a} \right). \quad (14)$$

If the fraction of charged groups is high enough, $i \gg i_{thr}$, one gets well-known results corresponding to the case of an

osmotic brush⁴¹

$$R_{corona}/a \sim i^{1/2} \tilde{m}, \quad (15)$$

$$F_{brush} = N_{br} f i \tilde{m} \left(1 + \ln \left(\frac{f}{\tilde{m}^2 i^{1/2}} \right) \right). \quad (16)$$

In Fig. 7 we plot gel degree of swelling vs surfactant concentration for the gels containing different fractions of ionic groups. Incorporation of charges into the gel subchains hinders stickers association because of an additional loss in the entropy of mobile counterions under gel physical cross-linking and resultant contraction. Due to this fact the range of C_{all} where the gel is collapsed becomes narrower as degree of gel ionization grows and entirely disappears at high enough values of i . In the swollen gel the effect of hydrophobic associating side chains is negligible, and the gel swelling ratio is defined by the balance of counterions osmotic pressure and Gaussian elasticity of subchains, $\alpha = \sqrt{Ni}$.⁴² Comparison of curves in Fig. 7 shows that ionization provokes swelling of the gel with hydrophobic stickers, and the gel volume in the highly swollen state is not influenced by the presence of associating chains and their hydrophobicity (see also Fig. 6). This conclusion accords with the experimental results on HM gels of poly(acrylic acid).¹² It has been shown experimentally that incorporation of ionic groups makes conformational transitions in polymer gels with associating side chains more abrupt, similarly to collapse of PE gels induced by solvent quality changes.⁴²

Due to abruptness of transitions between the swollen and the collapsed gel, a diagram of states of HM PE gel in a surfactant solution can be constructed. It is presented in Fig. 8 in the coordinates “surfactant concentration, C_{all} — degree of ionization, i .” The system parameters are chosen in such a way that the hydrophobicity and grafting density of stickers are high enough to provide their association at zero degree of gel ionization, $i = 0$, and in the absence of surfactant, $C_{all} = 0$.

One can see that the region of the collapsed gel state is limited by a certain surfactant concentration slightly lower than CMC and a certain critical fraction i^* of ionic groups which is high enough to induce disruption of hydrophobic aggregates. Thus, at a fixed surfactant concentration below CMC, the gel ionization causes its abrupt swelling at $i = i^*$.

The value of i^* is mainly defined by an interplay between counterion osmotic pressure and the energy gain

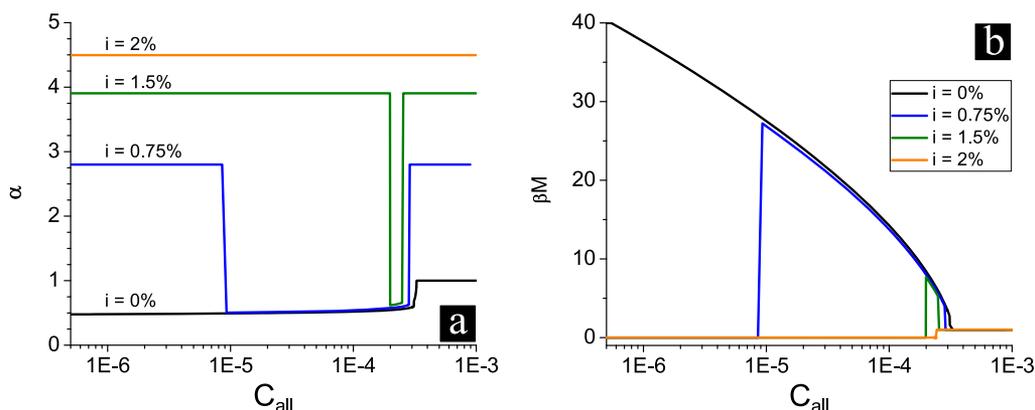


FIG. 7. Effect of the fraction of charged groups on the swelling of PE gel: (a) gel swelling ratio; (b) number of stickers in a micelle. Fraction of charged groups $i = 0\%, 0.75\%, 1\%, 2\%$; other parameters $\tau = 0$, $b = 5$, $\Delta F_{st} = 13$, $\Delta F_{surf} = 7$, $k = 3000$, $\sigma = 100$.

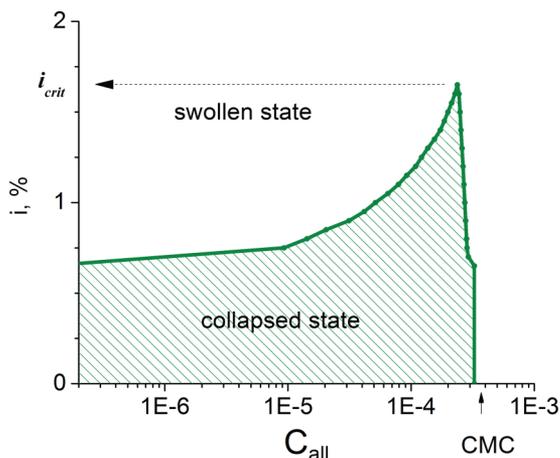


FIG. 8. Diagram of HM PE network state in surfactant concentration C_{all} and content of ionic groups i coordinates at $\tau = 0$, $b = 5$, $\Delta F_{st} = 13$, $\Delta F_{surf} = 7$, $k = 3000$, $\sigma = 100$.

from sticker/surfactant micellization. At increasing C_{all} the volume of the collapsed gel grows due to decreasing physical cross-links functionality f , and exerting osmotic pressure of counterions diminishes resulting in a higher i^* .

Thus, according to Fig. 8, the effect of the surfactant addition strongly depends on the gel ionization degree. If $i < i^*$ (for instance, at $i = 0.4\%$) the initially collapsed gel with aggregated stickers swells in the vicinity of CMC. At $i > i^*$ (for instance, at $i = 0.8\%$) an increase of the surfactant concentration can induce two consequent transitions: initially swollen gel first collapses upon surfactant/sticker micellization and then undergoes reswelling in the vicinity of CMC. Besides, if the gel ionization exceeds some critical value, $i > i_{crit}$, the gel is swollen at any surfactant concentration since the energy gain from micellization cannot overcome the loss in counterion entropy upon gel collapse.

C. Discussion

Nonmonotonic dependences of the gel swelling ratio α and the number of stickers in a micelle βM exhibiting extrema at intermediate surfactant concentrations qualitatively conform with the existing experimental data on the mixtures of HM linear polyelectrolytes with nonionic surfactants. In Ref. 7 it was found that the viscosity of 1% solution of linear sodium polyacrylate containing 3% of pendant $C_{12}H_{25}$ alkyl chains is also nonmonotonic function of nonionic surfactant $C_{12}E_8$ (dodecyl octaethylene glycol ether) concentration. Increasing amount of this surfactant, which forms micelles of only spherical morphology in the whole range of studied concentrations, induces first (i) the viscosity growth due to emergence of mixed cross-linking micelles and then (ii) a viscosity decrease referred to a rising amount of micelles with single sticker. Thus, hydrophobic aggregation regularities are rather common for polymer solutions and chemically cross-linked gels.

Some theoretical assumptions adopted in our consideration should be discussed in detail. First, micelles (brushes) in the neutral gel interior are starlike once the condition $R_{corona} \geq R_{core}$ is fulfilled. The core radius is given by

$R_{core}/a \sim (bM)^{1/3}$, while the estimation $R_{corona}/a \gtrsim \sigma^{1/2} f^{1/4}$ and $R_{corona}/a \gtrsim \sigma^{3/5} f^{1/5}$ are valid for the corona radius under Θ - ($\tau = 0$) and good solvent ($\tau = 1$) conditions, respectively, with equalities at $\bar{m} = \sigma$. Thus, micelles can be treated as starlike at low enough grafting density of stickers

$$\sigma \geq \begin{cases} (bM)^{2/3}/f^{1/2}, & \tau = 0 \\ (bM)^{5/9}/f^{1/3}, & \tau = 1 \end{cases} \quad (17)$$

For PE gel these conditions ensure validity of starlike micelle approximations all the more since PE brush swelling is higher than that of neutral counterpart. Inequalities (17) are satisfied at the values of parameters chosen in the above calculations.

Second, approximation of a fixed mixed micelle aggregation number M , though adopted for simplicity, is sufficiently justified. Indeed, aggregation number of low-molecular-weight non-ionic surfactants is known to be almost independent on environmental conditions,³⁰ and in a wide range of surfactant concentration (everywhere except the vicinity of the gel collapse point) stickers are the minor component of mixed aggregates. Volumes of stickers and surfactant tails are assumed to be equal facilitating approximately constant aggregation numbers as well. In addition, changing micelle composition accompanied by variations in corona block length \bar{m} has marginal impact on the mixed micelles aggregation number owing to the latter for starlike micelles is virtually independent on \bar{m} .^{34,41}

The developed theory, considering the case of nonionic surfactant, can be generalized to describe the case of ionic surfactants which was extensively studied experimentally.^{13,43,44} Micelles containing ionic surfactants possess nonzero charge. Surfactant counterions can be partly trapped in the vicinity of charged micelles to reduce the electrostatic energy and only mobile counterions would create exerting osmotic pressure and promote gel swelling. If interaction of HM polyelectrolyte gel with ionic surfactants is considered, peculiarities of ion exchange reactions and electrostatic interactions between micelles and gel subchains should be also taken into account.^{35,36,45}

IV. CONCLUSION

In this paper we propose a theoretical model to describe conformational behavior of a polymer gel with hydrophobic side chains in a surfactant solution. We take into account a possibility of sticker aggregation as well as mixed surfactant/sticker micelle formation within the gel. The hydrophobic aggregates act as additional physical cross-links causing gel shrinking. Gel internal structure is represented as a set of spherical polymer brushes consisting of network subchains tethered to spherical mixed micelles. This approach allows to apply scaling arguments for polymer brushes, and scaling results in different regimes are unified by appropriate interpolating formulas.

Surfactant is shown to considerably affect hydrophobic association in HM polymer gels and their swelling. Depending on the initial gel structure, different scenarios of the gel behaviour can be realized. If the hydrophobicity and grafting density of hydrophobic network moieties are high enough

to provide their aggregation within the gel in a surfactant-free solution, addition of surfactant results in surfactant non-cooperative absorption with incorporation into existing hydrophobic domains. As the concentration of surfactant in the solution grows, the fraction of surfactant in the mixed micelles increases, the effective degree of gel cross-linking diminishes and eventually the gel swelling occurs. If the initial gel in surfactant-free solution is swollen (this case is realized at relatively low content and hydrophobicity of stickers), an increase in surfactant concentration can induce two consecutive jump-like transitions of the gel volume. First, addition of surfactant provokes formation of joint surfactant/sticker aggregates within the gel acting as additional cross-links and resulting in the gel collapse. At that, surfactant sorption proceeds in a cooperative manner. Then further growth of surfactant concentration leads to a decrease of the fraction of stickers in the mixed micelles and gel reswelling.

The amount of surfactant, needed to induce gel collapse and reswelling, as well as the gel volume in the collapsed state are governed by sticker grafting density and surfactant hydrophobicity. The use of surfactants and/or network side chains containing photosensitive groups opens the way to tune gel conformations by light. Ionization of the gel subchains diminishes the region of hydrophobic aggregates stability within the gel and promotes gel swelling. Thus, variations of pH and solution ionic salinity can serve as additional tool controlling gel volume.

The developed theoretical approach could not only rationalize the existing experimental data on HM polymer gel/surfactant complexes but also serves as a background for directional design of highly responsive systems with desired properties.

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