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ORIGINAL CONTRIBUTION

Influence of vacuum on the formation of porous polymer films via water droplets templating

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Abstract We report on the formation of ordered arrays of micron-sized holes on the surface of polymer films cast from volatile solvents in the presence of humidity in vacuum. A lower pressure in a vacuum chamber can accelerate the evaporation of solvent in the same way as the accelerating action of the air flowing across the solvent surface and results in the formation of porous films via the "breath figure" templating method. This vacuum technique has a good reproductiveness for the fabrication of the well-ordered porous films in a large area. It is very controllable to prepare the porous films in a vacuum chamber via controlling the vacuum level. The pore sizes can be easily tuned from 5.6 to 17.1 μm by changing the vacuum level. The mechanism for the formation of the porous films in vacuum was also discussed. The polymer films with ordered porous structure and tunable pore sizes have potential applications in many areas such as microarrays and as scaffolds for tissue engineering.

Keywords Porous film · Breath figure · Template · Polymer · Vacuum

Introduction

Porous polymer films with pore sizes in the micrometer and submicrometer ranges have elicited much interest recently for use as membranes for separation and purification [1, 2], solid supports for sensors and catalysts [3, 4], scaffolds for tissue engineering [5], low-dielectric constant materials for microelectronic devices [6], and photonic band gap materials [7, 8], etc. A variety of self-assembled templating methods have been developed to create two-dimensional (2D) and three-dimensional (3D) porous structures, including using colloidal crystals [9], emulsions [10], rod-coil polymers [11], etc. Microporous films formed by colloidal crystals templating involve self-assembly of colloidal microspheres on a solid substrate to form 2D or 3D crystalline structure, infusion of other materials into the voids of the self-assembled microspheres, solidification of the material, removal of the template microspheres through either calcination or solvent extraction [9–11]. However, it is difficult to obtain a good self-assembly of template microspheres in a long range order, and any defects in the self-assembly result in a disordered structure of the film.

Recently, a templating method based on evaporative cooling and subsequent water droplet templating to form ordered array of breath figures was developed and used to produce porous films made of various materials [12–14]. Some efforts have been made to prepare porous polymer films using the breath figure method. Porous films have been prepared using nanoparticles [13, 15] and a variety of polymers [16–24], such as homopolymers [16], block copolymers [17, 23, 24], star or graft polymers [14, 18],

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conjugated rigid-rod polymers [19], and organometallic polymers [20]. In most cases, such porous films are prepared under a moist airflow over the solution surface [25]. However, use of the air flow may cause nonuniformity of humidity over a big surface and has a negative effect on the reproductiveness and quality of the films. The airflow often destroys the honeycomb structure of the films. As is well known, a rapid evaporation of solvents is necessary for the formation of ordered porous films via the breath figure methods. Lower pressure can accelerate the evaporation of solvent in the same way as the accelerating action of the air flowing across the solvent surface [25]. Therefore, it is possible that the air pressure has an effect on the formation of the porous film by the breath figure method. In this work, a new method was developed to prepare the porous films with an ordered honeycomb structure in a vacuum chamber without using moist airflow by the "breath figure" templating technique. The influence of vacuum levels on the formation and pore size of the porous polymer films was investigated. The mechanism for the formation of the porous films in vacuum was also discussed. Using this method, large-scale porous films with uniform pore structure can be obtained, and the throughput of the production is high.

Experimental

Materials and methods

Polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene (PSEBS, 31 wt.% styrene), and all solvents were obtained from Sigma-Aldrich. α,ω-dicarboxy terminated polystyrene (PS-2COOH, M_n=99.0 kg/mol, M_w/M_n=1.10) and polystyrene-block-poly(4-vinylpyridine) (PS-b-P4VP, M_n^{PS}=20.0 kg/mol, M_n^{P4VP}=19.0 kg/mol, M_w/M_n=1.09) were purchased from Polymer Source. Monodispersed polystyrene microbeads (2.6% solid latex) were obtained as an aqueous suspension from Bangs Laboratories.

Preparation of honeycomb-structured porous polymer films

PS-b-P4VP was dissolved in toluene to form a 20-mg/ml polymer solution. PS-2COOH was dissolved in benzene to form a 10-mg/ml polymer solution. A mixture of PS-b-P4VP and PSEBS (1/1, *w*/*w*) was dissolved in a mixture of toluene and benzene (7/3, *v*/*v*) to form a 5- to 30-mg/ml polymer solution. Equal amount of the solutions (about 120 µl) were cast onto clean glass substrates (15×15 mm) in a sealed 300 l chamber at room temperature, and then the chamber was immediately vacuumized to an appropriate vacuum level within 8~50 s. At the same time, the humidity in the chamber was maintained at 70–95 r.h.%. After drying, porous polymer films were obtained. The setup for the preparation of the ordered porous polymer films in a vacuum chamber by the "breath figure" method is schematically illustrated in Figure S1 (see Supplementary material).

Patterning of polystyrene microbeads on the porous polymer films

A glass slide covered with porous polymer films was inserted into a 0.05-wt.% suspension of 9.95 µm polysty-

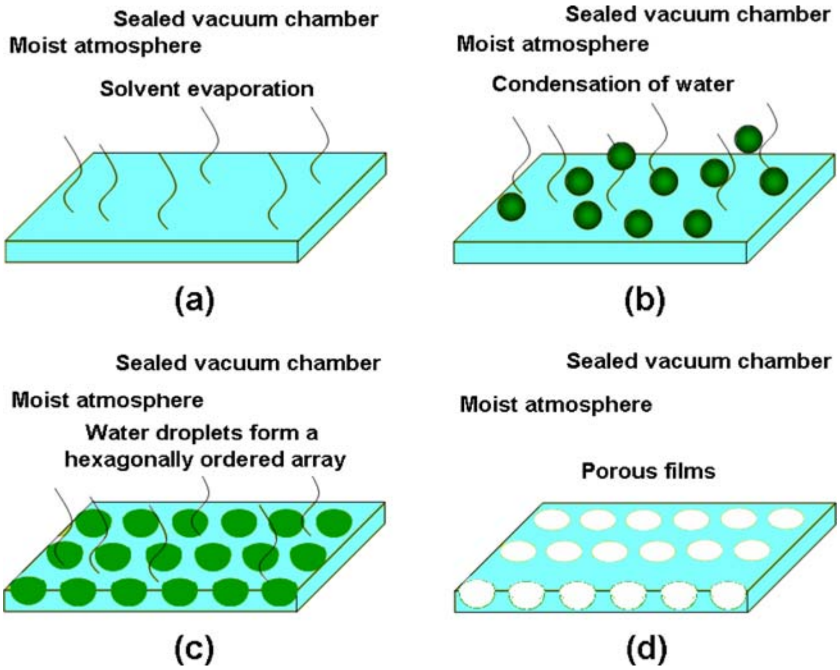

Fig. 1 Schematic diagram of formation of breath-figure films in a vacuum chamber

rene microbeads in a vial. The vial was then shaken on a shaker to allow beads to settle in the pores by the gravity. After the microbeads were dispensed into the arrayed pores, the surface of the porous films was washed with water to remove the excess beads. The film then dried at room temperature.

Characterization

Scanning electron microscope (SEM) images were taken using a FEI QUANTA 200 FEG SEM operating at 10 kV. A thin layer of gold was sputtered onto the samples prior to imaging. Bright-field optical images were obtained using an optical microscope (Axiostar plus) with a 50-W mercury lamp. A charge-coupled device (CCD) camera was used to capture optical images.

Results and discussion

A rapid evaporation of solvents is necessary for the formation of ordered porous films via the breath figure method. A moist air flow or some volatile solvents such as carbon disulfide and Freon [26] is usually used for preparation of porous polymer films using the breath figure method, to accelerate the evaporation of solvent and formation of ordered hexagonal array of water droplets in polymer solution. As is well known, a lower pressure can accelerate the evaporation of solvent in the same way as the accelerating action of the air flowing across the solvent surface. This "breath figure" method for preparing porous films can be improved by using a vacuum chamber. A schematic drawing is given in Fig. 1 to show the formation of porous polymer films in vacuum. Porous polymer films with well-ordered honeycomb structure could be formed when a polymer solution is drop-cast onto a glass slide in a vacuum chamber with moist atmosphere. The vacuum causes a rapid evaporation of the volatile solvent (e.g., toluene and benzene), and subsequently a rapid cooling of the solution, similar to other breath-figure methods by using a flow of moist air, and then, submicrometer- or micrometer-sized water droplets are formed on the surface of the cold solution [27]. Convection currents induced by temperature gradients and capillary forces between the water droplets favor a regular stacking of the water droplets with a narrow size distribution [28–30]. After the solvent evaporates completely, a polymer film is formed with the water droplets in the film. After the water droplets evaporate, a porous film with well-ordered pore structure is formed. In this chamber, many samples can be prepared at the same time. Vacuum plays the same role as the air flow usually plays in the breath-figure methods, but is more controllable.

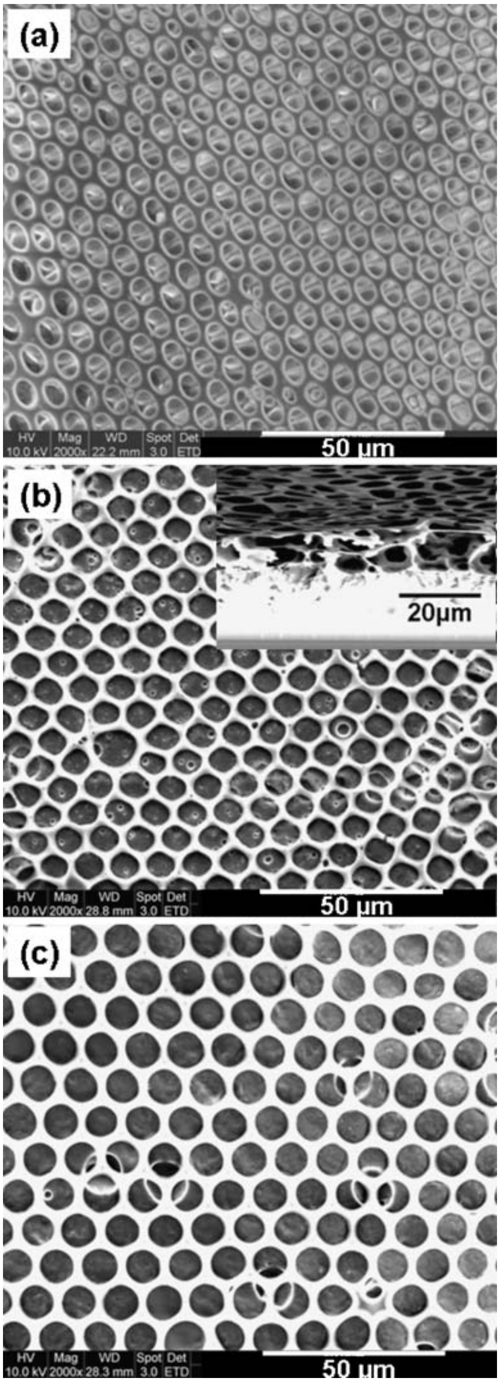

Fig. 2 SEM images of porous polymer films made of **a** PS-2COOH, 10 mg/ml solution in benzene, vacuum −50 kPa, relative humidity 82 r.h.%.; **b** PS-b-P4VP, 20 mg/ml solution in toluene, vacuum −50 kPa, relative humidity 89 r.h.%.; and **c** blend polymer of PS-b-P4VP and PSEBS (1/1, *w*/*w*), 15 mg/ml in a mixture of toluene and benzene (7/3, *v*/*v*), vacuum −50 kPa, relative humidity 82 r.h.%. The *inset* in (**b**) shows the cross-section image of the PS-b-P4VP film, demonstrating a 3D multilayered pore structure of the film

SEM images of porous polymer films made of PS-2COOH, PS-*b*-P4VP, and a blend of PS-*b*-P4VP and PSEBS are shown in Fig. 2. The porous films exhibit two-dimensional and periodical structures with hexagonal array of pores in a long-range order. The pore sizes are on the microscale. For PS-2COOH, besides benzene, ordered pore structure can also be easily prepared by using toluene, THF, carbon disulfide, and dichloromethane as the solvent. No good films are prepared when using chloroform as the solvent. For PS-b-P4VP, benzene, dichloromethane, and toluene can be used. The cross-section image of the porous PS-b-P4VP film in the inset of Fig. 2b shows that the film has a three-dimensional (3D) and multilayer porous structure with about three layers. The formation of the 3D polymer scaffold is related to the density of the solvent. When the water droplets are denser than the solvent, the water droplets easily sink into the solution. Once the solution surface is free, the whole process of evaporative cooling, water droplet condensation, and subsequent ordering repeats itself. This leads to the 3D architecture observed upon complete evaporation of the solvent. Once the film returns to ambient temperature, the condensed water and residual solvent evaporate, leaving behind the 3D polymer scaffold. However, the surface tensions also have an effect on the sinkage of the water droplets. For PS-P4VP solution in toluene, the water droplets sink into the solution, being denser than the solvent, because surface tensions can not counterbalance their weight. After these water droplets are evaporated, the films with multilayered pores are obtained [31].

More detailed studies were performed on porous films made of the PS-b-P4VP/PSEBS blend polymer because PSEBS is an elastomer, and the PS-b-P4VP/PSEBS blend polymer has better mechanical properties than the other two polymers. A suitable solvent was carefully chosen, as the solvent has demonstrated to be a key factor to affect the formation of porous films and their honeycomb pore structure [32]. The volatility of the solvent cannot only affect the pore sizes, but also the long-range order of the

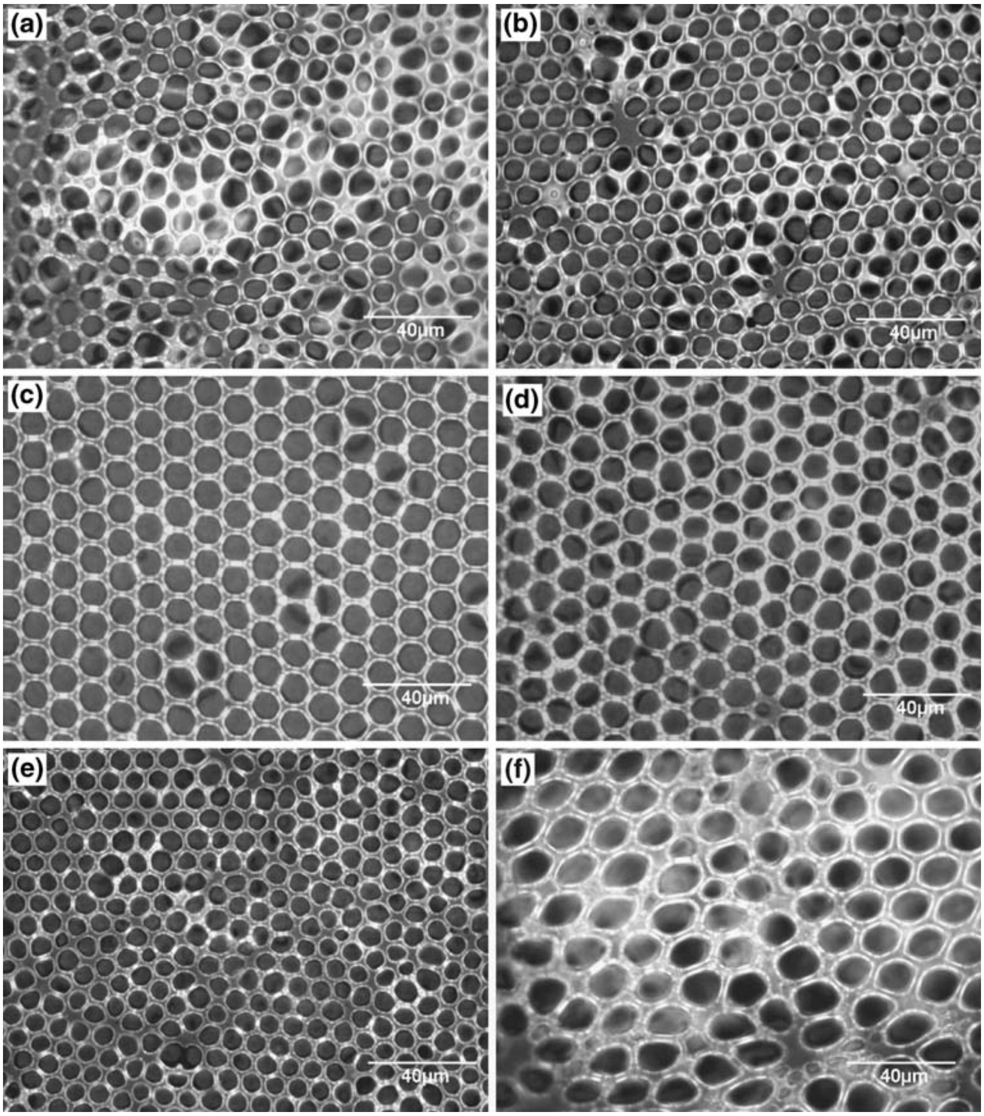

Fig. 3 Optical images of the PS-b-P4VP/PSEBS porous films. The percentage of PSEBS in the blend of PS-b-P4VP and PSEBS is: **a** 100%; **b** 80%; **c** 60%; **d** 40%; **e** 20%; and **f** 0%. The vacuum levels is −50 kPa, the relative humidity is 82 r.h.%, and the polymer concentration is 15 mg/ml in a mixture of toluene and benzene (7/3, *v*/*v*)

pore structure. In our experiment, it was found that the PS-b-P4VP/PSEBS blend polymer cannot form good porous films with ordered pore structures in toluene or benzene along. Toluene evaporates too slowly, while benzene evaporates too fast. By mixing the two solvents, the evaporation speed can be adjusted. PS-b-P4VP/PSEBS polymer was dissolved in a solution of mixed toluene and benzene, and porous films with long-range honeycomb structure were prepared in vacuum. Figure 3 shows the optical images of the porous films prepared from a blend of PS-b-P4VP and PSEBS with different fractions in a mixture of toluene and benzene (*v*/*v*, 7/3). Well-ordered porous polymer films could not be obtained by using a solution of PS-b-P4VP (or PSEBS) only. When the percentage of PSEBS is within the range of 40~60%, the films with ordered pore structure are obtained. Figure 4 exhibits the optical images of the films made from a blend of PS-b-P4VP and PSEBS, in a mixture of toluene and benzene with different ratios. It is found that highly ordered porous films can be obtained when the volume ratio of toluene and benzene is within the range from 70:30 to 40:60. These results suggest that two kinds of polymers with different properties can be used to fabricate well-ordered porous polymer films in some special solvents by the breath figure method.

The pore sizes of the films were altered by controlling the air humidity and vacuum level in the vacuum chamber. Optical images of the films made at different vacuum levels are given in Fig. 5, and the relationship between the pore diameter and vacuum level is shown in Fig. 6. The pore diameter increases linearly with vacuum level and increases from 5.6 to 17.1 μm when the vacuum level increases from −20 to −70 kPa, with a fixed polymer concentration of 15 mg/ml and a fixed relative humidity of 82 r.h.%. The size distribution of the pores is narrow. As is well known, previous literatures

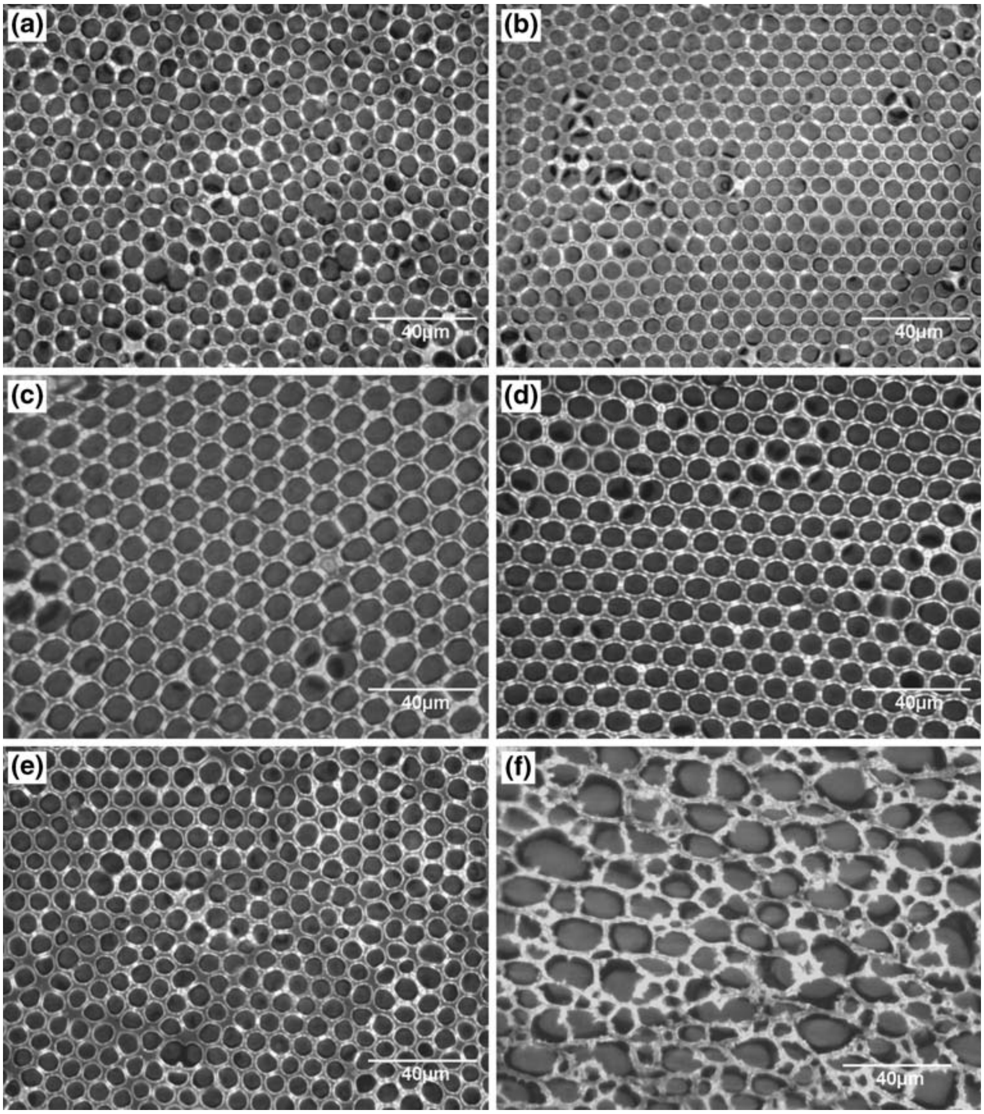

Fig. 4 Optical images of PS-b-P4VP/PSEBS (1/1, *w*/*w*) porous films. The Solvent is a mixture of toluene and benzene, with a volume ratio of: **a** 100:0; **b** 80:20; **c** 70:30; **d** 40:60; **e** 20:80; and **f** 0:100. The vacuum level is −50 kPa, the relative humidity is 82 r.h.%, and the polymer concentration is 15 mg/ml.

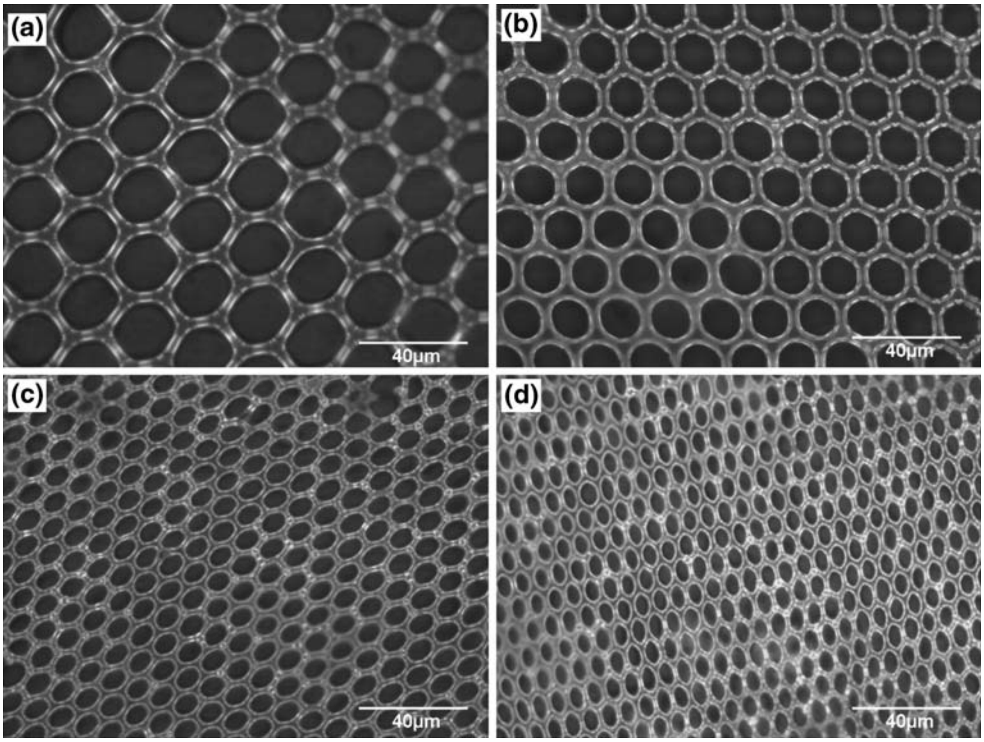

Fig. 5 Optical micrographs of the PS-b-P4VP/PSEBS (1/1, *w*/*w*) porous films made at different vacuum levels: **a** −70 kPa, **b** −50 kPa, **c** −40 kPa, and **d** −30 kPa. The relative humidity is 82 r.h.%, and the polymer concentration is 15 mg/ml

reported that the pore sizes would grow linearly with time [21]. Figure 7a displays that the evaporation time of the polymer solution decreases as the vacuum level increases. The evaporation time is the time when the polymer solution on the substrate was fully evaporated. We found that the pore sizes increased with the increase of the vacuum level, although the evaporation time decreased with the increase of the vacuum level. At a high vacuum level, the solvent evaporates very fast, and the temperature at the surface of the solution is reduced rapidly. As a result, water droplets are formed quickly on the solution

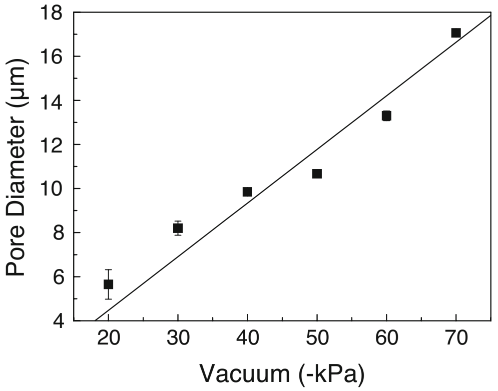

Fig. 6 The pore diameter of the PS-b-P4VP/PSEBS (1/1, *w*/*w*) porous film as a function of the vacuum level when the relative humidity is 82 r.h.%, and the polymer concentration is 15 mg/ml in a mixture of toluene and benzene (7/3, *v*/*v*)

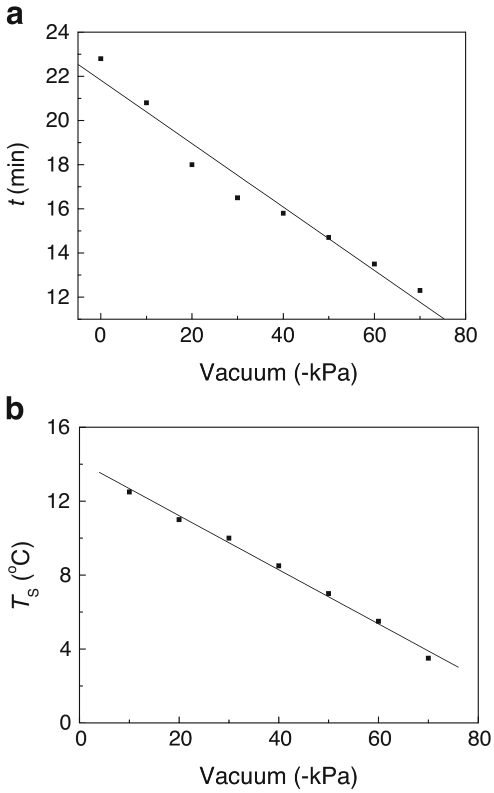

Fig. 7 The evaporation time (**a**) and surface temperature (**b**) of the polymer solution (0.075ml/cm^2) with a mixture of toluene and benzene (7/3, *v*/*v*) at a different vacuum level

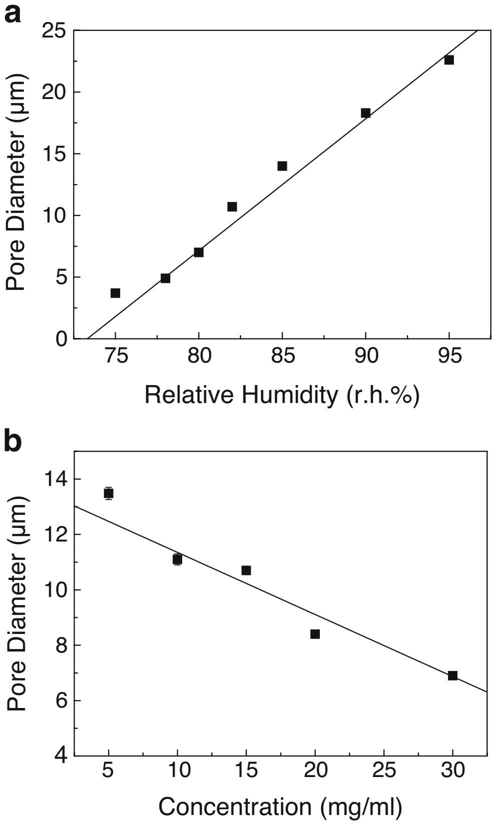

Fig. 8 **a** The pore diameter of the PS-b-P4VP/PSEBS (1/1, *w*/*w*) porous film as a function of the relative humidity when the vacuum level is −50 kPa, and the polymer concentration is 15 mg/ml a mixture of toluene and benzene (7/3, *v*/*v*); **b** The pore diameter of the PS-b-P4VP/PSEBS porous film as a function of the polymer concentration when the relative humidity is 82 r.h.% and the vacuum level is −50 kPa

surface and grow bigger and bigger. As such, porous films with big pores are formed. The growth law of water droplets can be described using Eq. 1 [33]:

$$R \sim \left[t \Delta p^{3/2}\right]^{1/3} \tag{1}$$

$$\Delta p \sim \Delta T^{0.8} \tag{2}$$

Where R is the radius of an isolated droplet, t is the growing time, Δp is the difference in the saturation pressure at temperature T_S and T_G. T_S is the surface temperature of the solution on the substrate, and T_G is the temperature of the air, $\Delta T = T_G - T_S$. According to Eq. 1, the pore size is related to not only t, but Δp or ΔT. ΔT increased due to the decrease of T_S (Fig. 7b), and t decreased as the vacuum level increases. According to Eqs. 1 and 2, ΔT and t have a contrary effect on the pore size. In our experiments, the pore size increased with the increase of vacuum level. The cause maybe is that ΔT has more effect on the pore size than the evaporation time in this experiment. It was also found that only disordered array of pores formed in the films when the vacuum level went below −20 kPa, due to the slow evaporation of the solution. Lower vacuum level causes slower evaporation of the solution so that the temperature at the solution surface may not decrease fast enough, and as such, convection currents induced by temperature gradients and capillary forces between the water droplets do not exist in the solution. Therefore, no water droplets even formed on the solution surface, and no porous polymer films are obtained. The vacuuming time is very short compared to the evaporation time for the solution, so the vacuuming process has little influence on the quality of the porous films.

The humidity in the vacuum chamber also plays a very important role in the formation of the porous films. Figure 8a shows the relationship between the pore diameter and the humidity when the polymer concentration and vacuum level were fixed. The pore diameter increases linearly with the humidity, as large water droplets are formed in the chamber with a high relative humidity. The pore diameter increases from 3.7 to 22.6 μm when the humidity increases from 75 to 95 r.h.%, with a fixed polymer concentration of 15 mg/ml and a fixed vacuum level of −50 kPa. Low humidity results in formation of transparent polymer films (no pores), while high humidity causes formation of disordered and coalesced pores in the films due to rapid condensing of water droplets, which is in consistency with the previous reports [16, 25]. The concentration of the polymer solution also affects the pore sizes of the porous films. The relationship between the pore diameter and the polymer concentration is also displayed in Fig. 8b. The pore diameter decreases from 13.5 to 6.9 μm when the concentration increases from 5 to 30 mg/ml, with a fixed relative humidity of 82 r.h.% and a fixed vacuum level of −50 kPa. The increase in the polymer concentration causes the increase of the viscosity of the solution and subsequently

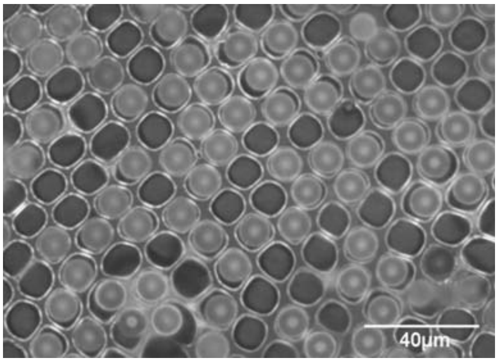

Fig. 9 An optical image showing the pattern of 9.95 μm microbeads on the ordered PS-b-P4VP/PSEBS porous polymer film

the formation of small water droplets in the solution and small pore sizes of the films. It is more difficult for the condensed water droplets to sink into the solution when the viscosity of the solution is higher. The pore wall is thicker when the concentration and viscosity of the polymer solution is higher, and smaller pores are produced [18, 30, 34]. At low concentration, the pore wall is thinner due to the low viscosity of the solution, and the condensed water droplets may fuse with each other to form larger water droplets, resulting in larger pore sizes. The thickness of the porous polymer films can be altered for the change of the polymer concentration. When the concentration increases from 5 to 20 mg/ml, the film thickness can increase from about 9.1 to 22.4 μm.

The porous polymer films can be used to pattern beads. Figure 9 exhibits the photograph of bead-based pattern on the porous polymer films. The beads are embedded within the holes on the porous films. The bead-based pattern on the porous polymer films can be applied to bead-based microarrays for the detection of biomolecules such as DNA and protein [35, 36]. The technique of preparing the microarray of DNA-based beads with the porous polymer films is in progress.

Conclusions

Porous polymer films via the breath figure method were prepared in a vacuum chamber without using any air or gas flow. Using the technique (using vacuum instead of air flow) we have developed, large-sized polymer films with long-range ordered pore structure were obtained. This vacuum technique has also a good reproductiveness for the fabrication of the well-ordered porous films. The pore size of the films can be more easily tuned by changing the vacuum level, the relative humidity in the chamber, or the polymer concentrations. The diameter of pores increased with the humidity and vacuum level and decreased with the polymer concentration. The polymer films with ordered porous structure and tunable pore sizes have potential applications in many areas such as microarrays and as scaffolds for tissue engineering.

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