Porous Polymer Films with Size-Tunable Surface Pores

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A novel method was developed to produce a porous polymer film with size-tunable pores on its surface. The porous film was produced using polystyrene microspheres as a template and the surface pore size can be tuned without changing the size of the template microsphere. Polystyrene microspheres were self-assembled on a substrate precoated with a thin layer of polystyrene and heated at an appropriate temperature, prior to infusion of a polymer precursor solution into cavities of the template microspheres, solidification of the polymer, and removal of the microspheres. The surface pore sizes can be tuned by changing the temperature and time for the heat treatment. With use of this method, porous films with nanosized surface pores can be produced using microsized spheres as the template, which can find applications in many areas.

Introduction

Porous polymer films with pore sizes in the micrometer and sub-micrometer ranges have elicited much interest recently for their 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] photonic band gap materials,[7−9] etc. Although a number of methods have been developed for producing porous materials, it still remains a great challenge in producing porous films with precisely controlled pore sizes, fully exposed pores (on the surface), and highly ordered periodic structure. Conventional methods based on electrochemical etching of alumina or silicon,[10] chemical etching of glasses,[11] and ion-track etching of polymers[12] can only produce porous films with essentially one-dimensional channel structures. Methods based on foaming of emulsion solutions[13] and sintering of ceramic particles[14] are capable of creating three-dimensional (3D) porous structures, but these methods have very little control over the pore size distribution.

Templating methods have been widely used for fabrication of porous materials with well-controlled structure, and self-assembled colloidal microspheres are usually used as a template for creating 2D or 3D highly ordered porous structure.[7−9,15−17] In these approaches, the voids between colloidal spheres are infiltrated with another material and subsequent removal of the template by either wet etching or thermal decomposition leads to the formation of ordered porous structure. 2D arrays of sub-micrometer spheres have been used as a template for producing porous polymer films and metallic half-shells.[18−20] Although many porous polymer films are prepared using the templating methods and their pore sizes are varied by using template microspheres with different sizes, the size of the surface pores on the films cannot be controlled. In this work, a new method was developed to produce a porous polymer film with ordered porous structure and size-tunable surface pores on the film, without changing the size of the template microspheres. With use of this method, porous films with nanosized surface pores can be produced using microsized spheres as the template, which can find applications in many areas, for example, membrane-based separation and purification and bead-based detection on microarrays.

Experimental Section

Materials. Monodispersed polystyrene microspheres with a diameter of ~2.68 μm (polydispersity less than 5%) were purchased

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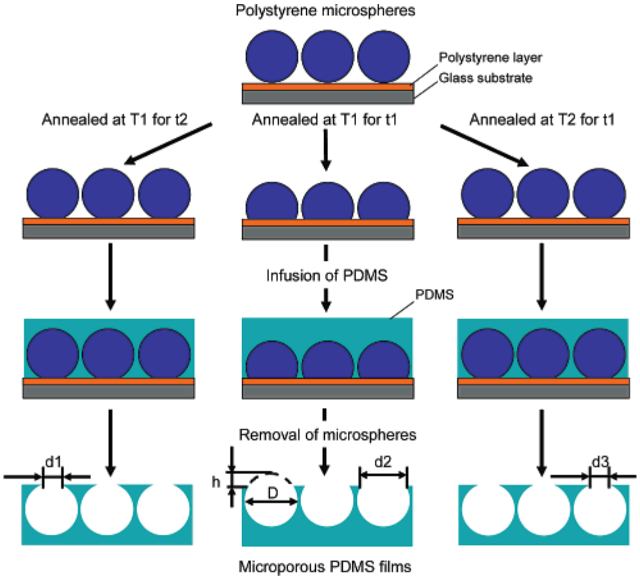

Figure 1. Schematic diagram showing how to prepare a porous polymer film with tunable pore sizes on its surface. The pore sizes can be tuned via heat treatment at different temperatures (T1, T2) for different times (t1, t2).

from Polysciences, Inc. Polystyrene (Mn = 140000) was obtained from Sigma-Aldrich, Inc. SYLGARD silicone elastomer base and SYLGARD 184 silicone elastomer curing agent were purchased from Dow Corning Corporation.

Preparation of the Porous PDMS Film. Three weight percent polystyrene solution in toluene was first spin-coated onto a clean glass substrate at 3000 rpm for 1 min using a spin coater and then dried at 70 °C for 6 h. Then a 0.1 wt % aqueous solution of polystyrene microspheres was spread on the polystyrene-covered glass substrate. After drying at room temperature for 8−12 h, polystyrene microspheres were self-assembled to form mono- or multilayers. After heat treatment at 70−90 °C in air, a mixture of silicone elastomer base and 10 wt % silicone elastomer curing agent was added to the microsphere-covered substrate and cured at 65 °C for about 5 h to form poly(dimethyl siloxane) (PDMS). After polystyrene microspheres were dissolved in toluene, PDMS films with well-ordered array of pores were obtained.

Characterization. Scanning electron microscope (SEM) images were taken using a FEI QUANTA 200 FEG SEM operating at 15 kV. A thin layer of gold was sputtered onto the samples prior to imaging.

Results and Discussion

The process of preparing the porous polymer film was illustrated in Figure 1. A thin layer of polystyrene was first spin-coated onto a glass substrate. Then a colloidal suspension of polystyrene microspheres was added onto the polystyrene-coated substrate and spread on the surface. After drying, the microspheres were self-assembled to form an ordered structure. After heat treatment at an appropriate temperature, a mixture of silicone elastomer base and 10% silicone elastomer curing agent was added to the microsphere-covered substrate, which was infiltrated into the voids between the microspheres driven by capillary action. The silicone elastomer base was then cured for polymerization and a solid poly(dimethyl siloxane) (PDMS) was obtained. The template microspheres were then removed by dissolving in toluene, resulting in a porous PDMS with well-ordered array of pores. Figure 2 gives some SEM images of the porous PDMS film obtained after the template microspheres were heated at 80 °C for 24 h. Both the large- and small-view images show that the film has a well-ordered porous structure with a hexagonal array of pores. The Fast Fourier Transforms (FFT) diffraction pattern (upper-right inset) suggested that the film has a two-dimensional porous structure with long-range order. The lower right inset in Figure 2b gives a cross-sectional SEM image of the porous PDMS film to show the internal pore structure. It was also found that swelling of PDMS by toluene has little effect on the final structure of the porous film.

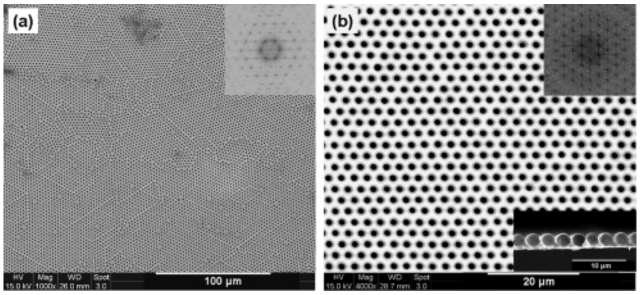

Figure 2. Low (a) and high (b) resolution SEM images of porous PDMS films made using 2.68 μm polystyrene microspheres as a template. The microspheres were self-assembled and heated at 80 °C for 24 h. The upper right inset shows two-dimensional Fast Fourier Transforms (FFT) of topography, demonstrating the long-range order of the porous structure. The lower right inset shows the cross-sectional SEM image of the porous PDMS film.

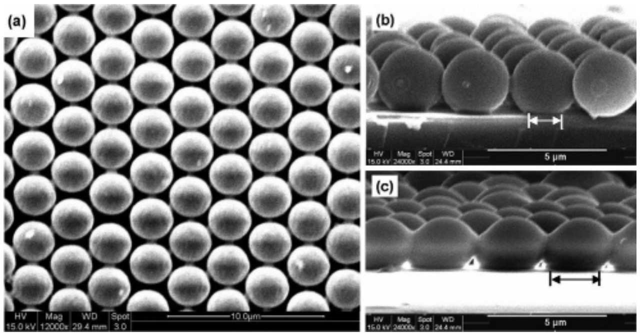

Figure 3. SEM images of self-assembled template polystyrene microspheres (a) and cross-sectional images of the microspheres after heat treatment at 90 °C for 12 h (b) and 36 h (c), respectively.

The SEM image in Figure 3a shows the top view of self-assembled polystyrene microspheres on the substrate. The microspheres were well-organized to form a two-dimensional ordered hexagonal array. After being heated at 90 °C, a temperature close to the glass transition temperature (*T*g) of polystyrene (∼94 °C), the microspheres started to deform. The bottom surface of the microspheres was melted and the microspheres were adhered to the polystyrene layer on the substrate to form necks between the microspheres and the polystyrene layer,[21−23] as shown in the cross-sectional images in Figures 3b and 3c. Comparing the neck radius for the two samples as shown in Figure 3, it was found that the necks became bigger when the microspheres were heated for longer time. It was also found that coating of a layer of

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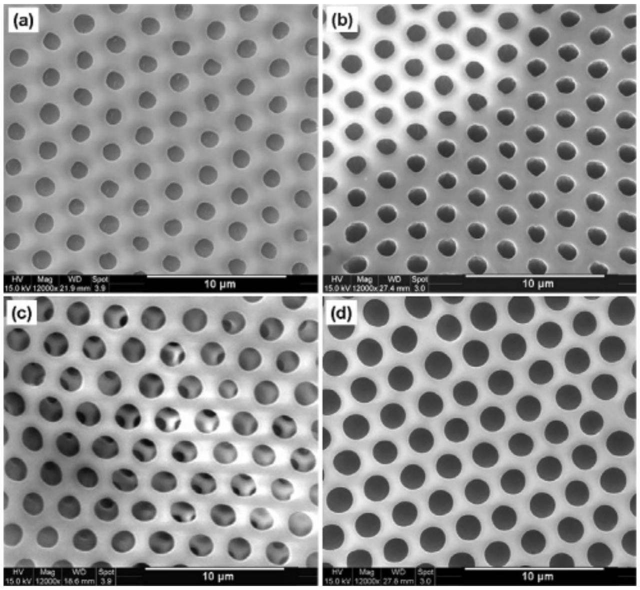

Figure 4. SEM images of porous PDMS films (using 2.68 μm polystyrene microspheres as a template) prepared via heat treatment at 90 °C for 3 h (a), 12 h (b), 24 h (c), and 36 h (d).

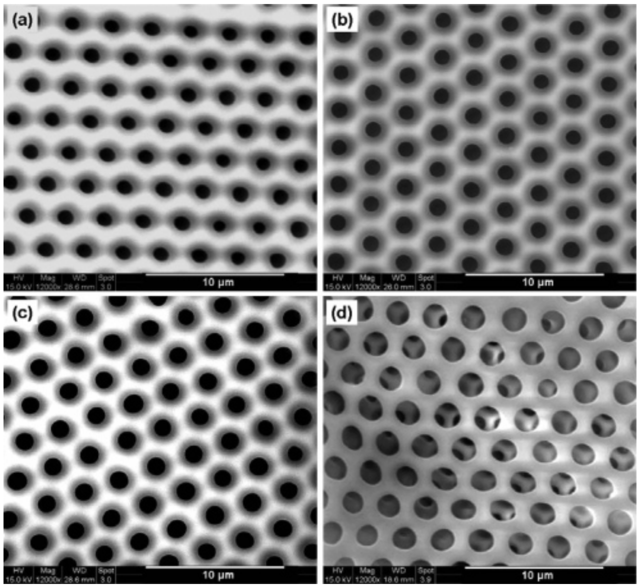

Figure 5. SEM images of porous PDMS films (using 2.68 μm polystyrene microspheres as a template) prepared via heat treatment at 70 °C for 16 h (a) and 24 h (b) and at 80 °C (c) and 90 °C (d) for 24 h.

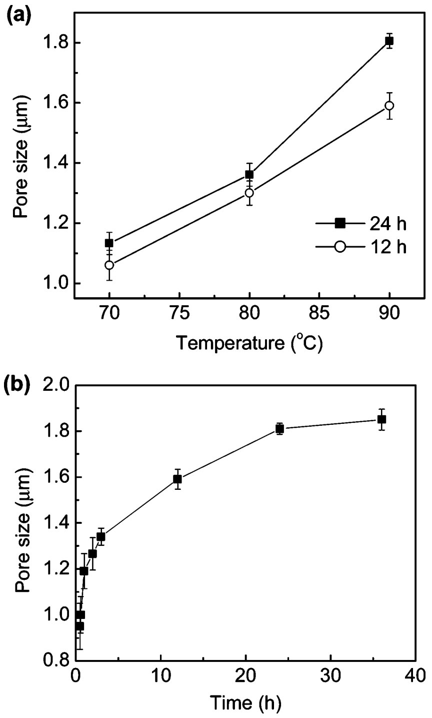

Figure 6. Size of the pores on the surfaces of porous PDMS films (using 2.68 μm polystyrene microspheres as a template) as a function of the temperature for heat treatment for 24 h (a) and the time for heat treatment at 90 °C (b).

polystyrene on the substrate was critical for the preparation of the porous film. It has been demonstrated that surface structure and property of a microsphere is very different from the interior of the microsphere.[24–27] The glass transition temperature (T_g) of the surface of the polystyrene microsphere (32∼67 °C) is much lower than that of the interior of the microsphere.[24–27] However, if polystyrene microspheres are self-assembled on the glass substrate directly, T_g of the bottom surface of the microsphere in contact with the glass is increased due to strong interactions between polystyrene and glass.[24,25,27–29] Then the microsphere is more difficult to deform and as such it is more difficult to form necks between the microsphere and glass. It was observed that, without coating of a layer of polystyrene on the glass substrate, pores could not be formed on the surface of the porous PDMS film (data not shown). Furthermore, PDMS may stick to the glass and could not be peeled off easily. Coating of a layer of polystyrene on the glass substrate may help to reduce the interactions between the microsphere and glass, and as such the microsphere can deform at a lower temperature to form necks between the microsphere and substrate.

The porous structure of the film is an inverse replica of the crystal structure of self-assembled microspheres. The size of the pores on the surface of the film is dependent on the size of the necks formed between the microspheres and the substrate. As such it is possible to control the size of the pores on the surface of the film by controlling the temperature and time for the heat treatment, without changing the size of the template microspheres. SEM images of the films obtained after the heat treatment at 90 °C for different times are given in Figure 4. The size of the pores increased with the heating time, due to the increase in the size of the necks formed between the microspheres and the substrate. The size of the pores could also be tuned by heat treatment at different temperatures. SEM images of the films obtained after the heat treatment at different temperatures for the same period of time, as shown in Figure 5, suggested that the size of the pores increased with the temperature.

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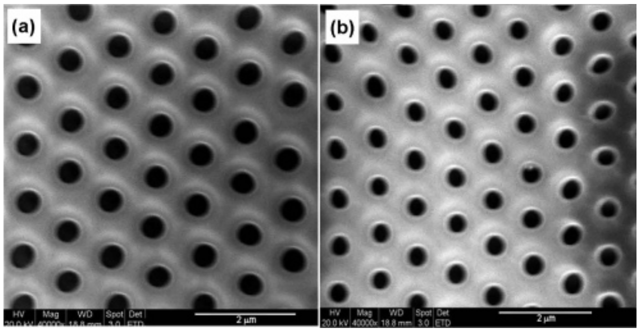

Figure 7. SEM images of porous PDMS films (using 1.09 μm polystyrene microspheres as a template) prepared via heat treatment at 90 °C for 2 h (a) and 40 min (b).

The pore size as a function of the heating time and temperature is given in Figure 6. The pore size increased with the heating temperature (with a fixed heating time of 24 h), from 1.06 to 1.85 μm as the temperature was increased from 70 to 90 °C. Furthermore, the pore size also increased with the heating time. With use of 2.86 μm microspheres as the template, the pore size could be altered from 0.92 to 1.85 μm by increasing the heating time from 30 min to 36 h, when heated at 90 °C. Meanwhile, the d/D ratio (d and D represent the sizes of the pores and polystyrene microspheres, respectively, as shown in Figure 1) increased from about 0.3 to 0.7. The pore size increased very quickly initially when the heating time was increased from 30 min to 3 h and after that increased slowly. This is closely related to the curvature of the bottom surface of the microsphere. As shown in Figure 1, the relationships between the pore size d, the microsphere size D, and the height of the spherical crown h are described as

$$d^2 = 4Dh - 4h^2 \tag{1}$$

where h is varied between 0 and $D/2$. According to eq 1, the smaller the h value, the smaller the d value. h increases with the heating time and temperature. When h is very small or near zero, d increases quickly with the increase of h, which agrees well with the data presented in Figure 6. This also suggests that although the pore size can be altered by controlling the heating time and temperature, the range of the pore sizes is limited. It is difficult to produce a porous film with very small and uniform pores when the d/D ratio is below 0.3. However, when using smaller microspheres as a template, porous PDMS films with smaller pores (even on the nanoscale) can be produced. As shown in Figure 7, when using 1.09 μm microspheres as the template, porous films with average pore sizes of about 400 and 300 nm were produced via heat treatment of the microspheres at 90 °C for 2 h and 40 min, respectively.

Conclusions

In summary, a new method was developed to produce porous polymer films with size-tunable exposed pores on the surface, using polystyrene microspheres as a template. The size of the exposed pores could be altered by controlling the temperature and time for the heat treatment to the template microspheres after they are self-assembled on a substrate. It was found that the pore size increased with the temperature and time for the heat treatment. Different from other templating methods in which porous polymer films with different pore sizes are usually produced by changing the size of the template microspheres, the pore sizes can be tuned by changing the temperature and time for the heat treatment to the microspheres, without changing the size of the microspheres. With use of this method, porous films with nanosized pores can be produced using microsized spheres as the template. We believe that this method can find applications in many areas, for example, use as a template to guide the patterning of microbeads, proteins, and some other biomolecules for microarray applications[30−32] and different polymers can be used to cater to different applications.

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