Formation of an Organic Thin Film by Photochemical Isomerization of a Surfactant with a Spiropyran Moiety

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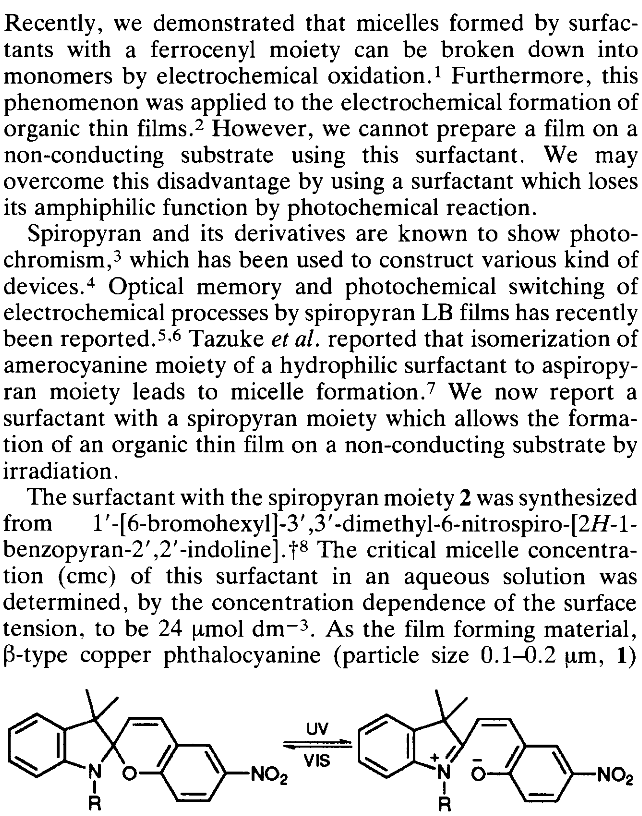
Copper phthalocyanine **1** thin film is prepared by irradiating an aqueous dispersion containing a surfactant with a spiropyran moiety **2**, ferrous sulfate and dispersed **1**.

Recently, we demonstrated that micelles formed by surfactants with a ferrocenyl moiety can be broken down into monomers by electrochemical oxidation.[1] Furthermore, this phenomenon was applied to the electrochemical formation of organic thin films.[2] However, we cannot prepare a film on a non-conducting substrate using this surfactant. We may overcome this disadvantage by using a surfactant which loses its amphiphilic function by photochemical reaction.

Spiropyran and its derivatives are known to show photochromism,[3] which has been used to construct various kind of devices.[4] Optical memory and photochemical switching of electrochemical processes by spiropyran LB films has recently been reported.[5,6] Tazuke *et al.* reported that isomerization of amerocyanine moiety of a hydrophilic surfactant to aspiropyran moiety leads to micelle formation.[7] We now report a surfactant with a spiropyran moiety which allows the formation of an organic thin film on a non-conducting substrate by irradiation.

The surfactant with the spiropyran moiety **2** was synthesized from 1′-[6-bromohexyl]-3′,3′-dimethyl-6-nitrospiro-[2*H*-1-benzopyran-2′,2′-indoline].†[8] The critical micelle concentration (cmc) of this surfactant in an aqueous solution was determined, by the concentration dependence of the surface tension, to be 24 μmol dm^{-3}. As the film forming material, β-type copper phthalocyanine (particle size 0.1–0.2 μm, **1**) was used, which is not soluble in water. Compound **1** may be dispersed by the surfactant, since this pigment is not soluble in most common organic solvents. A dispersion containing 2 mmol dm^{-3} **2**, 20 mmol dm^{-3} $FeSO_4$ and 10 mmol dm^{-3} **1** was prepared by sonicating for 10 min and stirring for 1 h. The dispersion was then irradiated from the side of the polyester plate by UV light (500 W Xenon lamp).



2: R = $(CH_2)_6(OCH_2CH_2)_{16.2}OH$

Scheme 1

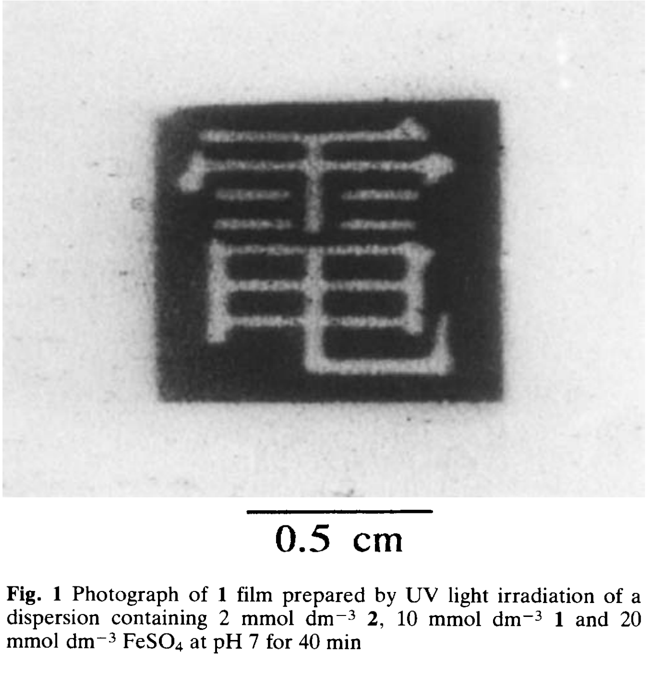


Fig. 1 Photograph of **1** film prepared by UV light irradiation of a dispersion containing 2 mmol dm^{-3} **2**, 10 mmol dm^{-3} **1** and 20 mmol dm^{-3} $FeSO_4$ at pH 7 for 40 min

A transparent blue film was formed on the polyester plate (thickness 0.1 mm) by irradiation with UV light of this dispersion for 40 min. A light image was also formed when a photomask was used. On the other hand, a film was not formed without $FeSO_4$. Absorption spectrum of an aqueous dispersion prepared by washing this film with 5 mmol dm^{-3} Brij 35 aqueous solution consisted of broad peaks and was very similar to that for a 5 mmol dm^{-3} Brij 35 aqueous dispersion of **1**.[9] The scanning electron micrograph of a cross section of **1** film shows that the film is of uniform thickness (approximately 1 μm for 40 min irradiation) and is composed of 0.1–0.2 μm particles which are the same as that used for the dispersion. This agreement indicates that this film is mainly made of **1**, and the crystalline form of **1** is maintained throughout the film preparation processes.

Such a film formation may be explained by a similar mechanism as that for electrochemical formation using the surfactant with ferrocenyl moiety:[2] surfactant **2** is isomerized to merocyanine derivative by irradiation which may form a complex with $FeSO_4$[3] and loses its function as a surfactant to adsorb on the surface of **1** particle due to enhancement of the tail group's hydrophilicity. The surfactant adsorbed on the particles are desorbed, which leads to the deposition of the particles on the substrate.

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Footnote

† Spectroscopic data for **2**: ^1H NMR (300 MHz, $CDCl_3$) δ 5.8–8.0 (9H, aromatic hydrogens), 3.5–3.7 (64.9H, $-OCH_2CH_2O-$), 3.1–3.4 [4H, $=NCH_2-$, $-(CH_2)_2CH_2O-$], 1.6–1.8 [4H, $-(CH_2)_2CH_2CH_2O-$, $=NCH_2CH_2-$], 1.2–1.4 [10H, $-(CH_2)_2CH_2(CH_2)_2-$, $-CH_3$]; ^{13}C NMR (300 MHz, $CDCl_3$) δ 18.9, 24.9, 25.1, 27.9, 28.6, 42.7, 51.6, 60.5, 69.1, 69.3, 70.3, 71.8, 105.9, 114.7, 117.7, 118.5, 120.8, 121.2, 121.9, 125.0, 126.9, 127.4, 135.1, 140.1, 146.3, 158.9.

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