Int. J. Microgravity Sci. Appl. Vol.31 No. 1 2014 (3–10)

IIIII Microgravity Experiments by Aircraft Parabolic Flights Ⅰ IIIII
(Original Article)

Effect of Microgravity on the Formation of Honeycomb-patterned Films by Dissipative Processes

Yuji HIRAI[1,7], Makoto NATSUISAKA[2], Takashi MASHIKO[3], Masaaki KANAHARA[4], Yuta SAITO[4], Hiroshi YABU[4], Masatsugu SHIMOMURA[4,5,7] and Kaoru TSUJII[6]

Abstract

Honeycomb-patterned porous polymer films can be prepared by casting a mixed solution of hydrophobic and amphiphilic polymers on a solid substrate utilizing the condensed water droplet arrays as templates. Due to the temperature non-uniformity of the solution surface resulting from the thermal convections, water condenses heterogeneously. The heterogeneous condensation of water droplets induces the formation of irregular-arrangement of domains in the ordered structure of microporous films. In order to evaluate the effect of gravity on the formation of honeycomb-patterned films, we have made microgravity experiments. Even under microgravity, we successfully prepared honeycomb-patterned films. And interestingly, some samples have multi-layered uniform microporous structures, which are formed with vanishing the relative density effect of solvent and water droplets. It is suggested that the microgravity affects the formation of honeycomb-patterned films considerably.

Keyword(s): Dissipative structure, Self-organization, Microgravity, Convection, Parabolic flight

1. Introduction

Microporous films are useful materials for membrane separation, cell culture scaffolds, catalyst supports and other practical applications.[1)] We have reported self-organized honeycomb-patterned porous polymer films can be prepared by casting a solution of hydrophobic polymer and an amphiphilic copolymer on a solid substrate by using condensed water droplet arrays as templates (**Fig. 1**)[2)]. The formation mechanism of the honeycomb-patterned films is considered as follows;

1) At first, polymer solution containing hydrophobic polymer (e.g. polystyrene, **Fig. 1(a)**), amphiphilic copolymer (e.g. synthesized polymer[3)], **Fig. 1(a)**) and volatile solvent (e.g. chloroform) is casted onto a solid substrate (**Fig. 1(a)**)

2) After starting evaporation of the solvent, humid airflow is added (**Fig. 1(a)**). Since the solution surface is cooled down by heat absorption due to vaporization (**Fig. 1(b)**1),2)), water-micro-droplets start to condense onto the solution surface (**Fig. 1(b)**3)). The droplets slightly sink into the solution due to difference in specific gravity between those.

3) Since the water droplets are stabilized by the amphiphilic copolymer, those get larger by absorbing water vapor in the humid airflow without fusing each other. This process keeps size distribution of water droplet uniform.

4) The water droplets are packed to form arrays by the lateral capillary force (**Fig. 1(b)**4)), and the polymers are gradually solidified with the solvent decreasing (**Fig. 1(b)**5)). The packing force arrays the water droplets like honeycomb at the late stage of this process.

5) After the solvent completely evaporating, water droplets also evaporate (**Fig. 1(b)**6)), when the temperature of the polymer film is recovered up to a room temperature, and the honeycomb-patterned porous polymer films is finally obtained. (**Fig. 1(c) - (d)**).

Uniformity of micropores is an important factor for above-mentioned practical applications. However, there are some defects and/or miss packing of the micropores observed on the obtained films (**Fig. 1(e)**). These defects and/or miss packing are caused by heterogeneous condensation of water droplets[4)] due to the non-uniformity of surface temperature of the solution, whichnon-uniform is induced by a thermal convection. The thermal convection arises from the temperature difference between the surface, which is cooled by heat absorption of the

1 Department of Bio- and Material Photonics, Chitose Institute of Science and Technology (CIST), 758-65, Bibi, Chitose, 066-8655, Japan
2 ISS Science Project Office, Institute of Space and Astronautical Science (ISAS), Japan Aerospace Exploration Agency (JAXA), 2-1-1 Sengen, Tsukuba, Ibaraki 305-8505, Japan
3 Graduate School of Engineering, Shizuoka University, 3-5-1, Johoku, Naka-ku, Hamamatsu, Shizuoka, 432-8561, Japan
4 Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, 2-1-1, Katahira, Aoba-ku, Sendai, Miyagi, 980-8577, Japan
5 Advanced Institute for Materials Research (AIMR), Tohoku University, 2-1-1, Katahira, Aoba-ku, Sendai, Miyagi, 980-8577, Japan
6 Graduate School of Science and Engineering, Chuo University, 1-13-27, Kasuga, Bunkyo-ku,Tokyo,112-8551, Japan
7 Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology Agency (JST), Hon-cho 4-1-8, Kawaguchi, Saitama, 332-0012, Japan
(E-mail: y-hirai@photon.chitose.ac.jp)

vaporization, and the bottom, which remains around a room temperature, of the solution. Hence, eliminating the thermal convection might lead homogeneous water droplet condensation and provide mono-domain honeycomb-patterned films. In this case, a convection type is considered as Rayleigh-Bénard according to the previous report[5]. It is well known that the thermal convection is governed by Rayleigh number (Ra)[6];

$$Ra = \beta g \varDelta T d^3/\kappa\nu \qquad (1)$$

where β is coefficient of thermal expansion, g is acceleration of gravity, $\varDelta T$ is temperature difference between solution top and bottom, d is a thickness of the solution, κ is a thermal diffusion coefficient, and ν is a kinematic viscosity. When Ra is higher than 1,700, the convectional flow occurs. According to the definition of Ra, the gravity is one of the important factors to control the convection. In fact, we revealed that hyper gravity strongly affected flow patterns and degraded film structures through centrifuge experiments[5,7]. Based on these results, we expected that microgravity could eliminate Rayleigh-Bénard convection and provide mono-domain, honeycomb-patterned films. In this report, we summarize the results of the parabolic flight experiments, which were carried out based on such motivations.

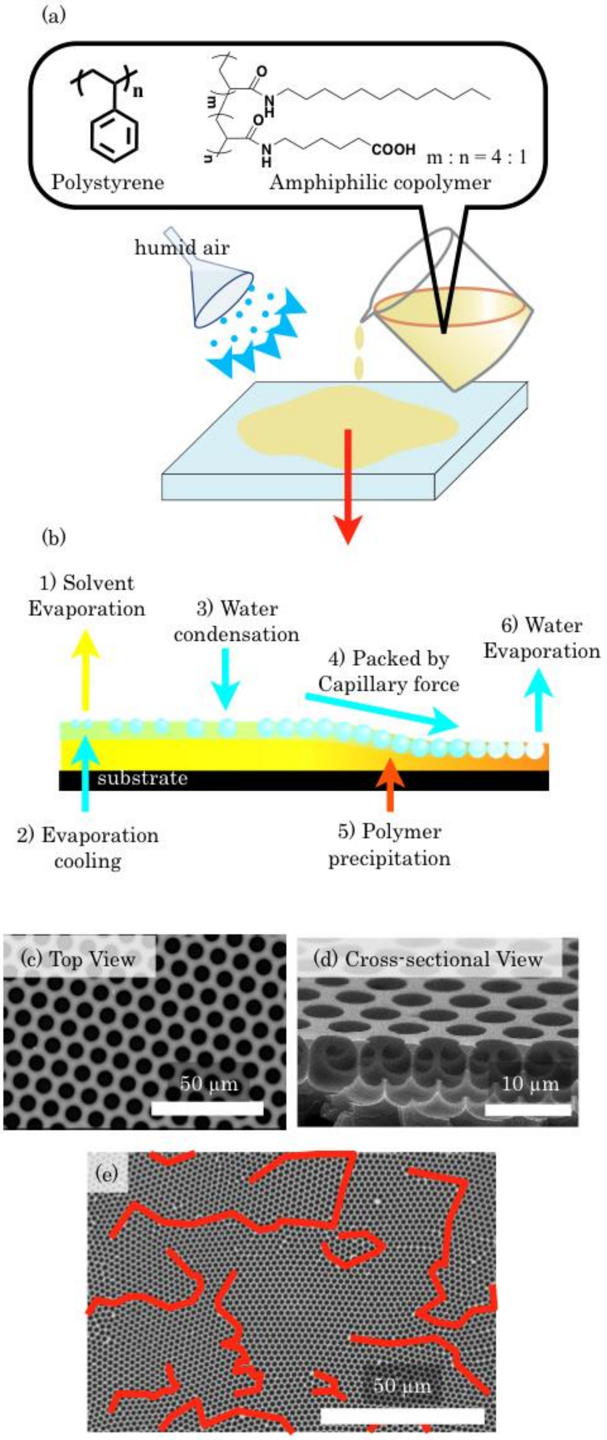

Fig. 1 Schematic Illustrations of (a) Preparation Methods and (b) Formation Mechanisms of Honeycomb-Patterned Films. (c), (d) SEM Images of Honeycomb-Patterned Films. (e) Boundaries of Domain Structures.

2. First parabolic flight experiment in March 2011

2.1 Preparation apparatus of honeycomb-patterned films 1

Researchers usually have about two weeks as one campaign. Five days including one spare day are allocated to the flight experiments in one campaign. 10 to 16 parabolic flights will be carried out every day. In our experiments, we obtained 15 parabolas in one day.

Figure 2(a) shows a schematic view of the preparation apparatus of honeycomb-patterned films, which was installed in the aircraft. **Figure 2(b)** shows its functional chart. The honeycomb-patterned film preparation cell consists of cupper plates, a PTFE spacer, and glass substrates (**Fig. 2(c), (d)**). A solution is filled onto the lower glass substrate and confined with the upper one and the PTFE spacer. Video cameras are placed below the cells to record images of entire processes of honeycomb-patterned film formation and white LED plates as back lights for the video cameras are placed above the cells, respectively (**Fig. 2(a), (b)**). A cylinder filled with humid air is heated at 25 degrees centigrade, which is almost the same as air conditioning temperature of the aircraft, with a rubber heater to keep the humid air vaporized by avoiding its condensation and connected to the two cells with a PFA tube. The temperature of the cell is not controlled since the temperature requirement for the process is not severe. The temperature range of the air conditioning of the aircraft is acceptable.

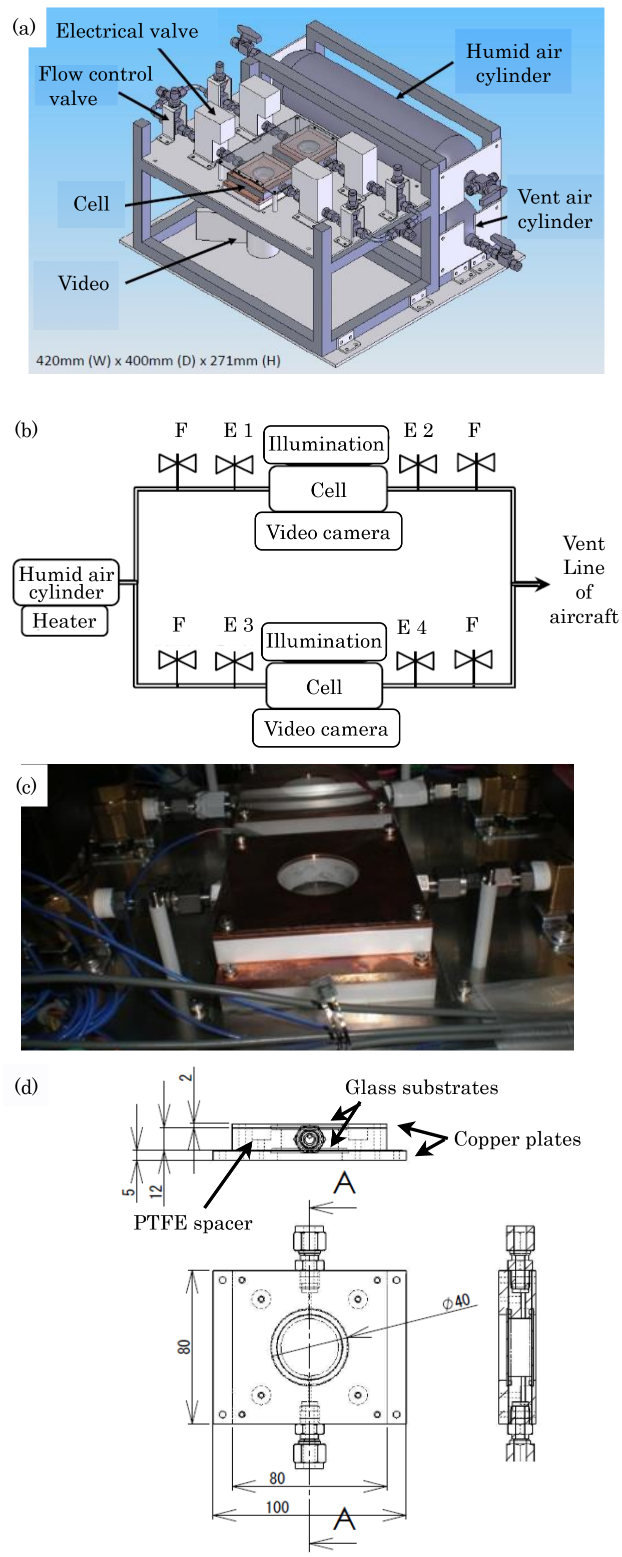

Fig. 2 (a) Illustrations of Honeycomb-Patterned Films Preparation Apparatus and (b) Functional Chart of the Apparatus. Here, F are Flow Control Valves and E are Electrical Valves. (c) A Photograph and (d) a Trihedral Figure of the Cell.

Since the cylinder and the cells are separated with electrical valves (E1 and E3 in **Fig. 2(b)**), the humid air isn't introduced into the cells before the experiments. The cells are also connected to the vent lines of the aircraft. The lines are also separated with electrical valves (E2 and E4 in **Fig. 2(b)**), the humid air and the evaporating solvent aren't evacuated into the vent line of the aircraft before the experiments. Flow rates of those lines can be individually controlled by flow control valves (Fs in **Fig. 2(b)**). Those electrical valves are controlled by a microcomputer, which monitors an acceleration level in the vertical direction of the aircraft. When the acceleration level becomes less than 0.25G, the microcomputer opens the electrical valves E1 and E3 to introduce humid air into the cells and, 2 sec after, opens the electrical valves E2 and E4 to evacuate the solvents. The air flow rate is determined so that the film can be formed within one parabola (about 20 sec). 3-axis accelerations, temperatures at an air inlet, an outlet, and a copper plate of the cells, room, and heater are individually measured with thermocouples and logged with a data logger.

The preparation apparatus of honeycomb-patterned films was fixed in the aircraft (Gulfstream II, operated by Diamond Air Service Incorporation).

2.2 Experimental conditions of the first flight

The polymer solutions were prepared by dissolving mixed polymers (polystyrene and amphiphilic copolymer) with chloroform. The concentrations of the mixed polymer solutions were kept at 5 g/ℓ (the volume ratios of polystyrene and amphiphilic copolymer were varied from 10 to 1), and the solution volumes of experiments were changed from 0.5 to 0.8 mℓ.

2.3 Results and discussion on the first flight

Figure 3 shows acceleration and temperatures profiles during an experiment. As shown in **Fig. 3(a)**, 15 parabolas were achieved in this experiment and the duration of one parabola was almost 20 sec as shown in **Fig. 3(b)**. In this experiment, the films were formed at the time of about 1000 sec (the 5th parabola). The cell temperature represented as "Cells" in **Fig. 3(c)** increased with the cabin temperature of the aircraft increasing. However, these temperature variations are acceptable in our experiments as mentioned previously.

Figure 4 shows the sequential photographs of the preparation process of honeycomb-patterned films under microgravity. Before attaining the microgravity, the solution surface was inclined since the aircraft was accelerated with ascending angle of 45 degree. Even after attaining the microgravity, the inclination remained since there was no recovery force under microgravity. As well, the meniscus of the solution raised under microgravity as shown in the length change of the white dotted arrows in **Fig. 4(a), (b)**, since the wettability was enhanced. After microgravity attained, the microcomputer opened the electric valves and humid air came into the cell through the air inlet attached to upper right part of the PTFE spacer, flowed to the solution surface in the direction of the white dotted arrow in **Fig. 4(c)**, and was evacuated from the air outlet attached to lower left part of the PTFE spacer. Right after this, interference colors appeared on the solution surface (**Fig. 4(d)**). This opaque, interference colored area spread over the whole solution surface

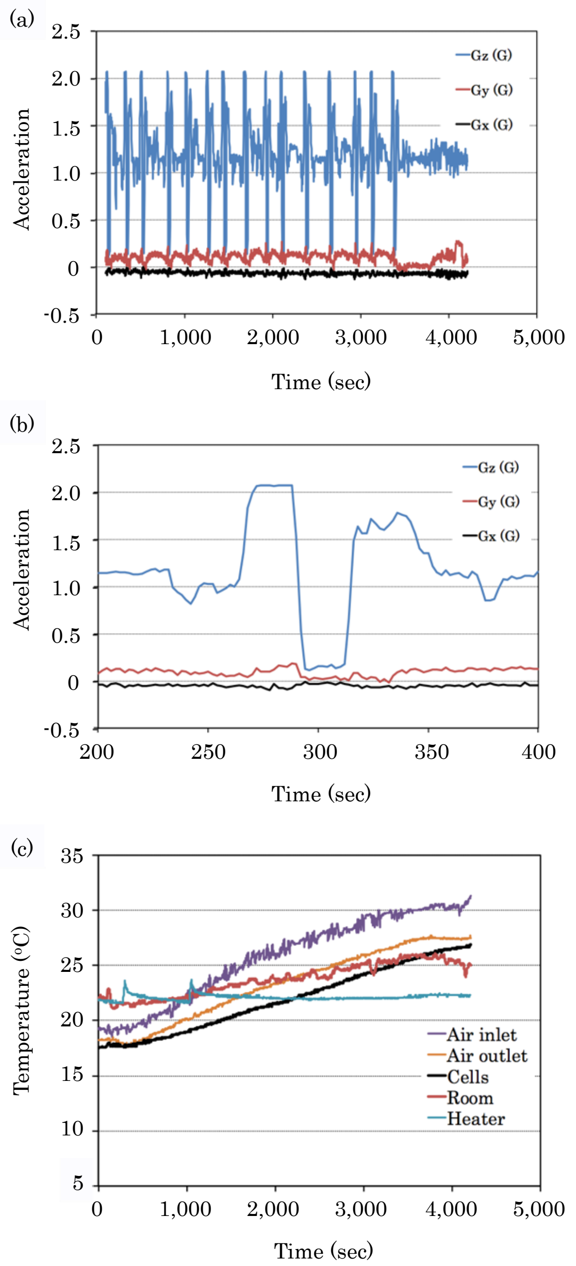

Fig. 3 Graphs of Obtained Date Logger Parameters. (a) Acceleration (Gx is Advancing Direction of aircraft. Gy is lateral direction. Gz is Gravity), (b) Magnified Graphs of (a) and (c) Temperatures.

until the end of the microgravity period (**Fig. 4(e)**). When the gravity came back, a little solvent remaining in the thicker part of the meniscus spread and redissolved some part of the opaque polymer film.

After the parabolic flight experiment was finished, the samples were picked up from the apparatus, and observed by an optical microscope. Though the opaque areas were decreased by redissolution, honeycomb-patterned films could be obtained (**Fig. 5**). As shown in **Fig. 5**, the pore diameters increased with the solution volume increasing[8]. However, there was no difference in the sample structures prepared under μG and on the ground (1G).

2.4 Summary of the first flight experiments

In the first parabolic flight experiments, the preparation apparatus was successfully operated on the aircraft, and we could obtain opaque honeycomb-patterned polymer films. However, some problems were found as follows; humid airflow was too strong for preparation of honeycomb-patterned films, and the solution surfaces were disturbed by the airflow. It implied that even if honeycomb-patterned films were formed, microgravity effect could not be observed correctly. In addition, solvent movement due to the gravity changes and tilting of the aircraft caused redissolutions of formed polymer films. We had to modify the cell structure and the apparatus to overcome these problems.

3. Second parabolic flight experiment in December 2011

3.1 Preparation apparatus of honeycomb-patterned films 2

A photograph of the modified preparation apparatus is shown in **Fig. 6(a)**. The modified points are as follows.

1) A swing arm was employed as a levelizer of the cells to prevent the tilt of the polymer solution surface.

2) The cell structure was also modified to prevent deformation of the solution surfaces. The cells were roughly divided into four parts. A glass substrate was fixed to the aluminum bottom spacer with the PTFE cell spacer. The sidewall angle of the PTFE cell spacer was made lower to prevent the meniscus from being raised due to wettability under microgravity. As well, the flow path of the humid air was redesigned to reduce the flow rate. The humid air flowed from the top of the cell and was evacuated with the evaporated solvent through the side vent. Dome-shaped main aluminum cell body was especially effective to make the flow rate of the airflow more moderate.

3) Furthermore, the oblique white LED illumination system was attached to the cells to obtain the clearer video images. A red LED was also added to the cell as a status indicator of the

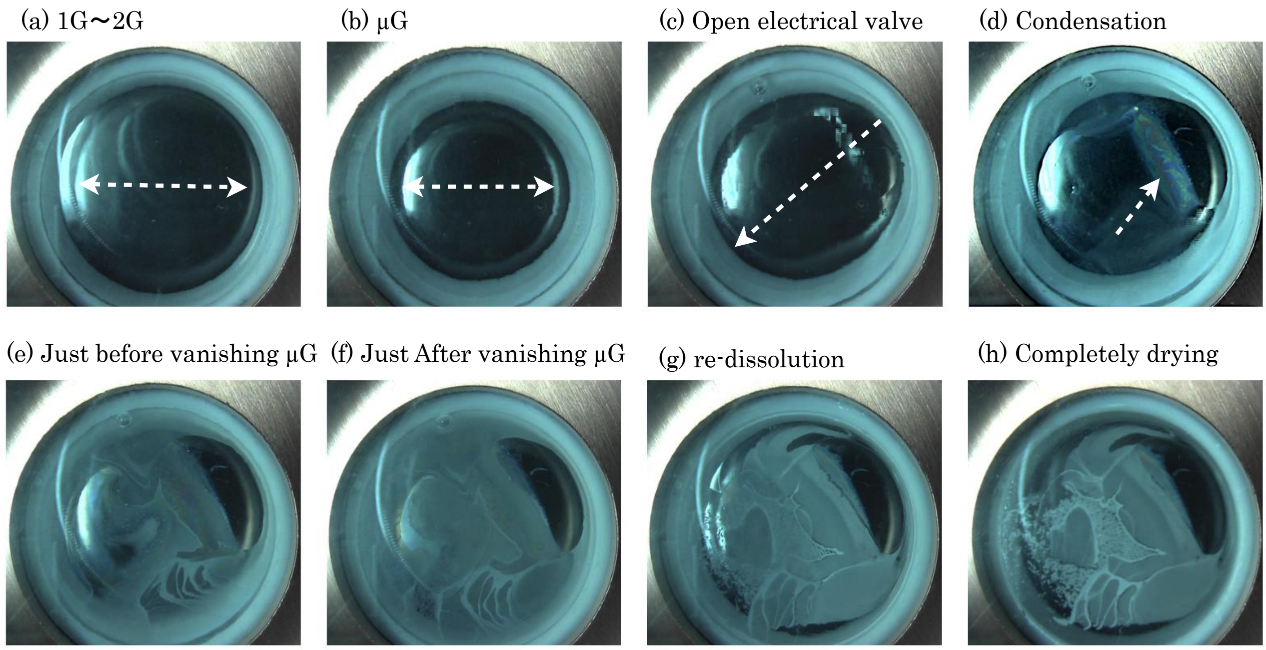

Fig.4 Continuous Photographs of Formation of Honeycomb-Patterned Films under Microgravity.

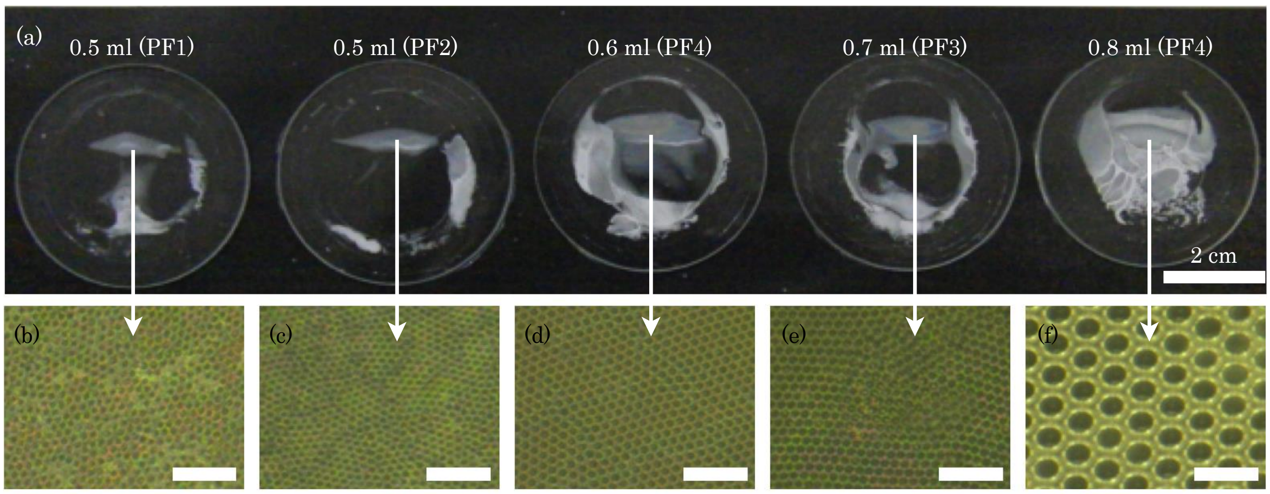

Fig. 5 (a) A Photograph of Honeycomb-Patterned Films Prepared under Microgravity. (b)~(f) Optical Microscope Images of Prepared Films. (Bars; 10 μm)

electrical valves. When the valves opened, the LED is illuminated. The modified apparatus was installed into the aircraft (MU-300, operated by Diamond Air Service Incorporation).

3.2 Experimental conditions of the second flight

The concentrations of the mixed polymer solutions were kept at 5 g/ ℓ (the volume ratios of polystyrene and the amphiphilic copolymer solutions were as varied from 10 to 1), and the solution volumes of experiments were changed from 0.7 to 1.8 m ℓ .

3.3 Results and discussion on the second flight

Figure 7 shows accelerations and temperatures profiles. In this experiment, 15 parabolas were achieved and one of those was used for the film processing. It is found that the temperatures were more stable than first flight from the comparison between **Fig. 3(c)** and **7(b)**. Although the temperature range of the air-conditioning of the aircraft is basically acceptable, the temperature near the room temperature is much suitable for the data comparison between μg and 1g. The reasons why the temperature behavior was different is not clear at present but may be use of a different aircraft or difference of an operation season.

Figure 8 shows the sequential photographs of the preparation process of honeycomb-patterned films under microgravity. Polymer solution was clear before microgravity. After the microgravity attained, the red LED was turned on, indicating that the electrical valves were opened, and then humid air flowed into the cells. Several seconds later, it was verified that water micro droplets were condensed onto the solution surface because interference colors could be seen. Although solution surface was perturbed a little during the formation of honeycomb-patterned films, the solution surface was still homogeneously opaque. It suggested that the formation of honeycomb-patterned films occurred successfully under microgravity.

We had four days for the parabolic flight experiments. The polymer films were successfully obtained without redissolution

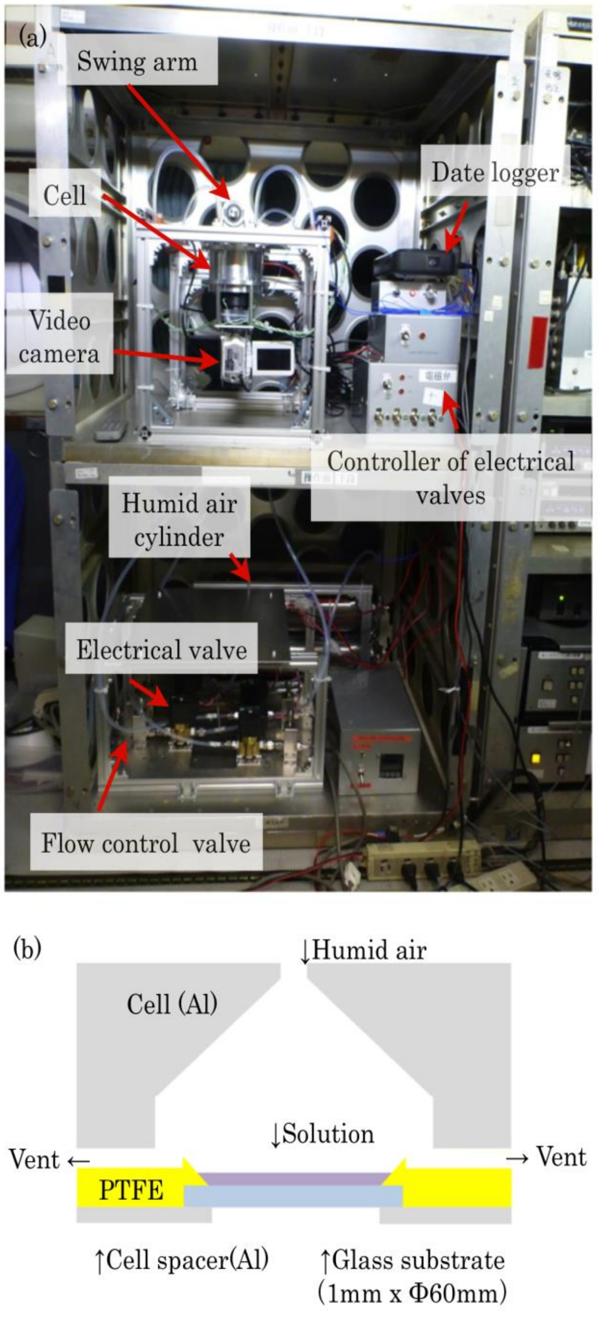

Fig. 6 (a) A Photograph of Honeycomb-Patterned Film Preparation Apparatus. (b) An Illustration of Inside the Cell.

every day. **Fig. 9(a)-(d)** show the optical microscopic images of the prepared honeycomb-patterned films under microgravity. **Figure 9(a)** shows flat polymer films without micropores. This result suggests that the solution volume was too small. Therefore, the solution was evaporated quickly before the water droplets were condensed. The other results show the micropores as shown in **Fig. 9(b)** to **9(d)**. These results suggest the solution volumes were suitable enough for the water droplets to condense. When the solution volumes were suitable enough, the film surfaces were opaque, and the microporous structures could be observed clearly with an optical microscope. It seems that not much difference exists in the microporous structures in **Fig. 9(c)** and **9(d)** as compared with the ground samples, that is, mono-layer films, though too much condensation and droplet fusions might occur during the film preparation in **Fig. 9(c)**. In addition, it seems that there is no relation between the solution volume and pore diameter. This issue will be studied in future.

The sample of **Fig. 9(b)** little differs from other samples. The sample could not be clearly observed with an optical microscope. Therefore, we used the secondary electron microscope (SEM) to observe the sample. **Fig. 9(e)** and **9(f)** show the SEM images of the honeycomb-patterned films prepared under microgravity. The images show “uniform”

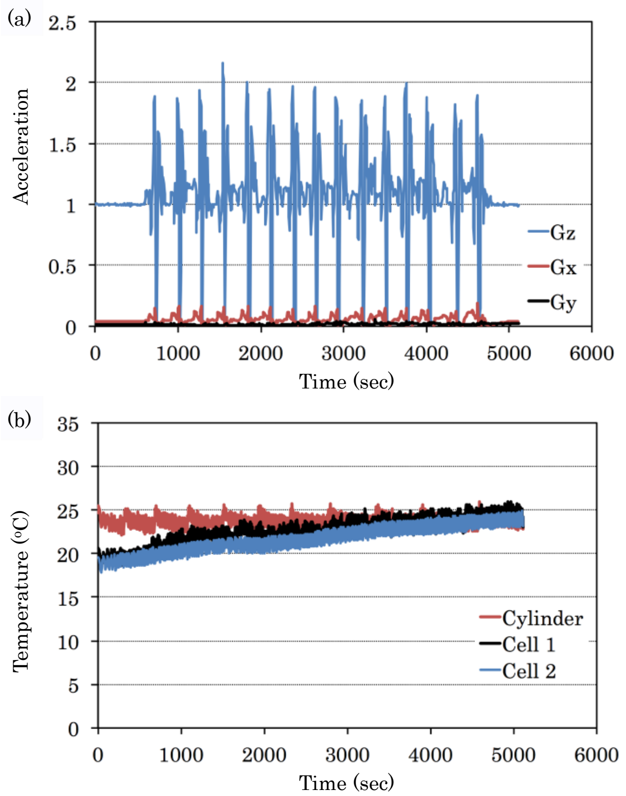

Fig. 7 Graphs of (a) Acceleration (Gx is Advancing Direction of Aircraft. Gy is Lateral Direction. Gz is Gravity) and (b) Temperatures of the Cylinder and Cells.

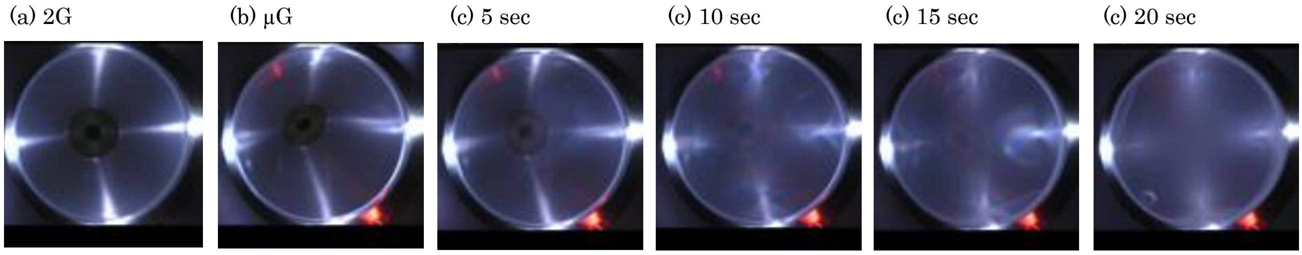

Fig. 8 Continuous Photographs of Formation of Honeycomb-Patterned Films under Microgravity.

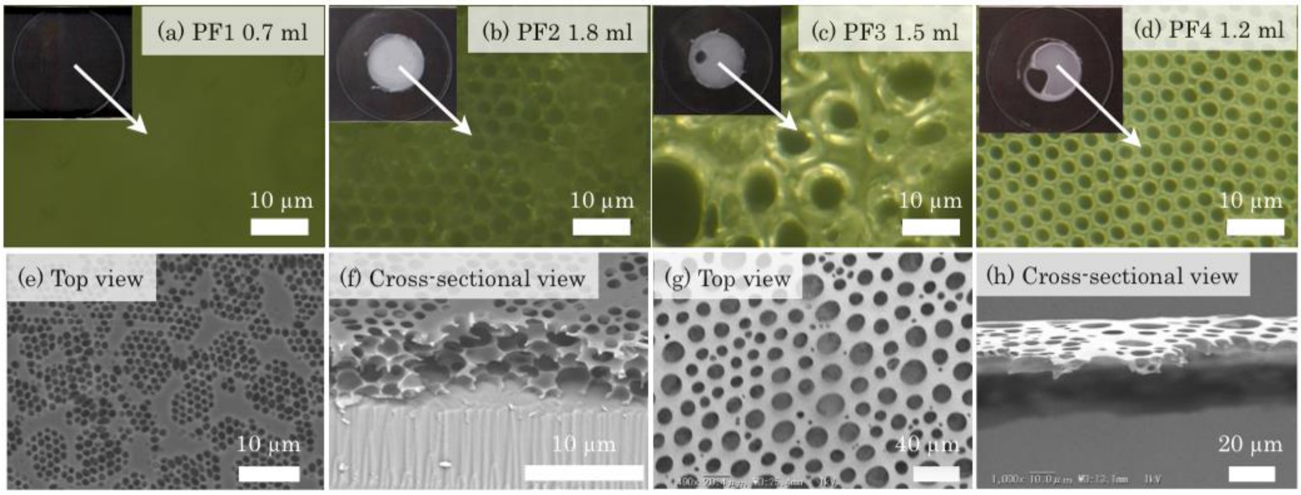

Fig. 9 Photographs and SEM Images of Honeycomb-Patterned Films Prepared under Microgravity (a)-(f) and SEM Images of a Ground Reference (g) and (h).

multi-layered microporous structures, which had never been obtained on the ground, although flat (non-porous) regions are partially seen on the surface. The multi-layered microporous structures are usually non-uniform when they are prepared on the ground because of fusions of condensed water droplets. The typical results on the ground are shown in **Fig. 9(g)** and **9(h)**. Due to the relative density difference between water and chloroform, water droplets were ordered at the solution surface on the ground. However, since the relative density difference is basically ignored in microgravity, water droplets may be uniformly mixed with the solution and fixed as "uniform" multi-layered microporous structures.

3.4 Summary of the second flight

In the second parabolic flight experiments, the preparation apparatus was successfully operated on the aircraft, and we could obtain opaque polymer films. In the second flight experiment, the improvement of the honeycomb-patterned films preparation apparatus enabled much better condition on the aircraft than the first microgravity experiment did. Namely, the swing arm could maintain the horizontality of the polymer solution surface. In addition, the obtained films were macroscopically much flatter than those in the previous experiments. This indicates that the new cell can flow the humid air more gently. The oblique white LED illumination improved visibility of the surfaces of the prepared films and the red LED illumination which was turned on when the electrical valves opened helped us to know which part of the video showed the film preparation. As the results of the surface observations with an optical microscope and SEM, the opaque polymer films had uniform micropores. In addition, some sample had "uniform" multi-layered microporous structure, which had never been obtained on the ground. It is suggested that the microgravity affects the formation of honeycomb-patterned films, because multi-layered uniform microporous structures cannot be obtained on the ground. On the other hand, there are still some problems, which have to be solved in future. The most important issue is the experimental duration. In our experiment, solvent could not be completely evaporated during a parabola (20 sec) and rapid evaporation degraded the sample structures. Neither a larger size film which enables the estimation of "domains" could be obtained. In order to obtain finer structures, a longer duration (several-minutes duration) microgravity experiment is necessary. The parabolic flight experiments may be suitable for more fundamental researches in our research, for example, in-situ observations of homogeneous micro-droplet nucleation, droplet formation on the liquid surface, and so on.

On the other hand, the domain size dependence on the time duration of evaporation and cell size must be investigated on the ground.

4. Conclusion

In this report, we summarized the experiment set-up, conditions, and results of the parabolic flight experiments performed in March and December 2011 to obtain mono-domain honeycomb-patterned films under microgravity. The preparation apparatus was successfully operated on the aircraft and honeycomb-patterned porous polymer films could be obtained in almost all the experiments. However, mono-domain honeycomb-patterned films, which have larger domain-size than prepared on the ground, could not be obtained because of limitation of preparation time, cell size and humid airflow rate.

But, in the second flight, a "uniform" multi-layered microporous structure, which had never been obtained on the ground, was obtained. The uniform multi-layered microporous materials can be applicable to 3D cell scaffold[9)], catalyst supports and so on. The mechanism yielding this unique structure has not been identified yet, but this might show a new possibility of the microgravity as a materials processing field.

Honeycomb-patterned films can be prepared from various hydrophobic polymers including engineering polymers and biodegradable polymers. When gravity effect is investigated and we can obtain homogeneous mono-domain honeycomb-patterned films, high-performance and practically valuable materials for photonic materials or high-efficiency membrane filters for material separation without the effect of inhomogeneous surface structures and/or boundaries will be obtained.

Acknowledgement

This research has been supported by research working group program coordinated by ISAS/JAXA. We thank Diamond Air Service Incorporation for their kind assistance during the parabolic flight experiments.

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(Received 31 Oct. 2013; Accepted 17 Jan. 2013)