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Water droplets as templates for ordered honeycomb-structured films prepared from PS-b-Peb-b-PS-MA

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ABSTRACT

Polystyrene-block-poly(ethylene-ran-butylence)-block-polystyrence-graft-maleic (PS-b-Peb-b-PS-MA) is an amphiphilic block copolymer which was recently synthesized by our group. By self-organization method, ordered honeycomb-structured PS-b-Peb-b-PS-MA films was achieved in a humid atmosphere. The effects of PS-b-Peb-b-PS-MA concentration, solvent, humidity and additive have been studied. Benzene was the best solvents because it owns the analogous elements with PS-b-Peb-b-PS-MA. The films with regular honeycomb-structure were formed when the PS-b-Peb-b-PS-MA concentration was 20 g/l, benzene as the solvent, and the relative humidity was 80%. With the increase of the benzene/acetone ratio, the pore size of the film became larger. The results showed that ordered honeycomb-structures could be formed by amphiphilic block copolymers and enlarged the family of materials which could be used to form ordered honeycomb-structured films. In addition, the investigation of surface tension which strongly influenced the pore size, strengthened the mechanism of the formation of ordered honeycomb-structure. Moreover, with the adding of acetone, better control of the pore size can be achieved.

Keywords: Honeycomb; Water droplets; PS-b-Peb-b-PS-MA; Surface tension; Solvent; High-humidity environment

1. Introduction

Ordered honeycomb-structured films have been attracted great attention due to their wild applications in chemical sensors [1], scaffolds for catalysis [2], biology [3], tissue engineering [4] etc. Using water droplets as templates is one of the most important methods for preparing ordered honeycomb-structured films. Under the moist atmosphere, the solvent evaporates and the temperature decreases. So the water evaporation is condensed on the surface of the solution, which acts as templates of the pores. This structure always called as "Breath Figures" is closely associated with the humidity of the atmosphere [5].

Francois [6] pioneered this method by casting a solution of star-shaped polystyrene in carbon disulphide onto a substrate and then films with honeycomb structure were obtained. Because of its convenience, researches about the material, the mechanism of patterning, the influencing factors of this method have been done. Julian [4] fabricated surfactant-free honeycomb-structured hydrophilic Poly($_{DL}$lactide) (P$_{DL}$LA) and Poly-($_{DL}$lactide-co-glycolide) P$_{DL}$LGA thin films by water droplet templating methods and suggested that they could be applicable as scaffolds for tissue engineering. Solvent, polymer concentration and humidity were found to be important factors in the formation of honeycomb structured thin films. Xu [7] prepared regular hydrophobic polysulfone (PSf) honeycomb film and discussed the effects of atmospheric humidity, solution concentration,

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and the PSf molecular weight on pore size. By adjusting the concentration or the types of the polymers, the strength of the surface thin film was controlled. PEK-C and PLEG (8:1) formed regular patterns at low concentrations but PPO required high concentrations. This phenomenon is mainly caused by the hydrophilicity of the polymers. PEK-C and PLEG (8:1) are hydrophilic polymers, and PPO is a hydrophobic polymer. Hydrophilic polymer molecules gather more easily on the solution surface than hydrophobic polymer molecules [8]. The amphiphilic copolymer includes hydrophobic chain and hydrophilic chain, whose law of forming honeycomb-structured film is different with above mentioned. Tian [9] studied the fabrication of honeycomb-patterned films from amphiphilic poly(L-lactide)-block-poly(ethylene glycol) (PLEG) in an atmosphere of high-humidity. By adding sodium dodecylsulfate to a concentrated solution of 1 g/l PLEG/CHCl3, regular pores could be obtained.

Recently, the literatures of amphiphilic polymers were extremely scanty. To study the formation mechanism of the ordered honeycomb-structure film of the new-style amphiphilic copolymer (PS-b-Peb-b-PS-MA), the effect of the concentration of PS-b-Peb-b-PS-MA, solvent, humidity, and the concentration of additive acetone on patterning were studied in details by SEM and a surface tensiometer.

2. Experimental

2.1. Material

Polystyrene – block - poly (ethylene – ran - butylence) – block – polystyrence – graft - maleic, abbreviated as PS-b-Peb-b-PS-MA, was synthetized by our group in Laboratory of New Materials Institute of Chemistry Chinese Academy of Sciences. Benzene, toluene, chlorylene, acetone were analytical reagents and purchased from Beijing Chemical Reagent.

2.2. Film preparation

PS-b-Peb-b-PS-MA was dissolved in solvent, and then it was stirred by SHZ-82 constant temperature shaker (Guohua Instrument Factory, Jiangsu, China) for 24 h to make the polymer dissolved completely. Then, PS-b-Peb-b-PS-MA solution was cast on a glass substrate and placed in a chamber, whose relative humidity could be controlled at room temperature. Water vapor was fed into the chamber, a few minutes later, the ordered honeycomb-structured film was formed.

2.3. Morphologies of the film

The surface morphologies of the films were observed using SEM (S-3400N, HITACHI). The films were dried prior to be coated with gold layer.

2.4. Surface tension of the polymer solution

The surface tension of the polymer solution was measured by a surface tensiometer (SEO-DST30M).

3. Results and discussions

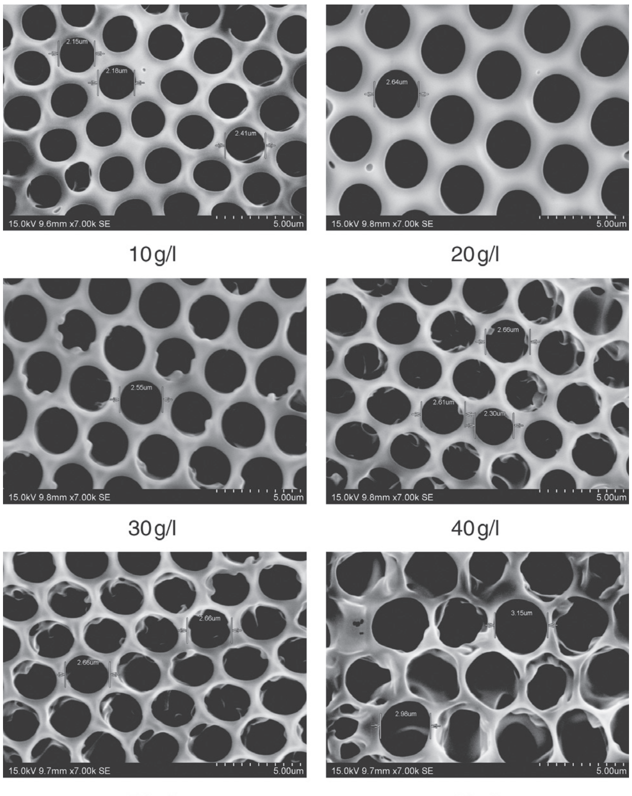
3.1. Influence of solution concentration

Benzene was chosen as the solvent to study the influence of the concentration of PS-b-Peb-b-PS-MA on patterning. In the chamber, the environmental temperature was room temperature and the relative humidity was 80%.

The surface tension showed the tendency of ascend first and decreased later. The maximum value was in 40~50 g/l of polymer solutions, and the minimum content was in 80 g/l of polymer solution (Table 1). Fig. 1 showed

Table 1
Surface tension of PS-b-Peb-b-PS-MA/benzene solutions for different polymer concentration (room temperature)

Concentration of polymer (g/l)	10	20	40	50	60	80
r (mNm^{-1})	26.768	26.847	27.244	27.244	25.188	24.951



10 g/l 20 g/l
30 g/l 40 g/l
50 g/l 60 g/l

Fig. 1. SEM images of films for different PS-b-Peb-b-PS-MA concentrations. Temperature: room temperature; Relative humidity: 80%; Solvent: benzene.

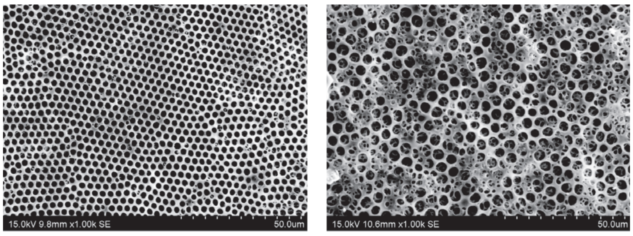
that the average pore size was stable around 2.6 μm when the solution concentration varied from 20 to 50 g/l, compared to 2.2 μm in 10 g/l and 3 μm in 60 g/l.

Under general conditions, it is believed that polymer tends to form an extremely thin surface film on the surface of the solution to both reduce the surface tension of the emulsion and stabilize the water droplets in the solution in order to ensure the uniformity of the water droplets. However, PS-b-Peb-b-PS-MA was an amphiphilic polymer, which had different property in comparison with PLEG, PPO and so on. In Fig.1, it was found that many pores were formed on the surface of the film when the polymer concentration was more than 30 g/l. When the concentration of PS-b-Peb-b-PS-MA was lower than 30 g/l, water droplets were condensed on the surface of the solution, and a higher surface tension helped to prevent the water droplets from easily immersing into the solution so that regular structure with smaller pores could be obtained; When the concentration of PS-b-Peb-b-PS-MA was higher than 30 g/l, the acting force between PS-b-Peb-b-PS-MA and water vapor increased and the surface tension decreased as the concentration of PS-b-Peb-b-PS-MA rose. Therefore, the larger pores were formed.

3.2. Influence of solvent

Benzene, chlorylene and toluene were chosen to study the influence of solvent on patterning. In the chamber, the environmental temperature was room temperature and the relative humidity was 80%.

When the polymer concentration was 20 g/l, it was shown in Fig. 2 that solvent benzene could get more regular honeycomb structure than chlorylene. And the pore size of the later was much larger than that of the former. Table 2 gave reason to this phenomenon that the surface tension of PS-b-Peb-b-PS-MA/benzene was higher than that of PS-b-Peb-b-PS-MA / chlorylene. When the polymer concentration was 80 g/l, Fig. 3 showed that the film with irregular pores was obtained from PS-b-Peb-b-PS-MA/ toluene while there were hardly regular honeycomb pores from PS-b-Peb-b-PS-MA/benzene. Table 3 illustrated that the surface tension of PS-b-Peb-b-PS-MA/benzene was much lower than PS-b-Peb-b-PS-MA/ toluene and could not prevent the coalescence of water droplets and finally led to an irregular pattern.

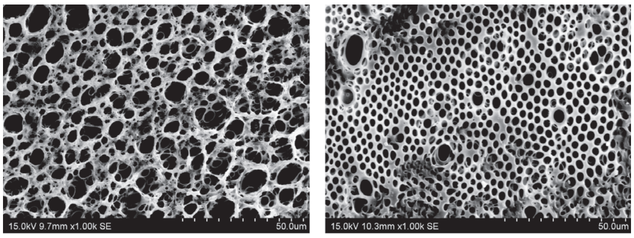


benzene chlorylene

Fig. 2. SEM images of films for different solvents. Temperature: room temperature; Relative humidity: 80%; Polymer concentration 20 g/l.

Table 2
Surface tension of PS-b-Peb-b-PS-MA solutions with different solvents
(T= room temperature, polymer concentration=20 g/l)

Solvent	benzene	Chlorylene
r (mNm^{-1})	26.847	23.209



benzene toluene

Fig. 3. SEM images of films for different solvent. Temperature: room temperature; Relative humidity: 80%; Polymer concentration 80 g/l

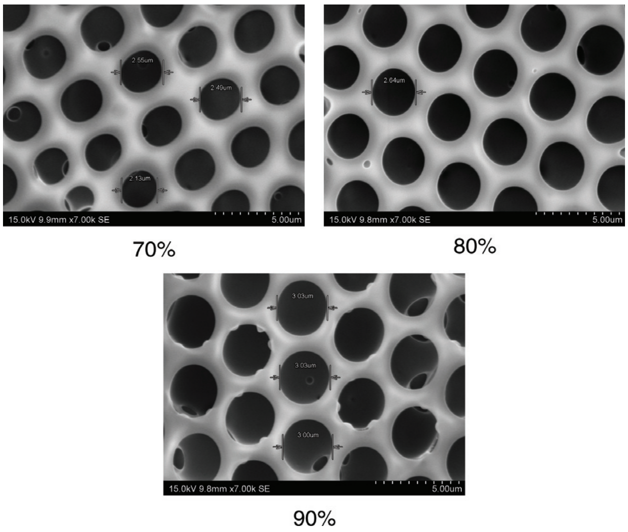
Table 3
Surface tension of PS-b-Peb-b-PS-MA solutions with different solvents
(T= room temperature, polymer concentration=80 g/l)

Solvent	benzene	Toluene
r (mNm^{-1})	24.951	26.517

3.3. Influence of humidity

The two-dimensional array of water microspheres is a template for the porous structure of the honeycomb film, and the size of a water microsphere is one of the determining parameters of the pore size, so the humidity of the atmosphere influences the water condensation at the air-polymer solution interface and, consequently, influences the pore size and regularity of the micropore arrangement [10,11].

To investigate the influence of humidity, PS-b-Peb-b-PS-MA films were prepared at relative humidity of 70%, 80%, and 90% when the environmental temperature was room temperature, polymer concentration was 20 g/l



70%

80%

90%

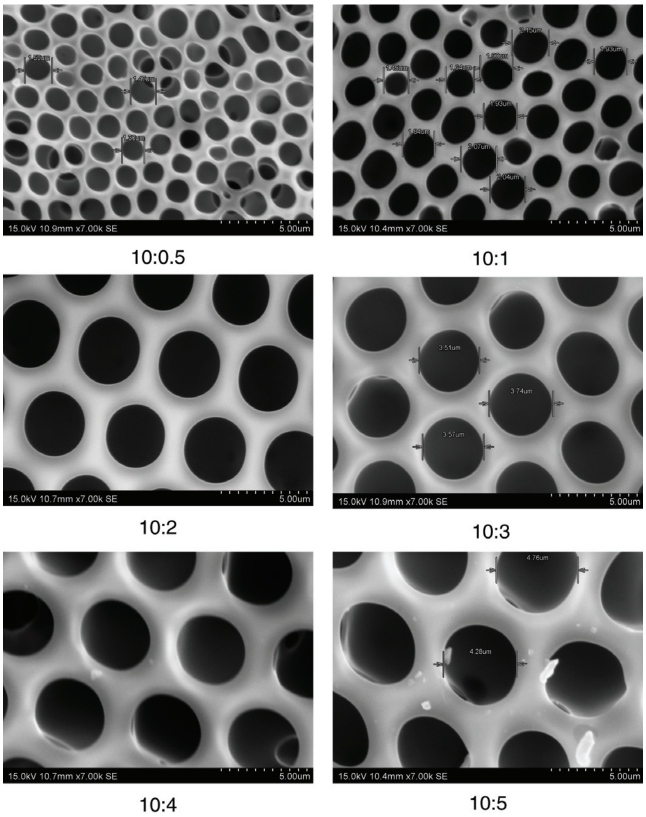
Fig. 4. SEM images of films for different humidity. Temperature: room temperature; Polymer concentration 20 g/l.

and the solvent was benzene. As shown in Fig. 4, regular structures were obtained under these circumstances. With the increase of relative humidity, the pore size enlarged from 2.4 to 3.0 μm. The optimal structure was obtained at the relative humidity of 80%.

3.4. *Influence of additive*

To better investigate the influencing factor on pore size and the mechanism, acetone was added to the solution as additive. Benzene was chosen as the solvent, and the concentration of PS-b-Peb-b-PS-MA was 20 g/l. In the chamber, the environmental temperature was room temperature and the relative humidity was 80%.

As shown in Fig. 5, the pore size enlarged as the proportion of acetone increased. Two reasons might be used to explain this phenomenon. With the adding of acetone, the concentration of PS-b-Peb-b-PS-MA reduced relatively so that the surface tension decreased (Table 4), which directly caused the enlargement of the pores. On the other hand, acetone changed the evaporation temperature of the solvent. The condensation of the water vapor could be divided into two stages: a fast nucleation stage and a slow growing stage. And it was believed that the key process to a uniform droplet size was a fast nucleation of droplets on the surface in conjunction with a very slow growth of their size [5]. Moreover, the increase of the radius of droplets R per unit time t is proportional to the temperature difference (ΔT, $\Delta T = Tr - Ts$), (Tr is the temperature of atmosphere, Ts is the temperature of surface), $dR/dt = \Delta T^{0.8}$. The boiling point of benzene is 80.10°C, while that of acetone is 56.48°C, which means acetone is much more volatile than benzene under the same condition, and a larger proportion of acetone lead to a fast evaporation and consequently, a larger ΔT. Considering the nucleation time was short enough to be regarded as the same for all solutions, solution with a larger proportion of acetone formed larger pores. In conclusion, tone can say that with the adding of acetone, which has a lower boiling point, the pore size increased.



10:0.5

10:1

10:2

10:3

10:4

10:5

Fig. 5. SEM images of films for different benzene/acetone. Temperature: room temperature; Relative humidity: 80%; Polymer concentration 20 g/l.

Table 4
Surface tension of PS-b-Peb-b-PS-MA/benzene solutions with different acetone
(T= room temperature, polymer concentration=20 g/l)

Benzene/Acetone (V/V)	10:0.5	10:1	10:2	10:3	10:4	10:5
r (mNm^{-1})	26.293	26.293	25.740	25.819	25.563	25.266

4. Conclusions

Ordered honeycomb-structured films have been successfully obtained by the amphiphilic copolymer (PS-b-Peb-b-PS-MA). As elevating the concentration of PS-b-Peb-b-PS-MA, average pore size had an increasing tendency. Benzene was a good solvent when the polymer concentration was lower than 30 g/l. With the increase of relative humidity, the pore size enlarged from 2.4 to 3.0 μm. By adding acetone to PS-b-Peb-b-PS-MA/benzene solution, the pore size of the film increased because of the decreasing surface tension and the higher differential temperature (ΔT). The ordered honeycomb structured film was successfully prepared that met the following conditions: benzene as the solvent, 20 g/l of the concentration of PS-b-Peb-b-PS-MA, 80% of the relative humidity, 10:2 of the ratio of benzene/acetone.

Acknowledgements

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