Bulk and Microscopic Properties of Surfactant-Bridged Hydrogels Made from an Amphiphilic Graft Copolymer

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ABSTRACT: Water-swollen hydrogels characterized by hydrophobic microdomains within an aqueous polymer network have been prepared and investigated. The microdomains consist of comicelles of sodium dodecyl sulfate (SDS) and alkyl grafts from a hydrophobically modified water-soluble polymer and form at concentrations below the critical micelle concentration of the surfactant alone. These aggregates behave like pseudo-cross-links, bridging together many polymer molecules to form a viscoelastic network. The comicelles have the ability to solubilize water-insoluble dyes; hence, these materials may be of use in separations and controlled release processes.

Introduction

In a recent paper,[1] we reported the formation of hydrogels from a nonionic water-insoluble graft copolymer in the presence of unmicellized sodium dodecyl sulfate (SDS). The gels are characterized by dispersed micelle-like hydrophobic aggregates. These aggregates bridge several copolymer chains, acting as cross-links. At concentrations higher than the critical micelle concentration (cmc) of pure SDS, the gels disperse. In this work we explore the composition and properties of the aggregates themselves with an eye toward exploiting the unique structure of these new materials in numerous applications.

Micelles consisting of insoluble side chains from graft copolymers have been shown to form in aqueous solutions of alternating copolymers with both ionizable and hydrophobic monomer units.[2-6] The existence and aggregation number of these micelles, as well as whether they are comprised of units from one or more polymer chains, depend on such factors as the flexibility of the backbone (as governed by the pH of the solution) and the length of the hydrophobic group. Under conditions where micelle formation is unfavorable, these copolymers are insoluble in water because of their relatively high hydrophobicity.

The polymer used in the present study, hydrophobically modified (hydroxyethyl)cellulose (HMHEC), is insoluble in water but soluble in high concentrations of surfactants, due to association of the hydrophobic polymer side chains with the surfactant.[7-11] The resulting aggregates are analogous to mixed micelles that form in solutions containing surfactant and free monomeric amphiphiles, which may or may not form aggregates on their own.[12-15] The size and composition of these mixed micelles vary with the molar ratio of surfactant to the monomeric amphiphiles in the bulk. Mixed micelles among surfactant molecules and alkyl grafts from an alternating copolymer are also known to occur.[6]

The composition of the aggregates in our nonionic polymer hydrogels will determine their ability to solubilize small molecules permeating the gel. The more hydrophobic the aggregate, the more likely hydrophobic solutes will be to partition into and remain within its interior. Thus gels with these immobilized "micelles" may be useful in chromatography or controlled release applications.

In this paper we present an analysis of the composition of the dispersed hydrophobic aggregates which form under various conditions in nonionic dispersed-phase hydrogels. We use steady-state fluorescence measurements to determine the size and composition of the aggregates.[13,16-18] We also examine the effect of aggregate composition on the dynamic rheological properties of the gels.

Experimental Section

Materials. Hydrophobically modified (hydroxyethyl)cellulose (HMHEC) (commercial name Natrosol Plus), MW $\sim 10^6$, with 3.7% molar substitution of ethylene oxide per anhydroglucose unit and 1.33% by weight $C_{12}H_{25}$ alkyl hydrophobe substitution, was a gift from the Aqualon Corp., Wilmington, DE. Sodium dodecyl sulfate (SDS), 99% pure, was obtained from Fluka and used as received. The critical micelle concentration (cmc) was found by conductivity to be 8×10^{-3}.

The fluorescence probe used was tris(2,2-bipyridine)ruthenium(II) chloride ($Ru^{2+}Cl^-$) (AESAR, 892 Lafayette Road, P.O. Box 1087, Seabrook, NH 03874-1087), emission wavelength maximum in SDS of 628 nm (excitation at 453 nm). The quencher was 9-methylanthracene. This probe/quencher pair was selected because it satisfies all of the requirements for use with this technique as discussed elsewhere[16] and has been used successfully to characterize SDS/water solutions.

Sample Preparation and Methods. From a fixed stock surfactant solution (8×10^{-2} M), a series of solutions ranging from 1×10^{-3} to 7.2×10^{-3} M surfactant and 100–600 mL in volume were prepared. A fixed amount (0.4 g) of polymer was stirred into the vortex of each solution, giving a ratio of surfactant to alkyl graft concentrations (C_s/C_a) overall of between 15:1 and 150:1. Microliter amounts of the probe and quencher were introduced into the solutions from stock probe and quencher solutions in ethanol. The solutions were then allowed to equilibrate for 2 h, leading to the formation of a gel phase and supernatant solution. By injecting the probe and the quencher during mixing, we were able to ensure the solubilization of all the quencher in the gel phase, as indicated by the lack of any fluorescence of 9-methylanthracene in the supernatant. A small but reproducible (to ±0.5%) amount of probe always remained in the supernatant. If the probe and quencher were introduced after the gel had formed, they remained in the supernatant.

Dynamic mechanical measurements of the gels were performed using a cone and plate Instron 3250 rotary rheometer operating in an oscillating mode. The torque and phase angle were measured with a Solartron frequency response analyzer, and the storage and loss moduli of the gels were obtained.

Steady-state fluorescence measurements were performed on a Spex Model 112A Fluorolog-2 fluorescence spectrometer.

Results

Below the critical micelle concentration (cmc) of the surfactant, the mixtures of polymer and surfactant always form a polymer-rich gel phase and a supernatant phase

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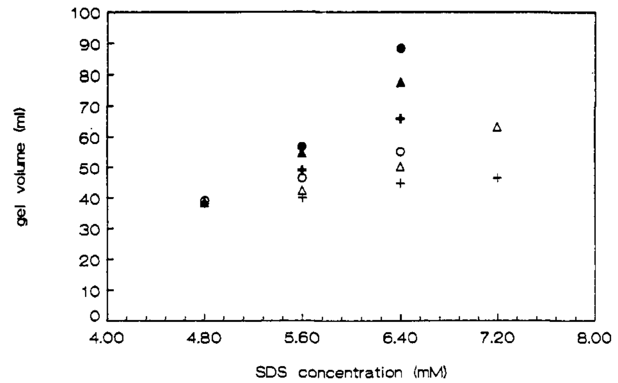

Figure 1. Effect of bulk solution composition on equilibrium gel volume: (+) 0.04 wt % HMHEC; (△) 0.02 wt % HMHEC; (○) 0.013 wt % HMHEC; (✚) 0.01 wt % HMHEC; (▲) 0.008 wt % HMHEC; (●) 0.006 wt % HMHEC.

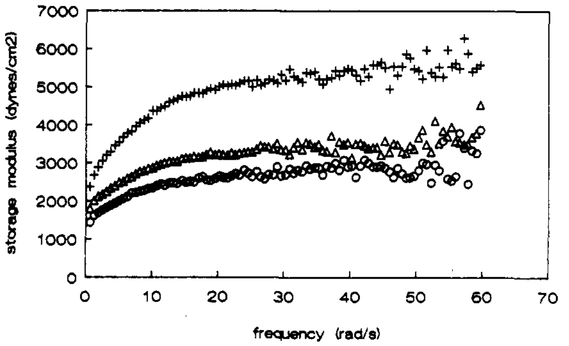

Figure 2. Dynamic storage modulus of hydrogels as a function of initial HMHEC concentration: (+) 0.04 wt % HMHEC; (△) 0.02 wt % HMHEC; (○) 0.013 wt % HMHEC.

composed primarily of surfactant and water. Only mixtures giving a supernatant with viscosity <1.5 cP were used, allowing us to neglect the presence of polymer in the supernatant for the purpose of our analysis. Thus all of the gels described here are assumed to have an identical polymer content equal to 0.4 g. It will be seen, however, that the volume of the gels (V_{gel}) containing this constant amount of polymer ranges from 37 to 88 mL depending on the composition of the initial solution.

The absolute gel volume increases with bulk surfactant (C_s) concentration and decreases with bulk polymer concentration (C_{pol}), as seen in Figure 1. The response of the gel volume to the ratio C_s/C_{pol} becomes increasingly sensitive to C_{pol} at higher C_s, reflected in the divergent behavior of the curves at high C_s. Note that the gel volume is not uniquely determined by the value of that ratio but depends in a complex manner on other factors, discussed below. For example, solutions containing 4.8×10^{-3} M SDS with 0.0133 g of polymer/mL and 7.2×10^{-3} M surfactant with 0.02 g of polymer/mL have the same C_s/C_a overall (45 molecules of SDS per alkyl graft) but give rise to gel volumes of 38 and 63 mL, respectively. At 4.8×10^{-3} M surfactant, the gel volume is less sensitive to polymer concentration, but the data still reveal the expected trend.

Typical rheological spectra of the gels are shown in Figures 2 and 3, showing the storage (G') and loss (G'') moduli, respectively. The plateau value of the storage modulus (G_n) is inversely proportional to the molecular weight between cross-links or entanglements (M_e) in network polymers.[19] G_n was obtained from our data by averaging the six values of G' spanning the frequency 30 rad/s, which was near the middle of the plateau for every gel. The plateau modulus decreases with increasing surfactant concentration as shown in Figure 4; thus the molecular weight between entanglement points, M_e, is rising. For a fixed surfactant concentration, M_e also rises with bulk C_s/C_a. This is consistent with the increase in volume observed with increasing C_s/C_a. M_e was calculated from $M_e = \phi\rho T/G'$,[19] where ϕ = volume fraction of polymer in the gel; ρ = density of the polymer = 0.6 g/cm^3, the bulk density of the dry control polymer (refer to manufacturer's literature); T = absolute temperature; and G' = plateau modulus. Results are summarized in Table I.

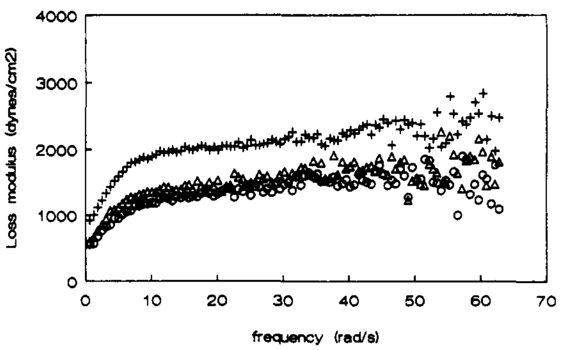

Figure 3. Dynamic loss modulus of hydrogels as a function of initial HMHEC concentration: (+) 0.04 wt % HMHEC; (△) 0.02 wt % HMHEC; (○) 0.013 wt % HMHEC.

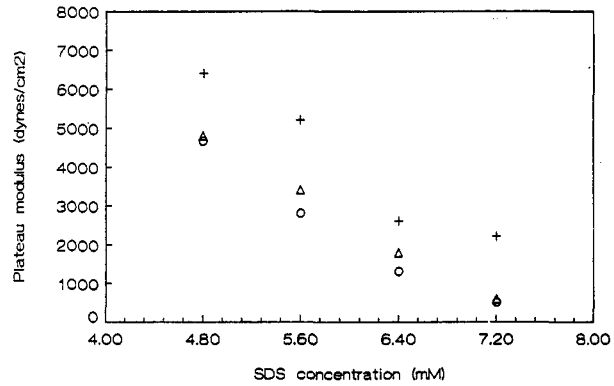

Figure 4. Effect of SDS concentration on the plateau modulus of HMHEC hydrogels: (+) 0.04 wt % HMHEC; (△) 0.02 wt % HMHEC; (○) 0.013 wt % HMHEC.

Figure 5 shows the relationship between M_e and the ratio of polymer to surfactant concentration (in grams of polymer per mole surfactant) in the gel itself. This ratio was calculated assuming that the surfactant concentration in the gel is equal to that in the starting solution, as discussed below. The results show excellent agreement for all gel compositions. However, note that this curve cannot be used to predict the effect of composition on M_e, since the gel volume, which is a parameter of the abscissa, cannot be predicted a priori from the composition (see below).

Steady-state fluorescence quenching is used to determine the aggregation number of surfactant micelles. We have adopted this method to investigate the microstructure of our gels. A fluorescence probe and quencher which are only sparingly soluble or completely insoluble in water will partition into hydrophobic regions in an aqueous system. The resulting fluorescence spectra provide a measure of the size, or aggregation number, of these regions, if they exist, according to the relation[16]

$$\ln (I_0/I) = [Q]/[M] \qquad (1)$$

where I_0 and I are the fluorescence emission intensity of the probe without and with quencher, respectively, [Q] is the quencher concentration in moles per liter, and [M] is the molar concentration of aggregates in the sample. The slope of this plot is thus the reciprocal of the molar

Table I
Summary of Gel and Microdomain Properties

alkyl graft concn, mM	SDS concn, mM	gel volume, cm^3	M_e	1/[M], (mol/L)$^{-1}$	N_s	N_a	N_{total}
0.105	4.8	39	5.3×10^4	10 820	48.7	8.3	57
	5.6	46.3	7.4×10^4	10 990	58.3	6.9	65.2
	6.4	55.1	1.3×10^5	11 214	68.4	5.8	74
0.157	7.2	63	2.9×10^5	10 556	73	4.7	78
0.32	4.8	38	3.9×10^4	11 259	50.7	8.8	59.5
	5.6	40	4.6×10^4	10 900	57.8	8.1	65.8
	6.4	44.6	8.3×10^4	10 703	65.3	7	72.3
	7.2	46.4	9.4×10^4	11 166	77	7	84

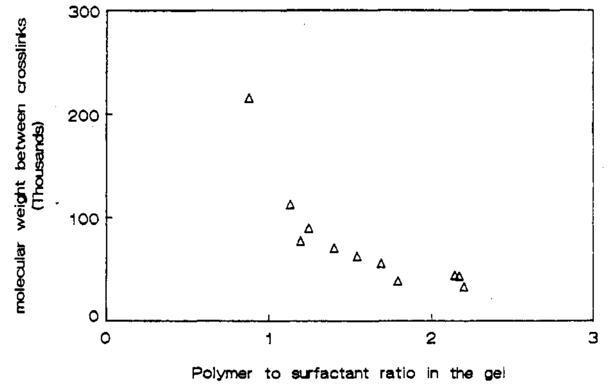

Figure 5. Effect of gel-phase composition on molecular weight between cross-links ($C_{s,gel} = C_{s,bulk}$; $C_{p,gel} = 0.4/V_{gel}$).

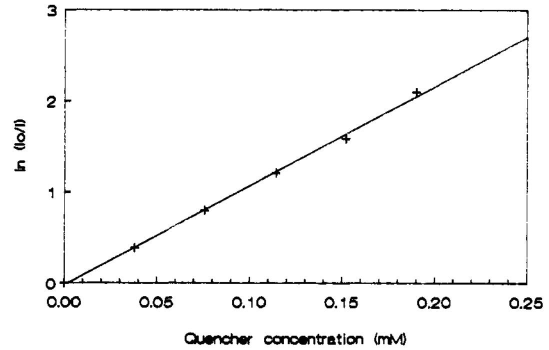

Figure 6. Typical plot of ln (I_0/I) vs quencher concentration, shown here for SDS and HMHEC concentrations of 5.6 mM and 0.04 wt %, respectively.

concentration of aggregates, and the aggregation number is given by [M] divided by the total moles of aggregated species.

Figure 6 shows the effect of quencher concentration on the fluorescence emission intensity of a Ru^{2+}Cl$^-$ probe solubilized in a typical gel with and without quencher. The slopes for various gels along with the corresponding compositions are presented in Table I. From the slope, the number of surfactant molecules (N_s) and the number of alkyl grafts (N_a) in an aggregate can be calculated as

$$N_s = ([\text{surf}]_0 - [\text{surf}]_{\text{free}})/[\text{M}] \qquad (2)$$

$$N_a = ([\text{alkyl}]_0 - [\text{alkyl}]_{\text{free}})/[\text{M}] \qquad (3)$$

where $[\text{surf}]_0$ and $[\text{alkyl}]_0$ are the total surfactant and alkyl graft concentrations in the gel, respectively, and $[\text{surf}]_{\text{free}}$ and $[\text{alkyl}]_{\text{free}}$ are, respectively, the surfactant and alkyl concentrations in the gel that are not part of an aggregate.

The total and free concentrations of the various species in the gel phase were estimated as follows. The conductivity of the supernatant, which is a measure of the concentration of charge-carrying species, is approximately equal to the surfactant solution conductivity in the absence of polymer. For lack of a better calibration, we assume this to mean that the total surfactant concentration in both the supernatant and the gel is the same and equal to the surfactant concentration in the starting solution, which is of order 10^{-3}. Values for $[\text{alkyl}]_0$ may be calculated from the data in Table I and are also of order 10^{-3}. The free surfactant and alkyl concentrations in the gel may be estimated from the cmc of mixtures of SDS and poly(oxyethylene) (POE) lauryl ether, which form mixed micelles at concentrations far below the cmc of SDS alone[12] in the mole fraction range corresponding to the value of C_s/C_a in our gels. The cmc of SDS in mixed micelles drops rapidly with increased concentration of cosurfactant, such that in our system the cmc in the supernatant phase, which contains relatively little alkyl side chain, will be significantly higher than that in the gel. We use values of 5×10^{-5} M and 3×10^{-4} M for the concentrations of free side chain and SDS, respectively, in the gels, based on studies with mixed micelles of SDS and POE lauryl ethers having six and eight ethoxy groups. It is clear from these values that N_s and N_a are not very sensitive to errors in the estimation of the free species. Note that the alkyl HMHEC side chains, which appear to be combining with SDS in our gels, have only one or two ethoxy groups, so these values represent only a best guess. The calculated values of N_s and N_a for each gel are given in Table I. The value of M_e may also be estimated from these data, by using the relationship M_e = (total grams of polymer per total volume of gel)/(total number of aggregates), where the total number of aggregates is given by 1/[M] (Table I). This gives values that average 1.65 ± 0.87 ($N = 7$) times those obtained from rheology.

The total aggregation number, $N_{total} = N_s + N_a$, of the SDS/alkyl group comicelles increases with increasing overall surfactant concentration, from 57 to 84 in the range studied (Table I) ($N_{SDS} = 57$[20]). The values for N_{total} are consistent with those of mixed monomeric micelles,[14] where N_{total} is greater than the aggregation number for pure micelles of either species. It may also be that larger assemblies are necessary to accomodate the bulky polymer "head group" from the cosurfactant in an assembly dense enough to exclude water from the interior. Note that our earlier results[1] showing a constant fluorescence signal of pyrene in the gels are not inconsistent with small variations in aggregation number such as those reported here, as this signal is not sensitive to variations of this order.[18] Figure 7 presents a summary of the aggregation number results on Table I, showing that, as the SDS concentration increases, the proportion of SDS in the aggregates increases as well. Thus SDS molecules displace the side chains. Note that the total aggregation number also increases linearly with surfactant concentration.

The effect of aggregate composition on the storage modulus of the gels is shown in Figure 8. As more side chains become incorporated into an aggregate, the network becomes more tightly entangled. The data lie on a smooth curve for all initial bulk compositions.

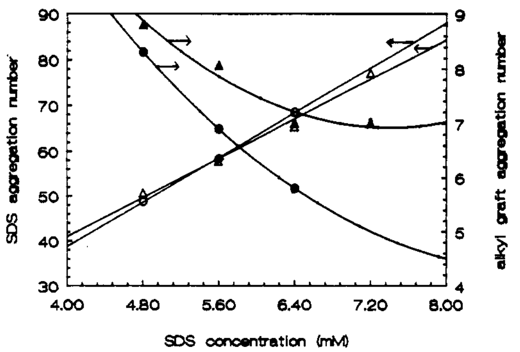

Figure 7. Effect of bulk solution composition on the composition of the microdomains: (△,▲) 0.04 wt % HMHEC; (○,●) 0.013 wt % HMHEC.

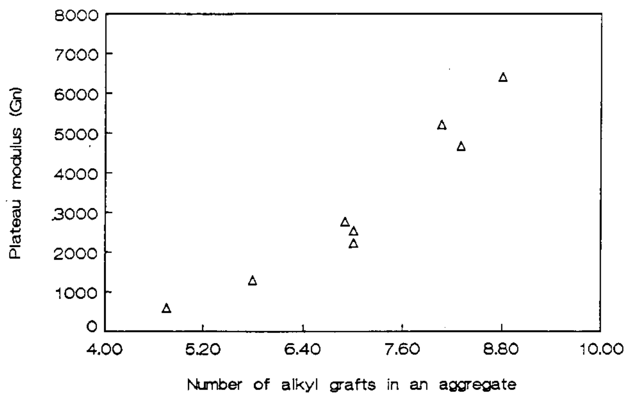

Figure 8. Effect of N_a on G'.

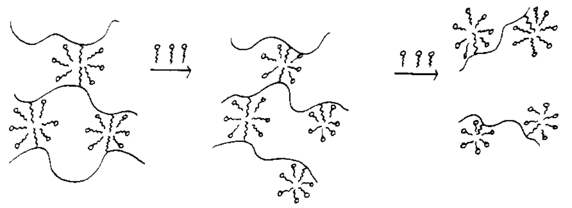

Figure 9. Schematic drawing of the hydrogel network.

Discussion

Under the same conditions where we observed the formation of both a gel and a supernatant phase with HMHEC, HEC formed a homogeneous solution. Thus clearly the gel structure must arise due to interactions involving the hydrophobic side chains. All of the evidence points to the formation of comicelles composed of SDS and alkyl polymer side chains. At low surfactant concentration there are as many as eight or nine alkyl grafts in each comicelle, providing a relatively tightly cross-linked network with a corresponding small volume, high G', and low M_e. As the concentration of surfactant increases, surfactant molecules replace side chains within the aggregates, with the result that the absolute number of cross-links goes down and M_e and the gel volume both increase. This is illustrated schematically in Figure 9.

The rheological results show that high gel volumes correspond to a high M_e, as expected. At the same time, the gel volume changes with the structure of the cross-links, as indicated by the fluorescence results. Several factors contribute to these effects. At high surfactant concentration, there are relatively fewer side chains per aggregate, i.e., more bound aggregates on each polymer chain, and a higher M_e. The resulting gain in entropy permits these longer chain segments to rearrange into a more extended configuration. At the same time, this increased number of aggregates gives rise to a higher static charge density on the polymer, which is also associated with a higher swollen gel volume.[21] Another effect that is important here is the fact that, as the surfactant concentration of the bulk solution increases, the solution becomes more hydrophobic and the polymer becomes more compatible with the solvent. This is in accordance with our earlier results showing that at very high surfactant concentration a homogeneous solution is formed.[1] It also follows from the fact that, for mixed micelles of SDS and POE lauryl ethers, the cmc increases above that of pure POE surfactant as the SDS mole fraction is increased, showing that POE becomes more soluble in the presence of SDS. Thus at high surfactant concentrations there may be a significant number of free (unmicellized) side chains in the gel, which would also give rise to a high M_e. It is not possible to determine which of these factors is the most significant in governing gel volume; however, they all would contribute in the same manner to the effects seen here.

By analogy with cross-linked polyelectrolyte gels, another parameter that contributes to the final swollen gel volume is the mobile ion concentration gradient between the gel and the supernatant. This is a very complex function in the case of these gels. The dissociation constant of bound surfactant molecules depends on the area available per head group in the aggregate. This area will be profoundly affected by the presence of cosurfactant and hence by the ratio of polymer side chains to surfactant molecules in the aggregates. There is polymer-bound surfactant in both the gel and supernatant phase in our system, with different ratios of the two species in the aggregates in each phase. There is also free dissociated surfactant present in both phases. Thus, although the total mobile ion concentration goes up with surfactant concentration, the mobile ion concentration gradient cannot readily be evaluated.

Conclusions

The results presented here demonstrate the tendency of a $C_{12}H_{25}(EO)_2$ molecule grafted to a cellulose polymer to form comicelles with sodium dodecyl sulfate. This is not unexpected in light of the huge literature showing the formation of comicelles among SDS molecules and cosurfactants[12] or long-chain alcohols[13-15] at concentrations below the cmc of pure SDS. When the cosurfactant is attached to a polymer, it is apparent from this study that the cmc of SDS is lowered, that mixed micelles composed of SDS and polymer-bound alkyl chains form, and the aggregation number of the mixed micelles is higher than that of pure SDS, by analogy with the case of mixed micelles consisting of SDS and long-chain alcohols. In this case, however, a stable polymer network of infinite molecular weight forms spontaneously as a separate phase. These networks behave much like cross-linked polyelectrolytes despite the absence of covalent bonds. This presents a new method of forming hydrogels with many of the desirable characteristics of cross-linked gels but without requiring additional reaction steps in the process.

The networks described in this work are composed of hydrophobic microdomains, which can solubilize a water-insoluble probe, dispersed throughout a water-swollen gel. These characteristics, coupled with the mechanical stability of the gels, make these new materials interesting candidates for such applications as chromatography or controlled drug release.

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Registry No. HMHEC, 9004-62-0; SDS, 151-21-3; Ru^{2+}Cl$^-$, 14323-06-9; Natrosol Plus, 117989-67-0.