# Preparation and Application of Electroconductive Films Electrooxidatively Polymerized in Ultrasonic and Centrifugal Acceleration Fields

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We succeeded in preparing three-dimensionally dense multilayer films of polyaniline, polythiophene and polypyrrole by the electrooxidative polymerization of the corresponding aromatic monomers under ultrasonic irradiation. As a practical guideline, it was indicated that aniline is polymerized in an acidic electrolytic solution under irradiation of ultrasound with a power higher than the cavitation threshould to form a highly uniform and dense polyaniline films available for electronic devices such as an electrolytic capacitor. On the other hand, a defectless monolayer films of poly(o-mercaptoaniline) could be prepared by polymerzing an o-mercaptoaniline adsorption monolayer self-assembled on a substrat electrode under ultrasonic irradiation. Centrifugal efffects on the polymerization of aniline leading to formation of the corresponding electroconductive polyaniline film were examined under a centrifugal acceleration force of 1 to 300 g. The polymerization rate, chemical and physical properties and morphological structure of the film were greatly affected by the cetrifugal field. The effects occurred anisotropically with regard to direction of the working electrode surface.

Key words: electroconductive film, electrooxidative polymerization, ultrasonic irradiation, centrifugal acceleration field

### 1. INTRODUCTION

Properties of polymer films 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<sup>[11]</sup> made the first successful attempt to prepare a two-dimensinally uniform and defectless monolayer film of polypyrrol by electropolymerizing the corresponding LB-monolayer of a pyrrole monomer adsorbed on an anode. However, in the LB-method, it is unavoidable to use the pyrrole 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<sup>[2-6]</sup>. Particularly, the effects on electroorganic reactions seem to be significant as demonstrated in our previous work<sup>[7-22]</sup>.

Osawa et al.<sup>[23]</sup> reported the formation of a macroscopically homogeneous polythiophene film by irradiating ultrasound during the electropolymerization. In the present work, we attempted to prepare three-dimensionally uniform

and dense multilayer films of polyaniline, polythiophene and polypyrrole using ultrasounds with powers higher than the ultrasonic cavitation In addition, the formation of a threshould uniform and defectless monolayer film of polyaniline without any bulky substituents was also examined by electropolymerizing the corresponding monolayer self-assembled on an anode under ultrasonic irradiation. Furthermore, it was attempted to electropolymerize aniline and thiophene in a centrifugal acceleration field to obtain the films with unique properties.

### 2. EXPERIMENTAL

The electropolymerization of aniline was cyclic-voltammetrically carried out in an ordinary procedure under electrolytic conditions as follows : anode and cathode, Pt plates (1 x 1cm) ; cell, undivided type ; temperature, 25 ± 1°C ; electrolyte, 0.1 M (M = mol dm<sup>-3</sup>) aniline / 4M HCl (aqueous solution) ; potential scanning range, 0.0-1.0V vs. SCE; scanning rate, 0.1 V s<sup>-1</sup>. Ultrasound (20 kHz, 7 W) was irradiated on the anode from a stepped horn (diameter, 0.6 cm) the during the polymerization. After polymerization, a polyaniline film formed on the anode was rinsed with 4 M 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.

An Au electrode (5 x 5 mm) was polished with

alumina powder (0.6  $\mu$ m), then was washed with conc. H<sub>2</sub>SO<sub>4</sub> and 0.2 M NaOH, and finally was rinsed with distilled water in an ultrasonic cleaning bath. Selfassembly of a monolayer of o-mercaptoaniline was accomplished by soaking the Au plate in a 10 mM omercaptoaniline / CH<sub>3</sub>CN solution for 60 min in the ultrasonic cleaning bath and the resulting Au plate was used as a working electrode for polymerizing omercaptoaniline self-assembled monolayer after being rinsed with acetone and hexane in the cleaning bath. The counter electrode was a Pt plate (10 x 10 mm). For polymerization of o-mercaptoaniline, the Au electrode was repeatedly potential-scanned between -0.2 and 1.0 V vs. SCE at 0.1 V s<sup>-1</sup> of scan rate in 0.5 M H<sub>2</sub>SO<sub>4</sub>.

Figure 1 shows centrifugal facilities equipped with a cylindrical electrolytic cell which is made with polyacrylate resin and has a 14 mm diameter and 7 mm length. Platinum discs (for working and counter) and an Ag | AgCl electrode (for reference) are electrically contacted with a potentio / galvanostat via silver rotating rings and carbon brushes. The entire cell assembly is suspended from the lid of a centrifuge tube with a polyethylene line. Surfaces of the platinum electrodes A and B face inward and outward, respectively, to the centrifugal acceleration force, as shown in Fig. 1. The forces on electrodes A and B are calculated to be 315 and 290 g, respectively, at 1500 rpm. One of the electrodes was covered with an insulating sheet remaining bare in the central part (6 mm diameter, 0.28 cm<sup>2</sup> area) as a working electrode. Electrode C is the electrode A at 1 g of the earth's gravity. After bubbling Ar gas into a 0.1 M aniline + 4 M HCl solution, it was injected into the cell. The electrooxidative polymerization of aniline was carried out by a potential scanning method at 50 cycles in a range of 0.1 - 1.1 V vs. Ag | AgCl at 0.1 V s<sup>-1</sup>, unless stated otherwise.



Fig.1 Centrifugal facilities equipped with an electrolytic cell.

The electropolymerization of thiophene and pyrrole was carried out in experimental procedures similar to those for aniline described above, unless otherwise stated.

## 3. RESULTS AND DISCUSSION

3.1 Polymerization under Ultrasonic Irradiation Figure 2 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 fact indicates that the polymerization rate with sonication is lower than that without sonication.



Fig. 2 Cyclic voltammograms in the course of polymerization of aniline at 50 times of potential scanning.

Surface of the film polymerized with sonication was visibly bright, while that without sonication seemed dull. Figure 3 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 sonicatiaon. 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  $(Mw/Mn \approx 2)$ . 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 electroactivity  $(3.8 \times 10^{-3} \text{ A cm}^{-3})$ <sup>2</sup>) as described above, while three-dimensional densities in the electroactivity (7.6 A cm<sup>-3</sup>) and gravity  $(12 \times 10^{-2} \text{ g cm}^{-3})$  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.3 SEM photographs of polyaniline films prepared at 50 times of potential scanning without and with sonication.

Table I 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.

As shown in Tables II and III, highly dense films of polythiophene and polypyrrole, respectively, could be obtained under ultrasonic irradiation.

 Table I. Thickness and density of polyaniline films

 prepared with and without ultrasonic irradiation

Ultrasonic	Thickness	Density	
irradiation	/ μm	Gravitational	Electrochemical
		/ x 10 <sup>-2</sup> g cm <sup>-3</sup>	/C cm <sup>-3</sup>
With	0.7	12	230
Without	19	2.6	100

Table II. Thickness and density of polythiophene films prepared with and without ultrasonic irradiation

Ultrasonic	Thickness	Density	
irradiation	/ µm	Gravitational	Electrochemical
		/ x 10 <sup>-2</sup> g cm <sup>-3</sup>	/C cm <sup>-3</sup>
With	0.6	11 .	88
Without	26	2.2	14

Ultrasonic	Thickness	Density	
irradiation	/ μm	Gravitational	Electrochemical
		$/ x 10^{-2} g cm^{-3}$	/C cm <sup>-3</sup>
With	0.7	10	210
Without	1.2	6	140

3.2 Polymerization of Monolayer Self-assembled under Ultrasonic Irradiation



Fig. 4 (a) Cyclic voltammograms of *o*-mercaptoaniline monolayer self-assembled, and (b) and (c) peak current  $(i_p)$  and potential  $(E_p)$  of poly(*o*-mercaptoaniline) monolayer, respectively, at different scan rates.

In the electropolymerization of an o-mercaptoaniline monolayer self-assembled on an Au anode, a set of redox peaks observed around 0.4 V, increased by repeating the scan, and saturated at the tenth scan, as shown in Fig. 4 (a).

Redox properties of the poly(*o*-mercaptoaniline) monolayer prepared above were examined by cyclic voltammetry at various scan rates. Fig. 4 (b) indicates that the anodic and cathodic peak currents (Ipa and Ipc, respectively) are proportional to the scan rate, while the anodic and cathodic peak potentials (Epa and Epc, respectiely) are independent on the scan rate as shown in Fig. 4 (c). The formation of poly (*o*-mercaptoaniline) monolayer could be reconfirmed by these facts.

Integration of the anodic and cathodic peaks indicates that surface coverages with aniline units are estimated to be 5.9 and  $6.0 \times 10^{-10}$  mol cm<sup>-2</sup>. These values seem to be reasonable as those for monolayers on an Au electrode, and also indicate a high reversibility for redox of the poly (o-mercaptoanililline) monolayer prepared.

3.3 Polymerization in Centrifugal Acceleration Field

The polymerization rate of aniline increased and decreased at centrifugal acceleration forces of 315 and 290 g on electrodes A and B, respectively, compared with electrode C at 1 g, as shown in Fig. 5. It should be noted again that the direction of the force to the surface of both electrodes is reversed. Therefore, it is suggested that the present anisotropical centrifugal effect is not caused by hydrostatic pressure approximately estimated to be about 1.2 and 1.0 atm on electrodes A and B, respectively, at 300 g. The shape of the second oxidation-reduction peak seems to be very slightly different between either electrode A or B and electrode C. It is also interesting to note that a decrease in the polymerization rate is observed under ultrasonic irradiation which is regarded to generate a mechanical energy field. Furthermore, it may be stated that a local and periodic shockwave acceleration is generated by ultrasonic cavitation which causes high speed jetstreams in a liquid-solid interface. As mentioned above, the comparison of the centrifugal effect with the ultrasonic one should be useful for a further mechanistic discussion.

Some properties of the polyaniline films are also greatly affected by the centrifugal field as summarized in Table IV. Additionally, the molecular weight is almost the same in all the polyanilines, while chemical bonding of the polyaniline molecules and doping current of the polyaniline films are also considerably affected by the field.

Table IV. Properties of polyaniline films prepared at 50 cycles of potential scanning

Electrode	Centrifugal acceleration force / g	Thickness / µm	Electrochemical density /C cm <sup>-3</sup>
A	- 315	13	89
В	290	9	59
С	1	14	65

The properties of polythiophene films prepared in the centrifugal acceleration field are shown in Table V.

Table V. Properties of polythiophene films prepared at 50 cycles of potential scanning

Electrode	Centrifugal	Thickness	Electrochemical
	acceleration	/μm	density /C cm
	force / g		
A	315	6	87
В	290	4	21
С	1	8	37



Fig. 5 Cyclic voltammograms during electrooxidative polymerization of aniline at 50 cycles of potential scanning at various centrifugal acceleration forces.

### 4. UTILIZATION OF POLYMER FILMS

As described above, the polymer films exhibit some unique physical and chemical properties, therefore their possible utilizations are expected as follows.

4.1 High-Performance Electrochemical Capacitor and Polymer Battery

It is noted that the polymer films prepared in ultrasonic and centrifugal fields have extremely high gravitational and electrochemical densities which are indispensable properties to not only high-performance but also ultra-micro capacitors and batteries. Consequently, the application to the capacitors is in progress.

### 4.2 Supramolecular Device

Since defectless monolayer polymer films sometimes have supramolecular functions, the films polymerized on substrates by the pre-sonication method may be applied to supramolecular devices.

#### 4.3 Molecule-recognizing Sensor

The polymer films prepared in centrifugal fields have highly regulated chemical structures, and such films may be used as molecule-recognizing sensors.

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