



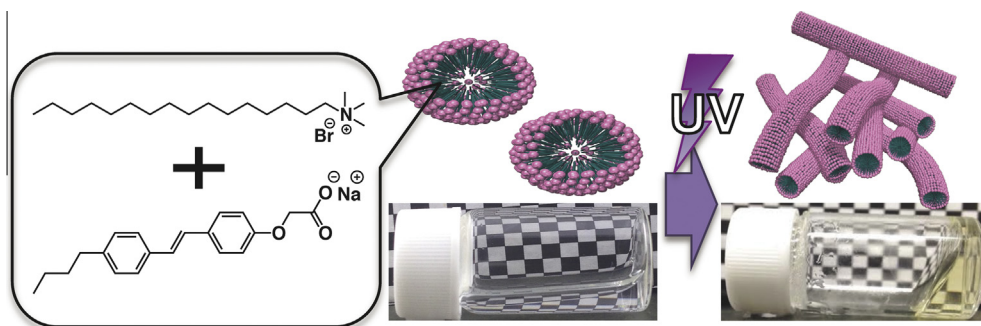
Photoinduced formation of threadlike micelles from mixtures of a cationic surfactant and a stilbene amphiphile



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GRAPHICAL ABSTRACT



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ABSTRACT

This study examined the influence of ultraviolet (UV) irradiation on aqueous surfactant solutions containing an anionic stilbene derivative (sodium [4-[(E)-2-(4-butylphenyl)ethenyl]phenoxy]acetate; C4StilNa) as a photoresponsive skeleton. Prior to UV irradiation, an aqueous solution of cetyltrimethylammonium bromide (CTAB) and C4StilNa was a low-viscosity fluid forming spheroidal micelles. Exposure of the low-viscosity fluid to UV light resulted in the formation of threadlike micelles and an increase in the viscosity of the aqueous CTAB/C4StilNa solution. ¹H nuclear magnetic resonance spectroscopy indicated that the photochemically induced isomerization and dimerization reactions of C4StilNa molecules had occurred in the aggregates due to UV irradiation. Overall, the structural transformation of the stilbene groups in the C4StilNa molecules with the photochemical reactions leads to an increase in the critical packing parameter and consequently a photoinduced transition of spheroidal micelles to threadlike micelles.

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1. Introduction

Threadlike micelles are entangled three-dimensionally in aqueous solutions and organic solvents. Therefore, the presence of threadlike micelles imparts viscoelasticity to the solutions. Mixtures of cationic surfactants with a long hydrophilic chain

and specific salts (e.g. sodium salicylate [1]) tend to form threadlike micelles. These threadlike micelles can be applied as drag-reducing agents in pipelines [2]. The formation of threadlike micelles in fluids leads to a transition from turbulent flow to laminar flow. Turbulent flow is effective in the transfer and diffusion of heat and material, whereas the laminar flow limits the loss of energy by friction between the fluid and the tube walls. Control of these flows is important in many engineering fields. The formation and disruption of threadlike micelles can lead not only to

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changes in the viscosities of the aqueous surfactant solutions, but also to a transition between turbulent and laminar states.

The application of external stimuli, e.g. pH variations [3,4], temperature [5,6], redox reaction [7], and light irradiation [8–10], to threadlike micelle solutions can result in the formation and disruption of threadlike micelles containing stimuli-responsive compounds. In particular, the use of light as an external stimulus is clean compared to the other stimuli and it is easy to handle temporally and spatially. Azobenzene, coumaric acid, and cinnamic acid derivatives have been used as light-responsive compounds in the control over the formation and disruption of threadlike micelles. Many studies have examined ways of modulating the formation and/or disruption of threadlike micelles containing mixtures of cetyltrimethylammonium bromide (CTAB) and azobenzene-containing amphiphiles [11,12] or cinnamic acid derivatives [13–15]. These studies reported that threadlike micelles form prior to exposure to ultraviolet (UV) light. The UV irradiation of aqueous solutions of threadlike micelles disrupts these micelles. However, there are no reports of the formation of threadlike micelles using a stilbene derivative as the light-responsive compound. Scheme 1 presents the photochemical reactions of stilbene derivatives. A number of photochemical reactions are induced by UV light [16,17]. (*E*)-Stilbene (*trans* isomer) is isomerized to (*Z*)-stilbene (*cis* isomer) by exposure to UV light of appropriate wavelength. Subsequent UV irradiation induces a conrotatory electrocyclic reaction in dihydrophenanthrene, and dehydrogenation to phenanthrene occurs in the presence of oxidants (e.g. iodine and oxygen). In addition, UV irradiation leads to a photochemical cycloaddition reaction, resulting in the dimerization of stilbenes. In other words, (*E*)-stilbene reacts photochemically through (*Z*)-stilbene to a dimer. The morphological transition of aggregates

formed from the surfactant with a stilbene skeleton has been reported [18,19].

A previous paper reported the formation of threadlike micelles by UV light irradiation in a mixed aqueous solutions containing CTAB and a light-responsive amphiphile, sodium [4-(4-butylphenoxy)acetate (C4AzoNa) [20]. The phenomenon resulted from a geometrical structural transformation with the photoisomerization of azobenzene groups from *trans* to *cis* isomers in aggregates formed from the mixture. In the present study, it is hypothesized that photochemical reactions of the stilbene derivative can be a candidate to induce the formation of threadlike micelles. Therefore, as a test molecule, a novel anionic stilbene derivative, sodium [4-[(*E*)-2-(4-butylphenyl)ethenyl]phenoxy]acetate (C4StilNa, Scheme 2), in which the azobenzene group in C4AzoNa is replaced with a stilbene group, was synthesized. This paper reports the influence of UV irradiation on aqueous solutions of CTAB/C4StilNa mixtures. The formation of threadlike micelles was induced by UV irradiation.

2. Experimental section

2.1. Materials and sample preparation

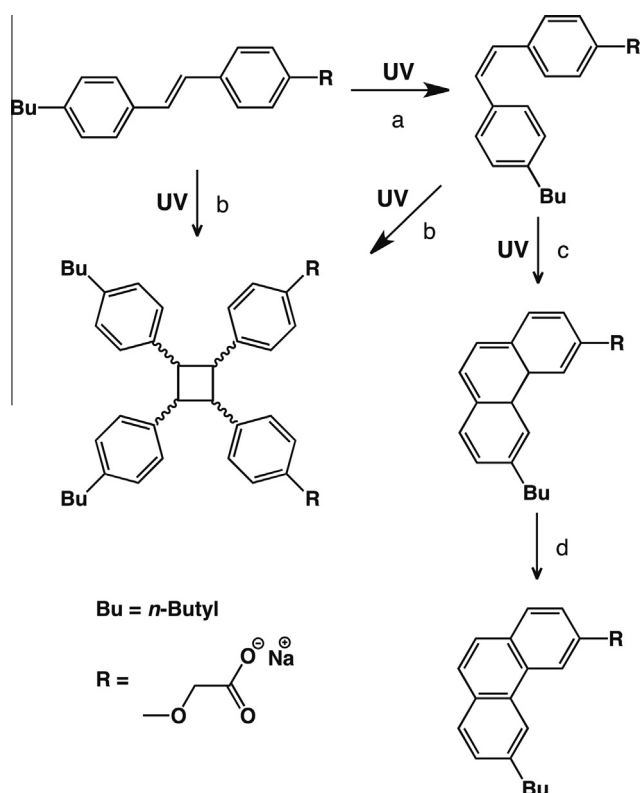
Cetyltrimethylammonium bromide (CTAB; reagent grade, >98.0%) was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan) and used without purification. Sodium [4-[(*E*)-2-(4-butylphenyl)ethenyl]phenoxy]acetate (C4StilNa) was synthesized according to Scheme 2. A 100 mM sample of an aqueous CTAB solution was prepared in high-purity H₂O (Milli-Q pure water; resistivity (*R*) = 18 MΩ cm, surface tension (γ) = 72.8 mN/m at 20 °C) and added to the desired amount of C4StilNa. These aqueous CTAB/C4StilNa solutions were stored at 30.0 ± 0.1 °C for at least 24 h to ensure equilibration. Each measurement was then carried out.

2.2. C4stilNa synthesis

C4StilNa was synthesized by the Williamson synthesis of 4-[(*E*)-2-(4-butylphenyl)ethenyl]phenol, which was prepared by Heck coupling with 4-vinylphenylacetate and *p*-butyliodobenzene, using ethyl bromoacetate, followed by hydrolysis in a sodium hydroxide solution (Scheme 2). 4-Vinylphenyl acetate (reagent grade, >98.0%) and ethyl bromoacetate (reagent grade, >98.0%) were purchased from Tokyo Chemical Industry Co., Ltd. *p*-Butyliodobenzene (reagent grade, 97.0+%) and 4-(dimethylamino)butyric acid hydrochloride were obtained from Wako Pure Chemical Industries, Ltd. (Tokyo, Japan). All other materials for synthesis of C4StilNa were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). The ¹H nuclear magnetic resonance (NMR) chemical shifts were determined by reference to the residual proton in CDCl₃ and *d*₆-DMSO (CDCl₃: 7.26 ppm and *d*₆-DMSO: 2.50 ppm [21]). The mass spectrometry (MS, JEOL JMS-SX102A) measurements were performed using the fast atom bombardment (FAB) method.

2.2.1. 4-[(*E*)-2-(4-butylphenyl)ethenyl]phenol (1)

The reaction mixture of 4-vinylphenylacetate (4.64 g, 28.6 mmol), *p*-butyliodobenzene (5.00 g, 19.2 mmol), 4-(dimethylamino)butyric acid hydrochloride (3.6 mg, 1.4 mol%), palladium(II) acetate (5.6 mg, 1.3 mol%), potassium carbonate (5.30 g, 38.3 mmol), and *N*-methyl-2-pyrrolidone (20 mL) was heated for 20 h at 130 °C. The crude product was extracted from the reaction mixture using chloroform. The resulting chloroform solution was washed with dilute hydrochloric acid and brine. After drying with anhydrous magnesium sulfate, the solvent (chloroform) was evaporated. The crude product was purified by column chromatography



Scheme 1. Photochemical reaction of the stilbene derivative, C4StilNa, by UV irradiation: (a) (*E*)/(*Z*) isomerization, (b) cycloaddition (dimerization), (c) conrotatory electrocyclic cyclization, and (d) subsequent dehydrogenation in the presence of oxidants.

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