## Application of Magnetically Simulated Microgravity for Preparation of Liquid and Solid Thin Films

Yoshifumi Tanimoto,<sup>\*1</sup> Hiromi Yamamoto,<sup>1</sup> Yoshihisa Fujiwara,<sup>1</sup> Masao Fujiwara,<sup>1</sup> and Akio Katsuki<sup>2</sup> <sup>1</sup>Graduate School of Science, Hiroshima University, Kagamiyama, Higashi-Hiroshima 739-8526 <sup>2</sup>School of General Education, Shinshu University, Asahi, Matsumoto 390-8621

(Received February 4, 2008; CL-080133; E-mail: tanimoto@sci.hiroshima-u.ac.jp)

Liquid thin films having 13–25-mm diameter of water, ethanol, benzene, etc., which cannot be prepared under the earth's surface gravity, were prepared on a metallic ring using magnetically simulated microgravity. In a magnetic field, poly-(vinyl alcohol) and poly(acrylic acid) solid thin films of 20-mm diameter were prepared, for the first time, from liquid films of the respective aqueous solutions.

A magnetic field is useful as an important tool to manipulate various chemical and physical processes in materials science.<sup>1</sup> An important utilization of strong magnetic fields is the generation of microgravity. Microgravity can be simulated using a strong magnetic field, as first reported for magnetic levitation of diamagnetic materials in 1991.<sup>2</sup> However, few studies related to the use of simulated microgravity have been reported,<sup>3–6</sup> despite their many potential applications.

Our group started investigation of chemical, physical, and biological phenomena of diamagnetic materials under magnetically simulated microgravity using a compact magnet, which can be used easily in a chemistry laboratory.<sup>6</sup> For instance, photoinduced convection of benzene and water solutions of photochromic compounds is affected remarkably by simulated microgravity, <sup>6a,6e</sup> X-ray spectroscopic qualities of protein crystal are improved by crystallization under magnetically simulated microgravity,<sup>6b</sup> and plastic chips can be separated using magnetically simulated microgravity.<sup>6c</sup> In previous papers,<sup>6g,6h</sup> we reported magnetic field effects on the surface phenomena of water and showed that a 25-mm-diameter water liquid thin film can be prepared using magnetically simulated microgravity, although a film of this size cannot be prepared under the earth's surface gravity. This paper reports for the first time, the preparation of polymer solid thin films, which have heretofore not been producible under the earth's surface gravity, using magnetically simulated microgravity.

A superconducting magnet (JMTD-LH15T40; Jastec, Inc.) was used for our experiment.<sup>6h</sup> This magnet had a room-temperature vertical-bore tube of 40-mm diameter. Its maximum magnetic flux density and the maximum magnetic force field (i.e., the product of magnetic flux density and its gradient) were, 15 T and 1500 T<sup>2</sup>·m<sup>-1</sup>, respectively.

Commercial distilled water, ethanol, methanol, benzene, poly(vinyl alcohol) (PVA; Wako Pure Chemical Industries Ltd., polymerization degree = about 1500), and poly(acrylic acid) (PAA; Wako Pure Chemical Industries Ltd., about 25%, polymerization degree = 8000–12000) were used as received.

Metal rings ( $\phi = 13$ , 20, and 25 mm) were made from a tin-coated copper wire ( $\phi = 1$  mm). Liquid films were prepared by soaking the ring in solvent or solution in a plastic vessel placed in the bore tube, where the magnetic force field is about

 $-1200\,T^2\cdot m^{-1};$  they were held in a magnetic field (about  $-900\,T^2\cdot m^{-1}).$  Solid polymer films were prepared by drying the liquid films in the magnetic field overnight.

To examine the potential application of magnetically simulated microgravity, preparation of liquid thin films of some solvents and solutions was attempted. Table 1 presents a list of solvents and solutions whose thin films are prepared using magnetically simulated microgravity, although no film of such size can be prepared under the earth's surface gravity. In the case of water, a large film ( $\phi = 25 \text{ mm}$ ) was prepared in the magnetic field, whereas a film larger than  $\phi = 13 \,\mathrm{mm}$  could not be prepared under the earth's surface gravity. Its surface area was about four times larger than that of the film prepared under the earth's surface gravity. It was mechanically stable even after it was taken from the bore tube. Liquid films ( $\phi = 13 \text{ mm}$ ) of ethanol, methanol, and benzene were also prepared. The magnetic susceptibilities of organic solvents are more or less mutually similar (-9.05 (water), -9.02 (ethanol), -8.29 (methanol), -8.82 (benzene)  $\times 10^{-9}$  m<sup>3</sup>·kg<sup>-1</sup>), but the film diameters of the solvents were much smaller than that of water, probably because the solvents' surface tensions are one-fourth that of water.<sup>7</sup> In the case of aqueous PVA and PAA solutions, large films ( $\phi = 20 \text{ mm}$ ) stable for more than 30 min could be prepared in a magnetic field, though they were only stable for less than 30 mm under the earth's surface gravity. These liquid films' respective thicknesses are less than 1 mm, as estimated from the diameter of the metal wire. The results described above indicate that large liquid thin films, which cannot be prepared under the earth's surface gravity, can be prepared using magnetically simulated microgravity.

As an application of liquid thin film preparation under magnetically simulated microgravity, the solid thin polymer film preparation is examined from liquid films of aqueous PVA and

 Table 1. Solvents and solutions for which liquid thin films are prepared using magnetically simulated microgravity in the magnet bore tube

Solvent/Solution	Surface tension $/mN \cdot m^{-1}$	Ring diameter <sup>c</sup> /mm		
		13	20	25
Water	72.8 <sup>a</sup>	М	М	М
Ethanol	22.6 <sup>a</sup>	Μ	S	
Methanol	22.6 <sup>a</sup>	Μ	S	_
Benzene	28.9 <sup>a</sup>	Μ	S	
<b>PVA Solution</b>	45.4 <sup>b</sup>	—	L	_
PAA Solution	—		L	_

<sup>a</sup>From ref 7. <sup>b</sup>Measured in the present study. <sup>c</sup>L, Film is stable in a magnetic field (about  $-900 \cdot T^2 \cdot m^{-1}$ ) for more than 30 min. M, Film is stable in the magnetic field for at least 1 min. S, Film is stable in the magnetic field for about 10 s.



**Figure 1.** PVA solid thin film (50- $\mu$ m thickness) prepared by solvent evaporation from a  $3.3 \times 10^{-2} \text{ g} \cdot \text{mL}^{-1}$  aqueous PVA film under magnetically simulated microgravity.

PAA solutions. A solid film is prepared simply by evaporation of the solvent from the liquid films overnight in a magnetic field. A solid PVA film ( $\phi = 20$  mm, about 50-µm thickness) that cannot be prepared under the earth's surface gravity was prepared from the 3.3 × 10<sup>-2</sup> g·mL<sup>-1</sup> aqueous PVA solution film, as presented in Figure 1. A solid PAA film (10–20-µm thickness) was similarly prepared from the liquid film of a 2 × 10<sup>-1</sup> g·mL<sup>-1</sup> aqueous PAA solution.

Under the earth's surface gravity, a liquid film, held parallel to the ground, sags in the middle because of gravity  $m \cdot g$ , where *m* is the film mass and *g* denotes gravitational acceleration. The solution drains downward from the edge of the ring, thereby forming a small pool at the center of the ring. The pool becomes larger as the film sags; finally the film breaks under the weight.

Under a magnetic field, magnetic force  $F_{\rm m}$ , which is given by eq 1, acts on the film,

$$F_{\rm m} = (m\chi/\mu_0)B(z)dB(z)/dz \tag{1}$$

where  $\chi$  is the mass magnetic susceptibility of the film,  $\mu_0$  is the magnetic permeability of vacuum, B(z) is the magnetic flux density at z in the vertical direction, and dB(z)/dz is its gradient. The film is considered to be placed under the simulated microgravity when  $F_{\rm m}$  is equal to  $m \cdot g$  and opposite the direction of  $m \cdot g$ . Under magnetically simulated microgravity, the film is weightless and is held on the ring by surface tension: the pool does not form. For this reason, the liquid films, which can not be prepared under the earth's surface gravity, can be prepared in magnetically simulated microgravity. Furthermore, a solid film will form on the ring when the solvent of the solution film is evaporated, keeping the magnetic condition given by eq 1. The magnetic force field necessary for putting a  $3.3 \times 10^{-2}$  g·mL<sup>-1</sup> aqueous PVA solution in the simulated microgravity is estimated as about  $-1370 \,\mathrm{T}^2 \cdot \mathrm{m}^{-1}$  from the magnetic susceptibility of PVA  $(-7.7 \times 10^{-9} \text{ m}^3 \cdot \text{kg}^{-1})$ , determined in this study, and that of water. In the present experimental condition, the magnetic force field at the position where a ring of a liquid film is held is estimated as about  $-900 \,\mathrm{T}^2 \cdot \mathrm{m}^{-1}$ . This fact indicates that the magnetic condition given in eq 1 need not hold rigorously.

The magnetic orientation of the PVA solid film prepared under the simulated microgravity might be negligibly small, if it exists at all, because the PVA film is amorphous.

In conclusion, for the first time, liquid and solid thin films of a large diameter, which had not been producible under the earth's surface gravity, were prepared on a metallic ring using magnetically simulated microgravity. By compensating the earth's surface gravity with magnetic force, liquid thin films with a large diameter were formed stably on the metallic ring. Solid PVA and PAA films were then successfully prepared from liquid films of the respective aqueous solutions by evaporation of water in a magnetic field. Present results demonstrate clearly that magnetically simulated microgravity is a new useful and economical physical environment for materials science to prepare thin films with two clean surfaces, which cannot be prepared under the earth's surface gravity.

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