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Photoinduced Reversible Change of Fluid Viscosity

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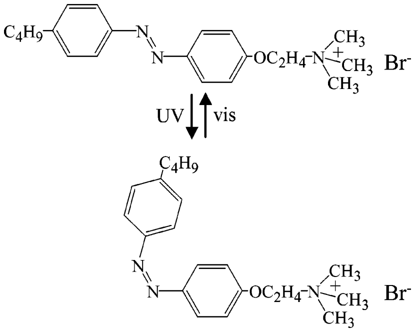
Reversible control of interfacial properties[1−4] and the formation and disruption of aggregates such as micelles[5−9] and vesicles[10−14] of surfactants in solution by external stimuli has attracted considerable attention. Our past studies demonstrated additional applications of the surfactant systems accompanying a dynamic aggregated state change, for example, active control of micellar solubilization[7−9] and the amount of model drug entrapped in vesicles.[12,14] Recently, we reported the control of the viscoelasticity of wormlike micellar solution containing a redox-active ferrocenyl surfactant [(11-ferrocenylundecyl)trimethylammonium bromide, FTMA] and sodium salicylate (NaSal) through the redox reaction of FTMA.[15] While the reduced solution exhibits a remarkable viscoelasticity due to an entangled network of wormlike micelles, the electrolytic oxidation causes the viscosity of the solution to dramatically decrease because of a significant change in aggregation state from wormlike micelles to monomers and/or smaller aggregates. This system will be a promising candidate for novel electrorheological (ER) fluid that would be useful for controlling the release rate of substances, such as dyes and perfumes, and as ink for inkjet printers and flow rate controlling systems.

This communication deals with a “photoresponsive” viscosity system, which is based, in part, on our past report on the viscosity control using a ferrocenyl surfactant.[15] The present system is fundamentally different in utilizing a dynamic change in the aggregated state of the photoresponsive surfactants from previously reported polymer systems[16] and organogels[17] that undergo a photoresponsive gel-to-sol transition. We used an azobenzene-modified cationic surfactant (4-butylazobenzene-4′-(oxyethyl)-trimethylammonium bromide, AZTMA; Scheme 1), which exhibits reversible *trans*−*cis* photoisomerization, as a “photoswitchable” agent. Cetyltrimethylammonium bromide (CTAB) is known to form wormlike micelles in water even at low concentrations when NaSal is added to the solution.[18,19] In the present system, a small amount of *trans*-AZTMA (10 mM) was mixed with aqueous CTAB solution (50 mM), and then NaSal (50 mM) was added to the solution to give viscoelastic wormlike micellar solution. AZTMA alone formed no wormlike micelles in water even in the presence of NaSal. The CTAB/NaSal/AZTMA solution (1 mL) was placed in a quartz cuvette (10 mm × 10 mm) and then irradiated with UV light (260−390 nm) using a Hg−Xe lamp (San-Ei Supercure-203S) while the solution was stirred. UV−vis spectra for the solution (see Supporting Information) showed that UV light irradiation decreased the absorption band at 344 nm assigned to the *trans*-isomer and caused an absorption due to the *cis*-isomer to appear at 440 nm. The irradiation for at least 120 min was required to lead to the photostationary state for AZTMA in our condition. Visible light irradiation (>410 nm) after the UV light irradiation changed *cis*-AZTMA back to its *trans*-isomer, but not completely. However, repeated UV and visible light irradiation resulted in reversible *trans*−*cis* photoisomerization of AZTMA.

Scheme 1 *trans*−*cis* Photoisomerization of AZTMA



Panels a and b of Figure 1 show the photographs of an aqueous CTAB/NaSal/AZTMA mixture before and after UV light irradiation, respectively. The viscosity of the mixture irradiated with UV light (Figure 1b) was obviously lower than that of the nonirradiated one (Figure 1a).

Figure 2 shows the dependence of storage (G') and loss (G'') moduli on angular frequency (ω) measured using a stress-controlled cone-plate rheometer (CSL 100, Carri-Med, Ltd.). Addition of *trans*-AZTMA to wormlike micellar solution of CTAB and NaSal shifted the G' and G'' curves to the low-frequency side, which indicates an enhancement in the degree of entanglement of wormlike micelles. For the nonirradiated solution, a plateau appeared on the G' curve and a maximum on the G'' curve. This viscoelastic behavior corresponds to a Maxwell model behavior as reported for typical wormlike micellar solutions.[18−20] On the other hand, the UV-irradiated solution had no plateau on the G' curve in the measured frequency range. This rheological behavior is similar to that observed for unentangled chain polymer solutions.[21]

We estimated their solution viscosity in terms of the zero shear viscosity (η_0). Figure 3 shows the η_0 values of the mixture measured during the repeated cycles between *trans*-AZTMA and *cis*-AZTMA caused by UV and visible light irradiation. Addition of AZTMA (*trans*-form) to aqueous CTAB/NaSal solution increased its η_0 value from 60 to 100 Pa•s, which is 5 orders of magnitude higher than the viscosity of water. When UV light was irradiated on the CTAB/NaSal/AZTMA (*trans*-form) solution, the η_0 value decreased 4 orders of magnitude (0.1 Pa•s) over that of the *trans*-AZTMA solution. The following visible light irradiation made the viscosity return to the value of the *trans*-AZTMA solution. This η_0 change was completely reversible between the *trans*- and *cis*-AZTMA solutions.

The drastic viscosity change reported here is likely to be attributed to a change in the aggregation state of surfactant

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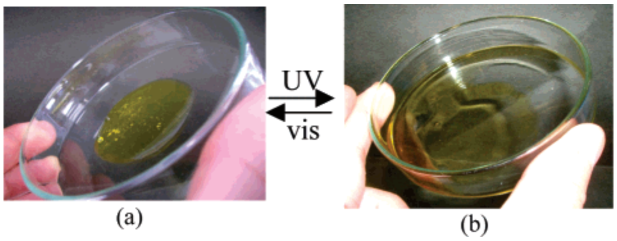

Figure 1. Photographs showing the appearance of aqueous CTAB/NaSal/AZTMA mixture (a) before and (b) after UV light irradiation.

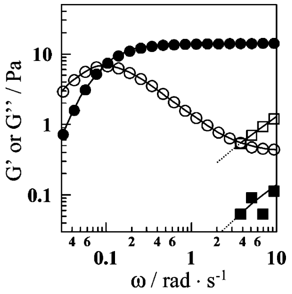

Figure 2. Storage modulus G' and loss modulus G'' as a function of angular frequency ω for aqueous 50 mM CTAB/50 mM NaSal/10 mM AZTMA mixture before (●; G', ○; G'') and after (■; G', □; G'') UV light irradiation.

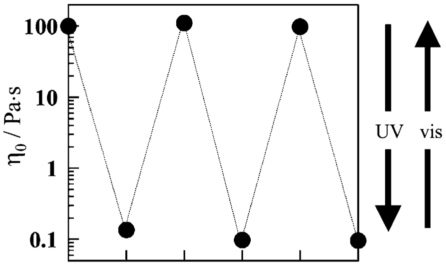

Figure 3. Zero shear viscosities (η_0) of aqueous solution of CTAB(50 mM)/NaSal(50 mM)/AZTMA(10 mM) measured during the repeated cycles of AZTMA between the *trans*-form and *cis*-form. The high values of η_0 correspond to *trans*-AZTMA solution, and the low values correspond to *cis*-AZTMA solution.

molecules. The reversible *trans*−*cis* photoisomerization of AZTMA (Scheme 1) causes changes in the geometrical structure and interfacial properties of the surfactant, thus leading to the reversible formation and disruption of molecular assemblies. *trans*-AZTMA is easily incorporated into wormlike micelles of CTAB and NaSal due to the linear structure of its hydrophobic tail. On the other hand, the bulky structure of *cis*-AZTMA is likely to destroy the network structure of wormlike micelles, and smaller aggregates (probably short rods) are formed in the solution. AZTMA incorporated in wormlike micelles, even though it is a minor component, permits a drastic change in solution viscosity through the *trans*−*cis* photoisomerization. The principle we report here thus can be generalized to other wormlike micellar solutions. We are now investigating changes in the aggregation state by cryo-transmission electron microscopy (cryo-TEM). These results will be reported elsewhere soon.

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Supporting Information Available: UV and visible light irradiation method, and UV−vis spectra and zero shear viscosity for aqueous CTAB/NaSal/AZTMA solution. This material is available free of charge via the Internet at http://pubs.acs.org.

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