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Foam Superstabilization by Lamellar Liquid Crystal Gels

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Highly stable microbubble dispersions with mean bubble radii of less than 100 μm stabilized solely with nonionic surfactant of glyceryl monostearate are reported, and the stability was sustained for more than 10 months which is attributed to the presence of lamellar liquid-crystal gels. The elastic response of the interface provides a physical barrier to collapse of dispersed microbubbles. Our study identifies a route to fabricate extremely stable dispersions of microbubbles.

Micrometer-sized bubbles are unstable and, therefore, difficult to make and store for substantial lengths of time. Short-term stabilization is achieved by the addition of amphiphilic molecules, which reduce the driving force for bubble dissolution. Surfactants, proteins or polymers, whose molecules cover the air/liquid interface to prevent collapse of the microbubbles, are generally effective in increasing the foam stability.[1] Nanoparticles exhibit similar properties by adsorbing at the interface and act as emulsifier of oil/water emulsion and excellent foam stabilizer.[2] Liquid crystals have also been reported to improve the foam stability in both aqueous and nonaqueous systems.[3] More recently, Stone and co-workers reported that low-gas-fraction dispersions through interfacial faceting or domain bending on certain surfactant-coated microbubbles were retained more than a year.[4] When the surfactant molecules crystallize on the air/liquid interface, the lifetime of individual bubbles may extend over a few months.[5] However, very few studies of foams stabilized by liquid-crystal gels are reported, and the lifetime of the obtained foams is only several hours.[6]

In the present contribution, we report extremely stable aqueous foams persisting for more than 10 months utilizing suspensions of glyceryl monostearate (GMS) at a concentration of 5 wt %. The originality in our study is that the presence of lamellar liquid-crystalline gels covered at the gas/liquid interface plays a more pronounced effect on the stability of macrodispersed microbubbles compared to foams formed in a variety of systems, including conventional surfactants, proteins or polymers, nanoparticles, and liquid crystals (with a lifetime from hundreds of seconds to tens of hours).[1–3] The simplicity and versatility of the prepared microbubbles with a binary composition of single-surfactant–water have an advantage over the microbubble dispersion systems generated from the ternary composition of a highly viscous glucose syrup (75 wt %) with water (23 wt %) and sucrose stearate (2 wt %) as the stabilizer reported by Stone and co-workers, both of which show different interfacial structures, although the present system displays shorter lifetime than the latter.[4] The surfactant solutions were mixed at higher temperature (60 °C) and then stirred at high speed (6000–8000 rpm), starting with 100 mL of surfactant solution, until a constant volume of white creamy foams was prepared. The foamability was estimated by measuring the foam volume immediately after preparation. The foam stability was assessed by monitoring the volume of foam column and the liquid drained as a function of time. The structure of microbubbles was observed with an Olympus BX-51 microscope in the differential interference contrast (DIC) and crossed polarizing modes. Differential scanning calorimetry (DSC) was carried out with a model DSC 200 calorimeter at heating and cooling rate of 5 °C min^{-1} to determine melting points, melt enthalpies, and the type of gel phases, α gel or coagel, present. Bulk viscosity of surfactant solutions and foams was measured at 25 °C at fixed shear rate of 50 s^{-1} using an RV-30 rheometer.

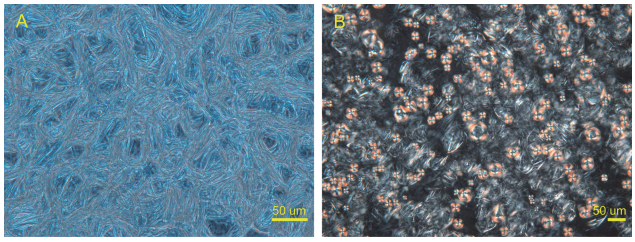

Figure 1. Optical micrographs of GMS solutions. (A) DIC mode; (B) cross polarizing mode.

The phase behavior of GMS–water systems was analyzed before we studied the microstructure of foams generated from this surfactant. Figure 1A shows an optical micrography picture of a 5 wt % GMS dispersion subjected to heat treatment of first heating up to 60 °C then lowering the temperature under the Krafft temperature of 53 °C. One can clearly discern both water and lipid are now homogeneously distributed and form a continuous, ordered matrix consisting of silk-like aggregates. In some areas the lipid layers form closed, spherical to ellipsoidal shells with a diameter of approximately 20 μm. With increasing surfactant concentration a similar but much denser supramolecular aggregate was observed. Under a light microscope with cross-polarized light, the resulting micrographs typically featured strongly birefringent spherical particles of approximate diameter ranging between 10 and 20 μm. Furthermore, the particles displayed a Maltese cross-like interference pattern which in surfactant dispersions, are indicative for lamellar liquid-crystalline (L_α) materials or multilamellar vesicles, as depicted in Figure 1B. Combined with DSC, SAXS, and viscosity analyses, we can distinguish that the GMS–water dispersion is not only displaying microstructure of lamellar liquid crystal but also exhibiting properties of a gel phase.[7]

As for microbubbles stabilized solely by GMS surfactant, the photomicrographs observed in the ordinary and crossed polarizing mode are shown in Figure 2. The gas phase, which occupies gas volume fraction about ca. 0.76 of the resulting foam, is divided into surfactant-covered bubbles, or gas microcells, whose size ranged from tens of micrometers (Figure 2A). The majority of the bubbles have radii of about 50 μm and are

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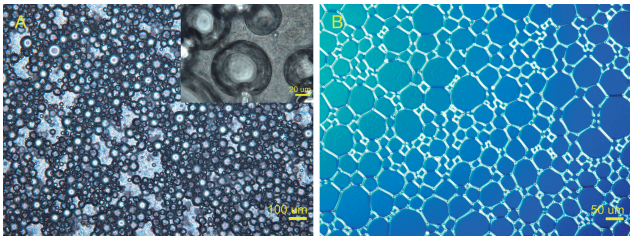

Figure 2. Optical micrographs of foams prepared by GMS solutions. (A) DIC mode; (B) cross polarizing mode.

stabilized by crystallization of lamellar liquid-crystalline phases located at the air/water interface resulting in the formation of a gel phase, which is birefringent as confirmed by optical micrographs viewed under crossed polarizing mode. The lamellar liquid-crystal gel (white) is located at the interface between gas and liquid as presented in Figure 2B. This phenomenon could be explained by the phase behavior of the GMS surfactant solutions as above discussed.

DSC experiments have been performed on microbubble dispersions prepared from commercial monoglyceride and water systems. Figures 3A and B present the thermal behavior of microbubbles immediately made and stored for 5 days, respectively. In this study, microbubbles were prepared from aqueous GMS solution subjected to heat treatment of heating above the Krafft temperature (up to 60 °C) and then cooling down at room temperature, in which the process of melting of β crystal has taken place. When the emulsifier, originally in the β-crystalline conformation, is heated in water (above the Krafft point), a lamellar phase is formed through molecular self-assembly. This consists of nonrigid lipid bilayers separated by water that is dissolved between the polar head groups. Upon cooling (lower than the Krafft point), the lipid chains rearrange into a rigid conformation and the lamellar phase turns into an α gel. The α-gel phase consists of monoglyceride bilayers, whose alkyl chains are partially frozen, separated by water layers. The structure remains similar to the lamellar sheet structure, although the hydrocarbon chains are in a crystalline state. The chains are extended and tilted. It is believed that the water layer in the α gel improves the ability to move the lipid bilayers relative to each other. Thus, these flexible layers can easily cover the bubble surfaces and create a stabilizing film.

It is apparent that only α-gel phase existed within instantly prepared microbubble dispersion because there is not enough time for α gel transforming into coagel, a crystalline phase, consisting of a network of plate-like β crystals.[8] As found in Figure 3A, therefore, two sequences of peaks were observed between 0 and 70 °C. Both the first and second heating curves exhibit identical α-gel transition into L_α phase (Both the same transformation temperature of 53 °C and melting enthalpies of 4.7 J g^{-1}). However, the metastable α-gel phase can be transformed to the coagel phase, on a time scale depending on composition, previous conditions of treatment and storage conditions, which also can incorporate a large amount of water. As a consequence, the coagel phase formation occurred within the prepared foams stored for 5 days, as shown in Figure 3B. The first heating curve presents only one peak corresponding to the melting of coagel phase (melting enthalpies of 9.05 J g^{-1}). In a second heating curve appearing peak indicates that the

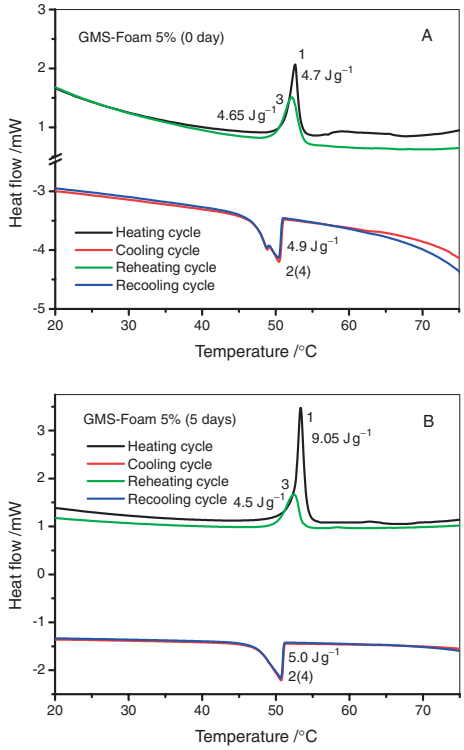

Figure 3. DSC thermograms of aqueous foam stabilized by GMS.

α gel converts into L_α phase (melting enthalpies of 4.5 J g^{-1}). Transition enthalpies and temperatures are shown in Figure 3. The enthalpy of melting of coagel is about twice the value obtained from the melting of α crystals. This difference in melting enthalpies can be employed to monitor the kinetics of the α gel to coagel phase transition. We can conclude from the above analyses, that the α-gel phase plays an important role in stabilization of microbubbles at the initial storage time. As the microbubble dispersions have been stored for a certain time, the α gel may transform into coagel phase under specific conditions, which contributes to the further enhancement in microbubble stability.

The foamability of the saturated monoglycerides in the crystalline β state is very poor (or even no foams could be obtained) due to absence of a surface-active effect. If the β crystals are melted in water and then cooled, an α-crystalline emulsifier is formed, with marked lower interfacial tension displaying surface-active crystals.[9] The α-gel emulsifier could be adsorbed on the air/water interface through vigorous mixing with good foaming characteristics. The crystals at the interface will expose a hydrophobic surface toward the air core and a hydrophilic surface toward water. The formed interfacial membrane may arrest Laplace-pressure-driven dissolution due to the ordered and tight stacking of GMS molecules. This specific structure is also thought to be advantageous for foam stabilization because of its ability to spread onto a surface being firm enough to stabilize the surfaces toward coalescence (see Supporting Information).[13] Therefore, the stability of prepared microbubbles could be improved distinctly with a lifetime up to 10 months longer.

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The α-gel phase formed from monoglycerides is thermodynamically unstable. When stored at room temperature, this phase in turn may transform to the coagel phase, which may take minutes or many months. This is due to capillary forces and because in the aqueous environment the molecules crystallize with their hydrophilic, water-attracting headgroups at the outside of the crystals. As for microbubbles here stored for 5 days, the α gel has converted into coagel phase resulting in enhancement in mechanical rigidity of interfacial film with denser packing (about 18.5 Å^2 cross section per chain) than that of α-gel phase (about 20 Å^2 cross section per chain), which causes strong interchain van der Waals attraction.[10] Furthermore, the birefringence is continuous from one air bubble to the next observed in Figure 2B, suggesting the existence of a continuous soft solid network. The forming three-dimensional networks extend through the continuous phase of the system and further enhance the lifetime of microbubble dispersion system. Interfacial crystallization as well as the formation of a three-dimensional network of GMS in the continuous phase determined the stability against coalescence and viscoelastic character of the microbubbles.

We also measured the viscosity of the prepared foam system. The viscosity of this system (621 mPa s) is lower than that of foams prepared from an aqueous AEO system (1516 mPa s) with the presence of lamellar liquid-crystalline phase.[11] However, the GMS-microbubble stability (even several months) appears significantly higher than that of the latter system (tens of hours). Thus, the present results showed that only viscosity is not directly related to the observed long-term stability of months to years and also demonstrated that the high stability is not a consequence of lamellar liquid-crystalline phase, but because of lamellar liquid-crystal gel.

Based on the above discussion, we propose an interfacial microstructure model on microbubble stabilized by lamellar liquid-crystal gel phase, as depicted in Figure 4. The amphiphilic molecules located at the air/water interface displaying ordered multilayers. The soapy shell has an inner surface and an outer surface. The hydrophilic headgroups keep in contact with the bulk liquid, whereas the hydrophobic hydrocarbon tails point to the gas bubble. With this orientation, the microbubbles are inhibited from coalescence and the diffusion of entrapped gas. The GMS molecules adsorbed at the air/water interface with stacked crystalline monoglyceride and water bilayers exhibiting double effects of lamellar liquid crystal and gel phase on stabilization in microbubbles.[12] The role of the liquid-crystal gel phase in stabilizing a microbubble can be related to its effect on several mechanisms involving the ordered and tight packing of GMS molecules located at the air bubble interface arresting the Laplace-pressure-driven dissolution and the interfacial crystallization as well as the formation of a three-dimensional network of GMS in the continuous phase against the coalescence of the microbubbles. The simplicity and versatility of this approach are expected to aid the formulation of stable wet foams for a variety of applications in materials manufacturing, food, cosmetics, ultrasound imaging, and drug delivery, among others.

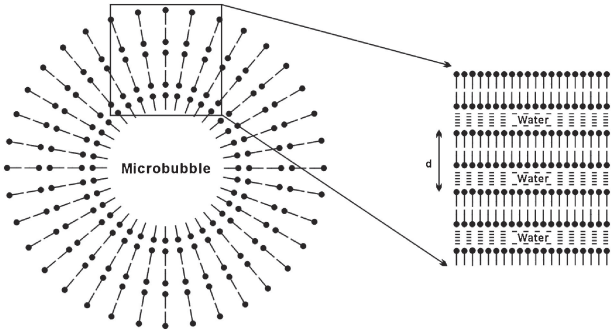

Figure 4. Schematic of the shell surrounding the microbubble.

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13 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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