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## INTERACTION OF SULFONATED POLYSTYRENE WITH CATIONIC SURFACTANTS IN AQUEOUS SOLUTION

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### ABSTRACT

The interaction of sulfonated polystyrene (SPS) with cetyl trimethylammonium bromide (CTAB) and myristyl trimethylammonium bromide (MTAB) in aqueous solution was investigated. It was found that the solution viscosity increases rapidly at the molar ratio of CTAB/ $-\text{SO}_3\text{Na} = 0.5$  or MTAB/ $-\text{SO}_3\text{Na} = 0.6$  (the first viscosity maximum) and CTAB/ $-\text{SO}_3\text{Na} = \sim 1.5$  or MTAB/ $-\text{SO}_3\text{Na} = 2.0$  (the second viscosity maximum). Both the first and the second viscosity maxima are related closely with the hydrophobic domains formed in solution, which can be detected using methyl orange as a spectral probe or *N,N*-dimethylamino flavone as fluorescent probe. In the higher concentration of [SPS], such as  $>0.05$  M ( $-\text{SO}_3\text{Na}$  unit), the SPS/CTAB solution converts to gel suddenly at CTAB/ $-\text{SO}_3\text{Na} = \sim 1.5$ – $1.7$  region, but with a further addition of CTAB or SPS, the gel collapses quickly. A term “micelle crosslinking” was proposed to explain the conversion of solution/gel and the reversible nature of gel  $\leftrightarrow$  solution.

*Key Words:* Sulfonated polystyrene; Cationic surfactant; Spectral probe; Fluorescent probe; Micelle crosslinking.

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## INTRODUCTION

The interactions of polyelectrolytes and amphiphilic molecules, especially surfactants, have attracted more and more attention (1,2). One of the reasons is that the interaction in question is very similar to that existed in protein and lipid and is also considered as a model interaction of protein and nuclei acid in cell (3). Another reason is that most of the complexation processes of amphiphilic molecules exhibit high self-assembly characteristics (4,5). It was confirmed that the surfactant molecules bind with the polymer chains in an aggregation form rather than as a single molecule (6,7). A micelle-like domain was formed via the hydrophobic interaction of sodium dodecyl sulfate (SDS) with gelatin or collagen (8) and a similar structure was observed in the system of poly(2-acrylamido-2-methylpropane sulfonic acid) and *N*-alkylpyridinium salt (9). Recently, we revealed a specific phenomenon in solution composed of SDS and cationic copolymer of 4-vinyl pyridinium salt and styrene (PVp-S): the solution viscosity rises suddenly to approximately two magnitude orders of its original value at a specific molar ratio of SDS/cation, then falls rapidly as the ratio increases further (10). In this article, we report the viscosity behavior of the anionic polyelectrolyte-cationic surfactant systems composed of sulfonated polystyrene (SPS) and cetyl trimethyl ammonium bromide (CTAB) or myristyl trimethyl-ammonium bromide (MTAB). The results show that the sudden rise and rapid fall of the solution viscosity in the SPS-CTAB or SPS-MTAB system also occurs and is very similar to that observed in the SDS-PVp-S system. Furthermore, we confirmed that, in this article, the dramatic changes of the solution viscosity are closely related with the hydrophobic domains existing in the solution.

## EXPERIMENTAL

### Materials

CTAB, MTAB, and methyl orange (MO) were purchased from ACROS and used as received. *N,N*-dimethylaminoflavone (DMAF) is a contributing sample, which was synthesized according to Reference (11), from Professor Wu, Institute of Photographic Science, Chinese Academic of Science. The SPS was prepared according to the method mentioned in Reference (12) with some modification as follows: polystyrene (PS, 1.04 g, 10 mmol) was dissolved in 10 mL of 1,2-dichloroethane (DCE), then a sulfonation agent—acetyl sulfate formed by dissolving acetic anhydride (10 mmol) and concentrated sulfuric acid (10 mmol) in 10 mL DCE, was added. The mixture was then heated at 80°C for 2–10 h, and 15 mL of H<sub>2</sub>O was added to dissolve the SPS. The aqueous solution in which the SPS dissolved was separated from DCE and neutralized with 0.1 N NaOH to pH ~7.

Diazo-resin, a polycondensation product of diphenylamine-4-diazonium salt with formaldehyde, was prepared according to the method described elsewhere (13),  $|\eta_{sp}/C = 0.15 \text{ dLg}^{-1}$ , corresponding  $M_n \sim 2600 \text{ g/mol}$ .

### Determination of Sulfonation Degree of SPS

The SPS, with greater than a 30% sulfonation degree, is water soluble and is difficult to separate from the aqueous solution containing sulfuric acid and inorganic salts. We have confirmed that the SPS reacted with diazoresin (DR) to form SPS-DR complex and was separated as a precipitate from the solution containing sulfuric acid or inorganic salts. The sulfonation degree of SPS can be calculated from the S% of the complex in which the combination of  $-N_2^+$  and  $-SO_3^-$  follows the 1:1 stoichiometric relation. The sulfonation degree of SPS is variable in the region of 30%–60% according to the sulfonation times (2–10 h).

### Viscosity Determination

The viscosity of SPS-CTAB or SPS-MTAB aqueous solution was determined with a capillary viscometer, which has a glass coat for running water from a thermostat. The relative viscosity  $\eta_r$  was calculated as a ratio of  $t_s/t_0$ , where  $t_0$  and  $t_s$  represents the time of the SPS solution running through the viscometer in the absence and presence of surfactant, respectively. The experiment was carried out as follows: into a 50-mL small beaker containing 10 mL of 0.02 M ( $-SO_3Na$  unit) SPS aqueous solution, the CTAB or MTAB (0.05M in water) was added from a titration tube in batches. The mixed solution was stirred (electromagnetic) 5–10 min for every batch, then sucked into the viscometer and the  $t_s$  of the solution at 30°C was determined.

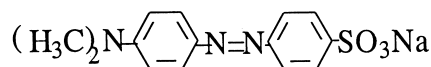
### MO Used as a Spectral Probe to Detect the Hydrophobic Domain

The hydrophobic domain in SPS-CTAB or SPS-MTAB aqueous solution can be detected by using methyl orange (MO, Struct. 1) as a spectral probe, which has the  $\lambda_{max} = 460$  nm in water and shifted to  $\sim 420$  nm in the presence of hydrophobic domain (14,15).

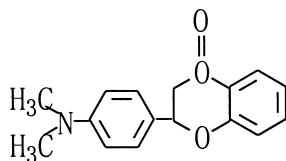
As an amphiphilic molecule with a block hydrophobic moiety, MO is successfully enters the hydrophobic domain. As a result, its  $\lambda_{max}^{UV}$  (wavelength of maximum absorption) shifts to a shorter wavelength.

### DMAF Used as a Fluorescent Probe to Detect the Hydrophobic Domain

A fluorescent probe used to detect hydrophobic domain has been widely investigated (16–18). A flavone derivative, *N,N*-dimethylamino flavone, (DMAF,



**Structure 1.** The formula of MO.



**Structure 2.** The formula of DMAF.

Struct. 2) has been confirmed to be an excellent fluorescent probe in detecting the hydrophobic domain in aqueous solution (19). The  $\lambda_{\max}^F$  (wavelength of maximum fluorescence) of DMAF will shift to a shorter wavelength, and its intensity of maximum fluorescence  $I_{\max}^F$  will greatly increase in the presence of hydrophobic domain (19).

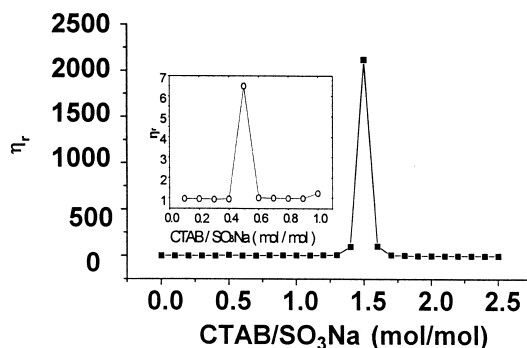
### Laser Light Scattering (LLS) Measurement

The experiment was carried out as follows: into a 50-mL small beaker containing 10 mL of 0.02 M ( $-\text{SO}_3\text{Na}$  unit) SPS aqueous solution, the CTAB (0.05M in water) was added from a titration tube in batches. The mixed solution was stirred (electromagnetic) 5–10 min for each batch, then diluted to 100 times with water and super centrifuged. The liquid obtained was used for determination of LLS (argon ion laser, output power = 200 mV,  $|\lambda_0 = 514.5 \text{ nm}$  at  $30.0 \pm 0.1^\circ \text{C}$ ).

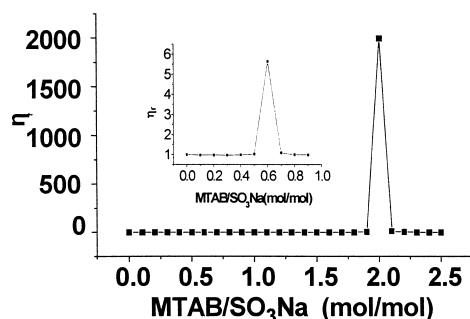
## RESULTS AND DISCUSSION

### The Viscosity of the Solutions

The relative viscosity ( $\eta_r$ ) of SPS-CTAB or SPS-MTAB aqueous solution rises or falls suddenly at a specific molar ratio of CTAB/ $-\text{SO}_3\text{Na}$  (or MTAB/ $-\text{SO}_3\text{Na}$ ) as shown in Figures 1 and 2. The results show that the first and second



**Figure 1.** The relative viscosity of SPS-CTAB aqueous solution at various  $[\text{CTAB}]/[-\text{SO}_3\text{Na}]$ ;  $[\text{SPS}]$  ( $-\text{SO}_3\text{Na}$  unite) = 0.02 M,  $30^\circ \text{C}$ .



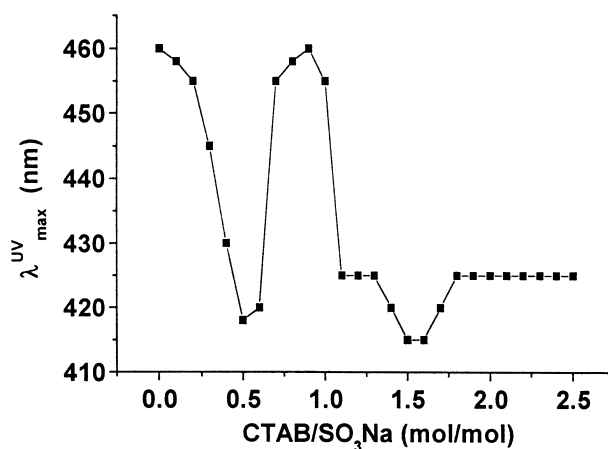
**Figure 2.** The relative viscosity of SPS-MTAB aqueous solution at various [MTAB]/[-SO<sub>3</sub>Na]; [SPS] (-SO<sub>3</sub>Na unite) = 0.02 M, 30°C.

maxima of viscosity appear at  $\sim 0.5$ ,  $\sim 1.5$  for CTAB/-SO<sub>3</sub>Na and  $\sim 0.6$ ,  $\sim 2.0$  for MTAB/-SO<sub>3</sub>Na, respectively. The increasing viscosity should be attributed to the physical combination of polymer chains via CTAB and MTAB molecules, which aggregate easily in water at critical aggregation concentration (CAC) to form micromicelle (20,21) and at a critical micelle concentration (CMC) to form micelle. We think the first and second maximum viscosities are related to the presence of hydrophobic domain, especially the formation of micromicelle and micelle.

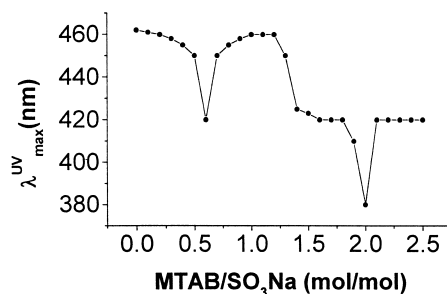
### The Detection of Hydrophobic Domain

With MO as a Spectral Probe

The relationship between the  $\lambda_{\max}^{\text{UV}}$  of MO and the molar ratio of CTAB/-SO<sub>3</sub>Na (or MTAB/-SO<sub>3</sub>Na), (Figs. 3 and 4) show that the  $\lambda_{\max}^{\text{UV}}$  (460 nm) of MO



**Figure 3.** The relationship of  $\lambda_{\max}^{\text{UV}}$  of MO and molar ratio of [CTAB]/[-SO<sub>3</sub>Na] in SPS-CTAB aqueous solution [SPS] (-SO<sub>3</sub>Na unite) = 0.02 M, 30°C.



**Figure 4.** The relationship of  $\lambda_{\max}^{\text{UV}}$  of MO and molar ratio of [MTAB]/[-SO<sub>3</sub>Na] in SPS-MTAB aqueous solution [SPS] (-SO<sub>3</sub>Na unite) = 0.02 M, 30°C.

in water moves to ~415 nm in solution at CTAB/-SO<sub>3</sub>Na = ~0.5 and to ~420 nm at MTAB/-SO<sub>3</sub>Na = 0.6, respectively, at which point the first viscosity maximum appears (see Figs. 1 and 2). It was considered to be related to the micromicelle formation in solution at CTAB/-SO<sub>3</sub>Na = ~0.7-0.9 (or MTAB/-SO<sub>3</sub>Na = ~0.6-1.2), the viscosity drops almost to the  $\eta_r = 1.0$  and the  $\lambda_{\max}^{\text{UV}}$  of MO return to ~460 nm because the complex precipitates (as a powder-like solid) in this region. With the further addition of CTAB or MTAB), the  $\lambda_{\max}^{\text{UV}}$  decreases, due to the dissolution of the complex and the hydrophobic domain forms again. At CTAB/-SO<sub>3</sub>Na = ~1.5 (or MTAB/-SO<sub>3</sub>Na = ~2.0), the second viscosity maximum appears (see Figs. 1 and 2) and the  $\lambda_{\max}^{\text{UV}}$  of MO moves to ~415 nm (Figs. 3 and 4).

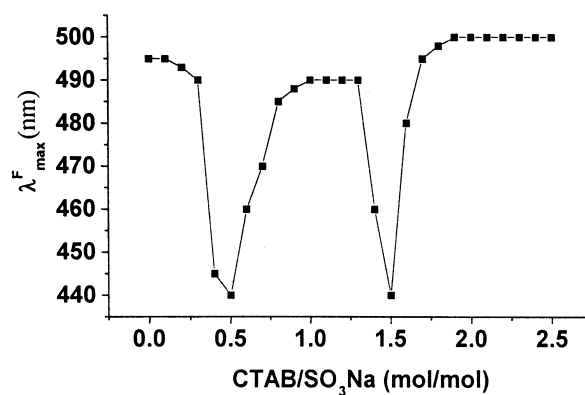
It is noteworthy that with the further addition of CTAB (or MTAB), the solution's viscosity falls (see Figs. 3 and 4), but the  $\lambda_{\max}^{\text{UV}}$  of MO shows almost no change. It may be attributed to the presence of normal micelles in this region (CTAB/-SO<sub>3</sub>Na > 1.8 or MTAB/-SO<sub>3</sub>Na > 2.2).

#### With DMAF as Fluorescent Probe

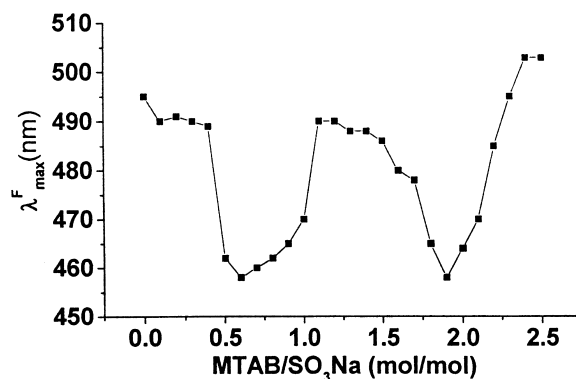
Using DMAF as a fluorescent probe, the wavelength of maximum fluorescence  $|\lambda_{\max}^{\text{F}}$  and the maximum fluorescence intensity  $I_{\max}^{\text{F}}$  changes with CTAB/-SO<sub>3</sub>Na (Figs. 5 and 7) and MTAB/-SO<sub>3</sub>Na (Figs. 6 and 8). From Figures 5 and 7, the  $\lambda_{\max}^{\text{F}}$  of DMAF appears two minima and the  $I_{\max}^{\text{F}}$  appears two maxima at CTAB/-SO<sub>3</sub>Na=0.5 and 1.5, at which two viscosity maxima appear (see Fig. 1). Figures 6 and 8 show the similar results obtained in SPS/MTAB system, i.e., the  $\lambda_{\max}^{\text{F}}$  of DMAF appears two minima and the  $I_{\max}^{\text{F}}$  appears two maxima at MTAB/-SO<sub>3</sub>Na=0.6 and 2.0, at which two viscosity maxima appear (see Fig. 2).

### The Hydrodynamic Radius $R_h$

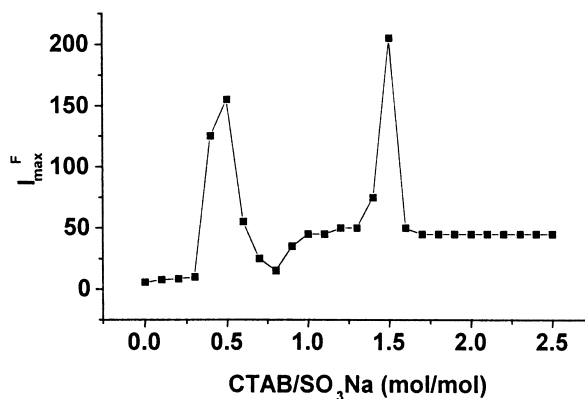
The hydrodynamic radius  $R_h$  of SPS/CTAB solution determined by laser light scattering (LLS) shows that  $R_h$  changes with molar ratio of CTAB/-SO<sub>3</sub>Na



**Figure 5.** The relationship of  $\lambda_{\max}^F$  of DMAF and molar ratio of [CTAB]/[-SO<sub>3</sub>Na] in SPS-CTAB aqueous solution [SPS] (-SO<sub>3</sub>Na unite) = 0.02 M, 30°C.

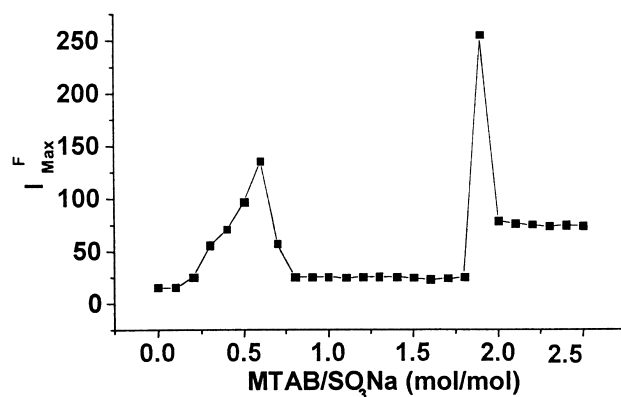


**Figure 6.** The relationship of  $\lambda_{\max}^F$  of DMAF and molar ratio of [MTAB]/[-SO<sub>3</sub>Na] in SPS-MTAB aqueous solution [SPS] (-SO<sub>3</sub>Na unite) = 0.02 M, 30°C.



**Figure 7.** The relationship of  $I_{\max}^F$  of DMAF and molar ratio of [CTAB]/[-SO<sub>3</sub>Na] in SPS-CTAB aqueous solution [SPS] (-SO<sub>3</sub>Na unite) = 0.02 M, 30°C.



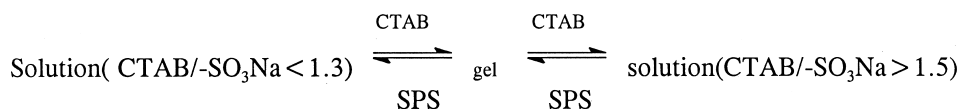


**Figure 8.** The relationship of  $I_{\max}^F$  of DMAF and molar ratio of  $[\text{MTAB}]/[-\text{SO}_3\text{Na}]$  in SPS-MTAB aqueous solution  $[\text{SPS}] (-\text{SO}_3\text{Na unite}) = 0.02 \text{ M}$ ,  $30^\circ\text{C}$ .

and shows two maxima of  $R_h$  appear at  $\text{CTAB}/-\text{SO}_3\text{Na} \sim 0.6$  and  $\sim 1.6$  (Tab. 1), which is in accordance with the result of two viscosity maxima by viscosity determination (see Fig. 1).

### The Micelle Crosslinking

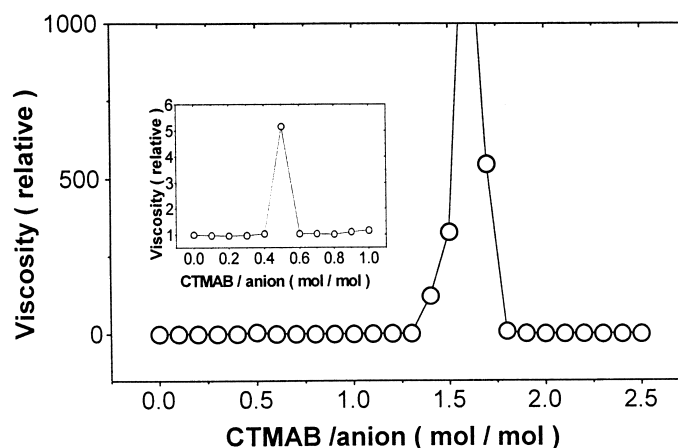
A specific phenomenon was observed in SPS-CTAB or SPS-MTAB solutions with the higher concentration of SPS ( $>0.05 \text{ M}$ ), the solutions converts to gel suddenly in  $\text{CTAB}/-\text{SO}_3\text{Na} \sim 1.5\text{-}1.7$  region as shown in Figure 9 (the phenomenon is similar in SPS-MTAB solution). The term “micelle crosslinking” was used to describe the gelation occurring in polyelectrolyte-surfactant system. It is very interesting that the crosslinking is reversible, i.e., with the further addition of CTAB or SPS, the gel (or solution) will convert to solution (or gel). The molar ratio of CTAB/SPS plays a key role in this process and can be represented as follows:



The change from solution to gel should be attributed to the physical combination of the polymer chains via CTAB. The change from gel to solution, we think, may be that with addition of excessive CTAB, the normal micelle forms. The driven force for forming normal micelle causes the CTAB molecules moving from the polymer chain and the gel collapses. It is also verified that a suitable amount of water was added into the solution, which just converted from gel due to addition of CTAB, the gelation will occur again. With the addition of water, the

**Table 1.** The  $R_h$  of SPS / CTAB solution determined by LLS at Different CTAB /  $-\text{SO}_3\text{Na}$ 

| CTAB / $-\text{SO}_3\text{Na}$ (mol/mol) | 0.0 | 0.4 | 0.5 | 0.6 | 0.8 | 1.0 | 1.3 | 1.6 | 1.7 | 2.0 |
|--|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| $R_h$ (nm)                               | 0   | 8   | 8   | 45  | 9   | 9   | 10  | 395 | 9   | 8   |

**Figure 9.** The gel formation in SPS-CTAB solution with higher [SPS] [SPS] ( $-\text{SO}_3\text{Na}$  unite) = 0.05 M, 30°C.

concentration of CTAB is diluted to less its CMC, thus, the normal micelle will be destroyed and the CTAB molecules, departed from the micelle, will participate in the combination of the polymer chains.

The sensitivity of gel  $\leftrightarrow$  solution (or solution  $\leftrightarrow$  gel) to the molar ratio of surfactant and positively charged polyelectrolyte may be found a practical application.

## CONCLUSION

The viscosity rises suddenly in the SPS-CTAB (or SPS-MTAB) aqueous solution at a molar ratio of CTAB/ $-\text{SO}_3\text{Na}$  (or MTAB/ $-\text{SO}_3\text{Na}$ ) =  $\sim 0.5$  (or 0.6) (the first maximum of viscosity) and at  $\sim 1.5$  (or 2.0) (the second maximum of viscosity).

The first and second maxima of viscosity are closely related to the physical combination of polymer chains originating from the aggregation of SPS molecules via CTAB (or MTAB) at CAC and CMC, respectively.

Using methyl orange (MO) as a spectral probe, *N,N*-dimethylamine-flavon (DMAF) as a fluorescent probe and laser light scattering, the hydrophobic domains that existed in the SPS-CTAB (or SPS-MTAB) solution at the first and second viscosity, increasing regions have been detected.

The reversible conversion of gel  $\leftrightarrow$  solution occurs in the SPS-CTAB (or SPS-MTAB) solution at higher SPS concentration can easily be regulated with CTAB/ $-\text{SO}_3\text{Na}$  (or MTAB/ $-\text{SO}_3\text{Na}$ ) molar ratio.

The term "micelle crosslinking" was used to explain the reversible conversion of gel  $\leftrightarrow$  solution in polyelectrolyte-surfactant systems.

### ACKNOWLEDGMENT

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### REFERENCES

1. Dubin, P., Ed. *Microdomain in Polymer Solutions*; Plenum Press: New York, 1985.
2. *Surfactants with Polymers and Proteins*; CRC Press: Boca Roton, FL, 1993.
3. Bowman, W. A.; Rubinstein, M.; Tan, J. S. *Macromolecules* **1997**, *30*, 3262.
4. Fundin, J.; Brown, W.; Vethamuthu, M. S. *Macromolecules* **1996**, *29*, 1195.
5. Ponomarenko, E. A.; Waddon, A. J.; Bakeev, K. N.; Tirrell, D. A.; MacKnight, W. J. *Macromolecules* **1996**, *29*, 4340.
6. Henriquez, M.; Abuin, E.; Lissi, E. *Colloid Polym. Sci.* **1993**, *271*, 960.
7. Taylor, P. *Colloid Polym. Sci.* **1996**, *274*, 1061.
8. Henriquez, M.; Lissi, E.; Abuin, E.; Cifferi, A. *Macromolecules* **1994**, *27*, 6834.
9. Okuzaki, H.; Osada, Y. *Macromolecules* **1995**, *28*, 380.
10. Zheng, X.; Cao, W. *Polymer Int.* **1998**, *46*, 285.
11. Wang, B. Doctoral Thesis, Institute of Photographic Science, Academic Institute of China: China, 1993.
12. Makowski, H. S.; Lundberg, R. D.; Singhal, G. H. U. S. Patent 3,870,841, 1975.
13. Cao, S.; Zhao, C.; Cao, W. *Polym. Int.* **1998**, *44*, 142.
14. Wang, G.; Engberts, Jan B. F. N. *Langmuir* **1994**, *10*, 2583.
15. Kim, W.; Seo, K. J. *Polym. Sci.* **1998**, *27(A)*, 389.
16. Anderson, S. R.; Weber, G. *Biochemistry* **1969**, *8*, 371.
17. August, J.; Palmer, T. F. *Chem. Phys. Lett.* **1988**, *145*, 273.
18. Antonietti, M.; Contendin, J. *Macromol.* **1989**, *17*, 798.
19. Shi, X.; Sun, C.; Wu, S. *Photogr. Sci. Photochem.* **1998**, *16*, 161.
20. Hecht, E.; Hoffmann, H. *Langmuir* **1994**, *10*, 86.
21. Abuin, E. B.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6274.

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