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Formation of Polystyrene Latex Thin Films by Micelle Disruption Method

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Synopsis. Polystyrene latex thin films were prepared on an indium tin oxide electrode by controlled-potential electrolysis of an aqueous solution containing a nonionic surfactant with a ferrocenyl moiety and dispersed latex particles. Thermal treatment rendered the film more transparent, and made the ITO electrode covered with the film inert against electrochemical reaction of hexacyanoferrate(II) due to the disappearance of the intergranular space in the film.

Recently we presented a novel technique for electrochemical formation of organic thin films of a wide variety of pigments using a nonionic surfactant with a ferrocenyl moiety (FPEG) (Fig. 1).[1—5] In these system the pigment is dispersed by the surfactant and not incorporated into the micelles.[3,5] The pigment particles are released when the surfactants adsorbed on the particles are electrochemically oxidized and finally the particles deposited on the electrode. In this paper, we report the preparation of thin films of polystyrene latex using this technique. This demonstrates a potentiality of the technique for preparing thin films of a wide variety of polymers on an electrode.

Experimental

Materials. The preparation of poly(oxyethylene)(12.3)-11-ferrocenylundecyl ether (FPEG) is described in previous papers.[1,4] Poly(oxy-1,2-ethanediyl)(20)sorbitanemono-9-octadecenate (Tween 80, Tokyo Chemical Co.) was used without further purification. Sodium dodecyl sulfate (SDS, Wako Pure Chemical Industries) was recrystallized from ethanol. β-Type copper phthalocyanine (Dainichiseika Color and Chemicals, **3**) and 4,4′-diamino-1,1′-bianthracene-9,9′,10,10′-tetrone (Ciba-Geigy, **4**) were used as blue and red pigments, respectively.

Preparation of Polystyrene Latices. Two polystyrene latices were prepared by an aqueous phase dispersion polymerization technique using hydrogen peroxide as the initiator in the following manner.[6] Two grams of styrene, 16 ml distilled water, 2 ml methanol, and 0.15 g Tweeen 80 for latex **1** (0.30 g SDS for latex **2**) were emulsified ultrasonically using a Honda 100 Watt Ultrasonic Multi Cleaner for 1 h. A 0.4 ml aliquot of 20% hydrogen peroxide was added to the emulsion. The emulsion was kept in a water bath maintained at 70±2 °C for 6 h. The resulting precipitate was removed by filtration.

Purification of Latices. The latices obtained as above contain oxidation products and the surfactant, which were removed as follows. The latices were redispersed by sonication with a small amount of distilled water (0.1 M LiBr aqueous solution for latex **2**; 1 M=1 mol dm^{-3}). Excess methanol was added to the latex dispersion, and this solution was then centrifuged (Kokusan Cetrifuge H-13B) at 3000 rpm for 30 min. This treatment was repeated five times. Finally, the latex was dried at 50 °C for a week.

The average sizes of latices **1** and **2** particles, as determined by scanning electron micrography (SEM) on a JEOL JSM-T20, were 0.2 and 0.08 µm, respectively. Both latices were almost monodisperse.

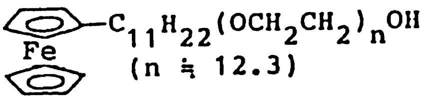

Fig. 1. Molecular structure of the nonionic surfactant with a ferrocenyl moiety (FPEG).

Preparation of Latex Dispersion. Fifty milligrams of powdery latex was added to a 10 ml aqueous solution containing the surfactant and 0.1 M LiBr, then the mixture was sonicated for 30 min followed by stirring for three days. This dispersion was used for cyclic voltammetry and film formation.

The electrochemical cell and purification of an indium tin oxide (ITO) electrode were described previously.[3,4] The electrochemical measurements and film formations were done at 25 °C under N_2.

Results and Discussion

Film Formation. The cyclic voltammogram (CV) of an aqueous solution containing 0.2 mM FPEG and 0.1 M LiBr at a glassy carbon electrode showed a quasi-reversible step with a $E_{1/2}$ of +0.20 V vs. SCE.[1,3,4] The CV of an aqueous solution containing 5 g dm^{-3} latex **1**, 0.2 mM FPEG, and 0.1 M LiBr showed also a step at the same potential as above. The film was formed by controlled-potential electrolysis of an aqueous solution containing 5 g dm^{-3} **1**, FPEG, and 0.1 M LiBr at a potential positive of the $E_{1/2}$ of the surfactant by about 0.1 V. This shift has been explained in terms of decrease in the concentration of free surfactant to a level below the cmc with concomitant desorption of the surfactant.[5] Taking account this shift into account, the potential for the electrolysis was maintained at +0.50 V vs. SCE for 120 min.

Whitish films were obtained by the electrolysis. These films were smooth and adhered better to the ITO electrode than the pigment films prepared by the same method. The adhesion force of the latex **2** film was stronger than that of the latex **1** film, probably due to a smaller size of **2** particles. Smaller particles exhibit stronger adhesion among particles and to the electrode. The optimum concentrations of FPEG were 0.6 and 0.8 mM for **1** and **2** latices, respectively, in view of the amount and smoothness of the film deposited on the ITO electrode. This slight difference arises from the

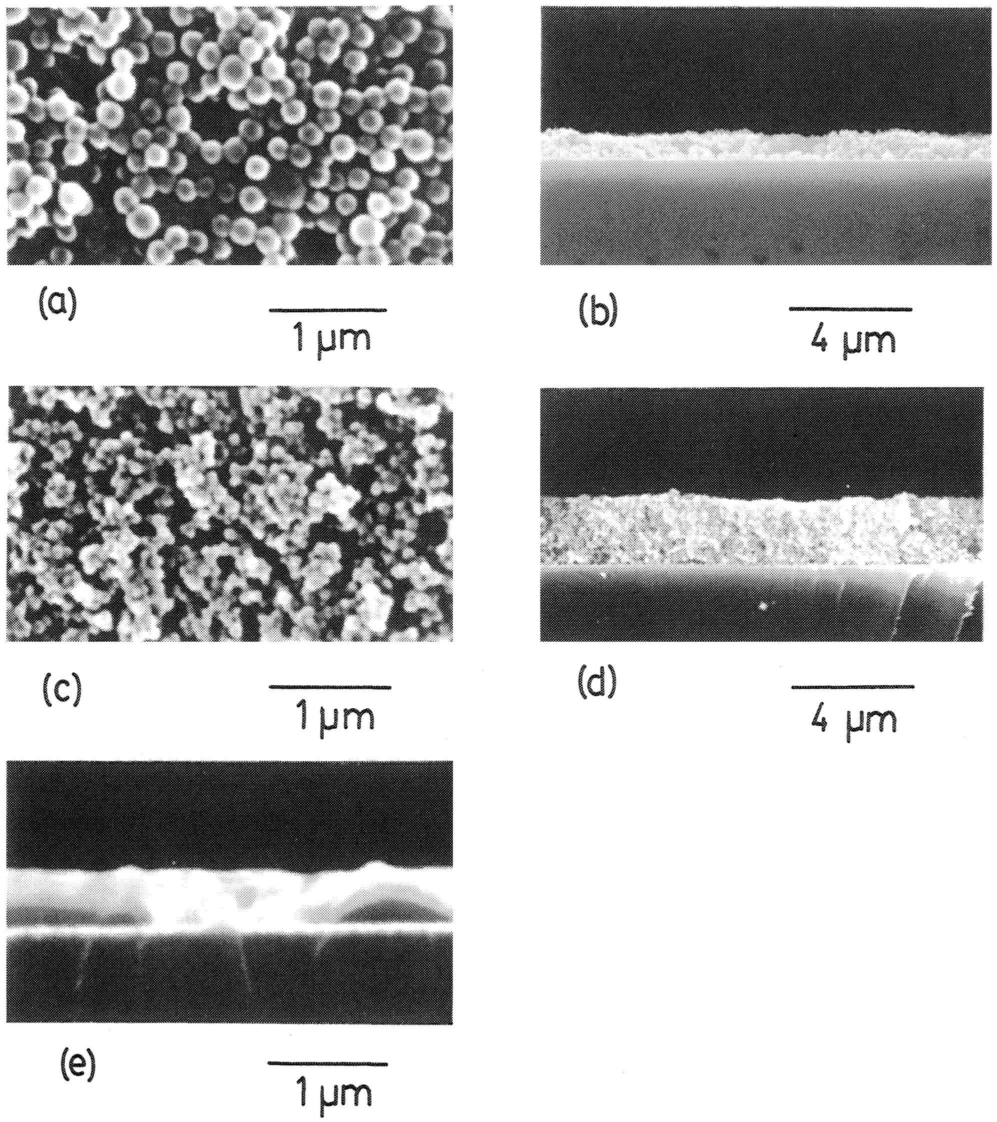

Fig. 2. Scanning electron micrographs of surface (a, c) and cross section (b, d) of the films prepared by electrolysis of an aqueous solution containing 5 g dm^{-3} latex **1** (**2**), 0.6 (0.8) mM FPEG, and 0.1 M LiBr at an ITO electrode at +0.50 V vs. SCE for 120 min (a) and (b); **1**, (c) and (d); **2**, (e); **1** film after treatment at 130 °C for 40 min.

larger area of the **2** particle surface than that of the **1** particle surface. Dispersion of particles with a larger area requires a corresponding larger amount of the surfactant. A lower and higher concentration of the surfactant than the optimum one yielded coarse and thinner films, respectively.

Figure 2 a—d shows the SEM photographs of latex **1** and **2** films prepared under optimum conditions. The films are composed of latex particles added to the solution. The cross section of these films (Fig. 2 b and d) demonstrates that these films are uniform with thickness of a few µm.

Treatment of latex **1** and **2** films at 130 °C for 40 min improved their transparency. The cross section of the latex **1** film (Fig. 2 e) shows that the latex particles disappeared completely.

The CV of an aqueous solution containing 2 mM $K_4Fe(CN)_6$ and 0.1 M KCl at the latex **1** film electrode without thermal treatment gave a reversible one-electron step at +0.42 V vs. SCE, and the peak current was 89% of that without the film at a scan rate of 50 mV s^{-1}. Thermal treatment stated above reduced the peak current to 7% of that at the bare electrode. This electrochemical inertness is due to the disappearance of intergranular space in the latex film. This phenomenon was applied to fabrication of the following films containing pigments **3** and **4**. A reddish mixed film of **1** with pigment **3** was prepared using an aqueous solution containing 3 g **1** dm^{-3}, 1.7 mM **3**, 1 mM FPEG, and 0.1 M LiBr. A bluish film was superposed on this reddish film by controlled-potential electrolysis of an aqueous solution containing 3 g **1** dm^{-3}, 2.3 mM **4**, 1 mM FPEG, and 0.1 M LiBr. On the other hand, the bluish **4** film was not superposed on the reddish film when the latter film had been thermally treated. In this case, the bluish film was formed only on a bare ITO electrode which had been protected by coating with an adhesive tape in the first film formation. Otherwise, to prevent the superposition of the film, the relevant part of the reddish film has to be electrically disconnected by etching of the ITO electrode.

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