

New Methodologies for Preparation of Highly -Regulated Structure Films of Conducting Polymers

Mahito Atobe and Toshio Fuchigami

Department of Electronic Chemistry, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8502, Japan

INTRODUCTION

Generally, properties of electroconducting polymer films are originated from their chemical (molecular) and physical (morphological) structures. In this point of view, it should practically be required that the structures of the polymer films can be controlled purposively for their utilization. However, few methods have been developed for controlling the physical structures so far, though the chemical ones can easily be controlled by changing molecular structures of the corresponding monomers and by selecting electrolytic conditions and procedures for the polymerization. From this aspect, we developed new methodologies for controlling the physical structures of the electroconducting polymer films by using ultrasound, centrifugal acceleration force, and ionic liquids, respectively, in the present work.

RESULTS AND DISCUSSION

1. Polymerization under Ultrasonication¹⁾

We succeeded in preparing a three-dimensionally uniform and dense film of polyaniline by the electrooxidative polymerization under sonication. The film surface was visibly bright and the SEM observation indicated a non-porous structure without grains.

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.

Very uniform and highly dense films of electropolymerized thiophene and pyrrole could be also obtained under sonication.

Table 1 Thickness and density of polyaniline films prepared with and without sonication

Sonication	Thickness / μm	Density	
		Gravitational / $\times 10^{-2} \text{ g cm}^{-3}$	Electrochemical / C cm^{-3}
With	0.7	12	230
Without	19	2.6	100

50 cycles of potential scanning in a range of 0 - 1.0 V vs. SCE at 100 mV s^{-1} in 0.1 M aniline + 4 M HCl aqueous solution.

2. Polymerization in Centrifugal Acceleration Field²⁾

Centrifugal acceleration force was produced by centrifuge facilities equipped with an electrolytic cell for the polymerization, as shown in Fig. 1. Two types of platinum electrodes such as the electrode A and B were used as a working electrode. Surfaces of the electrodes A and B face inward and outward, respectively, to the centrifugal acceleration force, as indicated in Fig. 1.

The rate of the electrooxidative polymerization of aromatic compounds like aniline, thiophene and pyrrole, to lead formation of the corresponding electroconductive

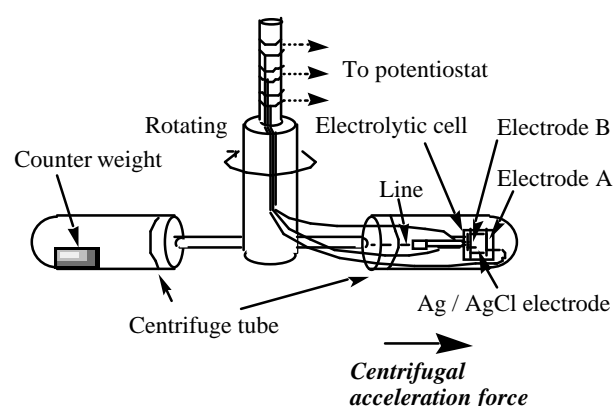


Fig. 1 Centrifuge facilities equipped with an electrolytic cell.

polymer films, was found to be increased on the electrode A, and decreased on B. This kind of an anisotropic phenomenon suggests that the centrifugal effect is caused by other than high static pressure. In addition, the chemical and physical properties and morphological structures of the films were also greatly affected by the centrifugal field.

3. Polymerization in Ionic Liquids

Ionic liquids are room temperature molten salts and have many interesting properties as electrolytes such as high ionic conductivity, thermal stability, non-flammability, non-volatility, and wide potential window. From this aspect, we focused on ionic liquids as a new electrolyte for the electrooxidative polymerization.

Fig. 2 shows SEM photographs of polypyrrole films prepared in an aqueous electrolyte and an ionic liquid like imidazolium trifluoromethanesulfonate. Large grains are observed in the film polymerized in the aqueous electrolyte, but there is no grain in that in the ionic liquid and surface of the film is very smooth.

It was also found that the use of the ionic liquid as an electrolyte could regulate the morphological structure of polyaniline and polythiophene.

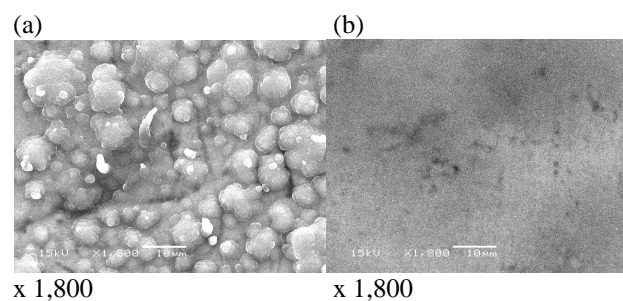


Fig. 2 SEM photographs of polypyrrole films prepared in (a) 0.1 M imidazolium trifluoromethanesulfonate / H_2O and (b) imidazolium trifluoromethanesulfonate (neat condition).

The authors are grateful to Prof. T. Nonaka of Tsuruoka National College of Technology and also to Dr. Ishii, Ms. M. Sekido, and K. Sekiguchi of Tokyo Institute of Technology for their helpful cooperations in experimental work and discussion.

References

- (1) M. Atobe and T. Nonaka, *Trans. MRS-J*, **2000**, 25, 81.
- (2) M. Atobe, S. Hitose and T. Nonaka, *Electrochem. Commun.*, **1999**, 1, 278.