1622 *Chem. Mater.* **2004,** *16,* 1622−1626

Polymer Membranes with Two-Dimensionally Arranged Pores Derived from Monolayers of Silica Particles

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Received October 21, 2003. Revised Manuscript Received January 16, 2004

This paper describes a simple method to prepare porous polymer membranes with closely packed two-dimensionally arranged pores ranging from approximately 20 to 1000 nm diameter. Mixtures of hydrophobized silica colloids and a polymerizable organic liquid, trimethylolpropane trimethacrylate (TMPTMA), were spread onto the surface of water-filled containers to form a wetting layer, in which two-dimensionally closed packed silica particles are embedded in a layer of the organic liquid in such a way that they penetrate through both the upper and lower interfaces. Photochemical cross-linking of the organic monomer and subsequent removal of the colloids give rise to a polymer membrane with pores of uniform size. The crucial factor of this method is to spread exactly the amount of silica particles necessary for the formation of a closely packed two-dimensional monolayer.

Introduction

The size selectivity and permeability of filtration membranes are determined by their average pore diameter, pore size distribution, overall porosity, and the thickness of the membrane.[1] The optimum performance will be achieved with membranes that are as thin as possible and bear densely packed holes of uniform diameter.[2] Porous materials with uniform pore size have been made via ion-track etching,[3,4] photo lithography,[5] and replica molding using mesoscopic templates such as micelles,[6] block copolymers,[7] or colloidal particles.[8] These methods usually generate bulk materials with three-dimensional porous structure. However, three-dimensional porous membranes have a comparatively large thickness, which easily leads to the trapping and adsorption of particles or large molecules in filtration applications.

Recently, we developed a technique to synthesize porous polymer membranes by using monolayers of silica colloids as templates.[9] The porous polymer membranes were prepared by spreading mixtures of silica colloids and polymerizable organic liquids onto a surface of a water-filled Langmuir trough. Lateral compression of the colloids to a dense monolayer, photochemical cross-linking of the organic liquid and subsequent removal of the colloids gave rise to porous polymer membranes. However, this method relied on the use of a Langmuir trough and was comparatively time-consuming.

Here, we show that (i) one can fabricate similar porous membranes in a much simpler way by replacing the Langmuir trough with a normal water container (e.g., a Petri dish) and spreading the right amount of particles on the air/water surface without a lateral compression described previously;[9] (ii) this method is effective to control pore sizes of membranes by choosing colloids of suitable sizes. Furthermore, we explore the upper and lower limits of pore sizes achievable by this method.

Experimental Section

Materials. Tetraethyl orthosilicate (98%), ammonia (NH_4OH, 25 wt % in H_2O), chloroform (99%), and ethanol (99%) were purchased from Merck and used as received. The polymerizable organic liquid trimethylolpropane trimethacrylate (TMPTMA, Aldrich) was made inhibitor-free by passing the liquid through a column filled with Al_2O_3, then 3 wt % of photoinitiator benzoinisobutyl ether (Aldrich) was added. Hydrofluoric acid (48%) was purchased from Fluka. Water used in this work (resistivity = 18.2×10^6 Ω/cm, total dissolved organic carbon < 5 ppm) was purified with an ion-exchange filter system (Millipore).

Particle Synthesis and Purification. Silica particles were synthesized following Stöber's method.[10] Five samples

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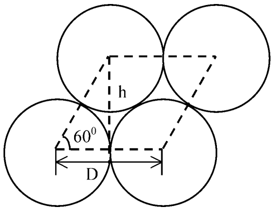
10.1021/cm035044w CCC: $27.50

Scheme 1. Schematic Illustration of Hexagonally Close-Packed Silica Spheres on a Water Surface (Top View)



of SiO_2 colloids: 33 nm ($\sigma = 9.43\%$), 119 nm ($\sigma = 5.57\%$), 334 nm ($\sigma = 2.78\%$), 558 nm ($\sigma = 2.14\%$), and 1184 nm ($\sigma = 4.24\%$) (σ refers to the relative standard deviation of the diameters, measured by the images of transmission electron microscopy (TEM); over 100 spheres were sized) were obtained by adjusting the reaction conditions. All of the SiO_2 colloids were hydrophobized by coating them with 3-(trimethoxysilyl)propyl methacrylate (TPM),[11] and subsequently washed with ethanol by four cycles of centrifugation and ultrasonic dispersion.

Calculation of the Spreading Amount of the Silica Particles. The starting point is the assumption that all of the silica colloids are hexagonally close-packed on the water surface (Scheme 1).

The area per particle A/n (A = area of the water surface, n = total number of particles on water surface) is given by the area of a parallelogram of width D (D equal to the diameter of the particle) and height h as indicated in Scheme 1.

$$\frac{A}{n} = D\cdot h = D^2 \sin 60° = \frac{\sqrt{3}}{2}D^2 \qquad (1)$$

The mass of a particle (m) is equal its volume ($V = (\pi/6)D^3$) multiplied by its density ρ (in our case,[12] ρ =1.9 g/cm^3).

$$m = \rho\cdot V = \frac{\pi}{6}\rho D^3 \qquad (2)$$

Thus the amount of particle dispersion (M) to be spread to form a closed packed monolayer of particles is given by the following:

$$M = n\cdot\frac{m}{\omega} = \frac{A}{A/n}\cdot\frac{m}{\omega} = \frac{\pi}{3\sqrt{3}}\cdot\frac{\rho DA}{\omega} \qquad (3)$$

Here ω is the mass fraction of the silica particles in suspension.

Preparation of Porous Polymer Membranes. Hydrophobized silica particles were suspended in a mixture of ethanol/chloroform (1:1 by volume) and the organic monomer TMPTMA (mass ratio of particles to TMPTMA = 3:1; mass ratio of particles to solvent = 1:100). These suspensions were spread onto the surface of a water-filled Petri dish, in such an amount as to yield complete coverage of the surface by the colloids (calculated from eq 3). After evaporation of the solvent, the organic monomers in the mixed monolayers were cross-linked by irradiation with UV-light of 360-nm wavelength. The solidified films were transferred to various substrates, such as metal electron microscopy grids, plastic plates, and mica sheets by horizontal transfer.[13] To remove the silica colloids, the transferred composite films were exposed to the vapor of hydrofluoric acid for 4−5 min in a sealed plastic container. (*CAUTION: Hydrofluoric acid is extremely corrosive and hazardous; it should be handled with care.*)

Characterization of the Porous Membranes. Scanning electron microscopy (SEM) images of porous membranes were measured on a DSM 962 SEM (Zeiss, Germany) or a field-emission scanning electron microscope (S-5200, Hitachi, Japan). A thin layer of Au/Pd alloy (about 5 nm) was sputtered onto the samples prior to imaging. Porous polymer membranes were directly transferred onto the gold grids (G204G, uncoated, Plano Co.) for TEM images. TEM images were performed on an EM 400T microscope (Philips, The Netherlands). All of the TEM images were obtained without additional contrast enhancement with the exception of the thinnest sample with a pore size of 18 nm. This film was very thin and almost transparent under standard TEM imaging conditions. To increase the contrast, a 1-nm thick gold layer was sputtered onto the membrane before the TEM characterization.

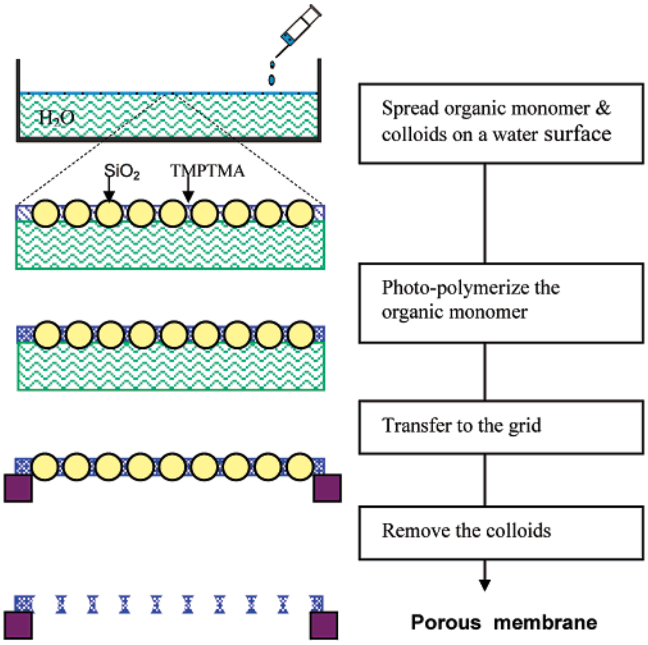


Figure 1. Scheme of the preparation of porous membranes on an air/water surface.

Results and Discussion

The general procedure used for the preparation of the porous membranes is shown in Figure 1. Mixtures of hydrophobized silica colloids, a nonvolatile organic liquid (TMPTMA), and a volatile solvent are applied on a water surface. After evaporation of the solvent, mixed layers of particles and the organic liquid are obtained. Polymerization of the organic liquid and subsequent removal of the silica particles yields polymer membranes with two-dimensionally arranged pores. The resulting porous membranes are transferred onto desired substrates.

Figure 2A and B show the TEM images of membranes prepared with 119-nm silica particles that have been transferred to electron microscopy grids. Before the removal of the silica particles, a composite membrane composed of colloids and cross-linked polymer is obtained (Figure 2A). It can be clearly seen that the silica colloids form a closely packed two-dimensional monolayer embedded in the continuous polymer layer. No overlaps of silica colloids can be found. The removal of silica colloids yields the corresponding porous membrane (Figure 2B). The pores are densely packed, giving a pore density of the membrane of 7×10^9 pores/cm^2. The pore size of approximately 105 nm and polydispersity of 5.3% reflect the size and polydispersity of the templating colloids. From the side view of the porous membrane supported on a mica sheet (Figure 2C), the size and shape of the pores can be clearly seen. The thickness of the membrane (approximately 80 nm) is even smaller

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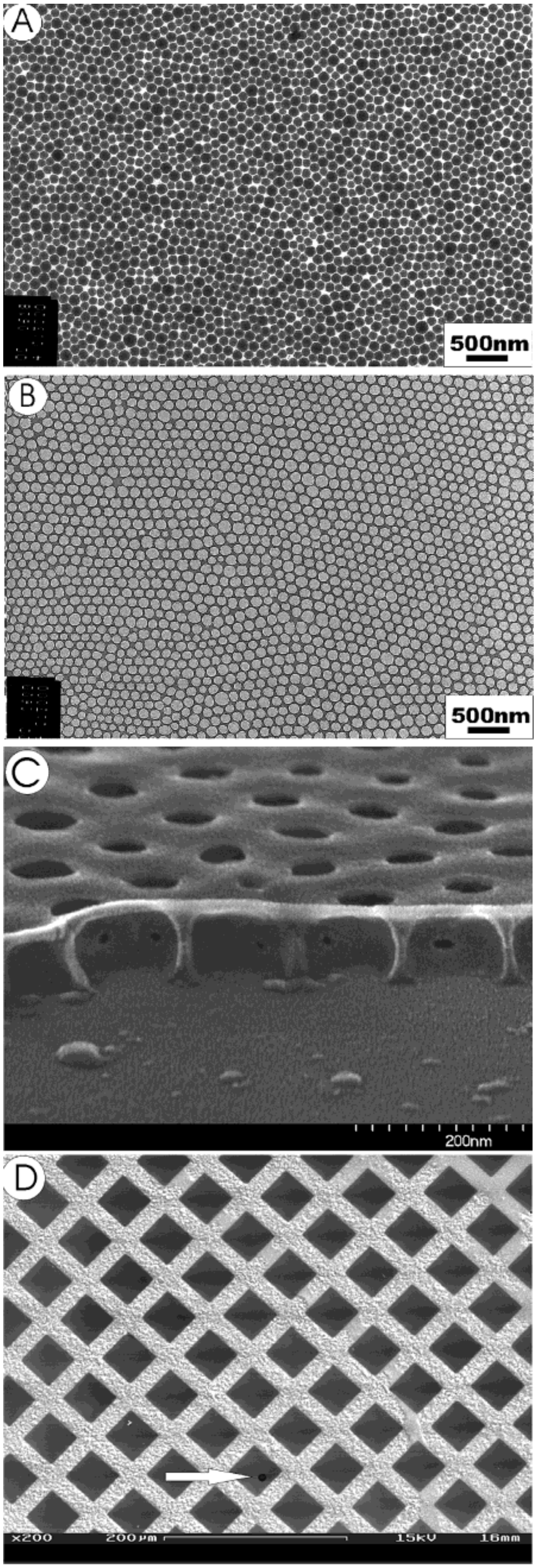

Figure 2. TEM images of membranes fabricated with 119-nm silica particles as templates, before (A) and after (B) removal of the silica particles. (C) High-resolution SEM image of the porous membrane (partially removed by ottransparent tape) supported on a mica sheet. (D) SEM image of the porous membrane transferred to a metal grid with 40-μm wide openings. The small defect indicated by a white arrow shows the contrast of a covered area to an uncovered area.

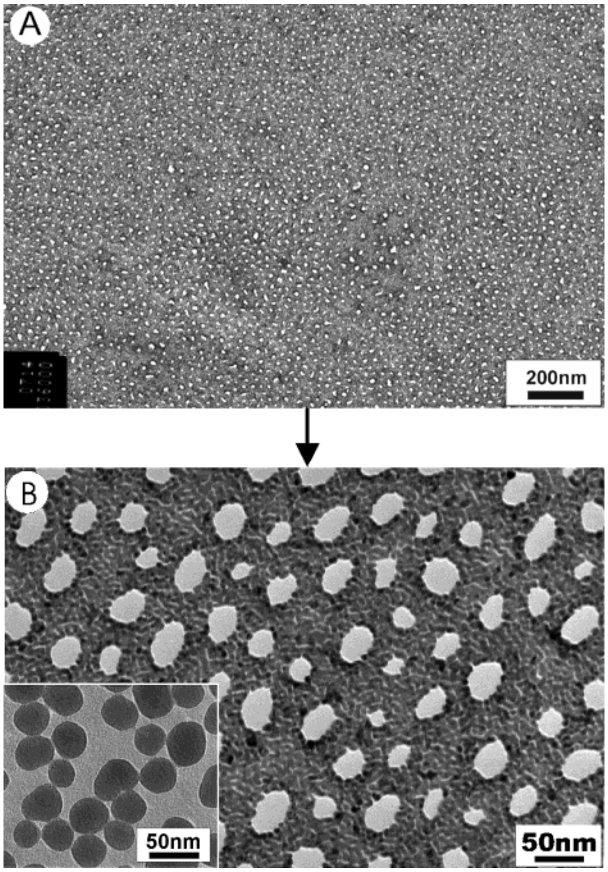

Figure 3. TEM images of a porous membrane prepared with 33-nm silica particles as templates. A 1-nm thick gold layer was sputtered onto the membrane to increase the contrast before the characterization. Inset in (B) shows a TEM image of the 33-nm silica particles.

than the size of the pores. All the pores on both the top and bottom surfaces of the membrane are fully open. This indicates that the silica colloids penetrate through both interfaces of the polymer membrane before the removal. Because the particles used here are spherical, the inner surfaces of the pores are concave. In the middle of the pore walls, one observes smaller inner openings in the walls between the pores. These openings presumably form in the position where two particles touch each other. This result further supports the observation of a close packing of the particles. Figure 2D shows an overview picture by SEM of such a porous membrane freely suspended on a gold grid. With the exception of a single defect (indicated by a white arrow), all of the 40-μm-wide openings of the grid have been completely covered. Though it is comparatively difficult to show all defects in such a membrane by electron microscopy, we estimate that there are approximately 2−5 such defects per square millimeter. Some of these defects could be caused by surface-active impurities on the water surface which were embedded in the continuous polymer layer.

The general appearance of the membrane is similar to that of the membranes fabricated on a Langmuir trough.[9c] However, the colloids used here are significantly smaller than the one used previously. To further explore the tunablility of pore sizes, we fabricated membranes using even smaller and bigger particles.

Figure 3 shows the TEM images of a membrane prepared with 33-nm silica particles by using the same approach as described above. The image of the porous membrane taken with lower-magnification (Figure 3A) reveals that the pores are evenly distributed on the membrane. Analysis of the image of a higher-magnification (Figure 3B) gives an average size of the pores of about 18 nm. In contrast to the membranes shown in Figure 2, most of the pores in this membrane are not spherical. This irregularity of the pores is due to the fact that the particles in this case are not ideal spheres (see the inset of Figure 3B). Such a deviation from spherical shape is usually attributed to the aggregation of smaller subparticles during the synthesis of silica particles of that small size.[14] Image analysis of this membrane yields a pore density as high as $\sim 8 \times 10^{10}$ pores/cm^2. This value is approximately 100 times that of porous polycarbonate films obtained by ion-track etching ($\sim 7 \times 10^8$ pores/cm^2).[15]

To increase the pore size of the membranes, silica particles of 334, 558, and 1184 nm have each been used as templates. Figure 4 shows SEM images of the corresponding three membranes with pore sizes of approximately 250, 410, and 1010 nm, freely suspended on the gold grids. All the pores in Figure 4A and B are closely packed. In contrast to the case of the smaller particles, the porous membrane fabricated with 1184-nm silica particles (Figure 4C) has a less regular structure and a higher amount of defects. It is important to keep in mind that the silica colloids we employ here have a surface modification to make them dispersible in organic media. However, the attraction force between the particles increases with their sizes, thus, the 1184-nm silica particles have a tendency to form aggregates either before or during the spreading process. As a result, the porous membrane has a relatively higher amount of irregular structures and defects.

In the previous work,[9] the particles were applied to the surface of a water-filled Langmuir trough at a coverage well below dense packing, and the closely packed monolayer was formed only after lateral compression. In the current work, we discovered that this lateral compression step actually can be omitted if the necessary amount of particles corresponding to complete surface coverage is spread directly onto the water surface. However, if a smaller amount is spread, the mixture of particles/monomers can only form small two-dimensional clusters on the water surface due to the attractive interactions (e.g., lateral capillary forces, dispersion force) among neighboring particles.[16] On the other hand, if we overspread, the monolayer will be partially covered by patches of excess particles on the top surface, and thus the thickness of the membrane becomes inhomogeneous and causes the overlapping of pores. Here, we calculated the area per particle and the spreading amount from simple geometrical arguments. It is worth pointing out that one can also obtain the area per particle from the lateral pressure/area isotherm measured with a Langmuir trough. If the particles are characterized correctly, the area per particle measured from the lateral pressure/area isotherm is close to the result calculated from eq 3. In the latter case, the Langmuir trough is used only as an analytical tool at the beginning of the experiments.

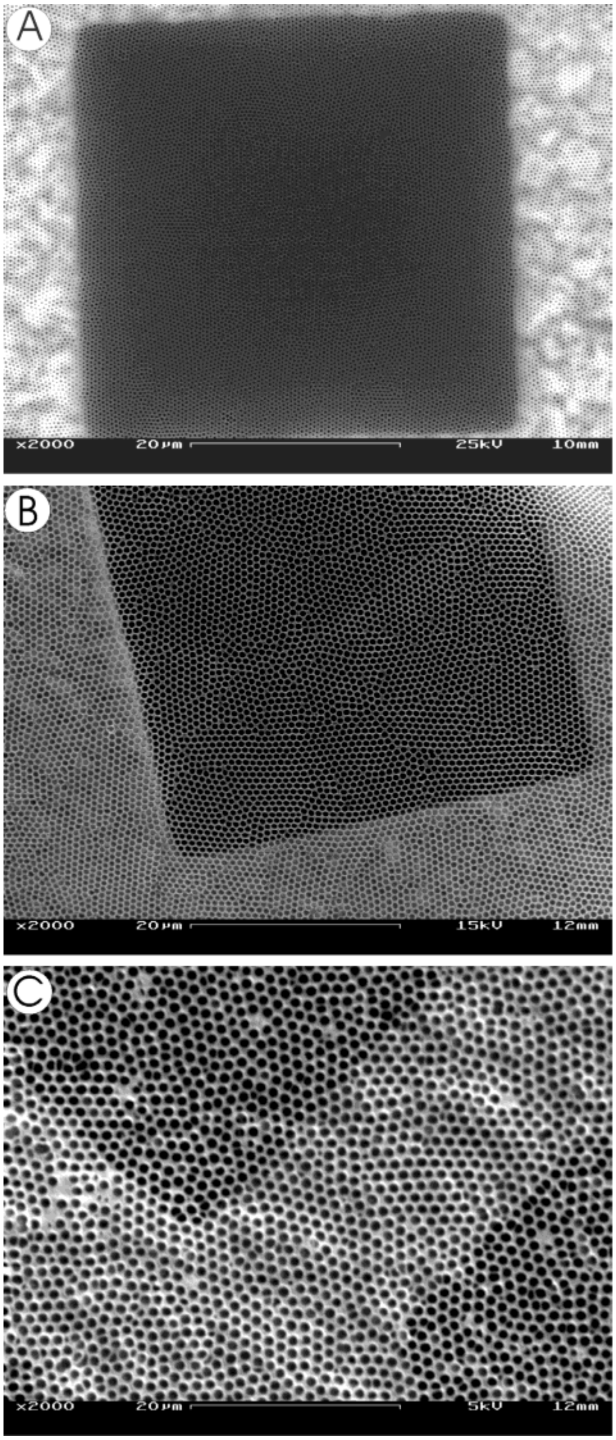

Figure 4. SEM images of porous membranes fabricated with (A) 334 nm, (B) 558 nm, and (C) 1184 nm silica particles as templates, respectively. All the membranes are freely suspended on gold grids with 40-μm-wide openings.

Conclusions

We have demonstrated a simple and effective way of making polymer membranes with two-dimensionally arranged pores. The Langmuir trough used previously has been successfully replaced by any desired water containers. Thus, the size and shape of the resulting

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porous polymer membranes are limited only by the area and shape of the water surface used. In this work, circular porous membranes with pores of uniform size as large as 23 cm^2 have been prepared on the surface of a water-filled Petri dish. With the technique used here, the upper and lower limits of achievable pore sizes are approximately 1000 and 20 nm, respectively. Although the resulting porous membranes prepared by this way are very thin, they are flexible and strong enough to be transferred to almost any desired continuous substrates or to be freely suspended over relatively wide openings. The porous membranes prepared in this way may be used as filtration membranes or as masks or molds for nanostructure fabrication.

Acknowledgment. The support by M. Möller, B. Rieger, and K. Landfester (University of Ulm), and H. Auweter and R. Iden (BASF) is greatly appreciated. We also thank Prof. P. Walther (University of Ulm) for high-resolution SEM measurement. This work was funded by the Deutsche Forschungsgemeinschaft (SFB 569, SPP 1052).

CM035044W