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Electrochemical Formation of Polymer Thin Films by Disruption of Micellar Complex

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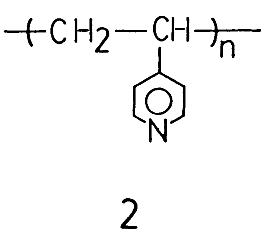
Polymer thin films of poly(4-vinylpyridine), and copolymer of methyl methacrylate and methacrylic acid were prepared by electrolysis of an aqueous solution containing a surfactant with ferrocenyl moiety and corresponding polymer. The film thickness increased linearly with the amount of electricity. The morphology of the films was investigated by scanning electron microscopy.

Polymer films have been prepared by casting, Langmuir-Blogett's,1) electrochemical polymerization,2) chemical vapor deposition (CVD), sputtering, and vapor deposition methods.3) For casting and Langmuir-Blogett's methods, polymers are used as the source materials, while for electrochemical polymerization, CVD, and sputtering methods, monomers are polymerized on substrates. Though the vapor deposition method is one of the most powerful methods for preparing inorganic and organic films, the use of it has been confined to a few polymers4-6) because most of polymers are thermally unstable.

Recently, we reported the preparation of organic thin films by a novel method using an aqueous micellar solution of (11-ferrocenylundecyl)trimethylammonium bromide (1^+). This method is based on the controlled release of a micelle-solubilized substance onto an electrode; the micelles formed by 1^+ are broken up into the monomers (1^{2+}) when 1^+ are oxidized electrochemically.7,8) A solubilizate is then released from the micelles and deposited on the electrode. The organic films of charged (1,1'-didodecyl-4,4'-bipyridinium dibromide)9) and uncharged (1-phenylazo-2-naphthol)10) materials have been prepared using this method.

The purpose of this letter is to show that this method used for preparing films of low molecular weight organic compounds is also useful in preparing polymer films. In the present investigation, poly (4-vinylpyridine) (2) and a copolymer (3) of methyl methacrylate with methacrylic acid were used as the film-forming materials. The former polymer was chosen because cast films of 2 have



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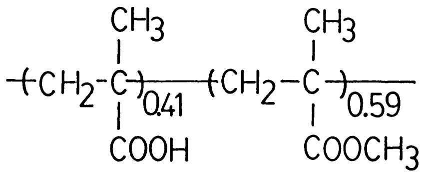

$$\text{-(}CH_2\text{-}\underset{COOH}{\overset{CH_3}{C}}\text{)}_{0.41}\text{-(}CH_2\text{-}\underset{COOCH_3}{\overset{CH_3}{C}}\text{)}_{0.59}$$

3

been used as coatings that have an attractive ion-exchange capacity and a counter ion retention property.$^{11)}$ The latter polymer was chosen because the cast films of poly(methyl methacrylate)$^{12)}$ and copolymers of methyl methacrylate with methacrylic acid$^{13)}$ have been utilized as electron beam resists.

Polymer **2**, molecular weight 50000, was obtained from Polysciences Inc. and used as supplied. Copolymer **3** was prepared by a method previously described in the literature.$^{14)}$ The molecular weight of **3** was determined to be 10^6 by gel permeation chromatography. Copolymer **3** was found to contain 41 mole percent of methacrylic acid using a standard titration technique,$^{15)}$ which was supported by IR and ^{13}C NMR analyses.$^{15)}$ The preparation of $\mathbf{1}^+$ has been reported in our previous paper.$^{8)}$ Its critical micelle concentration in 0.2 M Li_2SO_4 aqueous solution was determined to be 0.07 mM by dye solubilization method.

The electrochemical measurements were carried out at 25 °C under a nitrogen atmosphere. An indium tin oxide electrode (ITO) and a saturated calomel electrode (SCE) were used as a working and a reference electrode, respectively. Film thicknesses were determined by interferometric measurements.$^{16)}$

Cyclic voltammograms for (A), an aqueous solution containing 2.0 mM (1 M = 1 mol dm^{-3}) $\mathbf{1}^+$, 0.2 M Li_2SO_4, and 7.9 μM (3.8 mM monomer units) **2** and (B), an aqueous solution containing 3.0 mM $\mathbf{1}^+$, 0.2 M Li_2SO_4, and 8.2 nM (79 μM monomer units) **3** exhibited a redox wave with a half-wave potential of +0.15 V vs. SCE. This wave was attributed to the redox couple $\mathbf{1}^+/\mathbf{1}^{2+}$.$^{8)}$ Polymers **2** and **3** were electrochemically inactive in the potential range of -1.0 to +1.0 V vs. SCE. Film-formation experiments were carried out in stirred solutions by controlled-potential electrolyses at +0.3 V vs. SCE, where $\mathbf{1}^+$ was oxidized to $\mathbf{1}^{2+}$. The films prepared by the electrolyses of solution (A) and (B) were white and transparent, respectively.

Cyclic voltammograms of the film-coated ITO in 0.2 M Li_2SO_4 aqueous solutions exhibited a redox wave at about +0.23 V which may be due to the surfactant incorporated in the films. However, the value of the peak current for this wave was reduced to ca. 10% of its initial value after 20 redox cyclings between 0 and +0.5 V vs. SCE at a sweep rate of 20 mV s^{-1} in 0.2 M Li_2SO_4 aqueous solution. This suggests that ca. 90% of the surfactant

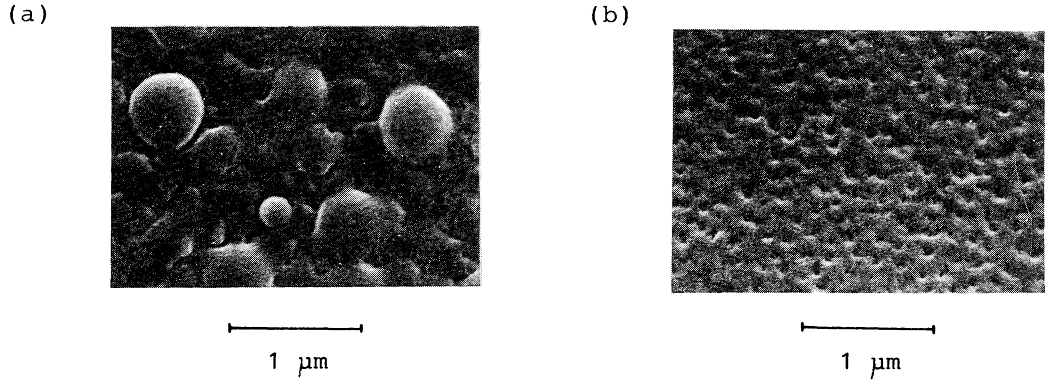

Fig. 1. Scanning electron micrographs (SEM) of the films prepared from (a) the solution (A) and (b) the solution (B).

incorporated in the films was removed by the treatment. All the films were cleaned by this post treatment and successive washing with water.

Figure 1 shows the scanning electron micrographs (SEM) of the films obtained by the electrolysis of the solution (A) (Fig. 1a). The amount of electricity passed through the ITO, Q, was 0.014 C cm^{-2}. Bulgy domains (the light area) and mossy domains (the dark area) were observed in the SEM image. Figure 1b shows a SEM image of a film obtained after the electrolysis of the solution (B) (Q = 0.1 C cm^{-2}). The integrity of the film was breached in places and the porous substructure became visible.

The absorption peaks in the electronic absorption spectrum of an ethanol solution prepared by washing the film prepared from solution (A) (Q = 0.019 C cm^{-2}) were the same as those in the spectrum of an ethanol solution of 0.25 μM 2, but were different from those in the spectrum of 1^+ under identical conditions. These results support the hypothesis that the thin film formed on the ITO is made up of 2.

FT-IR spectrum of the film prepared from the solution (B) (Q = 0.31 C cm^{-2}) was almost the same in positions as IR spectrum of 3 in a KBr pellet, indicating that the film on the ITO is made of 3.

Figure 2 shows the plots of the film thickness, d, vs. Q for the 2 film (●) and the 3 film (o). The value of d increased linearly with Q for both of the plots, indicating the possibility that control of the film thickness is governed by the value of Q.

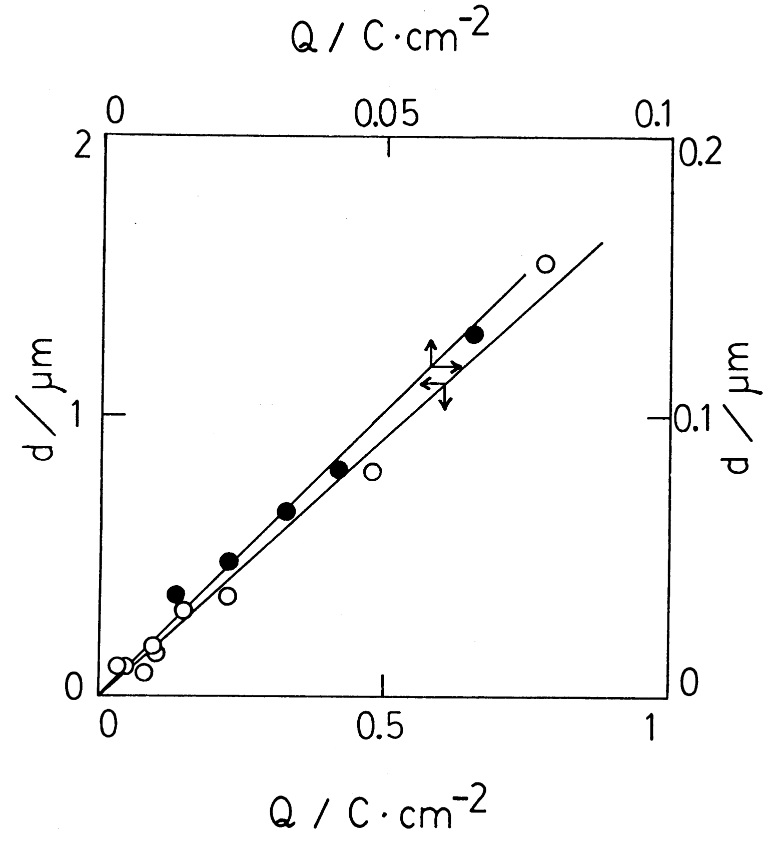

Fig. 2. The dependence of the film thickness, d, on the amount of electricity passed through the ITO, Q. ●: the 2 film; o: the 3 film.

Usually, water-insoluble polymers and cationic surfactants form complexes.$^{17)}$ Polymer 2 (or 3) solubilized in the 1^+ micellar solution may form a complex with the 1^+ micelles. Based on this assumption, the film formation may be explained by the following processes: (1) Mass transfer of the 2 or 3 complex and 1^+ from the solution bulk to the ITO, (2) Oxidation of the 1^+ surfactant bound to the polymer to 1^{2+} at the ITO surface, (3) Desorption of 1^{2+} from the polymer owing to the enhancement in the electrostatic repulsion among positively charged tail groups and in the hydrophilic character of 1^{2+},$^{8)}$ (4)

Deposition of the polymer on the electrode surface, and (5) Mass transfer of $\underset{\sim}{1}^{2+}$ to the solution bulk.

Present experiments show that such an electrochemical method also serves as a tool for preparing films of polymer materials which are soluble in a micellar solution. Considering the fine control of film thickness by controlling the amount of electricity, this method is promising in preparing polymer films and modified electrodes.

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