흐름장에 의한 계면활성제 용액의 미세구조 변화: 유변학적 거동과 응용

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Flow-Induced Microstructure of Surfactant Micellar Solutions: Rheology and Applications

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Introduction

Recently, considerable research efforts have been centered on the studies for predicting the microstructure-macroscopic property relations for microstructured materials under equilibrium and nonequilibrium condition. The microstructured colloidal dispersions include self-assembling complex fluids such as surfactants, block-copolymers and liquid crystals, and are known as *designer soft materials*. The presence of a suspended phase implies a strong interaction between external fields and macroscopic optical, mechanical, or electrical properties. Such a phase provides an opportunity for innovative manipulation of material properties through the understanding and control of the external field-microstructure interaction.

In the present study, we investigated the flow-induced microstructure changes by considering the effects of flow intensity, surfactant concentration, and various additives. The flow-induced microstructure was captured during in *situ* gelation through the sol-gel reaction of an alkoxide in the presence of worm-like micelles. It is well known that surfactant molecules form the worm-like micelles in the presence of the structure-enhancing additives. When the micelles form some types of supramolecular structure under a shearing flow, the structure grows in the direction of flow. As the shear rate increases, the micelles undergo coalescence or stretch in the direction of flow and the shear-induced structure continuously breaks and reforms. General feature of the microstructure evolution is strongly dependent on types of surfactants and additives, their concentrations, temperature, and flow intensity. A similar behaviour has been observed frequently in concentrated particle suspensions, such as shear thinning and thickening [1-2]. The worm-like micelles experience the complicated flow behaviour such as flow-induced coagulation and phase transition, which are strongly governed by the flow intensity, concentrations of constituent substances, and temperature. The rheological and rheo-optical studies have been performed on various sets of surfactants and additives [3]. The flow-induced structure in a dilute solution was associated with the shear-induced gelation in the self-assembly of surfactant molecules, which is accompanied by the shear thickening above a

critical shear rate [4-5].

Recent advances in the optical techniques enable us to measure directly the anisotropic properties such as birefringence and concentration fluctuation induced by an imposed flow. These studies are useful in obtaining the information about microstructural responses of the materials to the imposed flow direction. Most of the rheo-optical studies have been applied to polymer solutions [6], particulate suspensions [2], and structured micellar solutions [5]. Electron microscopy such as transmission electron microscopy, scanning electron microscopy, and optical microscopy is also useful for direct observation of the microstructure without an imposed flow. Several direct observations of flow-induced microstructure of complex fluids were conducted recently by use of optical microscopy in particle/polymer curing system [7], transmission shear microscopy in polymer blends [8], and a complicated freeze-fracture electron microscopy in micellar solution [9]. We investigated the flow-induced microstructure of worm-like micelles either in a shear flow or at equilibrium by *in situ* gelation [10].

Recently, molecular self-assembly of amphiphilics is frequently studied for the design of advanced materials and the fabrication of useful microstructures for advanced materials such as photonic and optoelectronic devices, catalysts, and sensors [11-13]. Many studies on the preparation of mesoporous or microporous materials have used the self-assembled structures of surfactants, block copolymers and organic molecules, especially for their potential applications as thin films, catalysts [14], sorbents and membranes [15]. In particular, many of studies have been performed on the effects of external fields, such as electric field [11], magnetic field [16], and flow field [17] on the synthesis of well-ordered structure for the functional materials. These external fields qualitatively endowed the prepared meso-phase with the long-range alignment and good pore quality. Patterning or orienting the mesoporous phase into a desired arrangement is essential for variety of potential applications. Thus the flow-induced microstructure must be probed by some means to control the materials properties. We discussed in last section the preparation methods of inorganic helical structure which was assisted by Taylor vortex flow.

Experimental

The surfactant used in the present work was cationic cetyltrimethylammonium bromide (CTAB: Sigma) and the structure-enhancing additive was sodium salicylate (NaSal: Aldrich), both used as received. The CTAB concentration was fixed at either 0.005M or 0.05M, and the NaSal concentration was varied with the molar ratio R= [NaSal]/[CTAB] fixed at R=1.0 or R=10.0. In order to capture the microstructure, the silica precursor tetramethyl orthosilicate (TMOS: Aldrich) in hydrochloric acid was selected as a gelation substrate and ammonium hydroxide was used as a catalyst for sol-gel reaction. The sample was prepared in a Couette flow cell between two coaxial cylinders. Shear rate was varied from 0.03 to 15s^{-1}, which was strong enough to induce the microstructure evolution. When the gelation was

completed, the samples were dried under vacuum for 3 hours and prepared for the scanning electron microscope. In addition, to confirm that these textures were formed by the presence of the worm-like micelles, SEM analysis was performed for the samples that were calcined to decompose the worm-like micelles. Calcination proceeded in an electric furnace at 450°C for 10 hours. Rheological properties were measured by using an ARES rheometer with cone-and-plate geometry (50mm diameter, 0.04rad) at room temperature.

For preparation of mesoporous materials, tetraethylorthosilane (TEOS) in hydrochloric acid was used as a precursor of the silica substrate to prepare the silica-micelle meso-phases via sol-gel chemistry. When the helical structure of the worm-like CTAB/NaSal micelles were formed by the coil-spring flow, the silicon alkoxide precursor was added into the flow cell to induce the sol-gel reaction. After the reaction was completed, the template of worm-like micelles was removed by solvent extraction (using ethanol and hydrochloric acid), as well as by calcination in an electric furnace leaving mesopores in their sites.

Results and Discussion

In Fig. 1, the shear viscosity of the equimolar micellar solution is plotted as a function of the shear rate for dilute and semi-dilute regimes. It can be seen that all of the CTAB solutions in the overall concentration range exhibited a typical non-Newtonian behavior of shear thinning. The shear viscosity is increased considerably as the CTAB concentration increases, which is because giant worm-like micelles form the entangled morphology. When CTAB concentration is 0.005M in equimolar solutions, the viscosity initially shear thins at low shear rates, then begins to shear thicken at a certain shear rate, and shear thins again at even higher shear rates. The shear thinning viscosity is clearly indicative of the flow-induced alignment toward the flow direction.

To gain the relationship between the rheological responses of the surfactant solutions and the development of flow-induced structure, the flow-induced microstructure was examined as functions of flow intensity and concentrations. In Figs. 2(a) and (b), the SEM images of the gelified sample was reproduced. It can be readily seen that the silica substrate was aligned to the flow direction in Fig. 2(a). It can be noted that the micron-sized zigzag morphology remained persistent at low shear rates. Thus, the shearing led to the flow-induced textures. The SEM image for the captured microstructure at the shear rate $15s^{-1}$ was shown in Fig. 2(b). The shear rate was above the onset of shear thickening. In this condition, the structure became less ordered due to interlayer coagulation caused by strong hydrodynamic forces.

When the outer cylinder is stationary and the inner cylinder rotates, Taylor instability is most likely to occur. Under these circumstances, the worm-like CTAB micelles are stretched and twisted along the coil-spring streamlines. The flow-induced microstructure of the worm-like micelles acts as a template for the preparation of the helical silica tubules of the mesopores. This method is very promising since a helical structure is easily

formed by the spring-coil flow and the orientational conformation of mesopores is controllable by the flow intensity. In Figs. 3(a) and (b), SEM images were shown in preparation of mesoporous structure with or without Taylor vortex flow.

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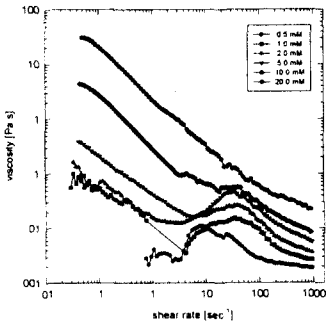
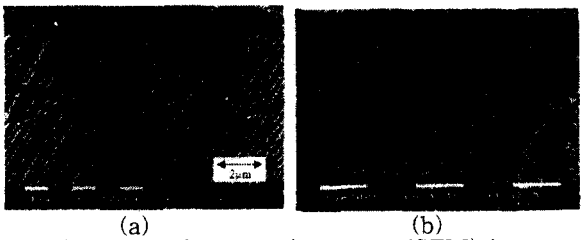
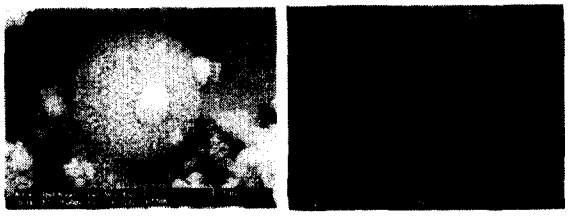


Fig. 1 Shear viscosity is plotted versus shear rate as a function of CTAB concentration. Molar ratio is fixed at R=1.0.



(a) (b)

Fig. 2 Scanning electron microscopy (SEM) images of the captured microstructure. The concentration of CTAB and NaSal were fixed at 0.005M. (a) under a shear rate 0.38s^{-1}; (b) under a shear rate 15 s^{-1}.



(a) (b)

Fig. 3 Scanning electron microscopy images of the preparation of mesoporous structures in the presence of worm-like micelle. The concentration of CTAB and NaSal were fixed at 0.005M. (a) without shear flow (b) Re=640.