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The formation of honeycomb structure in polyphenylene oxide films

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Abstract

The ordered honeycomb polyphenylene oxide (PPO) film was prepared by casting the solution on a solid substrate in a high humid environment in this paper. It was found that PPO/$CHCl_3$ solution could form regular microporous film in a large range of solution concentration (2–70 g/L) and their pore size was almost equal when the concentration varied from 5 to 30 g/L. Based on these phenomena, the mechanism of the formation of PPO honeycomb film was proposed. Moreover, several solvents were chosen to investigate the influence of the compatibility between PPO and solvents, and the volatility of solvents on the pattern regularity. It was found that good compatibility between PPO and solvents, and the appropriate volatility of solvents were important for the fabrication of honeycomb structure. Finally, some other affecting factors, such as the environment temperature and the molecular weight of PPO, were also tested.

Keywords: Polyphenylene oxide; Honeycomb films; Influences

1. Introduction

Microporous films with honeycomb structures received great interest in recent years, which might be applied in chemical sensors [1], optical apparatus [2], scafflold for catalysis [3], biology [4,5], tissue engineering [6], and micrographics [7], etc. A number of techniques were studied for fabricating microporous polymer membranes, such as lithography [8], photolithography [9], and emulsions [10], etc.

Recently, a new method utilizing water droplets as templates was used to form ordered porous films, which was first described by François et al. [11–14]. They cast the solution of polyparaphenylene in carbon disulfide onto a substrate in a high humid atmosphere. After the solvent and water droplets evaporated completely, a film with regular honeycomb pores was obtained, and they believed that the water droplets condensed on the surface of the solution acted as the templates. Because easily manipulated, this method aroused much attention [15–29], and many polymer materials were used to prepare honeycomb-like films. Initially, the study was mainly focused on those materials that contained some polar groups in their molecules, because it was thought that polar groups could increase the hydrophilicity of the polymers and stabilize the water droplets that condensed on the surface of the polymer solution. These materials included rod–coil block copolymer [30], star polymer [31], amphiphilic copolymer [32,33], organic/inorganic hybrid materials [34], and polyion complexes [35,36], etc. Recent years' research showed that a few hydrophobic polymers, without any polar end group in their molecule structures, also led to ordered porous films. Peng et al. [37] got honeycomb films by using polystyrene (PS) with linear structure and interpreted that honeycomb patterns was depended on the viscosity of the polymer solutions. Xu et al. [38] formed regular porous structures by polysulfone (PSF) and concluded that this appearance was caused by the self-assemble in the solutions of PSF.

Polyphenylene oxide (PPO) was a kind of high-performance thermo-plastic polymer with desirable characteristics such as resistance to heat and good endurance to water, which was widely studied in the field of membrane science [39,40]. However, using PPO to form honeycomb film did not been reported. In this paper, the fabrication of honeycomb structure of PPO in a high moist environment was researched. The mechanism of the formation of regular morphology in PPO films was discussed. Furthermore, the influences of the compatibility between PPO and Solvents, as well as the volatility of solvents on the pattern regularity were investigated. Besides, some other affecting factors such as the

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environment temperature and the molecular weight were also tested.

2. Experimental details

Polyphenylene oxide with two kinds of molecular weight ($M_w = 40$, 70 K) was purchased from Aldrich. The Solvents, spectroscopy grade, were purchased from Beijing Chemical Corporation, which included chloroform ($CHCl_3$), carbon bisulfide (CS_2), benzene, toluene, dichloromethane (CH_2Cl_2), and trichloroethylene (C_2HCl_3). Water was purified by a Millipore system (Milli-Q, Millipore). The honeycomb films were prepared directly by casting the PPO solution (100 μL) on glass substrates with controlled temperature and were placed into a chamber whose relative humidity was 95%. The surface morphology of the microstructured films was characterized by scanning electron microscopy (S-4300, Hitachi), operating at a 25-kV accelerating voltage. Wettability of PPO was characterized by the contact angle with bi-distilled water at room temperature by using a contact angle meter (FACE CA-D, Kyowa kaimenkagaku Co.). Surface tension of $CHCl_3$ and PPO/$CHCl_3$ solutions were also measured at room temperature (KSV Sigma703), following the Wilhelmy method.

3. Results and discussion

3.1. Formation of the honeycomb structure and its mechanism

After casting a drop of the PPO/$CHCl_3$ solution on a glass slide, the solvent began to evaporate and some phenomena were observed immediately. It was found that, with the volatilization of the solvent, the transparent polymer solution became turbid due to emulsification. When the solvent volatilized completely, an opaque and cream-colored layer left. Fig. 1 shows the SEM images of the films prepared by PPO/$CHCl_3$ solution with a series of concentrations. It could be seen that, regular pores were formed when the concentrations ranged from 2 to 70 g/L. This phenomenon was different from all other literatures which could obtain regular pores only in low concentrations [11–38]. It also could be seen from Fig. 1 that the optimal results were formed when the concentration varied from 5 to 30 g/L, whose pore size were all approximately 1.8–2 μm. When the concentration of the solutions was larger than 70 g/L, the diameter of the holes became small and finally vanished.

These special phenomena might be attributed to the molecular structure of the PPO. PPO was one kind of hydrophobic plastics, whose contact angle with water was

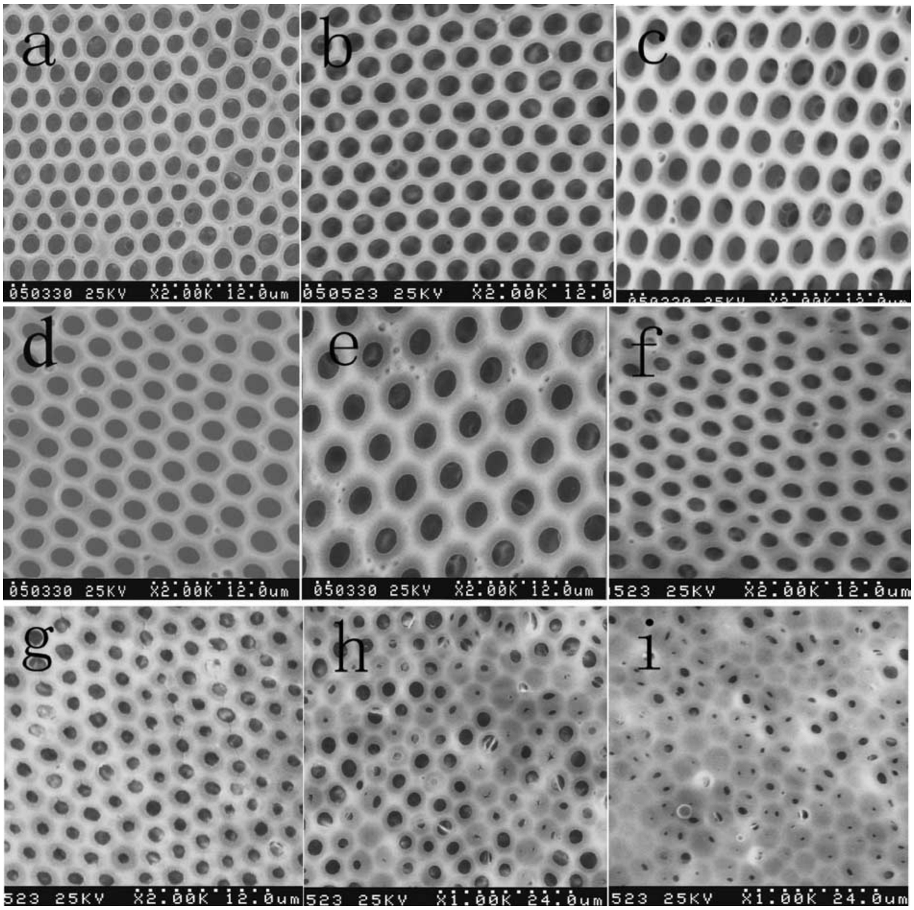

Fig. 1. SEM images of honeycomb structure in PPO films prepared from different solution concentration. (a) 2 g/L; (b) 5 g/L; (c) 10 g/L; (d) 20 g/L; (e) 30 g/L; (f) 50 g/L; (g) 70 g/L; (h) 80 g/L; (i) 90 g/L. Other conditions: temperature, 20 °C; relative humidity, 95%; spreading volume, 100 μL.

102.4° ($M_w = 70$ K), and there was no intense-polar groups in PPO molecule structure, which meant the formation of honeycomb structure in PPO films did not mainly rely on its hydrophilicity. Zhao et al. [41] reported that polyethers were easy to accumulate on the surface of the solution because of their ether group. For this reason, as a kind of polyether, PPO molecules should gather around on the surface of the solution and form an extremely thin surface film. This thin surface film might serve as a critical role in the shaping of the honeycomb models, which could not only reduce the surface tension of the emulsion, but also stabilize the water droplets in the emulsion.

When the aqueous vapors condensed on the surface of the polymer solution, the emulsion was formed because of the incompatibility of the water droplets and the solvent. The solvent and the water droplets acted as the dispersed medium and the dispersed phase, respectively. Originally, the water droplets were uniformly distributed in the emulsion, which increased the surface area of the system and led to the addition of the total energy. This was a non-spontaneity process. On the contrary, the decreasing of the overall energy (Gibbs free energy) of the system was spontaneous, which could be accomplished by reducing the surface area or the surface tension of the solution. As for pure solvent, the surface tension was unchanged when the temperature was constant and the only way to cut the total energy was the declining of the surface area. That is, the emulsion, which was composed of pure solvent and water droplets, was an unstable system, and the water droplets in the emulsion always had the tendency to coalesce with the purpose of cutting down the surface area. But for solution, the surface tension was related with the composition of the surface layer of the solution. It meant Gibbs free energy might be reduced by adjusting the amounts of the different components in the surface layer of the solution. If the solute could reduce the solution surface tension, it would try to gather on the surface. Otherwise, it trended to stay in the inner of the solution. As a result, once one wanted to decrease the free energy in the case of maintaining the initially stable emulsion, some additive must be added. PPO just performed the function of the additive to decrease the surface tension of the solution by assembling on the surface of the solution.

Whether PPO might aggregate on the surface of the solution could be proved by testing the alteration of the solution surface tension relied on Gibbs adsorption equation

$$\Gamma = -\left(\frac{c}{RT}\right)\left(\frac{d\gamma}{dc}\right) \tag{1}$$

where c is the concentration of the solution, γ is the surface tension of the solution. The concentration of the solution is always larger than that of the pure solvent, that is $dc > 0$. According to this equation, once the positive adsorption happened, namely $\Gamma > 0$, $d\gamma$ should has a negative value and the surface tension should decrease.

Table 1 shows the values of the surface tension of the solutions. It was found that the surface tension of the solution decreased at first and then increased gradually with the growing of the solution concentrations, and the surface tension γ of the polymer solutions was smaller than that of the pure solvent when the concentration was less than 70 g/L, namely, $d\gamma < 0$, which could testify that PPO molecules were congregated on the surface of the solution and formed a thin surface film. However, when the concentration of the solution exceeded 70 g/L, γ was larger than that of the pure solvent. This fact might be caused by the increasing amounts of the PPO molecules that gathering on the surface of the solution. These so many molecules not only formed a compact surface film, but also led to the increase of the solution viscosity, which both increased the solution surface tension and prevented the water droplets immerging into the solution. Moreover, it also could be seen from Table 1 that, the values of the surface tension changed slightly when the concentration ranged from 2 to 50 g/L, which might be interpreted from the characteristic of PPO molecule structure. It was well known that the polymers that had intense-polar groups could aggregate on the surface of the solution easily. However, PPO molecule contained weak polar groups and this character determined that even though there were a great many PPO molecules in the solution, the amounts of the PPO molecules that could gather on the surface of the solution were limited. As a result, although the concentration of the solutions varied from 2 to 50 g/L, the strength of the surface film did not change much. This was the reason why PPO/$CHCl_3$ solutions could form honeycomb films in a large range of concentrations and their pore sizes were similar.

Table 1
Surface tension of PPO/$CHCl_3$ solutions with different concentration ($T = 22$ °C)

Concentration (g/L)	r (mN/m)
0	26.92
1	26.17
2	25.58
5	25.49
10	25.44
20	25.47
30	25.51
40	25.83
50	25.97
60	26.27
70	26.87
80	27.87
90	28.94

3.2. Influence of the solvent

Peng et al. [37] discussed the influence of the solvent on formation of polystyrene films in high humid environment. They obtained honeycomb films using toluene or $CHCl_3$ as solvents but could not get regular membranes using CS_2 or THF. They thought the appropriate volatilization rate of the solvent was a key factor to fabricate honeycomb structures. However, other influences of the solvent on regular pattern formation might need to be taken into consideration. For instance, $CHCl_3$ and THF had similar volatility, according

Table 2
The properties of the solvents

	Molecular weight	Density (g/cm^3)	Boiling point (°C)
CH_2Cl_2	85	1.33	40
CS_2	76	1.26	46
$CHCl_3$	119	1.50	61
Benzene	78	0.89	80
C_2HCl_3	131	1.47	87
Toluene	92	0.87	110

to Peng's conclusion, similar patterns should be obtained, while, different pore structures were formed in Peng's study.

In order to study the influences of the solvent on the formation of the honeycomb structure, six types of solvents were used to dissolve PPO and form porous films. These solvents were chloroform ($CHCl_3$), carbon bisulfide (CS_2), benzene, toluene, dichloromethane (CH_2Cl_2), and trichloroethylene (C_2HCl_3). Their properties were described in Table 2. PPO was dissolved in these solvents and formed membrane in a high humid atmosphere, respectively. The morphologies of these films were discussed as follow.

3.2.1. Influence of compatibility between PPO and solvents

The solvents, which had similar boiling point and different compatibility with PPO, were chose to study the affection of the compatibility with PPO in the formation of honeycomb film. The degree of the compatibility could be estimated from the different interaction parameter x between polymer and the solvent by using the following expression [42]

$$x = \frac{V_m}{RT}\left[(\delta_{d1}-\delta_{d2})^2 + (\delta_{p1}-\delta_{p2})^2 + (\delta_{h1}-\delta_{h2})^2\right] \qquad (2)$$

where R is the ideal gas constant (8.314 J mol^{-1} K^{-1}), T is the environment temperature (298 K), δ_d, δ_p, δ_h are the Hansen's parameters [43–46]. V_m is a reference volume equaling to the molar volume of the specific repeating unit size of the polymer. It can be calculated by superimposing the molar volume of the group of the repeating unit [45]

$$V_m = \sum_i \alpha_i V_i \qquad (3)$$

where V_i is the molar volume of the group. α_i is the quantity of each group in the unit.

Table 3 shows the values of the interaction parameter x between solvents and PPO. By comparing the values of x and the solvents' boiling points, four solvents, CS_2, CH_2Cl_2, C_2HCl_3 and benzene, were selected and divided into two groups: CS_2/CH_2Cl_2 and C_2HCl_3/benzene. The solvents in each group had similar boiling points (the former were 46/40 °C, the latter were 87/80 °C) and different x values. Although the calculated x value of PPO/CS_2 ($x=1.50$) was much larger than that of PPO/C_2HCl_3 ($x=0.09$), CS_2 still could be considered as the good solvent for PPO based on the experimental fact that CS_2 and C_2HCl_3 could both dissolve PPO quickly. It cost 24 h for benzene ($x=0.54$) to dissolve PPO completely, while CH_2Cl_2 ($x=0.79$) could not dissolve PPO completely. As shown in Fig. 2, the porous films prepared from PPO/CS_2 and PPO/C_2HCl_3 solutions were more regular than those prepared from PPO/benzene solutions. Moreover, the porous membrane prepared from PPO/CH_2Cl_2 solution was completely irregular. Therefore, it could conclude that the formation of honeycomb structure depended on the good compatibility between polymers and solvents.

Based on the experimental phenomenon, the formation of honeycomb films of PPO could be deduced as follow steps: (1) PPO was dissolved in the solvent rapidly, and the long-chains of the macromolecules, which once accumulated together, were entirely dispersed in the solvent because of the overall solvation. (2) The polymer chains formed 'tiny spheres', which consisted of a single curly polymer chain and the solvent that was adsorbed by the chain. These 'tiny spheres' could perform Brownian motion in the solution freely (Fig. 3(a)). (3) Water droplets were condensed on the surface of the solution due to the cooling caused by the solvent evaporation, and the transparent polymer solution became turbid because of emulsification. (4) The emulsion was an unsteady system, and the water droplets in the emulsion tended to coalesce. PPO acted as an addictive in the solution, which could gather on the surface of the solution and form a thin surface film. This film could decrease the surface tension between the solvent and the water droplets (Fig. 3(b)). (5) With the volatilization of the solvent, the stable water droplets were closely packed on the surface of the solution under the drive of the capillary force (Fig. 3(c)). (6) After the water droplets and the solvent evaporated completely, honeycomb films were remained.

CS_2 and C_2HCl_3 were good solvents for PPO and they could totally dissolve the long-chains of PPO. These dissolved chains could perform Brownian motion freely in the solutions owing to the lower binding force and moved to the surface of the solution easily. On the contrary, because of the low

Table 3
Hansen's parameters of PPO and solvents and their interaction parameters

	δ_d [(cal/m^3)$^{1/2}$]	δ_p [(cal/m^3)$^{1/2}$]	δ_h [(cal/m^3)$^{1/2}$]	V_m (cm^3/mol^{-1})	x
PPO	9.41	1.3	2.4	114.1	
C_2HCl_3	8.78	1.5	2.6		0.09
$CHCl_3$	8.65	1.5	2.8		0.15
CS_2	9.97	0.0	0.0		1.50[a]
Toluene	8.82	0.7	1.0		0.52
Benzene	8.95	0.5	1.0		0.54
CH_2Cl_2	8.72	3.1	3.0		0.79

[a] The calculated data does not coincide with the experimental phenomenon; carbon disulfide can dissolve PPO immediately.

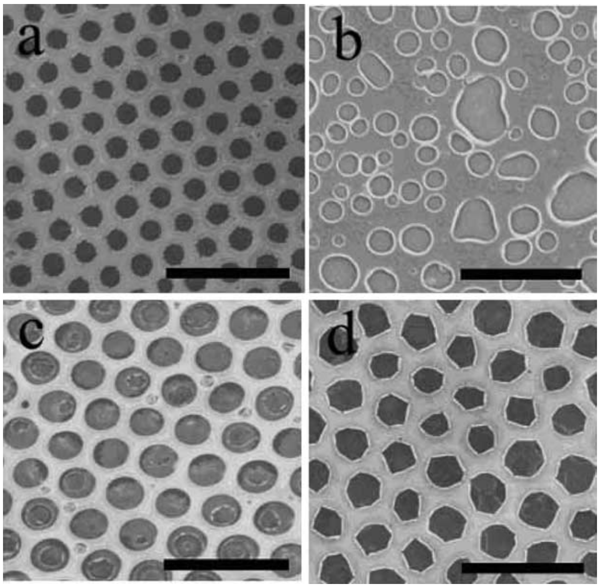

Fig. 2. SEM images of honeycomb structure in PPO films prepared from various solvents with different interaction parameters. (a) CS_2 1 g/L; (b) CH_2Cl_2 1 g/L; (c) C_2HCl_3 2 g/L; (d) benzene 2 g/L. Other conditions: temperature, 20 °C; relative humidity, 95%; spreading volume, 100 μL. Scale bar 10 μm.

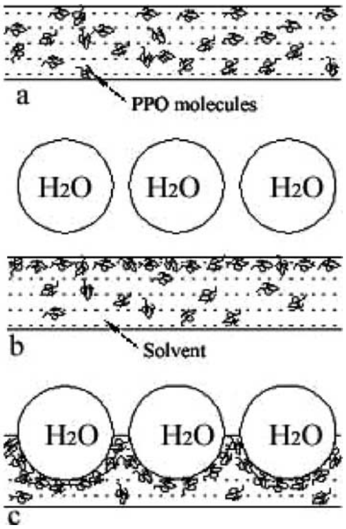

Fig. 3. The process of water droplets condensed on the surface of the PPO solution.

compatibility of PPO/benzene and PPO/CH_2Cl_2, PPO molecules could not fully dissolve in these two solvents. Therefore, the polymer chains would be restrained by intermolecular forces and could not move freely in the solution. The chains were not easy to congregate on the surface of the solution and forbid the coalescence of the water droplets. In a word, the lower compatibility between PPO and solvents led to the worse regularity of the holes.

3.2.2. Influence of the solvent's evaporation

CS_2, $CHCl_3$ and C_2HCl_3 were selected to study the influence of the volatility of solvents on the fabrication of regular porous structure. They had good compatibility with PPO and different boiling points. As shown in Fig. 4, all the solutions can form honeycomb films and the pore size of the films becomes large with the increase of the solvents' boiling point. When the boiling point increased, the volatility of the solvent decreased, and water droplets had more time to coalesce and grow on the surface of the solution, and the pores enlarged.

We then compared the porous patterns in PPO films prepared from another two different solvents: benzene and toluene. These two solvents had similar interaction parameters with PPO and different volatility. Fig. 5 shows the SEM images of films prepared by PPO/benzene solution and PPO/toluene solution. It could be seen that PPO/benzene solution forms porous structure, while the film fabricated by PPO/toluene solution nearly had no pores. This appearance possibly resulted from the low volatility of toluene, which made toluene evaporate too slowly to produce sufficient temperature difference. Thus aqueous vapor could not condense on the surface of the solution and act as templates for the honeycomb structure. The comparison of the results of Figs. 4 and 5 allowed one to conclude that the volatility of the solvent could not only influence the pore size of the honeycomb film, but also determined whether or not the regular porous structure could be achieved.

It must be pointed out that we fabricated honeycomb patterns in a static humid atmosphere, which had some difference from the dynamic moist environment reported in other literatures [6,37]. The process of the formation of honeycomb film in flowing wet air was that carrier nitrogen gas was bubbled through distilled water and sent with water vapor onto the solution surface. This method could accelerate

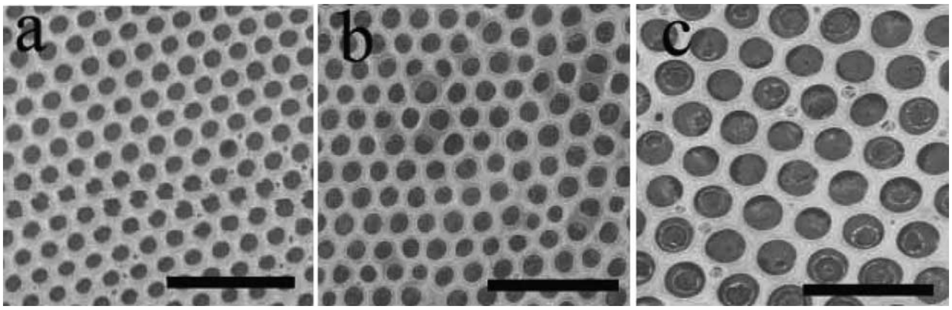

Fig. 4. SEM images of honeycomb structure in PPO films prepared from various solvents that have different boiling point. (a) CS_2; (b) $CHCl_3$; (c) C_2HCl_3. Other conditions: concentration, 2 g/L; temperature: 20 °C; relative humidity, 95%; spreading volume, 100 μL. Scale bar 10 μm.

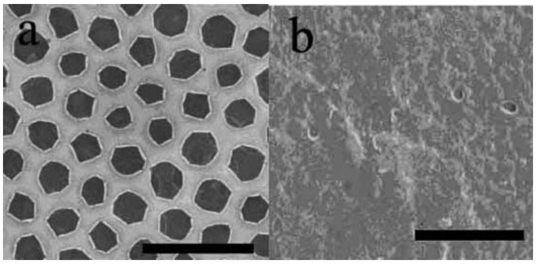

Fig. 5. SEM images of honeycomb structure in PPO films prepared from various solvents that have different boiling point. (a) Benzene; (b) toluene. Other conditions: concentration, 2 g/L; temperature, 20 °C; relative humidity, 95%; spreading volume, 100 μL. Scale bar 10 μm.

the evaporating speed of the solvent and made it possible to form essential temperature difference that caused the condensation of the vapor. The volatilization of the solvent in static humid conditions was slower than in dynamic one, and the temperature difference between the solution surface and environment was little. This was the reason why Peng et al. could obtain PS honeycomb film by using toluene as solvent in a mobile air, while PPO/toluene solution could not form pores in this paper. Therefore, in static surrounding, no other than the solvent had lower boiling point could form appropriate temperature difference and fabricate honeycomb structures.

3.3. Influence of the temperature

Fig. 6 shows the SEM images of the porous structure in PPO films prepared at different temperature. It was found that with the decreasing of the temperature, the pattern became regularity. Also, the width of the pore walls increased when temperature decreased. This result had a little difference with other report which did not obtain regular pores at low temperature [47]. They thought that the irregularity at low temperature was caused by low evaporation rate of the solvent. The slow evaporation of the solvent could not form enough temperature difference between the surface of the solution and the environment. The water droplets in air could not condense onto the surface easily and acted the template of the regular patterns. However, they only researched the influence of the temperature in low humid environment (RH% = 50%, 60%). In this paper, we used a high humid atmosphere, which could ensure enough water droplets to condense onto the surface of the solution. In this situation, the irregularity of the pore structure at high temperature should be interrupted by another viewpoint. The reason of less regular pattern at high temperature might be caused by the violent collision among the water droplets on the surface of the polymer solution. It was reported that the capillary attractive forces was an important factor during the formation of the honeycomb structure [48]. It was also indicated that the capillary force only acted locally [13,38]. Based on the observation of the initial stage of water droplets condensation after the evaporation of solvent, Peng et al. [37] deduced that at the first stage of the solvent evaporation, water droplets condensed on the surface of the solution and formed many isolated 'islands' with ordered structures. These 'islands' were then compactly arranged due to the Marangoni convection [49–51]. Xu et al. [38] considered that when the solution surface area decreased, these 'islands' were pulled together, and collisions occurred. These collisions led to irregular border between 'islands'. We believed that, the neighbor-isolated water droplets were arranged and collided along with Marangoni convection simultaneously. Whether or not the pores were regular depended on the competition of the arrangement and collision among the neighbor water droplets. After casting PPO/$CHCl_3$ solution onto a glass substrate, vapor condensed on the surface of the solution and then formed many isolated droplets at the first stage. In low temperature, Marangoni convection was slow, and the collision of the droplets was smooth. Regular arrangement was the main progress and an ordered pattern was formed (Fig. 6(c)). However, this thermocapollary convection was dramatic at high temperature, causing fierce collisions of the neighbor droplets, and leading to confusion of the pattern.

The large size of the pore walls at the low temperature was caused by the increasing of the viscosity of the solvent. When temperature decreased, the viscosity of the solvent increased, which led to more resistance for water droplets to immerge into the solution. Therefore, the width of the pore walls was large.

3.4. Influence of the molecular weight

Fig. 7 shows the SEM images of honeycomb patterns prepared from PPO with different molecular weight. It could be found that, when the concentration of the solution was 1 g/L, low molecular weight PPO ($M_w = 40$ K) could form honeycomb-like film (Fig. 7(d)). But the higher one ($M_w = 70$ K) did not fabricate regular structure (Fig. 7(a)). Moreover, when the concentration increased, these two polymers both could form

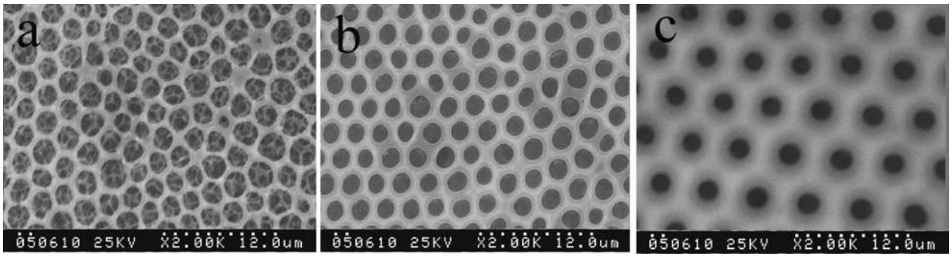

Fig. 6. SEM images of honeycomb structure of PPO films prepared in different temperature. (a) 30 °C; (b) 20 °C; (c) 10 °C; other conditions: concentration, 2 g/L; relative humidity, 95%; spreading volume, 100 μL.

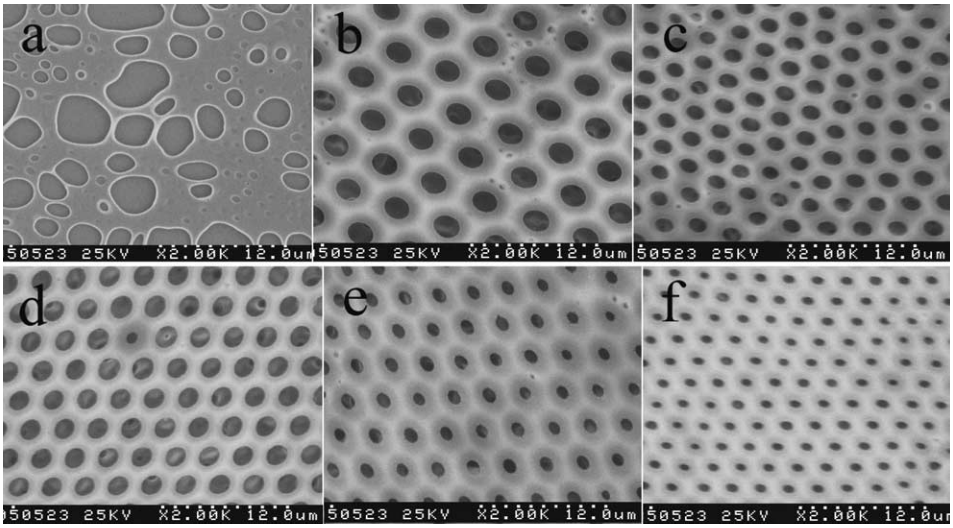

Fig. 7. SEM images of porous structure in PPO films prepared from different molecular weight PPO. (a)–(c) $M_w = 70{,}000$; (d)–(f) $M_w = 40{,}000$. Concentration: (a) and (d): 1 g/L; (b) and (e): 30 g/L; (c) and (f): 50 g/L. Other conditions: relative humidity, 95%; spreading volume, 100 μL.

regular pores. However, the pore sizes formed by low molecular weight PPO were lower than that of high molecular weight PPO at the same concentration. This phenomenon coincided with other reports [38]. There were two possibly reasons to interpret this phenomenon. One reason was that, low molecular weight PPO was easier to be dissolved by the solvent than the higher one, and its molecule chains could gather on the solution surface more easily. Therefore, low molecular weight PPO could construct a stronger surface film than that of being made by high molecular weight PPO. This surface film could prevent the coalescence of the water droplets. The other reason causing this appearance was that, the high the molecular weight had low mole fraction. It meant that when these two polymers had same mass concentration, low molecular weight PPO had more molecules in the solution, which can supply more molecules to fabricate the surface film. This surface film would compact at high concentration, which would prevent the water droplets immerging into the polymer solution. Therefore, the pore sizes formed by low molecular weight PPO were lower than that of high molecular weight PPO. In conclusion, low molecular weight PPO was easy to form stronger surface film and could fabricate honeycomb structure in a lower concentration.

4. Conclusion

As one kind of hydrophobic polymers, PPO could form honeycomb structures via water-assisted method in a large range of the solution concentration, and the best regular pores could be obtained by those solutions with the concentration ranged from 5 to 30 g/L, whose pore size were all approximately 1.8–2 μm. The good compatibility of PPO and solvent was very important to form honeycomb structure. The volatility of solvents not only could influence the pore size of the honeycomb film, but also could determine whether the regular porous structure could be achieved. By decreasing the environment temperature, more regular structure could be formed at the concentration of 2 g/L. The low molecular weight PPO could form honeycomb pattern at the lower concentration, while the high molecular weight PPO could not form. However, at the high concentrations, the pores' size of the high molecular weight PPO was larger than that of the low molecular weight PPO. According to the favorable performance of PPO in fabricating membranes, we expected this film had a great potential use in various fields.

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