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Fabrication and characterization of non-linear parabolic microporous membranes

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Abstract

Large scale fabrication of non-linear microporous membranes is of technological importance in many applications ranging from separation to microfluidics. However, their fabrication using traditional techniques is limited in scope. We report on fabrication and characterization of non-linear parabolic micropores (PMS) in polymer membranes by utilizing flow properties of fluids. The shape of the fabricated PMS corroborated well with simplified Navier-Stokes equation describing parabolic relationship of the form $L - t^{1/2}$. Here, L is a measure of the diameter of the fabricated micropores during flow time (t). The surface of PMS is smooth due to fluid surface tension at fluid-air interface. We demonstrate fabrication of PMS using curable polydimethylsiloxane (PDMS). The parabolic shape of micropores was a result of interplay between horizontal and vertical fluid movements due to capillary, viscoelastic, and gravitational forces. We also demonstrate fabrication of asymmetric “off-centered PMS” and an array of PMS membranes using this simple fabrication technique. PMS containing membranes with nanoscale dimensions are also possible by controlling the experimental conditions. The present method provides a simple, easy to adopt, and energy efficient way for fabricating non-linear parabolic shape pores at microscale. The prepared parabolic membranes may find applications in many areas including separation, parabolic optics, micro-nozzles / -valves / -pumps, and microfluidic and microelectronic delivery systems.

Graphical Abstract

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Non-linear parabolic polymer membranes

Introduction

The fabrication of non-linear microporous membranes inexpensively in large quantity using traditional fabrication techniques is scarce in literature^{1,2}. There are a number of non-conventional polymer flow based fabrication techniques that exploit intrinsic properties of materials³. These fabrication techniques include capillary force based clustering⁴, capillary force lithography⁵, capillary nanomolding⁶, microtransfer molding⁷ and multiphase laminar flow patterning⁸. Capillary force has also been utilized for fabricating simple energy efficient functional devices^{9,10}. The simplicity for these methods stems from the fact that the driving force behind the fabrication and functionality is intrinsic in nature and little or no external energy is required for the fabrication of the micropores.

In this manuscript, we report design, fabrication, and characterization of high aspect ratio non-linear parabolic micropores (PMS) with diameter in 150 μm - 5 mm range. The fabrication for PMS utilizes polymer flow properties including capillary and viscoelastic under gravitational forces. We demonstrate that our experimental results corroborated well with a simple mathematical model derived from Navier-Stokes equation of a non-compressible fluid and finite element analysis. This fabrication technique is energy efficient, and the fabrication protocol does not require any special equipment. This method was extended to fabricate an array of PMS that were used as templates for the fabrication of replicated PDMS microporous membrane. The final PMS membranes were independent of the roughness present in the starting substrate used in the fabrication procedure. This is an advantage for this fabrication method compared to many existing fabrication techniques where roughness in the mask or master structures can propagate to the fabricated daughter devices. These membranes may find potential applications in separation, biology, material sciences, electronics and medicine. For example, the polymeric microstructures can be used for the fabrication of parabolic micro-optics including mirrors and lenses, nozzles for the printing of biomolecules¹¹, fabrication of microfluidic and microelectronic delivery systems¹², polymeric mechanical valves and pumps¹³, and micro-bioreactors to study cell cultures and cell behavior in microfluidic channels^{14,15,16}.

Experimental Section

Microfabrication procedure

Glass and aluminum substrates were used for the fabrication of PMS. A Hitachi B13F 10" bench top drill press was used to drill pores (diameter $\sim$ 5 mm) in glass or aluminum substrate. The diameter of the hole in the substrate dictated the base diameter of PMS.

Sylgard 184 (Dow Corning) composed of 10:1 ratio of Part A (prepolymer) to Part B (curing agent) was degassed for 15 minutes prior to its use in the fabrication process¹⁷. Figure 1 schematically shows the steps involved in the fabrication of PDMS PMS. The polymer mixture (0.1 – 0.5 g) was then drop cast onto the glass/aluminum substrate (~25×25 mm²) with a hole in the center. The thickness of the drop cast PDMS film was in 200 µm – 1300 µm range. When necessary, the substrate was placed on a vortex instrument to produce a uniform PDMS coating. The polymer was then placed on a hot plate at 70°–120°C for 1–3 minute to enhance degree of polymerization. Next, a thin microscope cover glass (MCG) with an area density ~0.33 g/cm² was placed over the polymer film covering the hole in the substrate. The placement of MCG initiated polymer flow in two directions: a horizontal flow along MCG and a vertical flow along the wall of hole. The solidification of polymer was accomplished through application of heat resulting in the formation of PMS. Further, an array of parabolic PDMS micropores was fabricated by using an array of holes drilled in the substrate. Finally, a PMS array was subsequently used as a master template to fabricate an array of replicated PDMS micropores.

Surface modification of PDMS for template synthesis

In order to facilitate the peeling of mold from the template, PDMS surface was modified with a fluorosilane. The original protocol¹⁸ was modified by replacing the silane with fluorosilane to fit our needs. A fluorosilane solution composed of 95% (v/v) ethanol/water, 4% (v/v) tridecafluoro-1,1,1,2-tetrahydrooctyltriethoxysilane and 1% (v/v) acetic acid was used as a releasing agent in our experiments. The polymer-substrate assembly was fluorinated by immersing it in this mixture for approximately one hour. The assembly was dried under argon, and then baked for 10 hours at 110°C that facilitated peeling of the parabolic PDMS membranes from PDMS master.

Theoretical consideration

Understanding physics involved in the fabrication process demands utilization of powerful tools for solving multiple equations in three dimensions at continuum scale. For present problem, theory requires multiple parameters describing fluid flow, heat transfer, fluid-solid phase change, as well as free interface boundary conditions. The polymer in our system solidified while flowing along surfaces of the substrates. We have modeled the polymer flow using a simplified quasi-steady Navier-Stokes equation of a non-compressible fluid moving between two parallel plates with "*d*" spacing^{19,20,21}. Previous studies with a modified Navier-Stokes equation showed excellent agreement between theory and experiments for such systems.^{22,23,24,25} This encouraged us to utilize a similar theoretical approach for estimating the fluid flow behavior in our experiments

The Navier-Stokes equation is of the following form:²⁶

$$0 = \frac{\partial P}{\partial r} + \mu \frac{\partial^2 u}{\partial z^2} \quad \text{Eq. 1}$$

where *P*, *r*, *μ* and *u* are PDMS fluid pressure, radius of the drilled hole in the glass substrate, viscosity, and *z*-directional velocity of the PDMS fluid front respectively. Here, we assume

that inertial effects were negligible and that both the fluid properties (viscosity and density) and film thickness remained constant during experiments. Although, the viscosity, density, and surface tension changes in our experimental conditions, a simplified equation provides us useful information on the shape of the fluid front. Figure 2a provides a cross-section view of PDMS fluid, where δ , z and $r(t)$ represent initial thickness of the film, gravitational force along z -direction, and time-dependent radius of the top face of PMS respectively. The top and side views of fluid flow are depicted in Figures 2b and 2c respectively.

Balance of forces at the PDMS front required:

$$\Delta P(2\pi r)\delta = \gamma \cos\theta(2\pi r) \quad \text{Eq. 2}$$

Therefore, the pressure difference at the PDMS front yielded:

$$\Delta P = \frac{\gamma \cos\theta}{\delta} \quad \text{Eq. 3}$$

where θ denotes the contact angle of PDMS on the glass. From Eq. 2, we obtained:

$$-\frac{\partial P}{\partial r} = -\frac{\Delta P}{r(t)} = -\frac{\gamma \cos\theta}{\delta r(t)} \quad \text{Eq. 4}$$

The velocity of the PDMS front u is obtained by substituting Eq. 3 in Eq. 4

$$u(z) = \int_{z=\delta}^0 \frac{du}{dz} dz = \frac{\gamma \cos\theta \delta}{\mu r(t)} \left[\left(\frac{z}{\delta} \right) - \frac{1}{2} \left(\frac{z}{\delta} \right)^2 \right] \quad \text{Eq. 5}$$

We solved for the spatially averaged velocity (U) over the whole area which is given by:

$$U = \frac{\int_A^0 u(z) dA}{A} \quad \text{Eq. 6}$$

where $A = 2\pi r(t)\delta$. Solving Eq. 6 gave us the spatially averaged velocity in terms of $r(t)$ as follows:

$$U = \frac{\delta \gamma \cos\theta}{6\mu r(t)} \quad \text{Eq. 7}$$

This velocity is defined as follows:

$$U = -\frac{dr}{dt} \quad \text{Eq. 8}$$

Combining Eqs. 7 and 8 yielded the following equation for the instantaneous radius of PDMS:

$$\int_R^r r(t) dr = -\int_0^t \frac{\delta \gamma \cos\theta}{6\mu} dt \quad \text{Eq. 9}$$

Solving Eq. 9 for $r(t)$ provided the position of the PDMS front at a given time:

$$r(t) = \left[R^2 - \frac{\delta\gamma \cos\theta}{3\mu} t \right]^{\frac{1}{2}} \quad \text{Eq. 10}$$

Equation 10 predicts a $(1/2)$ power relation between the distance moved by the PDMS front with time (t). $R-t^{1/2}$ relationship is parabolic in nature confirms that the polymer fluid movement follows parabolic form. Our experimental data corroborates well with Eq. 10 (Figure 3).

Results and Discussion

Mechanism of parabolic membrane fabrication

The underlying principle involved in the fabrication of PMS membrane was discovered serendipitously when we observed a characteristic polymer flow in our earlier experiments where PDMS was used as an adhesive to sandwich two sheets of glass substrates²⁷. This phenomenon was analyzed and explored further to develop it into a simple microfabrication technique.

Figures 1(a – e) show a schematic of two-dimensional structure evolution-time for the PMS fabrication process. PDMS (green) was drop cast around a pore in a substrate (gray). The substrate was kept on a heating block for partial curing/solidification (Figure 1a). Figure 1b shows an initial PDMS flow pattern after placement of an MCG on the polymer film. The placement of MCG initiated a polymer flow along two directions: horizontally towards the center of MCG (blue line, Figure 1b) and vertically down along the pore wall (orange line, Figure 1c). Thermally curing of the polymer provided parabolic micropores whose shape is an interplay of horizontal and vertical polymer displacements at the time of solidification. The cured PMS implies that the polymer movement is negligible as compared to whole experimental time scale (many tens of seconds in duration). Thus, by controlling the polymer flow characteristics (capillary and gravitational forces) and curing kinetics (heating rate), the parabolic shaped micropores were controlled in size and shape (please see below). Cured PMS were removed to yield desired free standing membranes. The shape of PMS matches well with a parabolic curve (blue, Figure 1f). A schematic of cross-section and an SEM of the microstructures depicting parabolic pores are shown in Figures 1e and 1f respectively. An SEM micrograph of a free standing fabricated PMS without MCG and substrate is shown in Figure 1g. This PMS was used as a template for the fabrication of replicated PDMS membrane (Figure 1h).

Flow characteristics of fluids

Prior to the placement of MCG, the polymer did not flow over the edge of the macro-hole in the glass substrate. The polymer however formed a curved polymer-air interface at the edge of the hole due to surface tension of the polymer. The polymer movement along horizontal and vertical directions immediately occurred after an MCG was placed on the polymer film. The placement of MCG provided at least two crucial forces for the polymer flow. First, it provided a capillary force along the surface of MCG that induced polymer flow in the horizontal direction toward the center of MCG. Second, a gravitational force was induced

following MCG placement on the polymer film which facilitated a vertical polymer movement along the wall of the hole. The interplay between horizontal and vertical polymer flows yielded PMS after polymer curing. The radius of smaller pore (r) of PMS depends on the polymer curing rate and horizontal polymer flow rate. Whereas smaller r were formed with large horizontal polymer flow rate and slower curing rate, the larger r is a consequence of increased curing rate and slower horizontal polymer flow rate. The base radius (R) of PMS is relatively large and is close in dimension of the hole diameter in the glass or aluminum substrate. Interestingly, Eq. 10 provides a convenient way of controlling r by controlling t_{poly} . r can be made in nanometer scale (<100 nm) by appropriately controlling the experimental conditions (including polymer curing kinetics and MCG placement timing on the polymer film). For example, a slow polymerization kinetics can in principle provide non-linear parabolic pores where complete solidification occurs when r is in nanoscale dimension.

Two extreme cases for Equation 10 exist that will result in either cylindrical microstructures ($r \rightarrow R$) or completely closed parabolic structures ($r \rightarrow 0$). When $t \rightarrow 0$, $r \rightarrow R$; i.e., the polymer flow in the horizontal direction along MCG surface is insignificant relative to dimension of R at the time of complete polymer curing. This condition will provide cylindrical microstructures. In physical sense, $r \rightarrow R$ can happen if the polymer curing rate is extremely fast such that polymer front movement is extremely small as compared to R . A similar situation that would result in $r \rightarrow R$ when polymer flow is dominant by gravity and that horizontal flow is negligible. A second extreme case is noted when $t \rightarrow \infty$, i.e.; in this case, the curing rate is extremely slow such that r becomes infinitesimally small or $r \rightarrow 0$. These conditions will result in coalesce of the polymer front. This can happen for uncured polymer or for fluids that are not reactive and do not cure (please see, for example, videos 1 and 2 for uncured PDMS, glycerol, and water flow under similar experimental conditions).

Figure 3a shows a relationship between flow distance (L) and time (t_{poly}) for three polymer films with different area density (in mg/cm^2) at 72°C after MCG was placed on the film. L represents the fluid flow distance after an MCG was kept on the polymer film. The placement of MCG on polymer film provided activation energy for the polymer to flow both horizontally and vertically directions. L was measured using an optical microscope with a white light illumination by observing the polymer front. The error in our measurements was diffraction limit ($d_s = 2*\lambda/NA \sim 750$ nm; where $\lambda \sim 600$ nm is wavelength of the light, and $NA \sim 0.4$ is numerical aperture of the microscope) of the microscope. The value of L ranges between 0 (no fluid movement) and R (fluid covered the hole). PMS consistently yielded curved inner configuration for which the experimental data points fit well with $L-t^{1/2}$ parabolic equation (Figure 3a and Eq. 10). The parabolic shape of PMS was a result of polymer flow which can be represented using a simplified Navier-Stokes equation. Figure 3b shows an SEM of the cross-section of a PMS fabricated with smaller and larger diameters of $2r$ and $2R$ respectively. The experimental cross-section profile of PMS matches well with a theoretical parabolic curve shown by the blue dashed curve in Figure 3b. Video V1 shows flow characteristics of uncured PDMS under similar experimental conditions for the formation of cured PMS. In this video, at $\sim$ video 1s after placement of MCG, PDMS is seen flowing towards the center of MCG. At ~ 22 seconds in the video, the center of the hole is

zoomed in to show the convergence of the uncured PDMS. In the fabrication protocol, heating of PDMS resulted in the solidification of PDMS in the center yielding parabolic micropores. A careful observation of PMS cross-section in Figure 3b revealed a slight deviation in shape from ideal parabolic equation near the bottom of the larger pore diameter (indicated by green arrows in Figure 3b). The deviation of experimental data from ideal parabolic curve is not entirely clear at this point. It is attributed to surface-assisted capillary action enhancing the fluid flow rate when fluid thickness is small at the bottom of PMS. Due to surface tension of the polymer at polymer-air interface, the fabricated PMS were shown to possess smooth surfaces (see below). In the absence of air bubbles in pre-polymer and other defects due to curing and post-curing, the surface of PMS appeared smooth without defects. These smooth structures are useful for the fabrication of high-quality optical components where extremely smooth parabolic surfaces are sought.

Interestingly, the thickness of PDMS membrane was found to influence the polymer flow characteristics after an MCG was placed on it. For example, for a PDMS film with an area density of 0.32 mg/mm^2 deposited on a substrate took $\sim 650 \text{ s}$ to flow a horizontal distance of 3 mm along MCG after placement of an MCG on polymer membrane (red data points Figure 3A). However, it only required $\sim 150 \text{ s}$ to cover the same distance of 3 mm for a polymer membrane with an area density of 0.48 mg/mm^2 (blue data points, Figure 3A). The distance-time measurements were recorded by taking digital micrographs of the polymer at different times. Apparently, under the same experimental conditions, a thicker prepolymer film on a glass or an aluminum substrate showed enhanced horizontal flow rate after placement of an MCG on the membrane (Figure 3A). A possible explanation for enhanced flow rate for thicker PDMS films on MCG is that increased prepolymer weight film possibly required a smaller activation energy to cross the polymer-air surface tension barrier resulting in increased fluid flow rate after an MCG placement on the film. This was confirmed experimentally in our experiments when thick membranes ($> 2 \text{ mm}$) over flowed glass edges without placement of MCG on it.

Figure 4 shows the relationship between t_{MCG} and r , where t_{MCG} represents time for which PDMS coated on a substrate was allowed to polymerize before MCG was placed on PDMS film. In other words, t_{MCG} is a measure of polymer viscosity. With $t_{MCG} \sim 30 \text{ s}$, the smaller diameter (r) and apex angle (ϕ) of PMS were $\sim 300 \mu\text{m}$ and $\sim 30^\circ$ respectively. However, $t_{MCG} \sim 130 \text{ s}$ yielded PMS with r and ϕ of $2500 \mu\text{m}$ and close to 130° (i.e. a cylinder-like structure is resulted) respectively. ϕ is a measure of approximate apex angle because it does not take into account the curvature of PMS due to parabolic flow (Figures 3B and 1S). The apex angle ϕ is defined in Figure 1S. ϕ ranges from 0° to 180° . Interestingly, $\phi \sim 0$ gives when $r \sim R \sim 0$; whereas $\phi = 180$ when $r \gg R$ and $r \sim 0$. The former case ($\phi \sim 0$) will occur for an uncured fluid which will fill up the whole available space in the drilled hole (cylindrical structure). When the horizontal fluid movement dominates the vertical fluid movement will provide $\phi = 180^\circ$ (a thin polymer film-like structure). These results imply that a larger polymer viscosity due to increased polymerization resulted in smaller polymer flow rate before it was solidified. Thus, the polymer front underwent a larger displacement for smaller t_{MCG} providing smaller ' r ' and larger ' ϕ ' (Figures 4 and 1S respectively). These results suggest that with a careful control over polymer viscosity through tuning of t_{MCG} , the

dimension of PMS can be controlled. Photopolymerization provides an interesting opportunity for creating interesting PMS by controlling local prepolymer viscosity in space and time using photo-excitation of pre-polymer and monomers. Thus, this may allow the researchers to modulate spatial and temporal viscosity of the flowing polymer providing tuning of dimension and shape of PMS.

Effect of fluid properties

We studied the effects of viscosity and surface tension of fluids in an attempt to better understand how these properties of fluids may affect the formation of membranes. Both the fluid viscosity and surface tension also come in equations describing the fluid flow for our experiments (Eq. 10). We studied three additional fluids for their flow behaviors: water, dichloromethane (DCM) and glycerol. All the experimental conditions for these fluids were same except that these fluids do not solidify upon heating. The surface tension and viscosity values of these liquids were taken from standard reference sources²⁸. Table 1 provides viscosity, surface tension, density, and fluid flow characteristics of uncured fluids used in our studies. We observed that three fluids (PDMS, water, and glycerol) showed parabolic-like flow in our experiments whereas a gravity-induced vertical downward flow was dominant for DCM (video V2). DCM is a hydrophobic fluid with a dipole moment of 1.6D. DCM possesses a high density of 1.326 g/mL and an extremely low viscosity of ~0.45 cP (Table 1). In our experiments, both uncured PDMS and DCM are relatively non-polar and possess low surface tension; however, the flow characteristics of DCM differ considerably that from uncured PDMS (Table 1 and Figure 3S). These differences in the flow characteristics are likely due to large differences in the viscosity and density values of the two liquids. The viscosity of uncured PDMS >7000 times larger than that of DCM. PDMS prepolymer possesses long molecular chains providing viscoelastic properties which contributes to horizontal flow along MCG for PDMS. The viscoelastic property in DCM are absent. Further, a larger density for DCM contributed to increased vertically dominant flow for DCM. Thus, the placement of MCG provided an activation energy that led to a vertical dominant flow for DCM. However, although PDMS is a non-polar in nature, the viscoelastic and capillary force influenced its flow characteristics such that non-linear parabolic microstructures were obtained under similar experiment conditions.

Table 1. Various fluid, their properties, and their fluid flow characteristics in our experiments.

Interestingly, both water and glycerol showed both horizontal and vertical flow characteristics in our experiments (video V2). This flow is likely due to high polarity and surface tension for these fluids (Table 1 and Figure 3S) providing strong capillary forces when MCG was placed on fluid surface. Clearly, MCG surface provided fluids a means of overcoming surface tension-associated activation energy to move both along horizontal and vertical directions. Overall, the formation of parabolic polymer pore containing membranes appeared to require a balanced interplay between surface tension, capillary, viscous and gravitational forces. Curing of PDMS provided parabolic micropores where manipulation of these forces yielded controllable micropores. Although we have not fabricated parabolic micropores composed of different polymers, the above discussion suggests that non-linear

micropores with many other curable fluids are possible with some changes in the experimental conditions and physical parameters used in our experiments.

Influence of placement of MCG

The placement of MCG was observed to have a significant impact on the shape of the PMS fabricated with this technique. It is critical that the entire surface area of MCG comes in contact with the PDMS simultaneously to avoid uneven contact points on the polymer film. Any factors that may interfere with the isotropic flow of the polymer front may result in irregular or asymmetrical PMS or other structural defect in them. MCG placed parallel to PDMS film surface produced symmetrical parabolic micropores. We performed experiments by placing MCG on polymer film that was not parallel to the polymer membrane. This asymmetric MCG placement on polymer resulted in the formation of asymmetric PMS (Figure 5). The asymmetrical PMS formation is due to asymmetric PDMS flow because the gravitation force of MCG was not uniformly distributed over PDMS film. That is, the flow initiated first towards the center of the hole from those areas where MCG came in contact with the PDMS surface first. The movement of polymer front where MCG came in contact at a later stage was delayed, thus, this polymer front travelled a shorter distance prior to polymer curing compared to a polymer front that made contact with MCG at an earlier time. Consequently, the effect of non-parallel polymer-MCG contact resulted in asymmetric PMS with off-centered smaller pores (Figure 5).

The cleanness of MCG, that is, presence of dust or surface particles can also influenced the shape of PMS. For example, the presence of dust particles on the substrate and MCG may result in a non-uniform isotropic PDMS flow because the flow may get hindered or flow pattern may change due to presence of particles on MCG surface. The result of this hindered flow will be non-symmetrical PMS. Interestingly, this provides opportunities for creating a wide range of non-symmetric pores through careful control over MCG placement on polymer films, and by tuning MCG surface properties.

Influence of hole shape in the glass or aluminum substrate on PMS characteristics

Another interesting observation regarding PMS fabrication we made was the fabrication of smooth and circular polymer membranes when drilled holes in the substrates were rough at microscopic scale. We have found that the top polymeric surface of the fabricated PMS was always extremely smooth even the substrate hole had visual surface roughness at microscale (Figure 2S). To demonstrate this, we used a hexagonal shaped hole in the substrate instead of a circular hole previously used in our experiments and repeated the polymeric fabrication process as described above. Figure 2S shows that even though the fluid front started out as a hexagonal polymer front, it transformed into a circular cross-sectional pore (top view) after polymerization. The hexagonal to circular fluid flow transformation is a consequence of lowered surface energy of fluid front with less number of edges in it. The circular fluid front has a lower surface energy than for a flowing fluid front that contained edges in them. This also provides a flowing polymer front independent of surface roughness in the hole. Thus, the flowing polymer forms a smooth circular cross-section even if the holes were rough and non-circular in shape. These experiments demonstrated that the shape and roughness of the drilled holes had a little impact surface roughness of the fabricated PMS and that the smaller

openings possesses a circular geometry (Figure 2S). Unlike flow based fabrication technique such as demonstrated in this manuscript, other etching-based or photolithography-based fabrication processes may leave behind rough edges after fabrication process and may also need additional polishing and other related post-fabrication steps for its rectification. The self-rectification of rough edges is unique to the fluid flowing nature involved in this fabrication process. The parabolic shape and smooth surfaces of these structures is especially useful for micro-optical applications. For example, PMS and arrays fabricated using this technique may find potential applications in separation and parabolic micro-optical lenses and mirrors²⁹. Other applications of PMS are in nozzles for printing, delivery system, polymeric valves and pumps and template synthesis of different materials.^{11–16}

Fabrication of arrays and template synthesis

The technique described in this manuscript was further utilized for the fabrication of an array of PMS. An array of holes measuring 5 mm in diameter were drilled into an aluminum substrate (Figure 6a). Following the same protocol as described above, MCG measuring 22 mm × 40 mm and weighing 0.4 gm was placed on a spin-coated (<500 rpm) PDMS film. After fabrication of the membranes, PDMS containing the micropores were peeled off providing a freestanding polymer film with an array of PMS in it. Figures 6b and 6c show optical and SEM images respectively of a typical PMS array fabricated using this technique. These parabolic micropores were subsequently used as templates for the fabrication of replicated PDMS PMS containing membranes (Figure 7). Figures 7a shows two individual replicated PMS formed utilizing two different masters, whereas Figure 7b shows two replicated PMS formed from a single master. In principle, it is possible to fabricate many thousands of PMS of desired shapes and dimensions using this simple fabrication technique.

Porosity and ionic transport through PMS

Considering the diameter of larger pore of our PMS, the porosity of our membranes is considerably lower than commercially available polymer membranes. Thus, we expect that the transport flux of the PMS membranes is much lower than those for commercially available membranes. However, our membranes can be potentially useful for applications where individual pores needs to be addressed under an external stimulus (or stimuli). For example, our PMS may provide exciting opportunities for ions / molecular / particles transport under an electric field because individual pores are separated enough to allow for electric connections to them. Further, it will be interesting to investigate ionic flow behavior under electric field in nanoscale PMS where PMS may show a different electric potential-driven response as compared to those for cylindrical and conical pores.³⁴

Conclusions

We described a simple fabrication technique that employs controlled fluid flow and curing dynamics for the synthesis of non-linear parabolic micropores containing membranes. Our experimental results corroborate well with theoretical analyses based on simplified Navier-Stokes equation. The presented technique utilizes capillary, gravitational forces and viscoelastic forces for the fabrication of PMS. PMS membranes possess a smooth surface due to surface tension of pre-polymer. We discussed various ways to tune the

microfabrication protocol for fabricating desired parabolic microstructures. The shape and size of PMS can be readily manipulated by controlling the fluid and substrate properties. The fabricated PMS membranes were also employed for template synthesis of replicated microporous membranes. This technique can also be used to fabricate PMS composed of metallic, semiconducting or dielectric materials embedded in a polymer matrix that can provide parabolic microporous membranes with versatile properties without use of microscale masters or masks.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Highlights

1. We fabricate and characterize single and multiple parabolic pores in polymer.
2. The experimental data matched well with a simplified Navier Stokes equation.
3. Non symmetric parabolic pores and replica of parabolic pores were synthesized.
4. The effect of fluid properties on pore shape and size was also discussed.

Figure 1.

A two dimensional schematic of the structure evolution-time of the fabrication process. (a) PDMS (green) was drop cast around a pore drilled on glass or aluminum substrate (gray) and was kept on a heating block for partial curing/solidification. (b) and (c) show initial PDMS flow after placement of an MCG on the polymer film. The blue and orange arrows show horizontal and vertical polymer flow respectively. The interplay of polymer flow along these two directions yielded parabolic micropores in the polymer matrix. The base diameter ($2R$), tip diameter ($2r$), and height (H) of PMS are shown in (d). After complete solidification of the polymer, MCG and substrate were removed to yield the desired PMS. A schematic cross section and SEM of these PMS are shown in (e) and (f) respectively. The shape of PMS cross-section matches well with a parabolic curve (blue dashed line in f). An SEM micrograph of a free standing PMS without MCG and aluminum block is shown in (g). This structure was used as a template for the fabrication of daughter PDMS PMS replica (h). Scale bar is 1 mm.

Figure 2.

Theoretical analysis of parabolic microstructure. (a) Schematically shows the cross-section of the parabolic microstructure formation. $r(t)$ is the instantaneous radius of the pore. (b) Top view of figure in (a). (c) represents the movement of the polymer front with film thickness (ϕ) and polymer front velocity ($u(z)$) parallel to MCG.

Figure 3.

PDMS flow and microstructure parameters. (a) shows a relationship between L and t_{poly} . L represents distance travelled by the PDMS in time (t_{poly}). (b) An SEM of the cross-section of a typical parabolic microstructure fabricated with smaller diameter, larger diameter, and apex angle of $2r$, $2R$ and ϕ respectively. Scale bar is 1 mm. The blue dotted line in the figure represents a curve fit to a parabolic equation. The fit between the curve and micrograph of cross-section of the PMS clearly confirm its parabolic shape. (c) A top SEM view of a typical PMS.

Figure 4. Relationships between r and t_{MCG} . t_{MCG} represents time for which PDMS was heated before MCG was placed on the substrate. Heating of PDMS for longer time (larger t_{MCG} values) resulted in higher polymer viscosity and larger r value.

Figure 5.

An optical micrograph of an asymmetric PMS. The formation of a pore with its small opening offset from the center due to unparallel placement of MCG with respect to polymer film. The sides of MCG that contacted PDMS first and last are labeled in the micrograph.

Figure 6. Fabrication of an array of PMS. (a) A typical substrate with drilled holes used for the fabrication of PMS. Scale bar is 6 mm. (b) shows an optical micrograph of an array of PMS formed. Scale bar is 6 mm. (c) shows an SEM of PMS array. Scale bar is 500 μm .

Figure 7. SEM micrographs of replicated PDMS PMS fabricated using template-assisted synthesis. (a) SEM image of two separate PMS. (b) An array of two replicated PMS formed using a master containing two PMS. Scale bar is 50 μm for all the images.

Table 1

Various fluid, their properties, and their fluid flow characteristics in our experiments.

Fluid	Viscosity (cP)	Surface Tension (dyne/cm)	Fluid Flow characteristics
Uncured PDMS	3500 ^a	20 ^b	Parabolic flow was observed
Water	1.002 ^{c1}	72.75 ^{c2}	Both vertical and horizontal flows were observed
Glycerol	1412 ^{d1}	63.4 ^{d2}	Both vertical and horizontal flows were observed
Dichloromethane	0.449 ^{e1}	26.52 ^{e2}	Flow was vertically gravity dominated leading a small movement in horizontal direction

^a: Sylgard 184 technical sheet from Dow Corning. <http://www.dowcorning.com/applications/search/products/details.aspx?prod=01064291&type=PROD> Retrieved on May 7 2014.

^b: *Langmuir* **2000**, 16, 1256–1260

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