Electrooxidative Copolymerization of Aniline with *o*-Aminobenzonitrile in Centrifugal Fields

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It was demonstrated for the first time that centrifugal effects controlled not only the electrooxidative copolymerization ratio of aniline and *o*-aminobenzonitrile but also the morphology of the copolymer films.

In recent years, a variety of experiments in microgravity fields have received much attention from broad areas in science and technology. Although such fields can be generated by means of free fall, parabolic flight and artificial satellite, the experiments are costly and require huge facilities, and often last only a very short time.[1] Nevertheless, a number of experimental results obtained in microgravity fields suggest a new concept, namely that the gravity is not constant but variable when governing phenomena.[2]

Following the above point of view, the application of acceleration and deceleration forces stronger than the Earth's gravity (1 *g*) have naturally been considered.[3] Hence the experiments in high gravity fields can be much more easily and cheaply performed by using centrifuges which generate a centrifugal acceleration force as high as several hundreds (100 *g* values). The intensity of the force is very uniform and stable, and can also be continuously and precisely controlled in arbitrarily small increments by adjusting the length and rotation speed of the arm.

In a centrifugal field, the local flow of fluids occurs owing to convection, acceleration gradient, the Coriolis force, etc. Therefore, centrifugal effects on physical and chemical phenomena, particularly caused by mass transport, should be interesting from basic and practical aspects. However, it is noted that investigations of centrifugal effects on physical phenomena and chemical processes have rarely been reported except in spin-coating,[4] mechanical erosion,[5] spin-etching[6] and crystal growth.[7]

In the present work, we improved a commercially available centrifuge with a 17 cm of arm to generate a stable acceleration force of about 300 *g* during preparative electrolysis, and demonstrated clear and significant centrifugal effects on the electrooxidative copolymerization of aniline with *o*-aminobenzonitrile (*o*-ABN) leading to the formation of the corresponding copolymer film on the anode surface.

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 electrodes) are electrically contacted with a 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 faces inward and outward, respectively, to the centrifugal acceleration force, as shown in Figure 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^2 area) as a working electrode. Electrode C is electrode A at 1 *g* of the Earth's gravity.

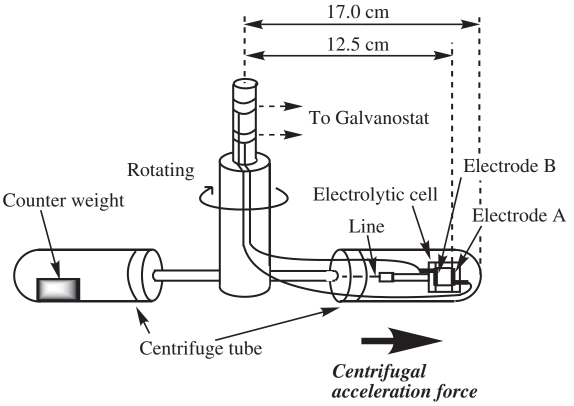

Figure 1. Centrifuge facilities equipped with an electrolytic cell.

After bubbling Ar gas into an electrolyte (1 M $HClO_4$ aqueous solution; $1\,M = 1\,mol\,dm^{-3}$) containinig aniline/*o*-ABN comonomers with arbitrary comonomer feed ratios, it was injected into the cell. The total concentration of the monomer was kept at 0.5 M. The electrooxidative copolymerization of aniline with *o*-ABN was carried out galvanostatically at $10\,mA\,cm^{-2}$ by passing 10 C at room temperature.

The proportion of *o*-ABN units in the copolymer film deposited on the anode was determined by an established method[8] using IR measurement. Experimental errors (deviation of data) were ±5%.

The specific density of *o*-ABN was measured by means of a pycnometer.

The copolymer film was also subjected to scanning electron microscopy (SEM).

Figure 2 shows a relationship between the proportion of *o*-ABN units in the copolymer film formed on the anode and the comonomer feed ratio in the electrolyte. Although the copolymerization ratio usually depends on the comonomer feed ratio as shown in curve (c) in Figure 2, the proportion of *o*-ABN units was increased and decreased at centrifugal forces of 315 *g* and 290 *g* on electrodes A and B, respectively, compared with electrode C at 1 g over a wide range of feed ratio: Especially at the 50% feed ratio both the increase and decrease in the proportion were remarkable. 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 was 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*.

A similar interesting centrifugal effect at 50 mol% of

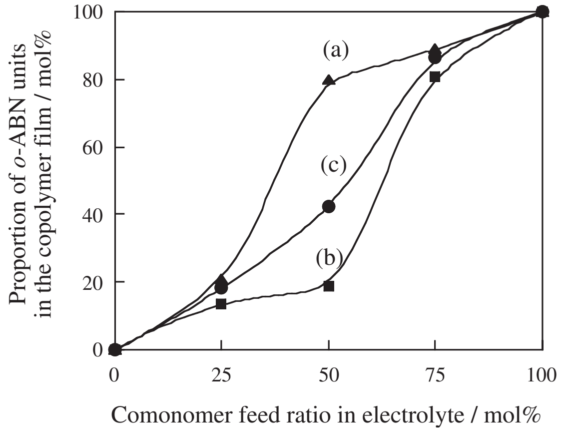

Figure 2. Relationship between the proportion of *o*-ABN units in the copolymer film formed on the anode and the comonomer feed ratio in electrolyte: (a) at 315 *g* on electrode A, (b) at 290 *g* on electrode B and (c) at 1 *g* on electrode C.

comonomer feed ratio was observed in wide ranges of centrifugal acceleration force as shown in Figure 3. The proportion is correspondingly increased and decreased on the electrodes A and B, respectively, with an increase in force, although the comonomer feed ratio was as constant as 50 mol%. This fact strongly supports a clearly and significantly anisotropical effect with regard to the direction of the force to the electrode surface.[9] It is well known that the copolymerization ratio is generally controlled by the feed ratio and the reactivities of comonomers. This result is the first example to control successfully the copolymerization ratio by using centrifugal effects. This interesting result can be explained in terms of the different specific densities of monomers (aniline: 1.022 g cm^{-3} at 25 °C;[10] *o*-ABN: 1.285 g cm^{-3} at 25 °C) and their oligomers.

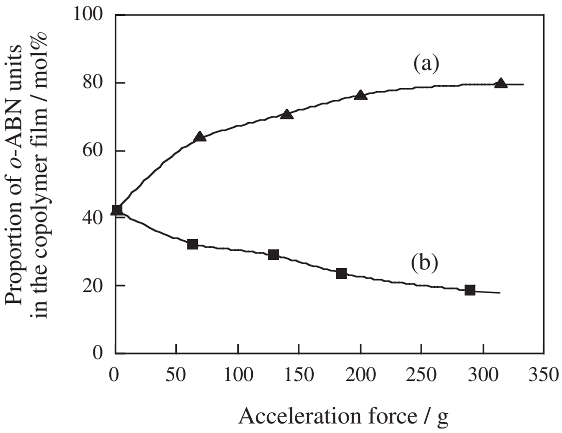

Figure 3. Influence of centrifugal force on the proportion of *o*-ABN units in the copolymer film formed on the anode: (a) on electrode A and (b) on electrode B.

From SEM observation, it was also found that the surface morphology of the copolymer films is greatly affected by the centrifugal effect, i.e. the surface structure of films deposited on electrodes A and B is smooth and rough, respectively, compared with that on electrode C.

Thus, the centrifugal effect can be usefully applied to control the proportion of each monomer unit in a copolymer film and the morphology of films.

A further investigation from mechanistic aspects is in progress.

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