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Fabrication and Optical Property of Self-Organized Honeycomb-Patterned Films

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By using self-organization of water droplets formed in casting process of polymers, we have fabricated polymer films with hexagonally ordered micropores, termed honeycomb-patterned films, and attempted to apply them as photonic crystals. Optical properties of the honeycomb films are measured by FT-IR spectroscopy. A broad band attributed to the periodic structure is newly observed in the IR absorption spectrum of the honeycomb film.

Key Words: Self-organization, Honeycomb pattern, Photonic crystal, Periodic structure,

INTRODUCTION

Recently, many groups have already reported the fabrication of well-ordered structures using various techniques and have also demonstrated photonic band gap^[1,2], in which photons are forbidden to propagate. It has also been reported that well-ordered structures or ordered arrays were fabricated by the colloidal assembly technique using nano- or micro-spherical particles and examined as two- or three-dimensional photonic crystals^[3,4]. Self-organization techniques as well are useful as ready fabrication methods to obtain ordered structures. Shimomura et al. have already reported the fabrication of hexagonal

ordered porous films using a self-organization technique.^[5] Although there are some complicating factors in the formation mechanism of the hexagonal ordered porous structures, such films, termed 'honeycomb-patterned' films, can be readily prepared through the simple casting of dilute solutions of various amphiphilic compounds under a humid atmosphere.^[6,7]

By the definition of photonic crystals, a hexagonally ordered porous film can be regarded as a periodic refractive index structure between amphiphilic polymers and air. It can further be said that this method is a direct fabrication of porous structured photonic crystals. Here we would like to report the photonic character of self-organized honeycomb structures.

RESULTS AND DISCUSSION

Figure 1(left) shows the chemical structure of the amphiphilic copolymer used in this study. The plain Cap polymer film was prepared on a quartz substrate using spin-coating. The film was measured by ellipsometer using He-Ne laser (wavelength = 632.8 nm) as a light source. The refractive index of the Cap polymer was estimated at 1.465.

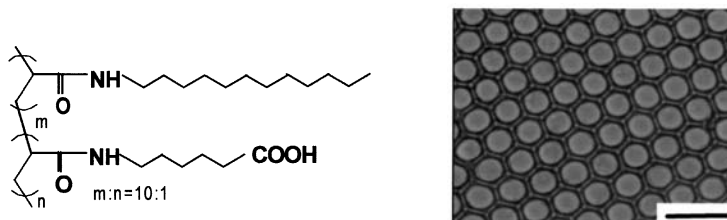


Figure 1. Chemical structure of polyacrylamide derivatives used in this study (left). Optical micrographs of a honeycomb-patterned film. Scale bar: $10\mu\text{m}$ (right).

Honeycomb-patterned films, formed via dissipative structure, were prepared by casting a benzene solution of Cap polymer on pure water under a humid atmosphere. The basic mechanism and details of preparation have been described.^[5,6,7] The films were prepared on the water surface then transferred to CaF_2 substrate. It was observed by transmission optical microscope that the film consisted of some well-ordered domains. Surface morphology was shown in figure 1 (right).

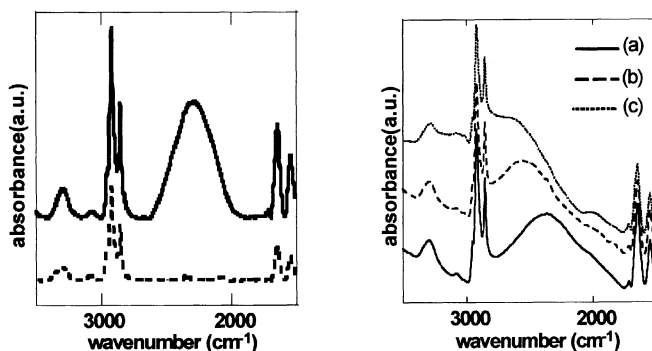


Figure 2.(left) FT-IR spectra of honeycomb-patterned and spin-coated films. solid line: honeycomb-patterned film; dashed line: spin-coated film.

Figure 3.(right) Effect of the pore size of honeycomb-patterned films. Pore sizes of honeycomb-patterned films is about 3.9 (a), 4.1 (b), 4.3 (c) μm , respectively.

This film was measured by FT-IR spectroscopy and compared with the spin-coated film. The result is summarized in figure 2. Solid and dashed lines represent honeycomb-patterned and spin-coated films, respectively. A broad peak was observed in the wave number of $2700\text{--}2000\text{cm}^{-1}$ in the spectrum of the honeycomb-patterned film. Since the spectrum of spin-coated film was the same as that of the bulk

polymer and all peaks were each assigned a chemical function, it is clear that this broad peak can be attributed to the honeycomb structure.

As the pore size of the films can be controlled by manipulating the rate of solvent evaporation, honeycomb films with differing pore sizes could be prepared which represented different periodic refractive index structures. Figure 3 shows the FT-IR spectra of three kinds of honeycomb-patterned films with pore sizes of about 3.9 (a), 4.1 (b), 4.3 (c) μm . These pore size values were calculated from the light scattering patterns and were consistent with microscopy observations. The results showed that the peaks attributed to the honeycomb structure shifted through the measurement of the three samples with different pore sizes. It was also confirmed that the peaks shifted on measuring under the oblique incident angle. These data indicated clearly that observed peaks are due to periodic structure of honeycomb film. The appearance of a strong peak is expected with the decrease in line defects between the ordered-domains in the films.

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