

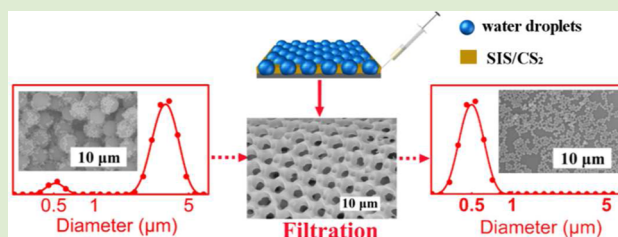
Robust Microsieves with Excellent Solvent Resistance: Cross-Linkage of Perforated Polymer Films with Honeycomb Structure

Can Du, Aijuan Zhang, Hua Bai, and Lei Li*

College of Materials, Xiamen University, Xiamen, 361005, People's Republic of China

S Supporting Information

ABSTRACT: Polymeric microsieves with uniform and tunable pores were fabricated with the breath-figure method and sequent vulcanization procedure using commercially available block copolymer polystyrene-*b*-polyisoprene-*b*-polystyrene. Uniform pore size and small film thickness endow the microsieves with high size selectivity and low operation pressure, while the cross-linked chemical structure gives them good mechanical properties and excellent chemical and thermal stability. These microsieves are able to separate particles in various media, including corrosive solvents, hot water, and organic solvents. The process reported in this communication is a simple and inexpensive method for the preparation of high-performance microsieves.



The process reported in this communication is a simple and inexpensive

Microsieves are one of the most outstanding micro-filtration membranes, with smooth surface, well-defined dense pores, and small thickness (generally smaller than the pore diameter).^{1–4} The morphological characters endow microsieves with insensitivity to fouling, a low flow resistance, and an excellent separation behavior. In past years, microsieves have been widely investigated for a variety of applications, including yeast cell and haze particles filtration of beer, bacteria and particle removal in pharmaceutical, and cell harvesting in biotechnology.^{1,5–7} Up to now, the commercially available monodispersed microsieve materials are mostly a silicon nitride membrane attached to a silicon support structure, which are produced using lithographic techniques similar to those used in the semiconductor industry.^{3,8,9} Evidently, the narrow choice in material and laborious fabrication process have a negative effect on the economical feasibility of the device to be developed. Alternatively, a broad spectrum of polymers has been employed to prepare microsieves by a phase separation micromolding (PS μ M) process because of the low cost, easy processability, and functionality.^{10–13} In this process, a hard mold consisting of pillars of several micrometers in height and diameter that protrude vertically from a flat solid substrate is used as a reusable mold for the casting of microsieves from solutions of suitable polymers. Although the technique is straightforward and cost-effective, the fabrication of hard mold still relies on lithographic techniques. Also, the release problems related to sticking, breaking, or other stress-related deformations of the polymer structure or the mold cannot be avoided. Therefore, a feasible and versatile methodology for the preparation of polymeric microsieves without the need of lithographic instruments is desired in both industrial and academic fields.

Breath-figure (BF) process is a facile and cheap strategy for the fabrication of highly ordered porous membranes with pore sizes varying from 0.20 to 20 μm without the need of lithographic techniques.^{14–17} It involves the condensation and

self-assembly of water droplets on the surface of a polymer solution during the drying of the solution in moist atmosphere. After complete drying of the solution, ordered pores are left on a polymer film templated from the water droplet array. Usually the pores are not through the film under conventional BF process; however, through-pore structured polymer films were fabricated via the BF process on special substrates, such as at the air/water^{18–20} or the air/ice²¹ interface, providing a new pathway to high-performance polymeric microsieves. However, the fabrication of perforated honeycomb films at these interfaces is confined to the use of amphiphilic copolymers or the assistance of surfactant.¹⁹ Furthermore, the regularity of the pore arrangement is easily fluctuated by the water surface.²²

In this communication we report a new reliable method to prepare robust polymer microsieves with excellent solvent resistance and tunable selectivity based on a modified BF technique and subsequent cold vulcanization. Our modified BF technique is applicable to various types of polymers, providing a wide choice of raw materials for the microsieves. Here, a commercially available triblock copolymer, polystyrene-*b*-polyisoprene-*b*-polystyrene (SIS) was used in our work. First, the SIS porous membranes with through pores (from 1 to 7 μm) were prepared with a modified BF method on glass substrate. In the following vulcanization, polyisoprene block is cross-linked, endowing the porous membranes with improved mechanical properties and chemical and thermal stability. The cross-linked porous membranes have a tensile strength of 14 MPa after a 20 min vulcanization and are suitable for separating microparticles in various media, including boiling water, strong alkali, strong acid, and polar organic solvents. The reported

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methodology provides a facile preparation of disposable polymer microsieves, circumventing the expensive lithographic technique and material cost.

In the BF process, the pores in the polymer film originate from the water droplets array. To fabricate through-pore structures, the floating water droplets must transpire the polymer solution film and come in contact with the substrate before the solution completely dries. However, the size of the water droplets are typically several micrometers, making it difficult to cast such a thin polymer solution film on solid substrate. That is why reported polymer films with through-pore structure were prepared on water, because the spread of the polymer solution on the water surface can produce a rather thin liquid film.^{18–21} Here, we developed a modified BF process to construct through-pore structures on solid substrate. The formation of through-pore structures is schematically shown in Figure 1. A 0.5 mL aliquot of 3 mg mL⁻¹ SIS/CS₂ solution is

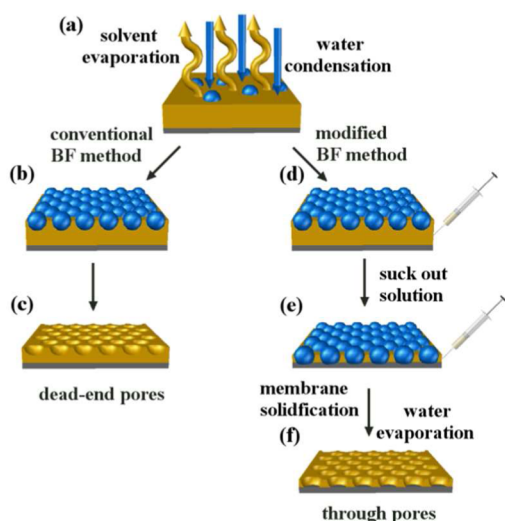


Figure 1. Illustration of the formation of honeycomb-structured polymer films with (a–c) dead-end pores and (d–f) through pores (microsieves).

typically cast onto the glass substrate with a size of 2.5 × 7.5 cm. The rapid evaporation of carbon disulfide decreases the surface temperature, resulting in the condensation of water droplets on the surface of the solution. The droplets floating on the surface of solution self-organize into hexagonal array by the capillary force. As water is a precipitator for SIS, it is worth noting that dissolved polymer will absorb at the water/solution interface to form a thin polymer layer which can stabilize water drops and prevent their coalescence. In conventional BF process, the solution was left to dry, resulting thick polymer film with pores on the surface, as shown in Figure 1b,c (Figure S1 for SEM). In our modified BF process, when the whole surface of solution becomes turbid, the excess solution underneath the surface is sucked out from the edge by a syringe equipped on a microinjection pump, as shown in Figure 1d,e. Most of the polymer solution is sucked out and water drops fall off with the descending solution surface to the extent that they can touch the surface of the glass. At that moment there exists a polymer layer between water drops and glass. Neutron reflection studies revealed that this polymer layer is a swollen layer of several nanometers²³ and radiolabel adsorption showed that it is under thermodynamic (reversible) control.²⁴

Therefore, this layer is easy to rupture when there is a force acted on the polymer layer. With further evaporation of the solvent, the droplets are squeezed by the descending solution surface and the substrate, resulting in a deformation of the thin interfacial polymer layer. Additionally, the surface of glass is rough (with a root-mean-square (rms) roughness of 5 nm; see Figure S2), which facilitates the rupture of the swollen polymer layer.²⁵ Consequently, the polymer thin films surround the water droplets are easy to rupture when they contact the glass substrate. As soon as the interfacial polymer layer ruptures, the adhesive force between the water droplets and hydrophilic glass comes into effect immediately. As a result, the water droplets adhere to glass and through-pore structures appear after complete evaporation of the solvent and water (Figure 1f). To support this process, we used an optical contact angle equipment to record the moment when a droplet touched glass in SIS/CS₂ solution (see Supporting Information, movie 1). From the video, it can be seen that when the droplet touched glass, it would adhere to glass immediately regardless of the thin weak polymer layer at the interface of water and polymer solution. It is worth noting that the solution concentration has significant influence on the formation of ordered through-pore structures. Increased viscosity causes the pumping out of solvent becomes difficult and perforation is unavailable. The desirable concentration of SIS/CS₂ solution is between 2 mg mL⁻¹ and 4.5 mg mL⁻¹.

The as-prepared membrane exhibits nacre color due to interface effects, as shown in Figure 2a, indicating the formation

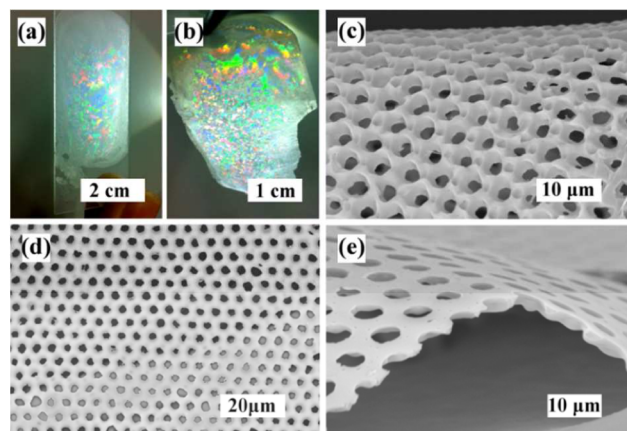


Figure 2. Digital photographs of (a) the SIS membrane supported on a glass slide before vulcanization and (b) the freestanding membrane peeled off from the glass slide after vulcanization. SEM images of honeycomb structured membranes with through-pores, prepared by SIS triblock copolymer after vulcanization: (c) top view of a curly membrane, (d) bottom view, and (e) cross-section view.

of highly ordered structures in a large area. Figure S3 shows the morphology of the as-prepared SIS film supported on glass, in which ordered through-pores with a diameter of 4.5 μm can be observed. It should be noticed that in the modified BF process the physical and chemical nature of the polymer plays a minor role in the formation of the through-pore structure, because the water droplet assay is forced to contact with the substrate by sucking out the excess solution. Therefore, polymers able to form honeycomb structure in conventional BF process can be fabricated into through-pore structures with modified BF process. Polystyrene (PS) and polystyrene-*b*-poly(acrylic acid) (PS-*b*-PAA) films with through-pores were successfully

prepared, as shown in Figure S4. Thus, our method is a universal way to produce polymer through-pore structures, which is important for the design of microsieves with particular properties and functions. For SIS film, the ordered structures are easily destroyed when it is peeled off from the glass substrate due to the soft nature of SIS. To improve the mechanical strength as well as the chemical stability, a cold vulcanization was carried out to cross-link the double bonds in polyisoprene block with sulfur monochloride (S_2Cl_2 ; the details are described in Supporting Information).²⁶ After cold vulcanization the membranes become self-standing and can be peeled off from the glass slide without damaging it (Figure 2b). The occurrence of the vulcanization can be judged from the decrease of the relative intensity of the band related with double bonds in infrared spectrum (Figure S5). Moreover, the nacre color in the cross-linked films indicates the formed ordered structures are well preserved. Figure 2c–e shows top, bottom, and cross-section views of the freestanding vulcanized SIS membranes. SEM image of a curly membrane (Figure 2c) shows that the pores are tapered with a bigger mouth at the top. Ordered pores can be found on both top and bottom surface of the film, and the substrate beneath the film can be observed through the pore (Figure 2d), demonstrating the through-pore structures. The thickness of the membrane is about 2 μm (Figure 2e), while the approximate porosity of 30% can be confirmed by calculating the area ratio of pores and the whole film.

A quantitative correlation between the vulcanization time and the mechanic properties of the membrane was characterized by tensile measurements. For comparison, the tensile strength of commercial filter papers and PTFE filter membranes were also measured. As shown in Figure 3, the

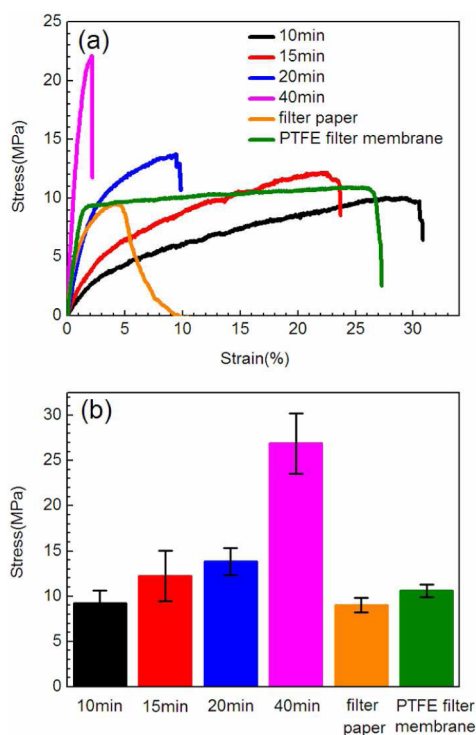


Figure 3. (a) Typical stress–strain curves and (b) graphical comparison of the tensile strength of the SIS membranes with different vulcanization times, commercial filter paper, and PTFE filter membrane.

tensile strength of a SIS microsieve membrane increases with the vulcanization time. A value of 12.5 MPa is achieved after a 15 min vulcanization, a value higher than that of filter paper (9.0 MPa) and PTFE filter membrane (10.6 MPa). In addition, the breaking elongation of the SIS membrane is higher than that of commercial filter paper and close to that of PTFE filter membrane, exhibiting excellent ductility. With the increasing vulcanization time, strength of 27 MPa is achieved. However, the breaking elongation of this membrane is reduced to 2.1%. Eventually, an optimum vulcanization time of 20 min is fixed to prepared microsieves for filtration experiments.

After vulcanized for 20 min, the double bond conversion of the PI blocks determined from FTIR is 46% (Figure S5). The high cross-linkage significantly suppresses the swelling of the PS component dispersing in the continuous PI matrix; thus, this ensures the size stability of the membranes in the organic solvents. To demonstrate the excellent chemical stability of the vulcanized SIS membranes, the membranes were immersed in various solvents for 10 h, and then their morphology and mechanical properties were rechecked. Thanks to the cross-linked chemical structure, the honeycomb patterned through-pore structures are maintained regardless of solvents (Figure S6). The tensile strength and breaking elongation of these SIS membranes treated with solvents, such as THF, toluene, NaOH aqueous solution and glacial acetic acid, are almost the same as the membranes without solvent treatment (Figure S7). The good chemical stabilities significantly broaden the application of the polymer microsieves, making it possible to separate particles in different corrosive media.

The separation behavior of these microsieves were demonstrated by separating 3 μm and 500 nm polystyrene (PS) particles from their blending dispersion by filtration using a membrane with an average pore diameter of 2 μm . The filtration experiments were carried out without additional pressure (Figure 4, inset), exhibiting easy pass-through for

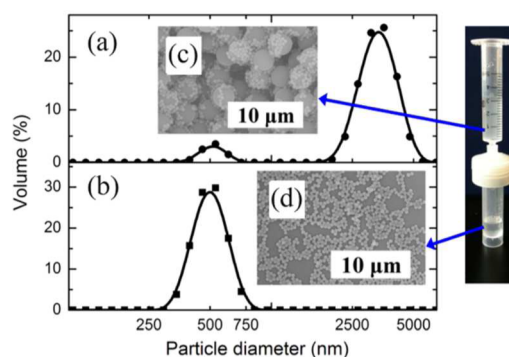


Figure 4. Size distribution of (a) the feeding particles comprised of 500 nm and 3 μm PS microspheres and (b) the filtrate obtained by filtering the feeding aqueous dispersion through the SIS microsieve. The corresponding SEM images of the particles (c) before and (d) after filtration.

particles and high energy-efficiency, due to short channel length. Also, the very low operating pressure combined with the short pore channels results in a relative insensitivity to fouling. It should be noticed that the filtration paper and PTFE membrane have a sponge-like or tortuous and long pore channel structure, which makes it difficult to clean the inside of these membranes.¹ Figure 4a,b shows the size distributions of mixed particles before and after filtration, determined by DSL.

The feeding dispersion has a dual distribution at 500 nm and 3 μm , which are in accordance with the actual particle diameters (Figure 4c). As was expected, the filtrate showed only a single narrow peak at 500 nm. Obviously, the cross-linked SIS microsieves show a high-selectivity separation performance. This high-selectivity can also be confirmed from the SEM images of the particles before and after filtration, as shown in Figure 4c,d. The high selectivity of the microsieves reveals the narrow size distribution of the pores in a large area, owing to the perfect self-assembly of the water droplets template during the BF process. The pore size can be adjustable by simply changing relative humidity and airflow rate in the BF process^{21,27} from 1 to 7 μm , as depicted in Figures S8 and S9. Therefore, the vulcanized microsieves with different pore diameters can be used for separating various nano/micrometer particles (Figure S10).

We further used our microsieves to separate particles in a harsh environment. The filtration experiment was carried out in 90 °C water and THF (good solvent for unvulcanized SIS). Because PS is soluble in THF, we use SiO₂ particles instead of PS particles to evaluate the size separation performance of the microsieves in THF. The SEM images of the particles before and after microsieving separation are shown in Figure S11. In both solvents, the particle mixture were successfully separated and only small particles were found in the filtrates. These results indicate that the pore structure of the microsieving is resistant to the above solvents due to the cross-linked chemical structure. Therefore, it is considerable that this kind of microsieving is suitable for filtration of particles dispersed in organic, acidic, or basic and hot solutions due to their excellent chemical and thermal resistance.

In summary, we developed a simple and inexpensive strategy for the fabrication of robust polymeric microsieves. The polymeric microsieves were prepared with a modified BF method using commercially available triblock copolymer SIS followed by vulcanization. Owing to the cross-linked chemical structure, the vulcanized SIS microsieves exhibit good mechanical property and excellent chemical and thermal stabilities. The pores on the microsieving forming in the BF process are highly ordered and tunable; thus, these microsieves can be used to separate different particles with high size selectivity and low operation pressure in various media, including hot water and organic solvents. These characteristics make the vulcanized SIS membrane an ideal microsieving, which has potential application in industry.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental details, morphology of SIS membrane with dead-end pores, AFM image of glass surface, SEM images of the as-prepared SIS membrane before vulcanization, other polymeric microsieves, vulcanization mechanism, morphology, and tensile test result after solvent and thermal treatment, the tunability of pore size, and separation behavior in a harsh environment. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: lilei@xmu.edu.cn.

Notes

The authors declare no competing financial interest.

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