Effect of Crosslinking Concentration on the Micelle Formation Inside the Polymer Gel Network and Mechanical Properties of Sensitive Hydrogel Polymer in Contact with Surfactant Solutions

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ABSTRACT: The variation of the swelling and mechanical properties of crosslinked nonionic poly (*N*-isopropylacrylamide) (NIPA) polymer gel immersed in tetradecyl dimethylaminoxide (C14DMAO) surfactant solutions at 0.1*M* NaCl, synthesized at different crosslinker concentrations was investigated. Also the aggregation behavior of C14DMAO surfactants inside and outside the polymer hydrogels has been studied through solubilization of Sudan III dye. The solubilization experiments indicated that, at the degree of ionization $\alpha = 0.5$ and 1, the surfactant concentration inside the gel is lower than that outside the gel at low crosslinker concentration. In the case of the nonionic C14DMAO at $\alpha = 0$, on the other hand, the surfactant concentration inside the gel and outside the gel was almost identical, irrespective of the crosslinker concentration. The elastic modulus, *G*, of the network polymer gel in contact with the C14DMAO solutions of 5 and 10 mM concentration was larger than that of the water solution irrespective of the degree of ionization ($\alpha = 0$ and 0.5). This difference in the elastic modulus, *G*, of network polymer gel may be attributed to the change of the rigidity of the polymer network. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 91: 3921–3926, 2004

Key words: tetradecyl dimethylaminoxide; NIPA gel; swelling; elastic modulus

INTRODUCTION

The interaction between polymers and surfactant is a subject of considerable current interest.[1] Many polymer–surfactant pairs are known to form micelle-like aggregates above certain surfactant concentrations, the so-called critical association concentration (cac). The polymer of *N*-isopropylacrylamide (NIPA) has received increasing attention because its aqueous solution exhibits a phase separation with lower critical solution temperature (LCST).[2] Since the earliest study by Eliassaf[3] on the binding of NIPA with sodium dodcylsulfate (SDS), various studies have been published in which the behavior of association was summarized.[4–8] The association is best viewed as a micelle formation in the polymer at a cac that is lower than the critical micelle concentration (cmc) of the pure surfactant. The interaction of gels with charged surfactants was studied in the last several years.[9–27] This process was shown to be governed mainly by electrostatic and hydrophobic forces. The electrostatic force prevails when a gel and a surfactant are oppositely charged, while, in other cases (surfactant and a gel of similar charges, uncharged gel/uncharged surfactant), hydrophobic interaction dominates. The hydrophobicity of NIPA chains depends on the temperature due to the dehydration of NIPA chains.[28] The binding isotherm of a surfactant onto NIPA gel has been measured to clarify the interaction between them,[5–7] which indicates that a conformational change of polymer chain was induced by the surfactant binding. The surfactant aggregation in the gel was affected by the gel network in the case of surfactants that form large cylindrical micelles in solutions.[6] Authors proposed that both the gel/ionic surfactant interaction and the surfactant aggregation in the gel have distinct effects on the swelling behavior of NIPA gel.[29] When hydrophobic interaction dominates, the gel swells upon the binding of surfactant. This is a consequence of the adsorption of the counterions of surfactant; the osmotic pressure exerted by these counterions being responsible for the gel swelling. The study of the polymer gel swelling is a simple experiment that can provide much information on the interaction between polymer gel and surfactant.[29–31] The polymer gel materials are useful for drug delivery systems, separation operations in biotechnology, processing of agricultural products, sensors, and actuators. In these applications, a fast response rate of hydrogel to the external stimuli is needed.

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To increase the response rate of NIPA gel to the external stimuli, several techniques were proposed: one is the submicron-sized gel.[32] Second are gels having dangling chains.[33,34] Third, macroporous poly-NIPA (PNIPA) gels are to start the PNIPA polymerization below the LCST of PNIPA and then elevate the temperature above it.[35,36] Another technique is to apply a radiation-induced polymerization method.[37] As far as we know, there have been no reports ascribing the effects of crosslinks concentration on the gel structure, the swelling behavior, and the mechanical properties of polymer gel in contact with mixed ionized surfactant. The present article investigates the swelling and mechanical behaviors of PNIPA gel in contact with mixed ionized surfactant (nonionic and cationic), in the presence of 0.1*M* NaCl, depending on the synthesis parameters such as crosslinks concentration, variation of the swelling, mechanical properties, and the relation between crosslinker concentration and micelles formation.

EXPERIMENTAL

Materials

Monomer and reaction accelerator for preparation of gel samples were NIPA (Kohjin Co., Ltd); *N,N′*-methylenebis (acrylamide) (a crosslinker; Nacalai tesque, Inc.); and *N,N,N′,N′*-tetramethylenediamine (an accelerator for polymerization reaction; Nacalai tesque, Inc.). Initiator used in gel preparation was ammonium peroxodisulfate. Tetradecyldimethylaminoxide (C14DMAO; nonionic surfactant; Fluka Chime AG) was prepared with differing concentrations and differing degrees of ionization. The nonionic C14DMAO sample was dissolved in water, and hydrochloric acid was added to protonate the amine oxide. The prepared solutions were freeze dried, and the solid samples of C14DMAO at different ionizations (α) were obtained.

Sample preparations

PNIPA gels were prepared by radical polymerization. A mixture of 3.96 g (700 mM) of NIPA monomer and crosslinker *N,N′*-methylenebis(acrylamide) concentration was varied between 1 and 20 wt % with respect to the monomer, and 120 μl of *N,N,N′,N′*-tetramethylethylenediamine was dissolved in pure water to make 50 mL of aqueous solution. The gel preparation temperature was kept at 5°C. For at least 30 min before polymerization, nitrogen gas was bubbled into the above solution to purge oxygen. An aqueous solution of ammonium persulfate (4 wt %) was bubbled by N_2 gas and a part of it (1 mL) was added to the above monomer solution. Polymerization reaction was performed under N_2 gas in a thin capillary or in a glass plate. Gel samples obtained were washed thoroughly with pure water. The cylinder gel of diameter 3–5 mm was employed for the swelling and mechanical measurements. The bulk gel prepared in a flat glass plate was cut into cubes several centimeters in diameter. These cut gels were used for determination of surfactant aggregate inside the gel via Sudan III solubilization.

Gel swelling experiment

The washed gel rods were immersed in bottles each containing 10 mL of aqueous surfactant solution at 25°C. The equilibrium swelling ratio, *W*, was defined as

$$W = (W_{\mathrm{Wet}} - W_{\mathrm{Dry}})/W_{\mathrm{Dry}}$$

where W_{wet} and W_{Dry} are the weights of gels in the equilibrium swollen state and dry state, respectively. The swelling ratio was measured after immersing the gel in the solution for almost 1 month at 25°C.

Solubilization of Sudan III by surfactant aggregates

The cube gels of almost 1 g (differing crosslinker concentrations, 1–20 wt %) equilibrated with surfactant solutions (10 mL). The surfactant concentrations of the solutions were 0, 0.05, 1, 5, 10, and 30 mM from C14DMAO, nonionic surfactant. Small amounts of Sudan III were added to the surfactant solutions containing the gel samples, and the solutions were allowed to be soluibilized. Equilibrium of the solubilization was obtained after 1 month at 25°C to attain the binding equilibrium of the surfactant onto the gel. The gels of differing crosslinkers concentrations were put in an injector and pushed under pressure. This pressure was high enough to squeeze out the solution inside the gel. Squeezed solution (0.5 mL) was analyzed by UV in determining the surfactant concentration inside the gel at maximum absorption of 500 nm.

Mechanical measurements

Stress–strain measurements were performed on PNIPA gel with differing crosslinker concentrations. All mechanical measurements were conducted in a thermostated room of 22°C. The schematic diagram of the apparatus used is shown in Figure 1.

A cylindrical gel sample of 4 mm in diameter and 10 mm in length was immersed in differing surfactant concentrations for 3 weeks and then was placed on a digital balance. A load was transmitted vertically to the gel through a rod. The force acting on the gel was calculated from a reading of the balance *m* as $F = mg$, where g is the gravitational acceleration, which is 9.8 m/s^2. The resulting deformation $\Delta l = l_o - l$, where l_o

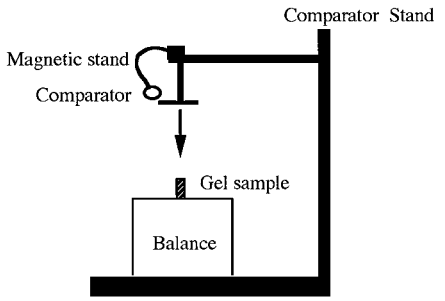

Figure 1 Schematic diagram of the compression apparatus for measuring stress—strain on NIPA gel.

and l are the initial undeformed and deformed lengths, respectively, was measured using a digital comparator (IDC type Digimatic indicator), which was sensitive to displacements of 10^{-3} mm. The force and the resulting deformation was recorded for 30 s of relaxation. The measurements were conducted up to a 30% compression. The deformation ratio $\alpha = 1 - \Delta l/L_o$. The corresponding stress $f = F/A$, where A is the cross-sectional area of the specimen, $A = \pi r_o^2$, where r_o is its initial radius. For uniaxial deformation, the statistical theories of rubber elasticity yield for Gaussian chains is an equation of the form[38]

$$f = G(\alpha - \alpha^{-2})$$

where G is the elastic modulus of the samples. The stress–strain data correlated according to the above-mentioned equation are shown in Figure 2 as filled symbols. The data were from two PNIPA polymer gels prepared separately but under identical conditions. The deviation from the linear relationships is obvious at small compressions. This deviation from theory can be attributed to the imperfect geometry of the surface of the samples, which results in relatively high deformations at low stresses. To correct this imperfection, the isotherm was redrawn by discarding the data at very low strains. The linear portion of the curve was then extrapolated to value of $-(\alpha - \alpha^{-2})$ at $f = 0$ (Fig. 2, dashed curves) from which the correct initial length was computed and the deformation ratios were adjusted. The data corrected are also shown in Figure 2 as open symbols.

RESULTS AND DISCUSSION

Figure 3 shows the weight swelling ratio, W, plotted against the surfactant concentration of C14DMAO at degree of ionization $\alpha = 0.5$ (mixed nonionic–cationic micelles), as the function of crosslinker concentration. All the swelling experiments were carried out at 25°C. At fixed surfactant concentration, the swelling ratio decreases and crosslinker concentration increases. As for a fixed crosslinker concentration, at high crosslinker content (5, 10, and 20%) the dependence of the swelling ratio on the surfactant concentration showed no distinct effects. This means that the crosslinker concentration was effectively dominant and affected the micelles formation. This may attribute to the decrease in the mesh size of the network with an increase in the crosslinker concentration, which slows down the diffusion of the surfactant into the gel network and limits the micelle formation. However, the dependence of the swelling ratio on the surfactant concentration showed remarkable change at low crosslinker concentrations (1 and 3%). Below 3% crosslinker concentration, the change in the swelling ratio of the gel network with surfactant concentration showed two regimes. In regime I, at low surfactant concentrations (0.05, 1, and 5 mM) the swelling ratio

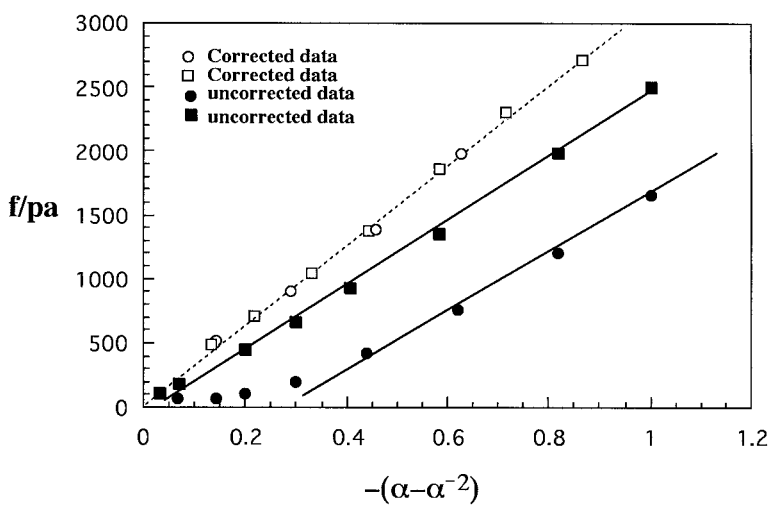

Figure 2 Stress—strain for two PNIPA gel samples. Crosslinker concentration = 3 wt %; (open symbols) corrected data (closed symbols) uncorrected data.

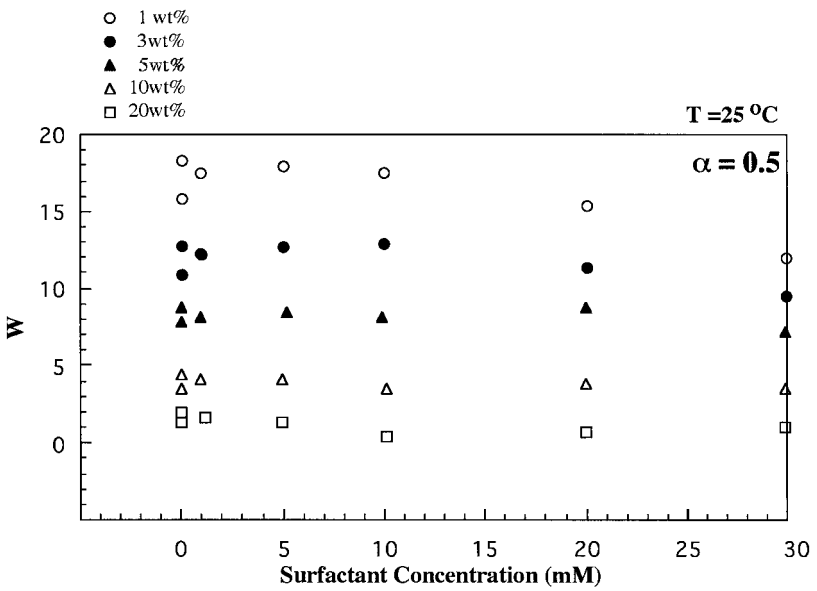

Figure 3 Swelling ratio (W) vs. surfactant concentration as a function of crosslinker concentration at degree of ionization $\alpha = 0.5$.

increases with increases in the surfactant concentration. In regime II, at high surfactant concentrations (10, 20, and 30 mM) the swelling ratio decreases with increases in the surfactant concentration. The increase in swelling ratio at low surfactant concentrations (regime I) commences as the adsorption of surfactant to NIPA chains via hydrophobic interaction. This increase is due mainly to the osmotic pressure contribution from the counterions. After swelling maximum, the gel begins to deswell (regime II); the reason for the deswelling is the surfactant concentration inside the gel is lower than outside the gel as indicated by the solubilization experiments.[29] This uneven distribution of the ionic micelles leads to the reduction of the swelling osmotic pressure of the gel (i.e., the decrease of the gel volume).[29] Therefore, it can be concluded that the micelles at $\alpha = 0.5$ cannot accommodate completely inside the gel due to both the exclusive space of polymer chains[39] and a decrease in the mesh size. This may be interpreted in terms of the micelles size increment at $\alpha = 0.5$ due to the existence of the hydrogen bonding between nonionic and cationic head groups.[40,41]

To investigate the effect of the degree of ionization of C14DMAO surfactant on the swelling ratio and micelle formation at fixed surfactant concentration 5 mM as a function of crosslinking concentration, the swelling ratio was plotted against α and shown in Figure 4.

Figure 4 shows two different behaviors. At 1 wt % crosslinker concentration, the swelling ratio increases with the degree of ionization increasing. While between 3 and 20 wt % the swelling ratio starts to decrease with the degree of ionization, and the decrease in the swelling ratio became more prominent at higher crosslinker concentrations (5, 10, and 20%). These results indicate that the micelles are less formed at $\alpha = 0.5$, especially at higher crosslinker concentrations. The decrease in surfactant concentration inside the gel, at $\alpha = 0.5$, may be explained in term of micelles size that cannot accommodate the mesh size of the gel. The gel network forbids the formation of large micelles due to unfavorable surfactant–polymer steric repulsion.[39]

Figure 5 shows the difference in absorbance of surfactant concentration of the bulk solution outside the

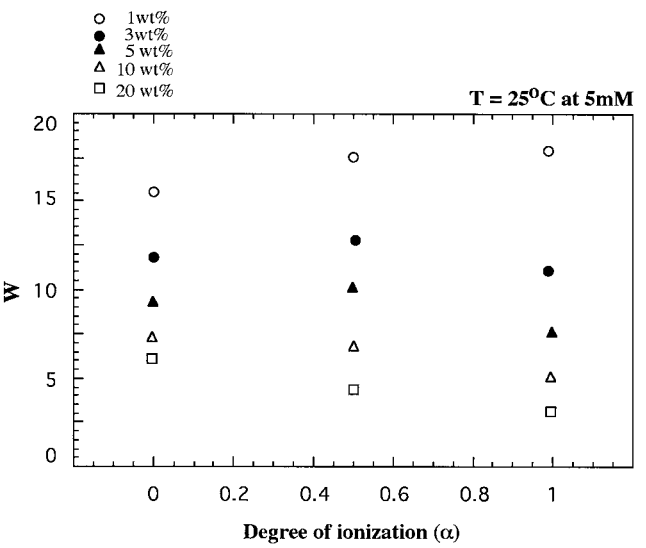

Figure 4 Swelling ratio (W) vs. the degree of ionization as a function of crosslinker concentration at the surfactant concentration 5 mM.

gel and inside the gel interior, $\Delta_{Abs} = A_{out} - A_{in}$, represented by UV absorption of Sudan III, plotted against the different degrees of ionization at 5 mM of C14DMAO. Different behaviors were observed, depending upon the association of the surfactant to the gel at different degree of α. It was found that, at $\alpha = 0$, the C14DMAO surfactant concentration inside the gel and outside the gel was almost comparable and Δ_{Abs} approached zero, irrespective of the crosslinker concentration. This means that the micelles inside and outside the gel are formed in a similar trend. On the other hand, at $\alpha = 0.5$, the decrease in surfactant concentration inside the gel became more apparent in comparison with that of the $\alpha = 0$ case.[39] So, the Δ_{Abs} of $\alpha = 0.5$ was higher than that of Δ_{Abs} of $\alpha = 0$ and $\alpha = 1$. Also, it can be seen that, at $\alpha = 0.5$ and 1, the Δ_{Abs} was a bit higher at lower crosslinker concentrations than the Δ_{Abs} at higher crosslinker concentrations.

Figure 6 shows the moduli of the network, *G*, in the case of $\alpha = 0$, as a function of crosslinker concentration at two different surfactant concentrations, 5 and 10 mM. Also, 0 mM surfactant concentration (i.e., water solution) was used as a reference. At surfactant concentrations 5 and 10 mM, a limited change was observed in moduli of the network as a function of the crosslinker concentration. However, a remarkable difference in the magnitude of *G* at 0 mM was observed in comparing the magnitudes of *G* at 5 and 10 mM. In general, a monotonal increase in *G* between 1 and 3 wt % of crosslinker concentration at the surfactant concentration used here (0, 5, and 10 mM) can be noted. Above 5 wt % of crosslinker concentration, the modulus values of the network are almost steady state irrespective of the surfactant concentration.

To investigate the effect of crosslinker concentration on the moduli of the network *G* as a function of degree of ionization of C14DMAO surfactant solution, the surfactant C14DMAO with $\alpha = 0.5$ was used.

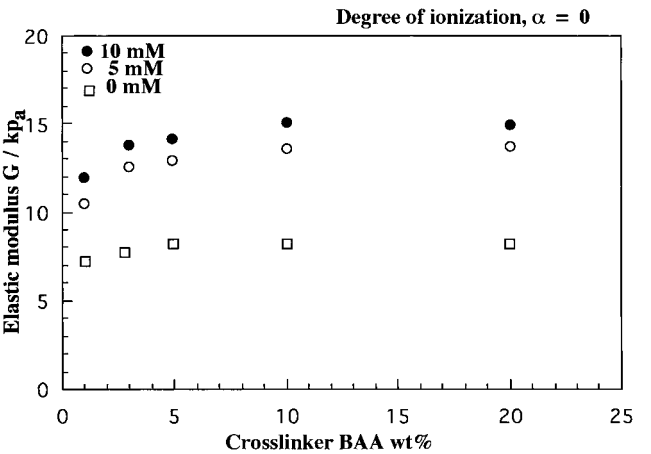

Figure 6 Elastic modulus of NIPA gel in the case of the degree of ionization $\alpha = 0.05$ vs. the crosslinker concentrations at 0, 5, and 10 mM.

Figure 7 shows the same trend of the change in *G* as a function of crosslinker concentration at $\alpha = 0.5$. Also a remarkable difference in *G* between the 5 and 10 mM cases and the 0 mM case can be noted, and the effect of the degree of ionization on the modulus *G* was not clearly observed. In general below 3 wt % crosslinker concentration, the elastic modulus *G* increases and reaches a steady state at high crosslinker concentrations (5, 10, and 20 wt %). In general, the difference in the *G* magnitude between the surfactant solution (5 and 10 mM) and the water solution (0 mM) may be attributed to the change of the rigidity of the polymer network. This rigidity results from the adsorption of the surfactant through the hydrophobic interaction between polymer and the hydrophobic part of the surfactant.[42,43]

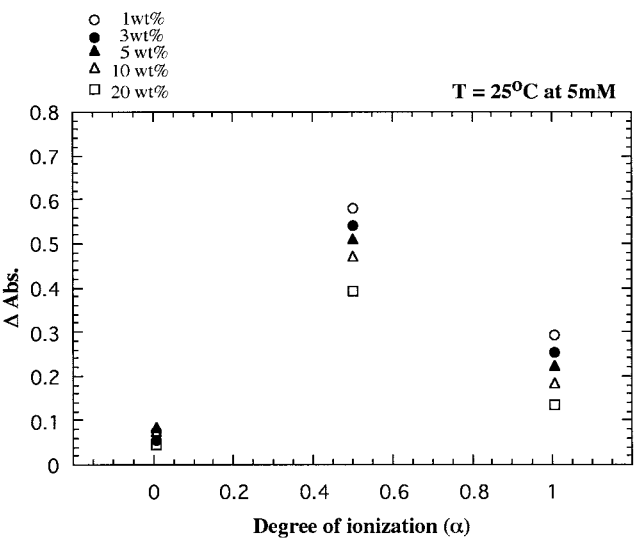

Figure 5 The difference in absorbance Δ_{Abs} vs. the degree of ionization as a function of crosslinker concentration at the surfactant concentration 5 mM.

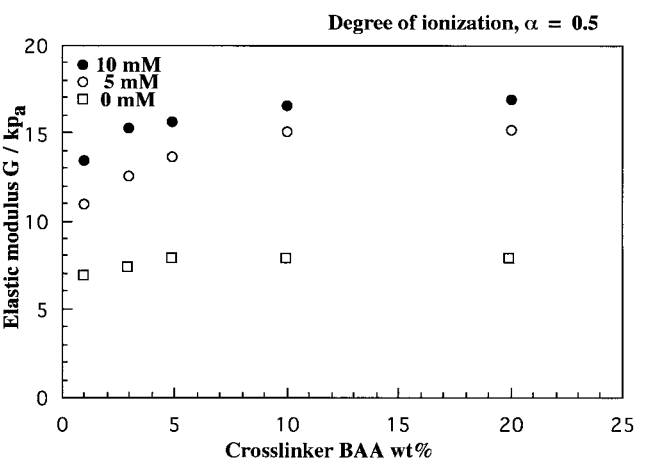

Figure 7 Elastic modulus of NIPA in the case of the degree of ionization $\alpha = 0.05$ vs. the crosslinker concentrations at 0.5 and 10 mM.

CONCLUSION

PNIPA networks were prepared by free radical crosslinking copolymerization in water using methylene(bis)acrylamide as the crosslinker. The synthesis parameter varied was the crosslinker concentration. The following conclusions were drawn from the experimental data:

- The solubilization experiments indicated that, at the degree of ionization of C14DMAO solutions $\alpha = 0.5$ and 1, the micelles formation inside the gel network are less formed at $\alpha = 0.5$, especially at higher crosslinker concentrations. The decrease in surfactant concentration inside the gel at $\alpha = 0.5$ may be explained in term of micelle size that cannot accommodate the mesh size of the gel. The gel network forbids the formation of large micelles due to unfavorable surfactant–polymer steric repulsion.
- At $\alpha = 0$, the C14DMAO surfactant concentration inside the gel and outside the gel was almost comparable and Δ_{Abs} approached zero, irrespective of the crosslinker concentration. This means that the micelles inside and outside the gel are formed in a similar trend.
- In general, the remarkable difference in the elastic modulus *G* of the polymer gel network in contact with the surfactant solution (5 and 10 mM) and the water solution (0 mM) may be attributed to the change of the rigidity of the polymer network. This rigidity results from the adsorption of the surfactant through the hydrophobic interaction between the hydrophobic part of the polymer and the hydrophobic part of the surfactant

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