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A study on formation of regular honeycomb pattern in polysulfone film

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Abstract

Regular polysulfone (PSF) honeycomb film with micron-sized cells was prepared by casting the solution in an atmosphere with high humidity. Water droplets acted as the template around which the PSF in the solution assemble. In this paper, the effects of atmosphere humidity, solution concentration, and the PSF molecular weight on pore size were discussed; the influence of storage time of casting solution on the pattern regularity was presented; the mechanism of pattern formation was proposed.

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Keywords: Polysulfone; Honeycomb films; Water droplet

1. Introduction

Highly regular patterned thin films have attracted much attention for their potential use in micro reactors [1], separation [2], or optical application [3,4]. Conventionally, they can be prepared by 'lithography' [5] or 'soft lithography' [6], a top-down engineering approach of printing a constructed pattern into the material. However, this method is expensive and complicated [7]. Moreover, self-organization approach requires a regular pattern of a template around which the material of interest is assembled. Block copolymers [8], colloids [9–11] and water in oil emulsions [12] can be used as templates.

Recently, Francois et al. [13–16] described their new method in preparing honeycomb films. They cast a solution of polystyrene–polyparaphenylene-*block*-copolymers (PS–PPP), or a polystyrene star polymer in carbon disulfide onto a substrate under moist air flow. After the solvent evaporated, films containing empty cells organized in a hexagonal array were obtained. They believed that in this method water droplets condensed from water vapor act as the template around which materials is assembled, a spherical polymer or a micelle in the solution support the regularity. Srinivasarao et al. [17] prepared 2D and 3D ordered macro porous layers and they thought this depends on the solvent density with respect to the density of water. Shimomura et al. used different kinds of compounds including organic–inorganic hybrid materials [18], amphiphilic copolymers [19–21], metal organic and saccharine-containing polymers [22] for patterning, and described the process of honeycomb pattern formation.

In this paper, a kind of novel honeycomb films with polysulfone was prepared in a humid chamber from its chloroform solution as the solvent evaporates. Polysulfone is a kind of high-performance thermo-plastic with such desirable characteristics as resistance to acidic and salt solutions and good resistance to detergents, hot water, and steam; they have been widely used to form various types of membrane. With this method, a kind of PSF membrane with regular pore size can be expected to obtain. The film structure was observed, the influences of the humidity, concentration and molecular weight on the pore size were discussed.

2. Experimental details

Polysulfone with two kinds of molecular weight (M_w = 44,000, 56,000) were purchased from Aldrich and one kind of molecular weight (M_w = 75,000) from Solvay. To prepare the ordered microporous polymer film, 100 μl of polymer

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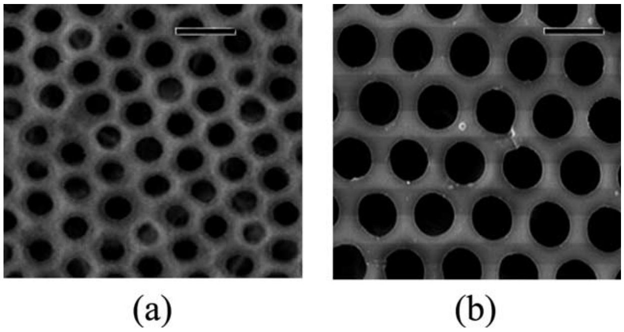

Fig. 1. SEM images of regular structures in PSF films obtained under different atmosphere humidity. Solution concentration, 0.3 wt%; polymer molecular weight, 75,000. Atmospheric temperature: 25 °C. Relative humidity: (a) 65%, (b) 85%. Scale bar 5 μm.

solutions (0.3, 0.6, 1 wt%) in chloroform were cast onto the glass substrate at 25 °C and were placed into a chamber whose humidity can be controlled (Solutions were stored for 30 days prior to the casting; one freshly prepared solution was cast for comparing). The surface morphologies of the obtained films were observed by scanning electron microscopy (JSM-35CF; JEOL, Tokyo, Japan).

3. Results and discussion

3.1. Influence of atmospheric humidity on the pore size

The PSF (M_w = 75,000, 0.3 wt%) chloroform solution was used to investigate the influence of the relative humidity on pattern formation. The humidity was set to 45%, 65%, 85% and 95%, respectively. When the humidity is 45%, no regular pattern was found; only transparent film was formed, because almost no droplet condenses onto the solution surface. The pore sizes of films with regular patterns were found to increase with increased humidity, as shown in Fig. 1. At a high humidity (>95% R.H.), the pore size distribution of obtained film was very broad because too many droplets condense onto the solution surface, the coalescence of water droplets can not be avoided.

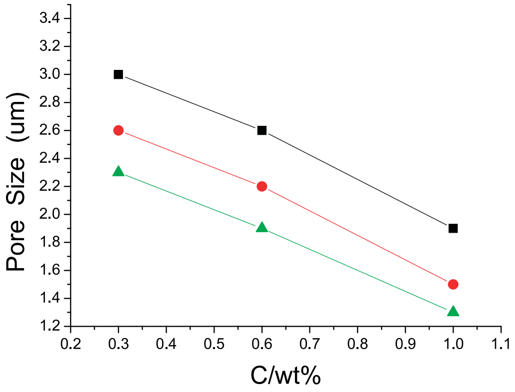

Fig. 2. Correlation between pore size and concentration of casting solution. Atmospheric conditions: temperature, 25 °C; relative humidity, 85%. (▲), M_w = 44,000; (●), M_w = 56,000; (■), M_w = 75,000.

3.2. Influence of concentration on the pore size

Three kinds of PSF with different molecular weight (44,000, 56,000, and 75,000) were prepared into solution of three concentrations (0.3, 0.6, 1 wt%), respectively, to investigate the influence of concentration on pore size.

As shown in Fig. 2, the pore size reduced as the concentration increases. Theoretically, Henry law (Eq. (1)) indicates that, the solvent in a more concentrated solution has a lower vapor pressure.

$$P = P_0(1 - X_B) \tag{1}$$

Where P is the vapor pressure of solvent in solution, P_0 is the vapor pressure of pure solvent, and X_B is the mole fraction of the solute.

Low vapor pressure slows the solvent evaporation, leading to a higher surface temperature for a more concentrated solution and vice versa. It was believed that the key process to a uniform droplet size is a fast nucleation of droplets on the surface in conjunction with a very slow growth of their size [23]. On the other hand, the increase of the radius of droplets R per unit time t is proportional to the temperature difference [24] ($\Delta T = T_r - T_s$), (T_r is the

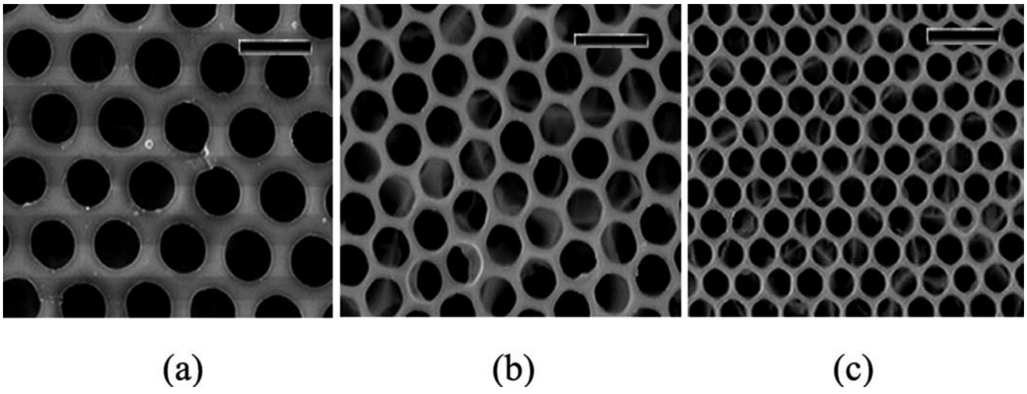

Fig. 3. SEM images of PSF honeycomb films obtained from different concentrations of casting solution. Molecular weight, 75,000; atmospheric conditions: temperature, 25 °C; relative humidity, 85%. Solution concentration: (a) 0.3 wt%, (b) 0.6 wt%, (c) 1 wt%. Scale bar 5 μm.

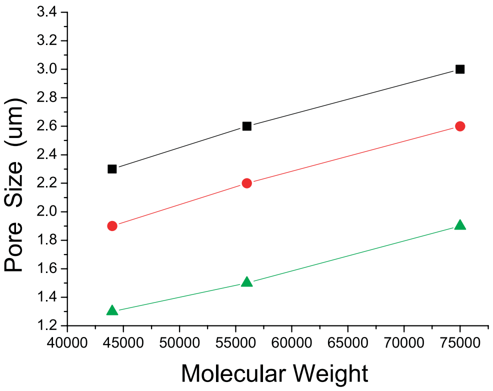

Fig. 4. Correlation between pore size and polymer molecular weight cast from PSF solution in chloroform. Atmospheric conditions: temperature, 25 °C; relative humidity, 85%. (▲), concentration: 1 wt%; (●), concentration:0.6 wt%; (■), concentration:0.3 wt%.

temperature of atmosphere, T_s is the temperature of surface).

$$dR/dt \sim \Delta T^{0.8}$$

At the nucleation stage, a more concentrated solution has a smaller ΔT, so the droplet's size increases much slower on its surface. Considering the nucleation time is short enough to be regarded as the same for all solutions, the droplet nuclears form on the surface of a more concentrated solution will be smaller. At the growing stage, the growth speed of the droplet size is very small, the droplet diameter R is observed to grow with time t according to $R \propto kt^{1/3}$, where k is a function of the velocity of the airflow and of the surface temperature [16]. Though the solvent in a more concentrated solution has a longer time to volatilize, the size of the droplets on it increases little more than on a diluter solution. So a conclusion can be drawn that the nucleation stage is the key process of determining the droplet size, and a more concentrated solution leads to a smaller pore size (Fig. 3). On the other hand, the viscosity of a more concentrated solution is higher, which consequently cased the delay of the droplets' growth.

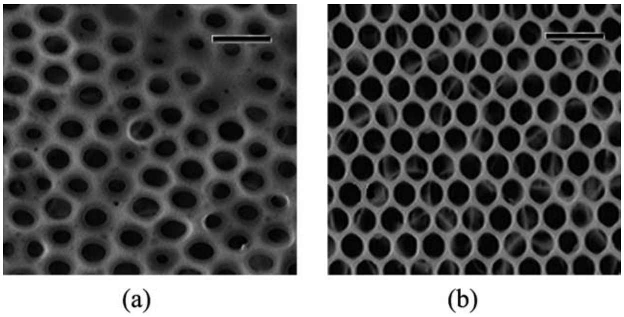

Fig. 6. SEM images of PSF honeycomb film with different storage time of casting solution (concentration: 1 wt%). Atmospheric conditions: temperature, 25 °C; relative humidity, 85%. Molecular weight: 75,000. (a) Freshly prepared. (b) Stored for 30 days. Scale bar 5 μm.

3.3. Influence of molecular weight on the pore size

As shown in Fig. 4, the pore size increases with molecular weight. In every three kinds of solution with the same weight concentration, the polymer molecular weights are different. The higher the molecular weight is, the lower its mole fraction is. According to Henry Law given above, the solution of a higher molecular weight polymer has a higher P, and the solvent evaporates fast. For the same reason above (detailed in Section 3.2), the pore size increased with the molecular weight (Fig. 5).

In the experiment, it has also been found when the chloroform solution of PSF was stored for 30 days prior to the casting, the film had much higher regularity than a freshly prepared solution (Fig. 6).

This kind of phenomenon might be caused by the polymer action in the solution. The polymer chains in the solution aggregate and form clusters after a period of time. As it was pointed out that a spherical-shaped polymer is easy to obtain high regularity [15], the film obtained from a solution stored for 30 days has a much higher regularity. Selvaraj et al. [25] found polysulfone cyclic dimer in polysulfone solution by high resolution mass spectroscopy, ^{1}H NMR, end-group analyses and SEC. The cyclic dimer of polysulfone has a tendency to crystallize in several days and

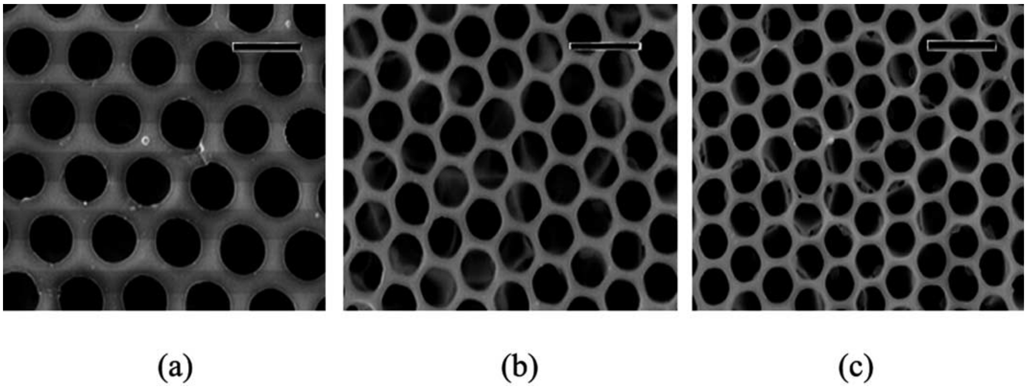

Fig. 5. SEM images of regular pattern in PSF films with different PSF molecular weight. Solution concentration: 0.3 wt%. Atmospheric conditions: temperature, 25 °C; relative humidity, 85%. Molecular weight: (a) 75,000, (b) 56,000, (c) 44,000. Scale bar 5 μm.

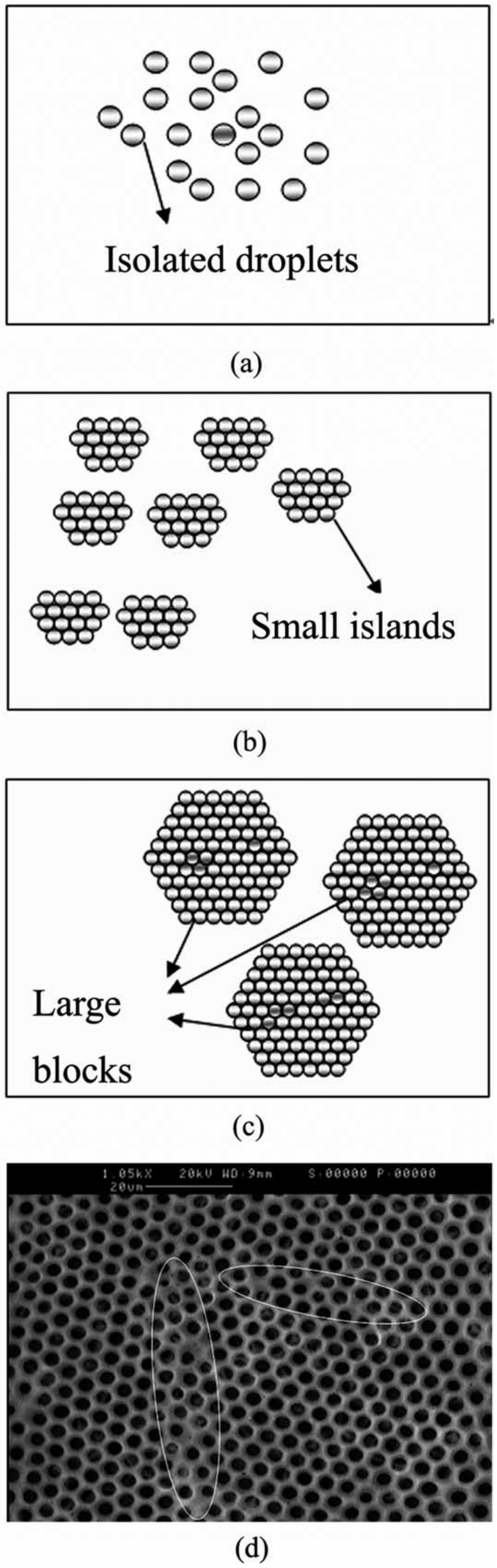

Fig. 7. Proposed mechanism of the formation of regular pattern. (a) Water droplets condense to cool solution surface and form isolated droplets. (b) A few water droplets arrange themselves into 'small islands' with ordered structures due to locally occurring capillary forces. (c) Surface currents force small islands into big blocks. (d) SEM image of a honeycomb film made of PSF. Large blocks are pulled together with the evaporation of solvent. The irregular border is pointed out with two white ellipses.

a slight precipitation may occur. So it was reasonable to regard that the increasing of regularity described above also has some relationship with the crystallization of polysulfone cyclic dimer. A more detailed understanding and description of this phenomenon is currently under investigation.

3.4. Mechanism of pattern formation

The mechanism of this ordered morphology formation has been widely investigated. It has been proved that the structures are formed around a honeycomb template of water droplets condensed onto the solution surface which vanishes after evaporation. The condensation phenomenon is called 'breath figures', which appears when a cold solid or a liquid surface is contacted with moist air [26,27]. When droplets condense onto a liquid surface, the interactions between the droplets can be modified, because the substrate is locally mobile and curved. A highly volatile solvent like chloroform evaporates rapidly from the cast polymer solution, and the temperature of the solution surface decreases (a temperature of $-6\,^{\circ}\mathrm{C}$ has been measured during evaporation of the solvent [28]). Initially the water vapor in the moist air condenses onto the cold solution surfaces, forming micron-sized droplets, as the density of water are less than that of the chloroform, the isolated droplets float on the solution surface. The capillary attractive forces are regarded as an important element in the formation of the honeycomb structure [14]. It allows each three droplets to locally arrange into a stable triangular geometry, while other droplets will arrange themselves onto each side of the triangle. Thus stable compact hexagonal small islands form (note: the capillary force acts only locally, over longer distances it is much smaller than the thermal energy $k_{\mathrm{B}}T$ [14]). Surface currents, which might not only be caused by the applied airflow and convection, but also by local variation of the superficial tension (Marangoni convection) [13], force the 'small islands' into hexagonal close-packing 'big blocks'. However, the surface currents are not strong enough (especially when the solution has a high viscosity, the surface currents are weakened) to regulate those 'big blocks' into a perfect hexagonal close packing array. Along with the evaporation of the solvent, the solution surface area decreases; the 'big blocks' are pulled together, and form an irregular border, as it is pointed out with two white ellipses in Fig. 7. The arrangements on each side of the ellipses are different.

In our case, the PSF in the solution precipitates at the interface between the solution and water and forms a monomolecular polymer layer. An X-rays experiment taken by Widawski indicates that [29] the characteristic length between the PPP [poly (p-phenylene)] cores of the micellar aggregates had been found to be about 209 Å in the case of featureless films (prepared in dried atmosphere), a smaller one (139 Å) was observed in the structured films (prepared in moisture). Pitios et al. [14] considered that this reduction of the characteristic length in the case of ordered films can be related to a ‘precipitated-like’ state for the polymer. Additionally, the capillary pressure at the three-phase line (air, water and solution) is strong enough to pull the polymer film to the top of the water droplet [30], just like an envelope, avoiding the coalescence of the water droplets.

4. Conclusions

We successfully prepared ordered microporous PSF films by a simple solution-casting method. The PSF film was formed around a template of water droplets, and the pore size was affected by the atmosphere humidity, solution concentration, and polymer molecular weight. The pattern regularity of PSF film was also affected by the storage time of PSF/chloroform solution. By varying these conditions, we were able to control the size of these films. Together with the excellent performance of PSF in preparing membrane, we can expect this film to have great potential use not only for cell culture substrates but also for membrane.

Acknowledgements

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