

Network Assembled Structures from a Series of Macromolecular Surfactants

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Abstract--Network assembled structures from a series of macromolecular surfactants were prepared on glass surfaces. When the content of the hydrophobic side-chains was increased from 10 to 90 mol%, the solutions exhibited a lower surface tension. In addition, these solutions ultimately formed thinner and more orderly network-based porous films on glass surfaces.

Keywords--associative behaviour; network structures; macromolecular surfactants; hydrophobic side-chains

I INTRODUCTION

The self-assembly behavior of surfactants on solid surfaces is of significant scientific and technological importance due to their relevance to biomacromolecular systems and potential for various industrial applications.[1] Macromolecular surfactants incorporate hydrophilic and hydrophobic monomer units that are attached to the same surfactant backbones,[2] and the self-assembly behavior of these surfactants can be influenced by their inherent structures, concentrations, mixing ratios among multi-component systems, and external stimuli. Generally, the self-assembled nanostructures of macromolecular surfactants can exhibit a wide range of architectural diversity, and these self-assembled nanostructures also tend to be more stable than the self-assembled structures of low molecular weight amphiphiles.[3]

In recent years, the development of surface modification techniques has led to the facile preparation of macromolecular films and facilitated the modification of surfaces.[4] However, the composition and homogeneity of these films were often poorly defined or differed from the expected composition. On solid supports, various kinds of macromolecular structures have been investigated, including those of linear block copolymers,[5] dendronized macromolecules,[6] special macromolecules incorporating siloxane blocks or fluorinated units, and composite macromolecular systems. However, further fundamental studies are required in order to advance our understanding of the formation and structure of macromolecular films.

Our interest in macromolecular surfactants began almost a decade ago, and a novel series of brush-like macromolecular surfactants with different side-chain compositions have been reported.[7-10] In the present work, the morphologies of the self-assembled films prepared from these surfactants with varying hydrophobic side-chain contents (ranging between 10 and 90 mol%) on solid supports were investigated. In addition to the morphologies of the surfactant films, the surface tension of solutions of these surfactants were also investigated. Upon

investigating the structures of the films on the surfaces, we were surprised to discover that the surfactant structure had a strong influence on the assembled structures on glass surface. This work will provide valuable insight into the design and preparation of macromolecular films with well-defined functional nanostructures that exhibit tunable properties.

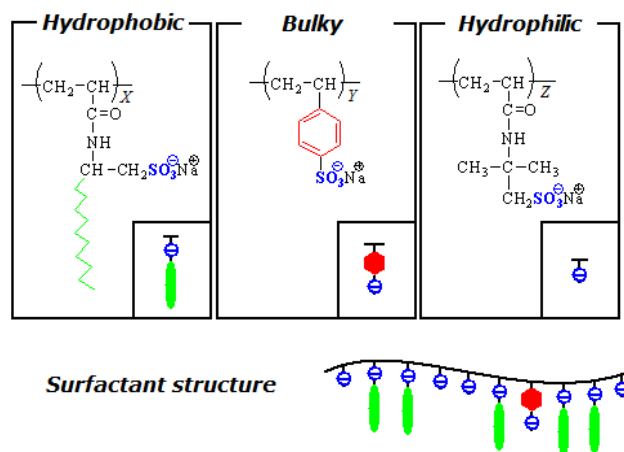


FIGURE I. ILLUSTRATION OF THE MACROMOLECULAR SURFACTANTS THAT INCORPORATED HYDROPHOBIC (AMC12S) UNITS, BULKY (SSS) UNITS, AND HYDROPHILIC (AMPS) UNITS. THE SUBSCRIPTS IN THE STRUCTURES SHOWN ABOVE REPRESENT THE MOL% VALUES FOR EACH UNIT, WHERE $X = 10, 30, 50, 70,$ AND 90 MOL%, $Y = 5$ MOL%, AND $Z = 95 - X$ MOL%.

II EXPERIMENTAL SECTION

A. Macromolecular Surfactants

The macromolecular surfactants incorporating 2-(acrylamido)-dodecane sulfonic acid (AMC12S, 10-90 mol%), sodium p-styrenesulfonate (SSS, 5 mol%), and 2-(acrylamido)-2-methylpropane-sulfonic acid (AMPS) units were synthesized, purified, and characterized according to the methods described in our previous report.9

B. Measurements

Sample solutions for surface tension, contact angle measurements, and SEM characterization were the same as that investigated in the previous work.9 Surface tension curves of the surfactant solutions were obtained by using the drop-volume method at 25.0 ± 0.5 °C. The contact angles were measured via axisymmetric drop shape analysis (ADSA) at room temperature. The morphologies of the assembled macromolecular films that had been formed on glass surfaces

were observed using a Hitachi S-530 scanning electron microscope (SEM).

III RESULTS AND DISCUSSION

The surfactants adsorbed at the air/water interface would interact with the aggregates in the solution phase as the solvent evaporates during the formation of film on the solid surface. The surface tension of the surfactant solutions could provide information about the adsorption of molecules at air/water interface. A plot of the variation of the surface tension versus the surfactant concentration is shown in Figure 2. There is no clear breakpoint for the surfactants with $fc12 = 10$ mol% and $fc12 = 30$ mol%, which implies that the adsorption of these two surfactants keep changing along with the increase of concentrations. This also suggests that the associative behavior of the surfactants possessing less of the amphiphilic AMC12S side-chains could have a stronger tendency to change with the increase of concentrations. The surface tensions of the surfactant solutions decreased when the concentrations were increased, indicating the progressive adsorption of the molecules at air/water interface along with the increase of concentrations. In addition, the surface tension of the surfactant solutions decreased when $fc12$ was increased, indicating that surfactants possessing more side-chains exhibited a lower surface tension.

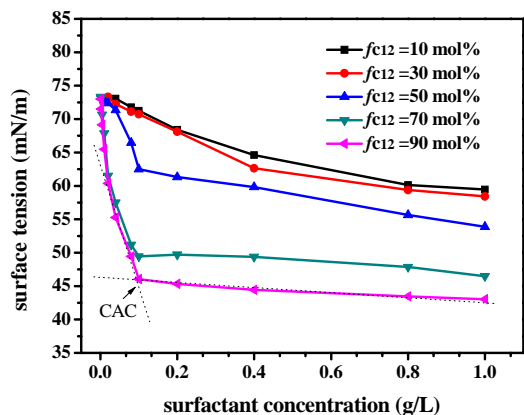


FIGURE II. PLOTS OF SURFACE TENSION AGAINST THE CONCENTRATIONS OF SURFACTANTS WITH VARYING $fc12$ VALUES.

In Figure 3, the morphologies of the films prepared from surfactants with varying $fc12$ values are shown. Regardless of their varying molecular structures, it was apparent that all of the surfactants yielded porous network structures. In addition, the arrays of these mesh-like structures became progressively more continuous and orderly for the surfactants with higher $fc12$ values. The films also became thinner when they were prepared from surfactant solutions that exhibited lower contact angles, and films of the surfactant with $fc12 = 90$ mol% appeared to exhibit a monolayer structure (Figure 3e). As mentioned earlier, this trend suggests that the thickness of the film is directly related to the contact angles of the surfactant solutions. Due to their long range nanoporous structures, the network-based films observed here could have various potential applications, such as gas separation, biosensors, or catalyst supports.

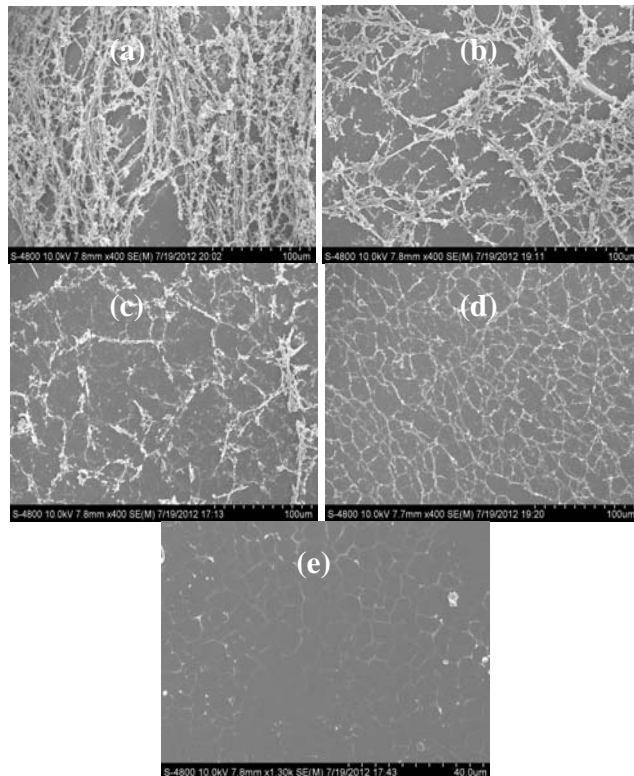


FIGURE III. SEM IMAGES OF SURFACTANT FILMS THAT HAD FORMED ON THE SURFACES OF GLASS SLIDES. THESE FILMS WERE COMPOSED OF SURFACTANTS WITH VARIOUS $fc12$ VALUES INCLUDING: $fc12 = 10$ (A), 30 (B), 50 (C), 70 (D), AND 90 MOL% (E).

IV CONCLUSIONS

The solutions of macromolecular surfactants with higher $fc12$ values would have a lower surface tension, and the solutions of the surfactants described in this report had surface tension in the range of 43-60 mN/m. The surfactant structures have obvious effects on the morphology of the films formed by the surfactants on surface. The solutions of surfactants with higher $fc12$ values formed thinner and more orderly network-based porous films covering the surfaces of glass slides, and the long range nanoporous structures of the films may find application in various fields.

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