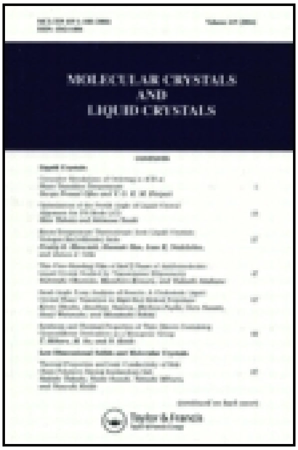

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Surface Properties of Self-Organized Honeycomb-Patterned Films

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Surface Properties of Self-Organized Honeycomb-Patterned Films

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This paper describes the preparation of honeycomb-patterned films from hydrophobic fluorinated copolymers. Micro-porous polymer films from fluorinated copolymers with hexagonally arranged micro-pores were prepared by casting polymer solution under humid condition. The pore size of the honeycomb-patterned film was controlled by changing casting volume. The water contact angles on the honeycomb-patterned films were measured with changing their pore sizes. The water contact angle increased up to 145°, when the pore size decreased. These values fitted the theoretical calculations.

Keywords: honeycomb-pattern; polymer film; self-organization; super hydrophobic

INTRODUCTION

This report describes the preparation of honeycomb-patterned film from fluorinated copolymers and their surface properties. It was reported that micro-porous polymer films from various polymers with hexagonally arranged micro-pores could be prepared by casting polymer solution under humid condition [1–4]. Hexagonally packed water

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micro-droplets are formed by evaporation cooling on the surface of the casting solution. The water droplets are transferred to the solution front by capillary force. After solvent evaporation, the honeycomb-patterned polymer film is formed with water droplet array as template. The template water droplets evaporate soon after solvent evaporation.

In this report, we describe prepared the honeycomb-patterned films from a fluorinated copolymer, **1**. The control of pore size and their surface properties are discussed.

EXPERIMENTAL

The fluorinated copolymer **1** was kindly provided by Asahi Glass Corporation. The copolymer **1** has fluorinated residue (n) and methyl-methacrylate (m), and its n:m ratio is 1:1. The copolymer was dissolved in AK-225 (mixture of $CF_3CF_2CHCl_2/CClF_2CHClF$, Asahi Glass Company, Japan) to prepare 10 g/L solutions. In all cases, homogenous solution of the compound (50 μL ~ 7.5 mL) was dropped onto glass substrates at ambient temperature. Humid air (relative humidity: 40 ~ 60%) was applied by an air pump (current velocity: 80 ~ 200 mL/min). The surface morphologies of the films were observed by scanning electron microscopy (SEM, S-3500N, Hitachi, Japan). The sizes of the prepared structures (pore size (d) and rim width (r)) were measured from these micrographs by using imaging software, the NIH image (National Institute for Health (NIH), USA). Contact angles of water on the prepared honeycomb-patterned films were measured by using a contact angle analyzer (G-1, ERMA Inc., Japan). Contact angles were measured 30 seconds after placing a water drop by the $\theta/2$ method. As a control experiment, a flat film was prepared by spin coating of 10 g/L polymer solution at 1,000 r.p.m.

RESULTS AND DISCUSSION

Hexagonally arranged micro-porous structure is clearly imaged by scanning electron microscopy (Fig. 1). Cross sectional image of the honeycomb-patterned film of **1** is also shown in the Figure 1. The spherical shape of the pores reflects the shape of template water droplets. Two layers of porous polymer sheet are stacked vertically by pillars at the vertex of hexagons.

The sizes of honeycomb structures are easily controlled by casting volume of polymer solution. The pore size of honeycomb-patterned film

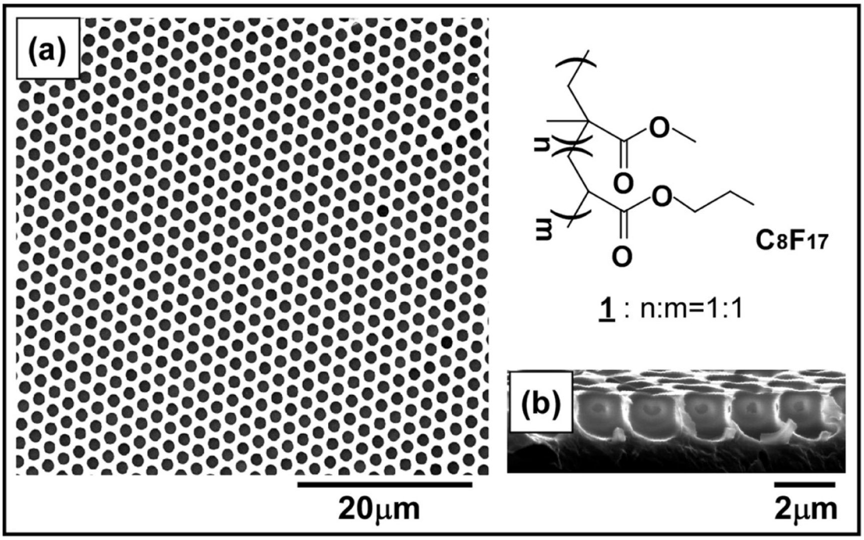

FIGURE 1 Chemical structure of the fluorinated copolymer **1** and scanning electron micrographs of (a) the honeycomb-patterned film of **1** and (b) its cross-section.

depends on the size of template water droplets. The size of the water droplets is dominated by the solvent evaporation time, which is equal to the water condensation time [5]. The pore size (d) and rim width (r) of honeycomb-patterned films were measured from each scanning electron micrograph by using the NIH image (Fig. 2(a), d: open circles,

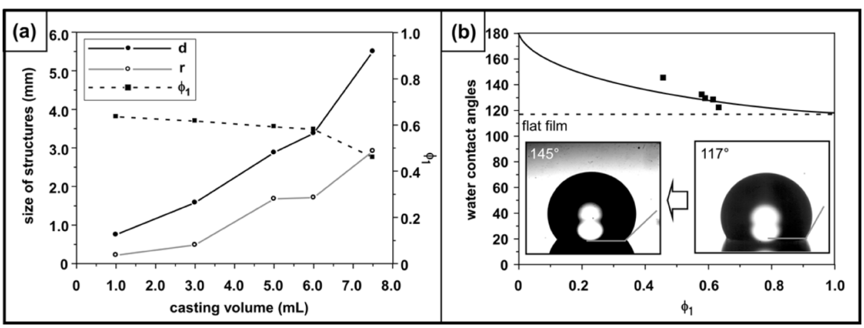

FIGURE 2 (a) The size (d, r) and surface area fraction of polymer (ϕ_1) change of honeycomb-patterned film. (b) The water contact angles on different ϕ_1 surface. The solid line shows the theoretical calculation.

r: closed circles). The averages of pore size and rim width of the films increased when large amount of polymer solution was cast. The average pore size of the hexagonally arrayed micro pores was ranged from 490 nm to 5.5 μm by changing casting volume from 20 μL to 7.5 mL.

The surface properties of the honeycomb-patterned films of **1** were measured by water contact angle measurements. The water contact angle of the flat film of **1** is 117°. In the case of honeycomb-structured film of **1**, the contact angle dramatically increases (Fig. 2(b), closed circles). Pore size dependence of the contact angle was observed. The maximum value of water contact angle on the honeycomb-patterned film is 145° (d = 0.75 μm). The superficial contact angle of the surface, which consists of two components (i.e., air and polymer), was described as a formula of fraction of surface areas of each proposed component reported by Cassie [6]. According to Cassie's law;

$$\cos\theta_c = \phi_1(\cos\theta_1 + 1) - 1 \tag{1}$$

where, θ_c is superficial contact angle; θ_1 and ϕ_1 are contact angles of flat film of polymer and surface area fraction of polymer, respectively.

According to the Eq. (1), large air void is required to achieve high contact angle. The ϕ_1 values of the honeycomb-patterned films of d = 0.75, 1.6, 2.9, 3.4, and 5.5 are calculated as 0.46, 0.58, 0.59, 0.62, and 0.64, respectively (Fig. 2(a), closed squares). The theoretical value of θ_c is calculated for each ϕ_1 and plotted as the solid line in Figure 2(b). The actual θ_c values are 145°, 132°, 129°, 128°, and 122°, respectively. The superficial water contact angles increased when the d decreased and the ϕ_1 values increased. These results show the water contact angle on the honeycomb-patterned films fitted Cassie's model.

We show the water repellent properties of the honeycomb-patterned films of the fluorinated copolymer. The micro-porous films of the fluorinated copolymers with different compositions are prepared. The fluorinated copolymer **1** forms well-arranged honeycomb-patterned films. The water contact angles of the honeycomb-patterned films are higher than the flat film. The value of water contact angles fitted the theoretical calculation.

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