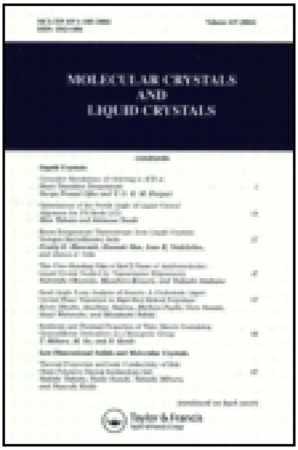

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PREPARATION OF MESOSCOPIC PATTERNS OF NANOPARTICLES BY SELF-ORGANIZATION

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Two-dimensional regular patterns consisting of ultra-fine particles were formed on honeycomb-patterned polymer film. Ultra-thin polymer films were prepared by simple casting of diluted amphiphilic polymer solution onto solid substrate. In the cast film, honeycomb patterns were observed as a result of evaporative cooling in the casting solution. Ultra-fine particles were introduced into the hole of honeycomb-patterned films by simple casting or dip-coating of aqueous ultra-fine particles dispersion. Densely packed ultra-fine particles were observed in only the hole of honeycomb pattern but not on the limb. The patterns of ultra-fine particles were expected to be the novel functional optical materials containing photonic crystals.

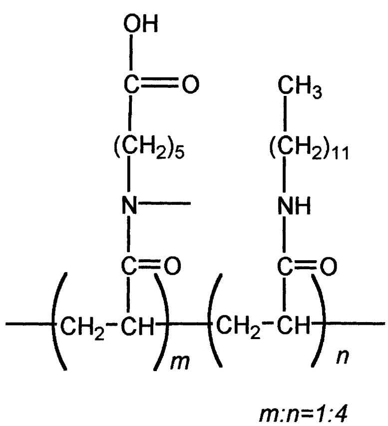
Keywords: dissipative structure; mesoscopic pattern; photonic crystal; self-organization; ultra-fine particles.

1. INTRODUCTION

Arrangement of ultra-fine particles is important for the application of photonic devices or electronic devices [1,2]. There are some methods for preparing the regular arrangement of ultra-fine particles, but a few approach using self-organization for arrangement and patterning of ultra-fine particles [3–7]. Recently, we have reported that some types of sub-micrometer-sized regular patterns were formed in cast films by simple casting of polymer solution or ultra-fine particles dispersion [8–12]. For example, regular stripe patterns were formed parallel to the receding direction of casting solution, when highly-diluted solution was cast onto freshly cleaved mica surfaces. Especially, in this paper, we paid much attention to the mesoscopic honeycomb structures in polymer film prepared by casting in highly-humid condition. By changing the casting condition, it is possible to control the hollow size and the pitch of the honeycomb patterns in the range from submicrometer- to millimeter-size. If organic or inorganic materials having high refractivities are adsorbed into the hollow of honeycomb patterns consisting of polymers, it was expected to be applied for the fabrication of the structure such as a photonic crystals. In this report, we will discuss about the investigation of the method for introducing of ultra-fine particles into the hollow of honeycomb-patterned polymer film.

2. EXPERIMENTS

Poly[*N*-caproic acid acrylamide-*co*-*N*-dodecylacrylamide] (CAP polymer, **1**), as an amphiphilic polymer, was synthesized in our group [10]. CAP polymer was dissolved in chloroform to the concentration of 1 g/l. Monodispersed aqueous silica particles dispersion (diameter: 100 nm) were kindly provided by Nissan Chemical Industries, LTD. The particles dispersions were diluted into proper concentration by purified water. Glass coverslips were washed with piranha solution (H_2O_2:H_2SO_4 = 1:1). Honeycomb-patterned cast films were prepared by the method which had been already reported [9,10]. In fact, 10 µl of CAP chloroform solution (1 g/l) was cast onto the surface of glass coverslip. The solvent of casting solution was evaporated at 25°C with blowing of humid air from a glass tube, and



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STRUCTURE 1

then, the cast film on a glass coverslip was naturally dried in the air. One μl of aqueous silica particles dispersion was deposited onto the surface of polymer films prepared. Water was naturally evaporated in the air at 25°C. Scanning electron microscopy (SEM) was performed by S-900 and S-3500N (HITACHI).

3. RESULTS AND DISCUSSION

SEM image of cast film consisting of CAP polymer is shown in Figure 1(a). As shown in the image, regular honeycomb-like networks were observed. As we have already reported, a film of the polymer was cast from homogeneous solutions of water-immiscible organic solvents. High atmospheric humidity favored the formation of honeycomb films. The mechanism of the pattern formation is described in detail by our research groups [13,14]. When diluted solution (~1 g/l) was dropped onto cleaned surface of solid substrate, on the evaporation of solvent, the condensation of water into a cooled surface of a water-immiscible solvent was caused. The micrometer-sized water droplets were regularly assembled along the three phase line of casting solution by the convection in casting solution. After water-immiscible solvent was evaporated, water droplet was evaporated leaving two-dimensional polymer network film. One microliter of silica particles dispersions were directly cast onto the surface of honeycomb-patterned polymer films. The casting dispersions were naturally evaporated at 25°C. Figure 1(b) and (c) shows SEM images of silica particles embedded in honeycomb-patterned polymer films. Densely packed silica particles were observed in the hollow of the honeycomb-patterned film. Silica particles

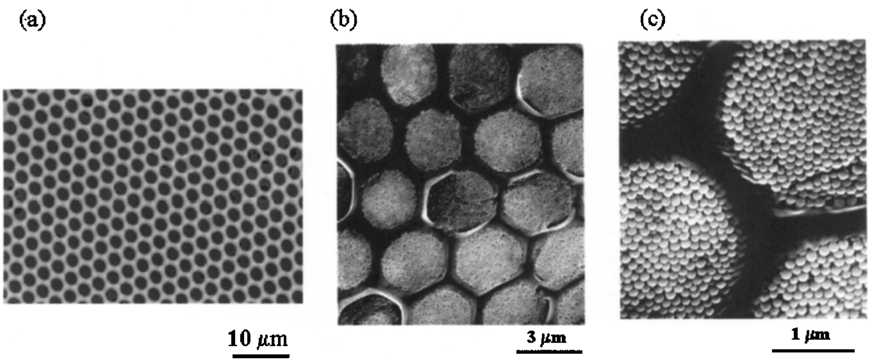

FIGURE 1 SEM images of (a) honeycomb patterned polymer film, (b), (c) silica particles (diameter: 100 nm) in the hollow of patterned film.

(<1 μm) could be inserted into the hole of the patterns. Because the height of the edge of honeycomb pattern was estimated to ca. 1 μm, the larger particles (>1 μm) were tend to get out of the hole of the patterns. For the application of photonic or electrical devices, we need to explore the possibility to isolate holes from each other. In this report, we described about silica particle patterns prepared by simply casting. We also succeeded to prepare honeycomb pattern-particles composite by using dip-coating and electrostatic adsorption between particles and solid substrate [15].

In conclusion, we have succeeded in introducing of ultra-fine particles into the honeycomb-patterned polymer films. Hierarchic structuring composite of colloidal nanoparticles (hexagonal particles packing) and regular arranged honeycomb-patterned polymer film can be expected to provide novel optical properties.

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