Nano-Sized Polymer Micelle Synthesized from Cationic Gemini Surfmer

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ABSTRACT

We examined the synthesis and characterization of polymer micelle using polymerizable cationic gemini surfactant (surfmer). Here, cationic gemini surfmer (GS) was newly synthesized and characterized. Also, a “monomer”-type surfmer (MS) was synthesized and characterized for comparison. The equilibrium properties in water and in the presence of 0.1 M NaBr were investigated by means of surface tensions of the surfmer, indicating the GS can show the characteristic properties of gemini surfactant. Micelles of GS were polymerized and characterized with dynamic light scattering (DLS) measurements and TEM observation. The particle-size distribution for polymer micelle indicates that the structure of polymer micelle synthesized from GS is quite uniform. The average diameter of the particle is about 3 nm. The TEM image show that the nano-ordered organic particles were formed whose diameter is similar to that obtained by DLS measurement.

Keywords: gemini surfactant, surfmer, polymer micelle

1 INTRODUCTION

In our life, we have used a lot of nanoporous materials for the gas purification, separation, and energy capacitor systems [1]. Recently, porous materials with new functions have been reported and applications by use of these materials have also been published. For instance, Kondo [2] and Kitagawa et al. [3] synthesized nanoporous Cu-complex whose pore width can be controlled by changing the organic ligands. This organic-inorganic hybrid material show a unique molecular adsorption effect which is different from that prepared with other techniques. Some researchers reported a “molecular valve model” for Cu-based solids by means of adsorption isotherm analysis of carbon dioxide and X-ray diffraction technique [4, 5], which means that this material can adsorb molecules after changing the crystalline structure at definite pressure (called gate pressure). Thus, the nanoporous materials having unique functions can produce a lot of possibilities to apply to the material for gas storage of methane and/or hydrogen.

In addition, a variety of solids having regular pore structure have been developed with many kinds of methods. Especially, templating synthesis is a quite important to produce regular pores. Kyotani et al. prepared carbon tubes whose pores belong to large mesopores with the aid of the aluminum oxide template [6]. Ryoo et al. succeeded in the preparation of mesoporous carbons, which are named CMK using the mesoporous silica as the template [7-10]. However, templating methods cannot be used to manufacture industrial products because they normally need relatively hard conditions such as high temperature, lower or higher pH, and so on. Therefore, we need other concepts to produce nanoporous materials having regular pores.

Here, organic nanoparticles are quite useful for various fields because of their relative convenience for synthesis and functionalization with a chemical reaction. It has been reported to synthesize the organic nanoparticles of polymer micelle by use of polymerizable surfactants [11, 12]. However, it is difficult to obtain the nanoparticles having uniform particle size. If we could develop a method to obtain the organic nanoparticles having regular structure, it can be applied to synthesize organic solids with regular nanopores and various kinds of functionalities.

In this study, we examine the synthesis and characterization of polymer micelle using polymerizable cationic gemini surfactant (surfmer). Here, gemini surfactants have been gathering much attention because of their outstanding surface porpoerties [13-15]. Also, gemini surfactants form micelles or other molecular assemblies at lower concentration, therefore, it is easier to control the particle structure without cohesion. Therefore, this paper also shows solution properties of polymerizable gemini surfactants which were newly synthesized in this work.

2 EXPERIMENTAL SECTION

2.1 Synthesis of Surfmers

Figure 1 shows chemical structures of cationic gemini surfmer (GS) and “monomer”-type surfmer (MS) used in this study. MS was synthesized as described elsewhere [16]. On the other hand, GS was prepared by reacting a 2:1 molar ratio of bromoundecyl methacrylate [17] to N, N, N’, N’-tetramethyl ethylene diamine (99.5 %; Aldrich) in anhydrous ethanol (99+ %; Wako) which were refluxed at 50 °C for 48 h. Then, the solvent was removed, and crystals of GS were obtained after recrystallizing in the mixture of acetone and methanol.

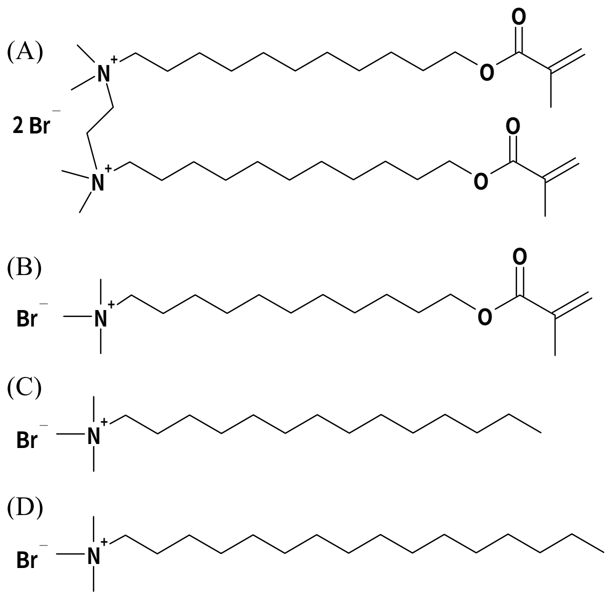

Figure 1: Chemical structures of (A)GS, (B) MS, (C) TTAB, and (D) CTAB.

2.2 Surface Tension Measurements

The surface tensions of each surfactant solution were measured 30 °C with a Wilhelmy surface tension meter (Model CBVP-A3, Kyowa Surface Science, Co. Ltd.) using a platinum plate. Here, the surface tensions of tetradecyltrimethyl ammonium bromide (TTAB) and cetyltrimethyl ammonium bromide (CTAB) were also measured for comparison. The critical micellization concentration (cmc) values and the surface tensions at each cmc value, γ_{cmc}, were taken at the intersection of the linear portions of the plots of the surface tensions against the logarithm of the surfactant concentrations. The saturated amount of surfactant adsorbed at the air/solution interface, Γ_{max}, was calculated using the Gibbs adsorption isotherm. Also, the area occupied by one surfactant molecule at the air/solution interface, A_{min} and the reducing surface tension, pC_{20} [17], were obtained.

2.3 Polymerization

The polymer micelle was obtained by the polymerization by using GS aqueous solution (20 mM) and 0.2 mM of 2, 2-azobis(2-methylpropionamidine). They are reacted at 60 °C for 2 h. The particle-size distribution of the sample was determined by measuring the dynamic light scattering (DLS) (NICOMP 380 ZLS, Particle Sizing System, Co. Ltd.). Also, the transmission electron microscopy (TEM) observation was carried out by H-7650 (Hitachi Co. Ltd.).

3 RESULTS AND DISCUSSION

To reveal the solution properties for each surfactant, we measured the surface tension and determine the interfacial parameters. Figures 2(a) and (b) show the surface tension as a function of logarithm of concentration for each surfactant in water and in the 0.1 M NaBr aqueous solution, respectively. Here, when we use electrolytic solution as a solvent of surfactants, we can obtain the interfacial parameters such as Γ_{max} or A_{min} more accurately for ionic surfactants. These figures show that surface tension at the cmc of GS in both media is lower than any other surfactants indicating an outstanding interfacial properties of a gemini surfactant.

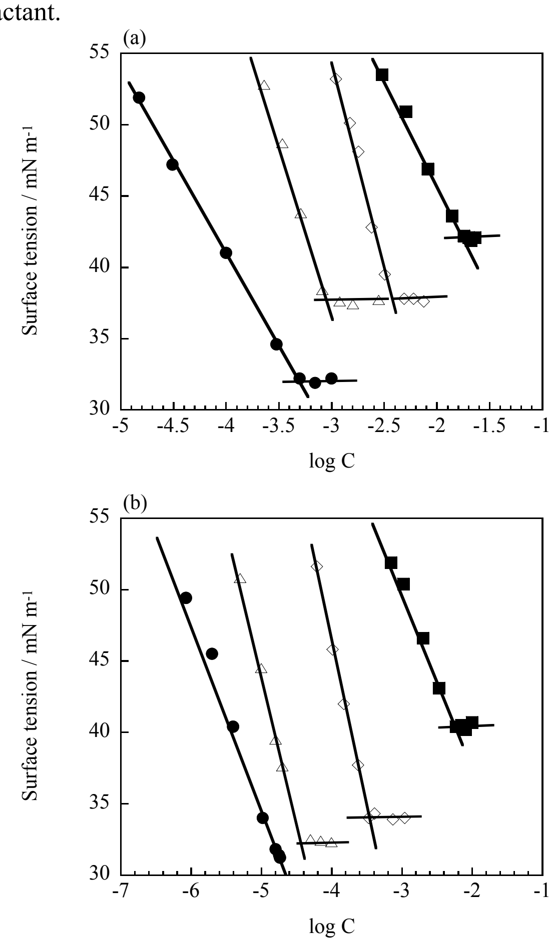

Figure 2: Relationship between the surface tension and concentration of each surfactant in (a) water and (b) aqueous solution of NaBr (0.1 M). (●: GS, ■: MS, ◊: TTAB, and Δ: CTAB)

Table 1: Interfacial parameters of each surfactant.

Surfactant	Media	cmc / mmol dm^{-3}	γ_{cmc} / mN m^{-1}	pC_{20}	A_{min} / 10^{-2} nm^2	Γ_{max} / 10^{-10} mol cm^{-2}
GS	Water	0.49	32.1	4.8	220	0.74
MS	Water	18.0	42.1	2.3	129	1.29
TTAB	Water	3.7	37.8	2.9	63	2.6
CTAB	Water	0.88	37.6	3.7	73	2.3
GS	0.1 M NaBr	0.0036*	n.a.	6.2	68	2.43
MS	0.1 M NaBr	5.7	40.5	3.1	75	2.22
TTAB	0.1 M NaBr	0.34	34.0	4.3	41	4.1
CTAB	0.1 M NaBr	0.034	32.4	5.3	44	3.8

*Measured at 40 °C

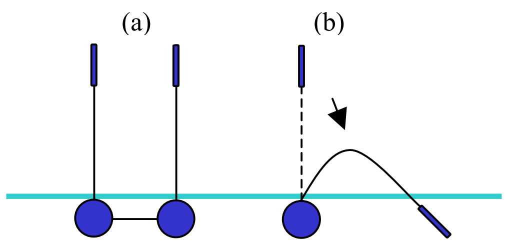

Figure 3: Schematic illustration ob molecular structure of (a) GS and (b) MS at the interface.

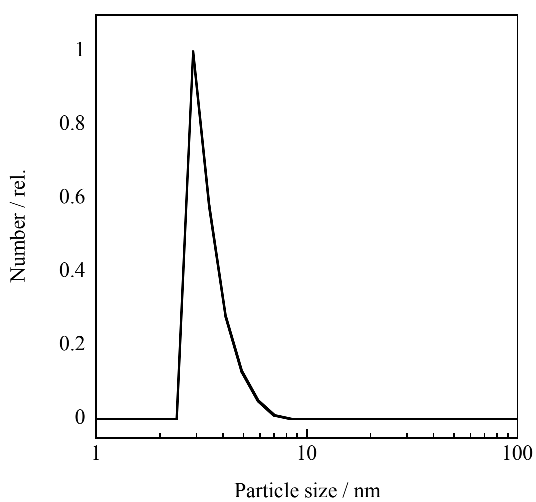

Figure 4: Particle-size distribution of polymer micelle synthesized from GS.

Table 1 summarizes the interfacial parameters obtained by the results shown in Figures 2(a) and (b). The cmc value of GS in both media is quite lower than any other surfactants indicating micelles can be formed at lower concentration and, therefore, these molecular assemblies are highly dispersed in aqueous solution. Here, the aim of this study is to prepare the nano-sized polymer micelle; the highly dispersed state of molecular assembly of GS is an excellent property to synthesize uniform polymer micelle without any flocculation of micelles. Also, the value of cmc for MS is higher in both media. The end of hydrophobic chain of GS and MS is composed of the metacryloyl group which shows less hydrophobicity. In the case of GS, the hydrocarbonic chain between two MS, which is generally called as spacer, can inhibit not to bend the hydrophobic chain to the hydrophilic part as shown in Figure 3, although it is possible for MS to bend the hydrophobic chain. Hence, the unique properties of GS used in this study come from both the gemini-type structure of surfactant.

Then, we synthesized and characterized the polymer micelle which was prepared from the polymerization of GS. Figure 4 shows the particle-size distribution of polymer micelle measured by DLS. This figure indicates that the structure of polymer micelle synthesized is quite uniform. The average diameter of the particle is about 3 nm. The TEM image of polymer micelles obtained from GSM is shown in Figure 5. The nano-ordered organic particles were formed whose diameter is similar to that obtained by DLS measurement. Also, the uniform shape of polymer micelle was observed stemming from the highly dispersed state of GS which can form micelles at lower surfactant concentration. Hence, we can synthesize the nano-ordered organic particles having uniform structure by using cationic gemini surfmer.

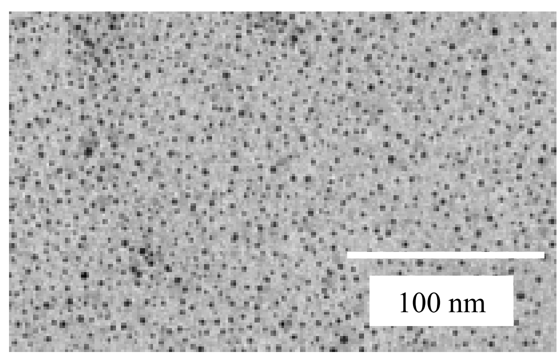

Figure 5: TEM image of polymer micelles.

4 CONCLUDING REMARKS

We could synthesize and characterize the polymer micelle using polymerizable cationic GS. The equilibrium properties in water and in the presence of 0.1 M NaBr indicate the GS can show the characteristic properties of gemini. The particle-size distribution for polymer micelle indicates that the structure of polymer micelle synthesized from GS is quite uniform whose diameter is about 3 nm. This result strongly agrees with the result of TEM observation.

5 ACKNOWLEDGEMENT

This work was supported by a Grant-in-Aid for Science Research (No. 17710102) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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