Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Self-Organized Hierarchy Structures Composed of Honeycomb-Like Polymer Films and Spider-Web-Like Particle Structures

Sachiko Matsushita [a b], Nobuhito Kurono [a] & Masatsugu Shimomura [a c]

[a] Dissipative-Hierarchy Structures Laboratory, RIKEN Frontier Research System, Saitama, Japan

[b] Department of Integrated Sciences in Physics and Biology, College of Humanities and Sciences, Nihon University, Tokyo, Japan

[c] Nanotechnology Research Center, Research Institute for Electronic Science, Hokkaido University, Sapporo, Japan

Version of record first published: 12 Mar 2007

To cite this article: Sachiko Matsushita, Nobuhito Kurono & Masatsugu Shimomura (2007): Self-Organized Hierarchy Structures Composed of Honeycomb-Like Polymer Films and Spider-Web-Like Particle Structures, Molecular Crystals and Liquid Crystals, 463:1, 93/[375]-99/[381]

To link to this article: http://dx.doi.org/10.1080/15421400601021554

Mol. Cryst. Liq. Cryst., Vol. 463, pp. 93/[375]–99/[381], 2007

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400601021554

Taylor & Francis
Taylor & Francis Group

Self-Organized Hierarchy Structures Composed of Honeycomb-Like Polymer Films and Spider-Web-Like Particle Structures

Sachiko Matsushita
Dissipative-Hierarchy Structures Laboratory, RIKEN Frontier Research System, Saitama, Japan and Department of Integrated Sciences in Physics and Biology, College of Humanities and Sciences, Nihon University, Tokyo, Japan

Nobuhito Kurono
Dissipative-Hierarchy Structures Laboratory, RIKEN Frontier Research System, Saitama, Japan

Masatsugu Shimomura
Dissipative-Hierarchy Structures Laboratory, RIKEN Frontier Research System, Saitama, Japan and Nanotechnology Research Center, Research Institute for Electronic Science, Hokkaido University, Sapporo, Japan

We demonstrate a self-organized system for fabricating a hierarchical structure, composed of a honeycomb-like polymer film and the dissipative structures of fine particles. The process is quite simple: Fine-particle water suspension was dropped on polymer organic solution under the exposure of humid air. The cracking of self-assembled particle dissipative structures caused the locally elongation of the honeycomb-like polymer film, and formed hierarchy structures in an one-step procedure.

Keywords: fine particles; nano-structures; opal; photonic crystal; self-assembly

The authors thank Ms. Hiromi Takemoto, Ms. Kaoru Ito and Ms. Sayori Yagi for valuable assistance, and Dr. Tetsuro Sawadaishi and Dr. Hiroshi Yabu for their fruitful discussions. This work has been supported in part by the Ministry of Education, Culture, Sports, Science and Technology, Japan (17029072).

Address correspondence to Masatsugu Shimomura, Dissipative-Hierarchy Structures Laboratory, RIKEN Frontier Research System, 2-1 Hirosawa, Wako, Saitama, 351-0198, Japan. E-mail: shimo@poly.es.hokudai.ac.jp

INTRODUCTION

Various production methods, such as conventional lithography, soft lithography, and self-assembly, are used to obtain nanoscale to microscale architectures. These architectures are considered extremely important from the point of view of applications such as photonic crystals [1,2], electron emitters [3], high-density optical storage media [4], and catalytic systems [5]. Among them, since Prigogine won the novel prize in 1977, the dissipative process has been well known to be potentially of great scientific and technological interest because the process is a simple, self-assembly-based, and inexpensive method of preparing a wide range of architecture, from nanometer to micrometer size. In particular, one of the important points of the dissipative process is its capability to realize hierarchy structures that will give birth to diversity and complexity, as living creatures do [6,7].

Among many dynamic-process-based structures such as dissipative structures, we focus on honeycomb-like films. This honeycomb-like structure can be formed in a volatilized process of polymer solution by exposure in humid air, and the final structure has hexagonally hole-packed air spheres (0.2–10 μm diameter) like those of combs of honeybees [8–10]. The template of the honeycomb morphology is a water droplet, which was spontaneously formed on the polymer solution surface. Possible applications of such honeycomb films include membranes for separation, microreactors, biointerfaces [11,12], catalysts, microstructured electrode surfaces, and photonics [13,14].

The authors had previously reported the preparation of hierarchy structures by inserting water-dispersible material in the water droplets. In this paper, we would like to suggest the utilization of the crack formation in particle's self-assembled structures during the honeycomb-like film formation to prepare another-type hierarchy structures.

EXPERIMENTAL

One-step fabrication of the combined structure of honeycomb-like films and particles has recently been reported by the authors [15]. The combined structure was a honeycomb-like film, in which halls fine particles were packed. In this experiment, we focused on the force of the fine particles aggregation to elongate the polymer of the honeycomb-like films. The procedure shown here is almost the same as that previously reported (Especially, the used polymer was same).

Synthesis of Surfactants

Typically, in our experiments, the honeycomb-like film was synthesized from two monomers. One monomer, N-(carboxyl pentyl)acrylamide, was obtained by the addition of a diethyl ether solution of acryloyl chloride into an aqueous solution of 6-aminohexanoic acid and NaOH. Another monomer, N-dodecyl acrylamide, was obtained through the general method. Polymerization of these two monomers was carried out using these acrylamide derivatives in the ratio of 1:10 (N-(carboxyl pentyl)acrylamide: N-dodecyl acrylamide) in the presence of azobisisobutyronitrile. The weight average molecular weight (Mw) and molecular weight distribution (Mw/Mn) of the resulting material, copolymer 1, estimated by gel permation chromatography, were 1.9×10^4 g/mol and 1.58, respectively.

Preparation of Combined Structures

Casting from homogeneous solutions of water-immiscible organic solvents, e.g., chloroform, or benzene under high atmospheric humidity can easily produce the self-organized honeycomb morphology of polymers. The condensation of water droplets leads to the formation of a hexagonal array. The droplets are spontaneously covered with the polymers. 30–50 μl of a benzene solution of copolymer 1 (concentration: 1 g/L) was spread over a nonfluorescent glass substrate (Matsunami). 10 μl of a water suspension of red fluorescent polystyrene particles ($\lambda_{ex}/\lambda_{em}$: 542/612 nm) of essentially the same dimensions (50 nm diameter; Polymer Microspheres Red Fluorescing, 1 wt% Solids, Duke Scientific Co.), or of silica microspheres (2 wt%, NIST Traceable, 0.49 μm ± 0.03 μm, Duke Scientific Co.), was dropped on the benzene solution of copolymer 1. The solution was evaporated to form a film by blowing humidified air (Fig. 1). The temperature was 20.0–20.6°C

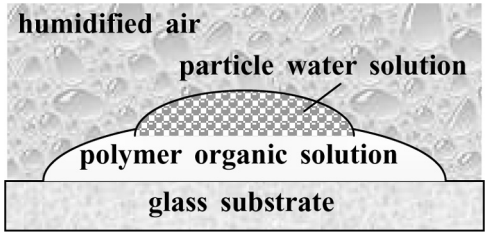

FIGURE 1 Schematic cross-sectional image of the experiments for the dissipative process. The entire procedure was done within 5 minutes.

and the humidity was 10.0–34.8%. The samples thus prepared were characterized by optical microscopy (BX-60; Olympus).

RESULTS AND DISCUSSIONS

Honeycomb-like films are basically made from water-in-oil emulsions covered with surface-active agents [16]. Thus, some amount of water particle suspensions were injected into the water-in-oil emulsions, and formed honeycomb-like film, as the authors previously reported [15]. When the particle size is small, another interesting phenomenon was observed.

It is well known that drying of a fine particle suspension forms dissipative structures such as stripes and dots [17]. Hence, in the case of our procedure, the dissipative structure of fine particles and the honeycomb-like structure of polymer were formed simultaneously. First, the surface of the organic solution, which is the area uncovered by the water particle suspension, became opaque due to the condensation of water vapor of the moist air. After the organic solvent evaporation, a thin honeycomb-like film was formed following the water particle suspension drying. An important point is that the dissipative structure formation of fine particles started during the honeycomb film formation. As a result, we obtained a combined structure (Fig. 2). Ladder-like (Fig. 2a) and spider-web-like (Fig. 2b) structures of red polystyrene particles were formed. The unit size of the dissipative structure is about 5–20 μm square. Interference fringes were observed as circular patterns in the large units. Some units involved honeycomb-like films. The pore size of the honeycomb-like film is about 1 μm. The magnified image (Fig. 2c) shows that partial plastic deformation of the film was spontaneously induced by the dissipative process of fine-particles. The dissipative process is not limited by the polystyrene particles. The drying process of 2 wt% SiO_2 particles, 500 nm in diameter, which is larger than red-polystyrene particles, could also cause the plastic deformation of the film (Fig. 3).

Nishikawa et al. have reported that various geometric patterns can be formed upon mechanical deformation of honeycomb-like film [18]. They used a degradable viscoelastic polymer, PCL. Its glass transition temperature is felatively low (−65°C). In our case, the glass transition temperature of copolymer 1 is higher (we should mention here that the temperature value is widely spread between 45°C and 100°C, implying low reproducibility, and differed with the molecular weight and the vials of the samples). We think the plastic deformation of the polymer observed here occurred before the polymers solidified, i.e., before the complete drying of the organic solvent.

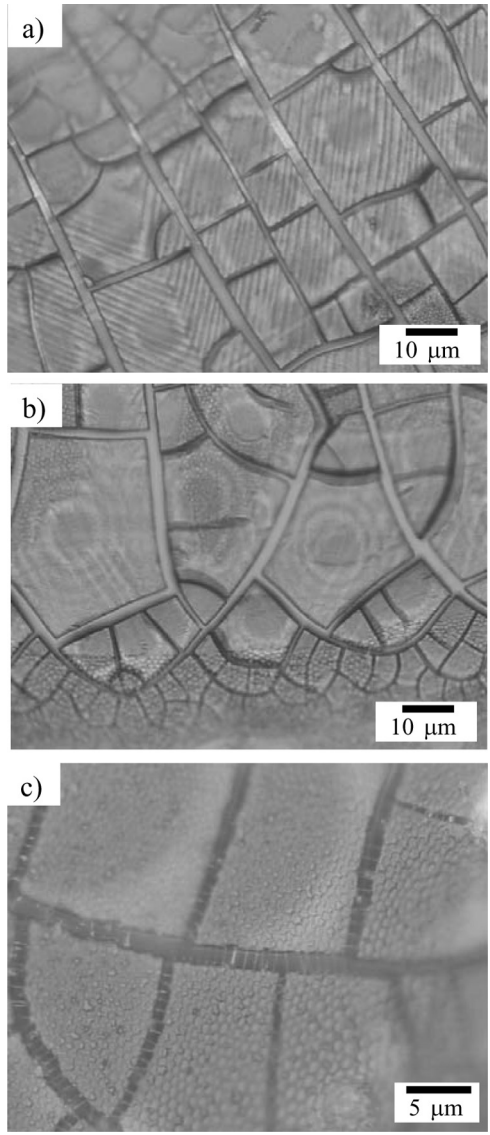

FIGURE 2 Optical microscopic images of spider-web-like self-assembled structure. 1 wt% red-fluorescent polystyrene particle (50 nm diameter) water suspension was used.

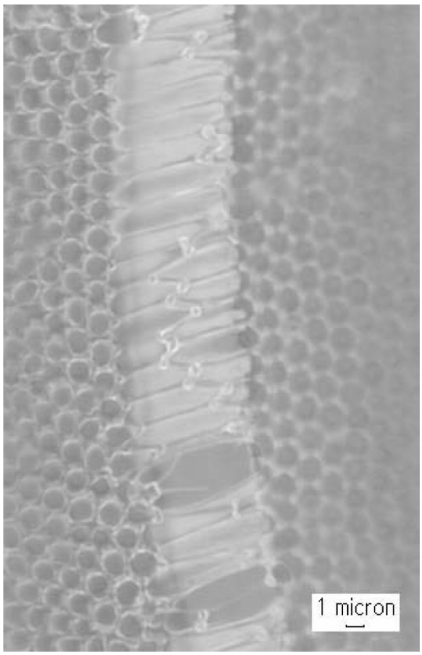

FIGURE 3 Optical microscopic image of combined structure. 2 wt% SiO_2 particle (500 nm diameter) water suspension was used.

In this paper, we suggest the utilization of the crack formation in the particle's self-assembly process for the preparation of hierarchy structures. We could prepare self-organized structure composed of honeycomb-like polymer films and spider-web-like particle structures in a simple, one-step procedure. Last, but far from least, the calm dissipative process enables us to achieve the delicate plastic deformation of the polymer and obtain the hierarchical structures.

REFERENCES

[1] Matsushita, S. I. et al. (2000). Light propagation in composite two-dimensional arrays of polystyrene spherical particles. *Langmuir*, *16*, 636–642.
[2] Matsushita, S. I., Fukuda, N., & Shimomura, M. (2005). Photochemically functional photonic crystals prepared by using a two-dimensional particle-array template. *Colloids and Surfaces A*, *257–258*, 15–17.
[3] Okuyama, S., Matsushita, S. I., & Fujishima, A. (2000). Preparation of periodic microstructured diamond surfaces. *Chem. Lett.*, 534–535.
[4] Micheletto, R., Fukuda, H., & Ohtsu, M. (1995). A simple method for the production of a two-dimensional, ordered array of small latex particles. *Langmuir*, *11*, 3333–3336.

[5] Matsushita, S. I., Miwa, T., Tryk, D. A., & Fujishima, A. (1998). New mesostructured porous TiO_2 surface prepared using a two-dimensional array-based template of silica particles. *Langmuir*, *14*, 6441–6447.
[6] Prigogine, I. (1997). *The End of Certainty*, The Free Press: NY.
[7] Camazine, S. et al. (2001). *Self-Organization in Biological Systems*, Princeton University Press: New Jersey.
[8] Widawski, G., Rawiso, M., & Francois, B. (1994). Self-organized honeycomb morphology of star-polymer polystyrene films. *Nature*, *369*, 387–389.
[9] Maruyama, N. et al. (1998). Mesoscopic patterns of molecular aggregates on solid substrates. *Thin Solid Films*, *327–329*, 854–856.
[10] Wang, S. X., Wang, M. T., Lei, Y., & Zhang, L. D. (2000). Mesoscopic self-assembling morphology of polymer based on emulsification. *Mater. Res. Bull.*, *35*, 1625–1630.
[11] Nishikawa, T. et al. (1999). Mesoscopic patterning of cell adhesive substrates as novel biofunctional interfaces. *Mater. Sci. Eng. C*, *10*, 141–146.
[12] Nishikawa, T. et al. (2002). Fabrication of honeycomb film of an amphiphilic copolymer at the air-water interface. *Langmuir*, *18*, 5734–5740.
[13] de Boer, B. et al. (2001). Supramolecular self-assembly and opto-electronic properties of semiconducting block copolymers. *Polymer*, *42*, 9097–9109.
[14] de Boer, B., Stalmach, U., Melzer, C., & Hadziioannou., G., (2001). Synthesis and self-organization of PPV-based block copolymers for photonic applications. *Synthetic Metals*, *121*, 1541–1542.
[15] Matsushita, S. I., Kurono, N., Sawadaishi, T., & Shimomura, M. (2004). Hierarchical honeycomb structures utilized a dissipative process. *Synthetic Metals*, *147*, 237–240.
[16] Karthaus, O. et al. (2000). Water-assisted formation of micrometer-size honeycomb patterns of polymers. *Langmuir*, *16*, 6071–6076.
[17] Sawadaishi, T. et al. (2001). Two-dimensional patterning of nanoparticles using dissipative structures. *Mol. Cryst. Liq. Cryst.*, *371*, 123–126.
[18] Nishikawa, T. et al. (2003). Micropatterns based on deformation of a viscoelastic honeycomb mesh. *Langmuir*, *19*, 6193–6201.