Ultrasonic Effects on Electroorganic Processes V. Preparation of a High Density Polyaniline Film by Electrooxidative Polymerization under Sonication

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1 INTRODUCTION

Supramolecular properties of polymers are originated from their highly-regulated molecular and morphological structures. Electroactive films of aromatic polymers deposited electrooxidatively on anodes have received much interest from fundamental and practical aspects, not only since they are electroconducting but also since they have unique chemical, physical and/or biological properties. Hence, if the structure of the films could be highly controlled, they might have supramolecular properties. From this point of view, this work aimed to develop a method for preparing the two- and three-dimensionally dense and uniform films.

Willcut and McCarely^{1,2)} made the first successful attempt to prepare a two-dimensionally uniform and defectless monolayer film of polypyrrol by electropolymerizing the corresponding LB-monolayer of a pyrrol monomer adsorbed on an anode. However, in the LB-method, it is unavoidable to use the pyrrol having extremely bulky hydrophobic substituents which may dilute supramolecular properties of the film formed.

A variety of ultrasonic effects on electrochemical processes have been reported so far.³⁾ Particularly, the effects on electroorganic reactions seem to be significant as demonstrated in our previous work.⁴⁻⁷⁾ Recently, we have also reported that a uniform and defectless monolayer film of poly (o-mercaptoaniline) without any bulky substituents can be formed in the electropolymerization of the corresponding monolayer self-assembled on an anode under ultrasonic irradiation.⁸⁾ Osawa *et al.*⁹⁾

reported the formation of a macroscopically homogeneous polythiophene film at high polymerization rate under ultrasonic irradiation during the electropolymerization. In the present work, we succeeded in preparing a three-dimensionally dense multilayer film of polyaniline having an high density (About 10 times as high as an ordinary one) by irradiating ultrasounds.

2 EXPERIMENTAL

The electropolymerization of aniline was cyclic-voltammetrically carried out in an ordinary procedure under electrolytic conditions as follows :¹⁰⁾ Anode and cathode, Pt plates (1 x 1cm) ; cell, undivided type ; temperature, $25 \pm 1^\circ\text{C}$; electrolyte, 0.1M (M = mol dm⁻³) aniline / 4M HCl (aqueous solution) ; potential scanning range, 0.0 ~ 1.0V vs. SCE ; scanning rate, 0.1 Vs⁻¹. Ultrasound (20 kHz, 7 W) was irradiated on the anode from a stepped horn (Diameter, 0.6 cm) during the polymerization. After the polymerization, a polyaniline film formed on the anode was rinsed with 4M HCl and then was dried at room temperature. Thickness of the film was measured by a polarization microscope and / or a roughness meter. Amount of the film was estimated from weight gain of the anode. Molecular weight of polyaniline was measured by GPC (Polystyrene standard) in THF.

3 RESULTS AND DISCUSSION

Figure 1 shows cyclic voltammograms in the course of polymerization of aniline at 50 times of potential scanning without and with sonication. Although their shapes seem to be almost similar to each other, the oxidation and reduction peak currents (Electroactivity) with sonication are much smaller than those without sonication. Almost equal currents to those at 50 times of scanning with sonication was obtained at 15 times without sonication. This

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Fig. 1 Cyclic voltammograms in the course of polymerization of aniline at 50 times of potential scanning

fact indicates that the polymerization rate with sonication is lower than that without sonication. In this point, an ultrasonic effect on the polymerization of aniline seems to be quite different from that of thiophene which is known to be preferably polymerized under irradiation of ultrasounds.⁹⁾ This also suggests that the mechanism of the ultrasonic effect may be different between the polymerization of aniline and thiophene.

Surface of the film polymerized with sonication was visibly bright, while that without sonication seemed dull. Figure 2 shows SEM photographs of the films dedoped. A porous structure with grains is observed in the film polymerized without sonication, but there is no grain in that with

sonication. The film prepared with sonication is so thin that linear traces derived from polishing scars of the Pt substrate appear on the photograph.

Molecular weight of polyaniline film prepared with sonication was a little lower than that without sonication, but the both polyanilines had similarly sharp (Monomodal) molecular weight distributions ($M_w/M_n \approx 2$). The film polymerized with sonication was much thinner than that without sonication. The films prepared at 50 times of scanning with sonication and at 15 times without sonication have an almost equal two-dimensional density in electroactivity ($3.8 \times 10^{-3} \text{ A cm}^{-2}$) as described above, while three-dimensional densities in the electroactivity (7.6 A cm^{-3}) and gravity ($10 \times 10^{-2} \text{ g cm}^{-3}$) of the former film are ca. 9 and 8 times, respectively, as high as those of the latter. Electroconductivity of the film prepared with sonication could not be measured because of difficulty of peeling off as a test piece from the anode substrate.

Fig. 2 SEM photographs of polyaniline films prepared at 50 times of potential scanning without and with sonication

Table 1 Properties of polyaniline films prepared without and with sonication.

Sonication	Potential scanning / time	Surface appearance		Molecular weight			Thickness / μm	Density / $\times 10^{-2} \text{ g cm}^{-3}$
		Visibly	SEM	Mw	Mn	Mw / Mn		
Without	50	Dull	Porous	3560	1800	1.98	120	3.7
Without	15	Dull	Porous	_{a)}	_{a)}	_{a)}	40	1.1
With	50	Bright	Dense	2090	1050	2.00	5	10

a) Not measured.

Table 1 summarizes some properties of the films. It should be noted that the densities of the film polymerized with sonication are remarkably high compared with those without sonication. This fact suggests that the film has a highly-regulated molecular and morphological structure and consequently may exhibit supramolecular properties. A further investigation for verification of the supramolecular properties and formation mechanism of the film is in progress.

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