Formation of ordered macroporous membranes from random copolymers by the breath figure method

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Abstract

In this paper, well-ordered macroporous membranes were fabricated from random poly(styrene-*co*-acrylonitrile) using tetrahydrofuran as solvent by the breath figure method. Influencing factors were investigated systematically including the relative humidity of atmosphere, the concentration of polymer solutions and the temperature. The pore size and the patterns were affected by these factors. The mechanism of pattern formation was also discussed.
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1. Introduction

Porous polymer membranes have attracted much attention because of their potential application in the fields of electronics [1], photonics [2,3] and biotechnology [4–7]. A number of techniques have been developed for the fabrication of well-controlled porous membranes, such as photolithography [8], soft lithography [9–11], phase separation of block copolymers [12,13] and templating methods [14–17]. Recently, Francois [18–20] reported a simple method called breath figure method to fabricate ordered pattern membranes. The method has shown its advantages in making highly ordered macroporous membranes [21–28]. When the solvent was evaporated under humid conditions, the surface of the solution was cooled, and the water vapor was condensed to form water droplets. The water droplets sank into the surface of the solution, while the solvent was evaporating. After the solvent and water were evaporated completely, the ordered traces (pores) were then obtained. The key point in this method was to stabilize the water droplets formed during the fabrication. Therefore, the complex-systems and amphiphilic block copolymers or homopolymers with polar terminal group were usually involved.

In the breath figure method, water-immiscible solvents, such as benzene, chloroform, carbon disulfide (CS_2), were often utilized. Francois and co-workers [18–20] prepared honeycomb porous structure from carbon disulfide solution of poly(*p*-phenylene)-*block*-poly-styrene, star polystyrene, and associative polystyrene. Jiang's group [29] observed honeycomb structure membranes by evaporating 4-dodecyl-benzenesulfonic acid-doped polyaniline solution in chloroform. Han et al. [30] investigated the influencing factors on the macroporous formation in polystyrene film systematically, in which the solvent and humidity of atmosphere played important roles. In such system, the ordered porous structure could not be obtained using polystyrene/THF solution. In general, it was considered that a water-miscible or partially miscible solvent was not suitable to fabricate ordered macroporous membranes by the breath figure method because of its affinity with water. However, Kim and co-workers [31] recently reported successful results by evaporating the THF solution of cellulose acetate butyrate (CAB), monocarboxylated end-functional poly-styrene (PS-*m*COOH) and poly(methyl methacrylate). Rabolt's group [32,33] showed that irregular porous structures were formed on the surface of fibers when polystyrene (PS) fiber was electrospun from THF solution under humid conditions.

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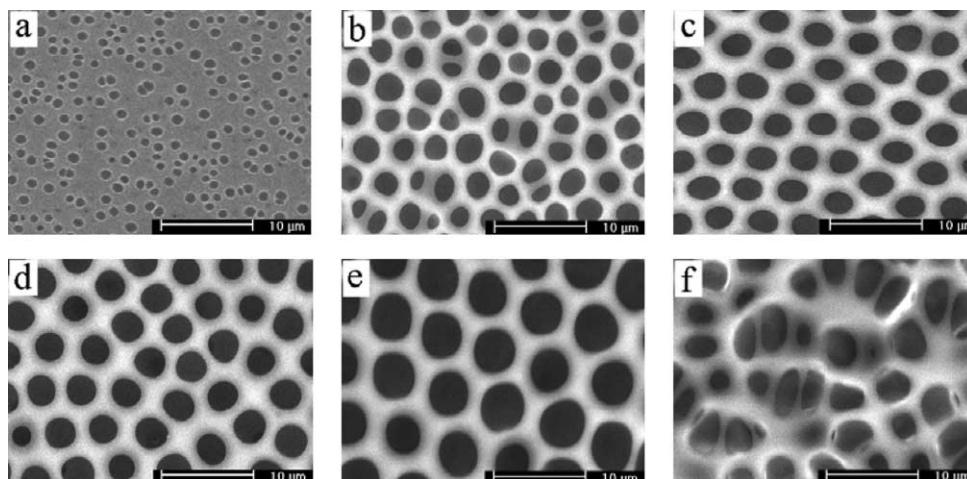*E-mail address:* nkulicx@yahoo.com.cn (C. Li).

Fig. 1. The ESEM images of the membrane surfaces by evaporating SAN/THF solution (0.08 g/mL) directly at various relative humidity at 25 °C. a: 30%, b: 40%, c: 50%, d: 60%, e: 70%, f: 80%.

In some cases, the water-miscible solvent THF was often involved, such as the preparation of molecularly imprinted polymer membranes [34,35]. In this paper, the well-ordered macroporous membranes were fabricated from random poly(styrene-*co*-acrylonitrile) (SAN) in THF via the breath figure method. We investigated the influence of concentration, temperature, and humidity of atmosphere on the membrane structure. SAN membranes overcame the fragility of polystyrene membranes for their good mechanical property to have many applications in antireflection coating, separation and catalysis, etc.

2. Experimental details

Random poly(styrene-*co*-acrylonitrile) (C.P.) was purchased from PetroChina Lanzhou Petro and Chemical Company. The number-average molecular weight (M_n) and polydispersity index (PDI) of SAN were 3.1×10^4 and 1.91, respectively, determined by gel permeation chromatography (Waters Co.) with polystyrene standard. The molar percent of acrylonitrile units was 25% by elemental analysis.

The membranes were fabricated in a glass box (1.0 m × 0.5 m × 0.5 m) equipped with a thermometer and a hygrometer to monitor the condition of the atmosphere in the box. The relative humidity (RH) of the atmosphere was controlled by changing the flow of carrier nitrogen bubbled through two-necked flask with distilled water. A small electric fan was used to keep convection of the atmosphere in the box. All the polymers were dissolved in dried THF at room temperature with 5 h of stirring. The SAN/THF solutions were cast on a clean silanized glass substrate under different conditions.

The surface morphology of the membrane was investigated by environmental scanning electron microscope (ESEM; XL30, Philips). The pore size and size distribution were obtained from the ESEM images using Scion image software (www.scioncorp.com).

3. Results and discussion

3.1. Influence of atmospheric humidity on the pore size and pattern

The breath figure method to fabricate well-ordered macroporous membranes utilized the condensed monodisperse water droplets as templates when the solvent of polymer solution was evaporated [18–28], therefore, the humidity of the atmosphere directly affected the surface morphology of the membranes. In order to investigate the effect of relative humidity of the atmosphere on the surface morphology of the membrane, the relative humidity is the only variable factor in this section. The membranes were fabricated using 0.08 g/mL SAN/THF solution by evaporating solvent directly at 25 °C at various humidity from 20 to 80%. The surface images of the membranes were shown in Fig. 1. At 20% humidity, the smooth and transparent membrane was formed (not shown in Fig. 1). Disordered pores began to be formed on the surface of the membrane with the increase of the humidity as shown in Fig. 1a, though the pores were distributed randomly. In this case, the membrane formed was also transparent. The relatively regular pores were obtained at 40% humidity (Fig. 1b), and the membrane became opaque. When the relative humidity was increased further to 50%, highly ordered pores were generated (Fig. 1c). The regular patterns were also observed at 60–70% humidity as shown in Fig. 1d and e, respectively. When the humidity was increased further to 80%, the pores became irregular (Fig. 1f).

These results showed that well-ordered macroporous membranes were successfully fabricated by evaporating SAN/THF solution at 50–70% humidity (Fig. 1c–e).
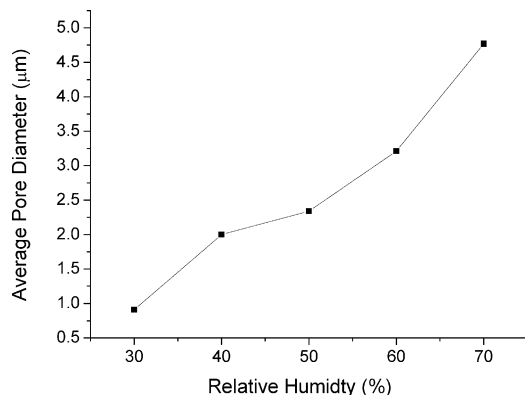
Fig. 2. Plot of the number average diameter (D_n) versus relative humidity of the atmosphere. Solution concentration: 0.08 g/mL. Atmospheric temperature: 25 °C.

Nonetheless, regularly ordered patterns cannot be obtained at the other humidity. A possible explanation is as follows: The growth of breath figure on liquids evolves through three stages [36]. In the initial stage, the water droplets grow as isolated objects with weak interdroplet interactions and the low surface coverage. The average diameter D_n of water droplets is increased with time t followed by the growth rule $D \sim t^a$, $a \approx 1/3$. The second stage is characterized by maximal surface coverage. The final stage is represented by constant surface coverage and coalescence between the water droplets. Enough water droplets could not be formed quickly to cover the whole surface at relative low humidity, therefore, there was no ordered patterns formed on the membranes (Fig. 1a). Although a number of water droplets covering the surface of solution were formed slowly at 40% humidity, the viscosity of solution increased with the

evaporation of solvent, resulting in the difficulty for the water droplets to sink into the solution, the coalescence of some water droplets could not be avoided. When the humidity increased to a much higher level, there were lots of condensed water droplets covering the surface of solution, which sank into the solution in a short period of time, and the viscosity of solution increased with the evaporation of the solvent to stabilize the water droplets [29,30]. On the other hand, the chains of SAN containing the polar nitrile groups were easily located near the water droplets and precipitated around condensed water droplets, which was different from the system of polystyrene in THF [30]. The polar groups may increase hydrophilicity of the chains to be favor to stabilize the water droplets. The water droplets could not be diffused rapidly in the viscous solution without stirring. When the solvent evaporated completely, ordered patterns were observed as shown in Fig. 1c–e. However, at 80% humidity, the water droplets were formed too quickly due to the high rate of nucleation, resulting in the coalescence, therefore, the regularity of the pores was destroyed as shown in Fig. 1f.

The average pore diameters (D_n) as shown in Fig. 2 were obtained by analyzing the ESEM images using Scion Image Software. According to the data, the pore diameters could be controlled by the change of the relative humidity. And the average pore diameter increased with the increase of humidity (Fig. 2). The average pore diameter (D_n) was 0.91, 2.02, 2.34, 3.21 and 4.77 μm, respectively, when the humidity were 30, 40, 50, 60 and 70%. Han and co-workers [30] described the same relationship between the average pore diameters with the relative humidity in polystyrene/toluene system.
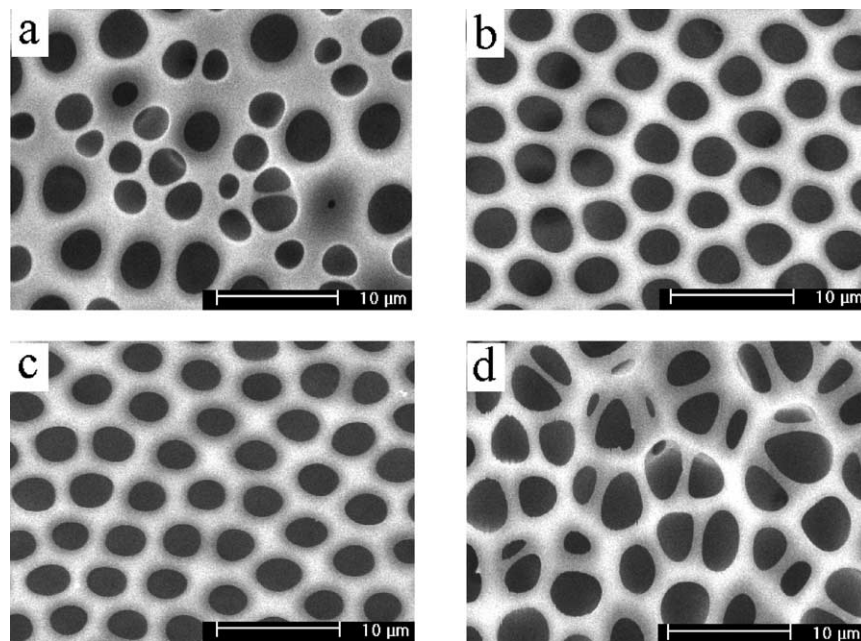

Fig. 3. The ESEM images of the membrane surfaces by evaporating varying concentrations SAN solution in THF at 25 °C at 50% humidity. a: 0.03 g/mL, b: 0.05 g/mL, c: 0.08 g/mL, d: 0.10 g/mL.

3.2. Influence of concentration on the pore size and pattern

The effects of concentration on the morphology of the membrane surface were shown as ESEM images in Fig. 3, which were fabricated from various concentration solution (0.03, 0.05, 0.08 and 0.10 g/mL) at 25 °C at 50% humidity. Well-ordered patterns could not be formed at 0.03 g/mL (Fig. 3a). During the experiments, the membranes were destroyed completely after the solvent evaporated, when the membranes were fabricated using the typical concentration (0.01 g/mL) solution at 25 °C at 50% humidity. Fig. 3b and c showed the well-ordered patterns fabricated from 0.05 to 0.08 g/mL SAN solution in THF. But irregular porous structures (Fig. 3d) were formed at 0.10 g/mL. We explain this phenomenon as follows. The water droplets were encapsulated and stabilized by the polymer solution with proper viscosity due to the water-miscibility of THF. Although the droplets were formed covering the surface of solution at less than 0.03 g/mL, the droplets would coalesce and even mix with THF solution because the solution could not stabilize them. The solution viscosity increased with the increase of the concentration, which was beneficial to stabilize the droplets. In addition, the convection was proved to favor the well-ordered packing of the water droplets. With the increase of the viscosity of solution, the convection in the polymer solution was weakened. And it was difficult for the droplets to sink into the solution surface because of the high viscosity when the solution of 0.10 g/mL was employed. The droplets floated on the solution surface, so the coalescence could not be prevented. After complete drying of the water and solvent, irregular patterns were formed. The solidification time of the solution became

longer with the decrease of the concentration under the same atmospheric conditions. Therefore, the growth time of droplets was prolonged with the decrease of concentration, which lead to larger pore size at lower concentration as shown in Fig. 3b and c.

3.3. Influence of atmosphere temperature on the pattern formation

In the breath figure method, the water vapor was condensed to form water droplets while the solution surface was cooled by the evaporation of the solvents. The temperature strongly affects the evaporation rate of the solvents. Based on this point, the effect of temperature on the surface morphology was investigated as shown in Fig. 4. In the serial experiments, no well-ordered porous membranes could be fabricated from 0.03 to 0.10 g/mL SAN/THF solution at 20 °C at various humidity. Our explanation was as following: The decrease of temperature decreased evaporation rate. Under low temperature condition, there were no enough condensed water droplets because of low evaporation rate of solvents, so some water droplets disappeared because the water droplets were miscible with THF. Irregular pores were formed and distributed randomly on the surface of the membranes finally shown in Fig. 4a and d, respectively. The evaporation rate of the solvents increased with the increase of the temperature. The fast evaporation led to low surface temperature, which is favor to form the droplets. And the water droplets would behave like 'solid' particle because the polymer solution was solidified quickly when the evaporation rate of solvents was suitable. In these cases, the well-ordered porous membranes
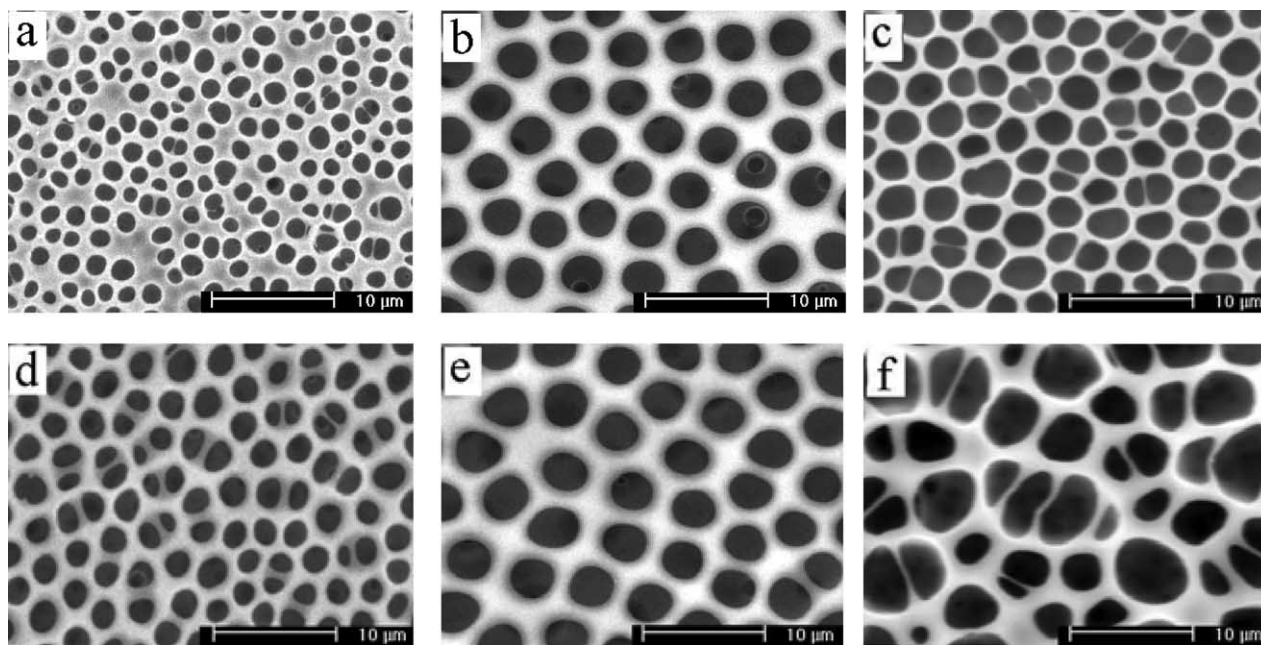

Fig. 4. The ESEM images of the membrane surfaces by evaporating 0.08 g/mL SAN/THF solution under different conditions. a: 20 °C, RH=50%, b: 30 °C, RH=50%, c: 35 °C, RH=50%, d: 20 °C, RH=60%, e: 30 °C, RH=60%, f: 35 °C, RH=60%.

were obtained from 0.08 g/mL SAN/THF solution at 25, 30 °C at 50, 60% humidity shown in Figs. 1c and d and 4b and e. But the irregular pattern was observed at 35 °C in Fig. 4c and f, because lots of droplets were formed due to the low surface temperature resulted from the quick evaporation of solvent at high temperature, on the other hand, the viscosity of the solution increased quickly due to the evaporation. The coalescence of the droplets took place on the surface, especially at higher humidity (Fig. 4f).

3.4. Mechanism of pattern formation

The mechanism of ordered patterns formation has been widely investigated. It has been proved that the structures are formed by an ordered template of condensed water droplets, which vanishes after evaporation completely. When water vapor in the moist air was condensed onto the cold solution surface, it appears in the form of uniform droplets. The close adjacent droplets are attracted to each other by the lateral capillary force. At equilibrium, the preferred packing arrangement of them will be that which corresponds to the lowest free energy [37]. The optimum-covering lattice is hexagonal. The ordered water droplets were trapped into the solution and formed the regular pore patterns after the evaporation of droplets and solvent. In our case, since the density of THF is less than that of water and THF is a hydrophilic solvent, the droplets will sink into the solution. Therefore, the following conditions are the determinant elements in the producing ordered patterns: The formation and arrangement of the droplets before they sink into the solution; the stabilization of the droplets. If there were too many droplets formed on the solution surface, or the droplets cannot sink into the solution in time, the coalescence cannot be inhibited. Finally, the irregular pores will be observed on the membranes. The ordered droplets are encapsulated and stabilized by the viscous solution after sinking into the solution; the water droplets would behave like 'solid' particle if the polymer solution was solidified quickly when the evaporation rate of solvent was suitable; and the chains of SAN containing the polar nitrile groups were easily located near the water droplets and precipitated around condensed water droplets. The polar groups may increase the hydrophilicity of the chains, which may facilitate to stabilize the water droplets. At last, water droplets and solvent evaporate and leave the regular pore patterns. If the droplets have no enough time to form the dense hexagonal packing before sinking into the solution, the regular patterns with slight imperfections are formed.

4. Conclusions

Well-ordered macroporous membranes were successfully fabricated from random copolymers (SAN) in THF in the range of 50–70% relative humidity. The results showed that the surface morphology of the membranes was affected by the humidity, the solution concentration and the temperature. The pore size and patterns could be controlled by changing the influencing factors. The pore sizes increased with increased humidity, and decreased with the increase of the solution concentration. There was no well-ordered macroporous membrane obtained at 20 and 35 °C. The results also showed that the polar groups might be favor to stabilize the water droplets if the water-miscible solvent was employed, such as THF. And the SAN membrane had many potential applications due to its better mechanical property than the polystyrene membrane.

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