Hydrophilic Interfacing for Thermal Micro Assembly of Polymers (HITMAP)

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This paper presents a simple approach to create microchannels in polydimethylsiloxane (PDMS) using basic hydrophobic–hydrophilic interactions of polymers. During polymerization, low molecular weight hydrophobic chains of PDMS expel hydrophilic moieties. This phenomenon has been used to create microchannels in PDMS. The process is simple, systematic, flexible in design, easy to implement, rapid, inexpensive and does not require lithography. Fabrication of microchannels in PDMS can be carried out using bench-top tools without the aid of any special facilities or equipment. With directed thermal polymerization over the hot plate, the expulsion of hydrophilic materials creates microchannels along the path traveled by particles. The approach is sensitive to the polymer viscosity, temperature profile and the surface chemistry of the particles. This work can have important implications in reducing the cost and time for prototyping polymer based applications in separation science, cell behavior studies, catalytic membranes and hydrogen storage. The membranes are characterized for electrical continuity and charge effects on conductivity.

Keywords: Hydrophilic Particles, Hydrophobic Polymers, Membrane Surface Charges, PDMS Membranes.

1. INTRODUCTION
Polydimethylsiloxane (PDMS) is an optically clear organosilane polymer commonly used to fabricate microfluidic channels using soft lithography. It has a very low glass transition temperature of \(-125{^\circ}C\), can withstand a wide temperature range between \(-100{^\circ}C\) to more than \(100{^\circ}C\), has a biologically relevant Young’s modulus, and is biologically inert.1,2 Various methods have been demonstrated to fabricate microfluidic devices with varying channel sizes and multilevel channel structures.3–10 Soft lithography has proved to be a powerful technique to fabricate channels, where a master is first fabricated using photolithography and the elastomeric stamp is then made with patterned relief structures. Inexpensive methods using nylon fiber and low energy templates have also been recently reported.11,12 Simple porous membranes with pore size of 4–6 \(\mu m\) are reported using water as porogen and these membranes have been used as pH sensors.13 On the other hand, commercial membranes are made by bombardment of heavy ions on polymer surface such as polycarbonate and polyethylene terephthalate, called track-etched membranes.14

PDMS has been the material of choice for electrical wire insulations for decades owing to its hydrophobic nature that is easily regained due to diffusion of low molar mass PDMS to the surfaces.15 During polymerization the macromolecules are connected into polymeric networks that are three-dimensional. The cross-linking reaction increases the molecular weight and the macromolecular network extends to the whole sample and coexists with loose branched networks that are not yet part of the network. This is known as the gel-point (GP). The network continues to grow until all remaining molecules are used as part of the one big network. The reactions at GP are crucial in determining the stiffness and viscosity of PDMS.16 At GP, phase transition of the prepolymer into a rubber-like material occurs. The process has an associated decrease in the entropy of the system which essentially results from the reduced number of configurations that molecular sub-units can have after polymerization.17,18 The configuration that the sub-units can take and the probability for these sub-units to become a part of a large network are independent of each other. The overall change in free energy can be separated into enthalpy and entropy components. It has been also reported that PDMS immersed particles do not get intercalated during polymerization.19 The work presented here gains its
strength from the hydrophobic–hydrophilic interactions between the interface of the PDMS as it polymerizes and nano/micro materials like beads, particles or droplets. The reduction in free energy results into useful enthalpy that pushes immiscible entities out of the resulting semi-solid polymer. This is the first demonstration for using this enthalpy to get useful work done in a quick, low-cost, bench-top fabrication technique for porous membrane fabrication, using inherent hydrophobic property of PDMS.

We present a simple approach to fabricate microchannels and porous PDMS membranes using bench-top tools. The fabrication does not require complex lithographic processes and does not take more than an hour. Magnetic nanoparticles and polyurethane beads are discussed as the materials of choice to implement this technique. Solvents like acetone and condensed vapor have also been used and these would be discussed in detail in forthcoming manuscripts. The proposed technique can be implemented with minimal need for special facilities or equipment. The formation of channels is based on the repulsion of hydrophilic particles by the hydrophobic polymer during polymerization.

2. EXPERIMENTAL METHODS

2.1. Hydrophobic–Hydrophilic Interaction Studies

Figure 1 shows the motivation and simple mechanism, where blue ink was homogeneously mixed in the liquid precursor of PDMS. As soon as the solution was exposed to heat from the bottom, the polymerization ensued from the bottom of the well. First, almost all ink droplets clumped together into clusters and then the clusters started rising away from the bottom (hot side) in the direction of the polymerization.

Polymerization reaction is generally an exothermic reaction. This means that heat is released from the reaction. This is followed by the conclusion that the enthalpy of such a reaction would be negative (\(-\Delta H\)). During polymerization, the base and curing agent are mixed in a specific ratio. The liquid pre-cursors or reactants undergo curing at elevated temperatures to form an elastic polymer. If entropy (\(\Delta S\)) can be understood as the extent of disorder present in a system, then it can be clearly seen that the phase change of the reactants from a comparatively dis-ordered and disperse liquid medium to a solid state would decrease the entropy of such a reaction to a considerable extent. Entropy of the reaction would be,

\[
\Delta S_{\text{reaction}} = \Delta S_{\text{products}} - \Delta S_{\text{reactants}} \tag{1}
\]

Since the entropy of the products would be less than that of the reactants, the net entropy of the reaction would be negative (\(-\Delta S\)). The phase change between the reactants and the reduced number of configurations that the polymer can assume favors the decrease in entropy of such reactions. The energy required for the

![Fig. 1. Images showing the behavior of homogeneously mixed blue ink in PDMS. As the PDMS polymerizes. (a) At time \(T = 0\), the ink is homogeneously mixed in the PDMS precursor. (b) At time \(T = 20\) min, the ink gradually forms clusters as low molar mass PDMS networks are formed. (c) At time \(T = 90\) min, the polymerization continues and a gradient of ink is seen. (d) The small clusters of ink rise as PDMS networks become large essentially pushing the ink droplets to the top.](image-url)
reaction to take place is a combination of both the enthalpy and entropy components and is given by Gibbs free energy, \( \Delta G \). It is the energy available for useful work after the loss to the surroundings is accounted for. It is given by the equation,

\[
\Delta G = \Delta H - T\Delta S
\]

(2)

If the \( \Delta H \) for the reaction is negative and that \( \Delta S \) is also negative, the sign of the free energy then depends on whether the factor of enthalpy is more negative than the factor of the product of temperature and entropy. But it can also be seen that the reaction proceeds in the forward direction without the application of external energy at room temperature. The PDMS with a thickness of 1 mm can be cured at room temperature if it is left undisturbed overnight. This proves that the reaction is spontaneous in the forward direction. On the basis of the above observation we can conclude that \( \Delta G \) for the above reaction is negative. The reaction proceeds in such a direction that \( \Delta G \) becomes less negative. At equilibrium \( \Delta G \) becomes zero. This equilibrium can be reached at an accelerated rate if the temperature is increased. This was observed experimentally and can also be deduced from the above equations and arguments.

When hydrophilic particles like iron-oxide nanoparticles or polyurethane beads are introduced into the system, the tendency of the hydrophobic polymer matrix is seen to be to expel the particles out. This can be attributed to the fact that the hydrophobic polymer matrix tries to maintain a minimal interfacial contact area with the hydrophilic particles. The energy required for this work is provided when the polymer matrix is cured at an elevated temperature. The reduction in entropy and the subsequent enthalpy produced in the above reaction is used for pushing the immiscible particles out of the polymer matrix.

We use this phenomenon to show techniques for simple bench-top porous PDMS membrane formation, and call this approach Hydrophilic Interfacing for Thermal Micro Assembly of Polymers (HITMAP). Such PDMS membranes can be manufactured for use in pervaporation experiments to remove organics, as soft elastic substances to study cell movement, for cell adhesion studies, hydrogen storage and for aligned microfluidics.\(^{20-22}\) The basic mechanism is believed to be the same for both of the materials used here.

Polyurethane beads, iron-oxide nanoparticles, and sylgard 184 were used as received. Ultrapure grade water with a resistivity of 18.2 M\( \Omega \)-cm was used in all experiments.

### 2.2. Polyurethane Beads

Polyurethane beads are hydrophilic and thus were used to fabricate aligned channels. The Lubrizol polyurethane beads (Tecoflex-EG-80A with a diameter range of 2.5–3.5 mm) were kept on a clean glass petridish and heated at 100 °C for 2 minutes. The PDMS was mixed in a ratio of 10:1 (with oligomeric curing agent) and poured into the dish on top of the beads. Temperature variation studies were done to tune the optimum temperature for the formation of the channels. These beads formed channels in the range of hundreds of micrometers. Figure 2 shows the confocal micrographs of 517 \( \mu \)m diameter channels. These structures were vertically aligned but closed from one end (bottom). The channel diameter was not uniform throughout the channel and slight constriction was observed at the bottom. These membranes were cut open from the bottom to obtain through channels. An important requirement to form these channels was the hydrophilicity of the bead surfaces. Interestingly, there was a range of temperature from 113 °C to 120 °C within which the channel formation occurred. Below and above this temperature, the beads/vapors were predominantly entrapped inside the polymer. It is important to note here that the track-etched membranes with conical pores have found many applications in biophysical studies.\(^{23}\) The pore with varying inner diameters can be defined in terms of the narrowest diameter, as that would be important for similar applications as that of conical pores. The curing temperature of PDMS was above the melting temperature of the polyurethane beads, so the beads melted and formed thick viscous naculations. The change in entropy and enthalpy at GP and diffusion of low molar mass hydrophobic PDMS chains slowly ‘kicked’ the molten beads out while the PDMS polymerized. This movement resulted in the trails/tracks in the form of empty channels in the PDMS bulk.

### 2.3. Iron-Oxide Nanoparticles

For precise channel formation, 30 nm iron-oxide particles were employed. The particles were kept on a petridish and PDMS was
poured on top of these nanoparticles. PDMS was polymerized on the hotplate while a magnet was used to align iron-oxide particles as the particles moved upwards. The magnet was used to give directionality and to align the channels.

In the presence of a magnetic field, the magnetic particles typically produce one dimensional (1-D) chains with their magnetic dipoles aligned head-to-tail, parallel to magnetic field. It can be seen in Figure 3 that the particles made 1-D linear pores. The resulting pore diameters ranged between 4–7 $\mu$m. The confocal micrograph of one channel is shown in Figure 4.

To prove the hydrophilicity of the iron-oxide nanoparticles and to establish that the magnetic force was not the driving force in pushing the nanoparticles out of the matrix, the above experiment was conducted in the absence of the magnetic field. SEM micrographs shown in Figure 5 clearly show the presence of the iron-oxide nanoparticles on the surface of the PDMS. This follows the proposed mechanism closely. But what was observed was that the force exerted by hydrophobic PDMS was not enough to push all the particles upward/out of the PDMS. The rate of polymerization at the particle-polymer interface was very fast. This was attributed to the fact that metal particles absorb heat quickly and in turn would lead to localized polymerization. This resulted in the capture of many particles rather than pushing them out. An external upward force in the form of controlled magnetic or conductive field served two purposes: (1) Moved all particles against the localized polymerization and (2) Aligned the nanoparticles.

The expected outcome was the formation of 30 nm channels, but the viscosity of liquid PDMS collapsed the chains, forming small bundles of particles in the range of hundreds of nanometers but mostly in micrometers. SEM micrographs shown in Figure 6 illustrate some of the pores obtained in the nanometer dimensions. The diameters of the pores are in hundreds of nanometers which are in accordance with the earlier conclusions. An important point here is that the alignment demonstrated using soft lithography is not as closely achieved by the approach presented here, but it essentially provides channels in the same range without the use of lithography. The whole process can be completed within 30 minutes. The precision in alignment versus cost and time are essential trade-offs here.

3. DISCUSSION

The study presents a systematic approach to create microchannels without the use of extensive lithographic techniques.
Fig. 6. SEM micrographs of pores obtained from iron-oxide nanoparticles. The diameters of the pores range from a few hundred nanometers to ~5 micron. The variation in size is because of the agglomeration of the iron-oxide nanoparticles.

These bench-top techniques can be employed in laboratories and research groups where microfluidic applications are required for preliminary analysis. The study explores the possibility to obtain uniform pore sizes with a certain degree of alignment. Tecoflex polyurethane beads also provide good channel characteristics because the bead placement can be controlled easily. Better alignment of nanoparticles can be achieved by accurate positioning of the particles on a charged substrate using techniques like self-limiting electrostatic interactions.27–29 However, the study employed only a magnet to align the nanoparticles.

Fig. 7. (a) Circuit equivalent to the membrane. (b) I–V data from membrane at different molarities. Resistance and calculated length is shown on each curve.

4. CURRENT–VOLTAGE MEASUREMENTS

Electrical Conductivity measurements are often used to characterize microfluidic chips for electro-osmotic characteristics (electro-osmotic velocity, mobility and zeta potential).30,31 In a similar vein, the membranes were tested for their continuity and permeability using ionic solution conductivity measurements. The characterization system employed here is similar to the one used for solid-state nanopores sensors.32,33 An N number of channels, with the same diameter and length, and filled with ionic solution of same molarity, can be considered to have the same resistance and conductivity, if we approximate the effects of surface changes from each channel wall to be equal (Fig. 7(a)). The equivalent resistance \( R \) of a network of \( N \) parallel and equal resistances \( R' \) is \( R' / N \). The current–voltage (I–V) data for a membrane with six was measured with a patch-clamp measurement system developed in-house. The voltage bias was applied across the membranes and the conductivity of KCl solution was measured across directly aligned channels. The membrane channels had diameters of 300 ± 10 \( \mu \)m. These channels were made using polyurethane beads. They were closed from the bottom and were sliced open to form through channels. The I–V data across these channels was measured at different concentrations of KCl solution and conductivity was calculated for different molarities using \( \sigma = nq\mu \) where \( \sigma \) was the conductivity of the channels, \( n \) was the number of ions; \( q \) was the unit charge and \( \mu \) was the mobility of the ions. The ionic mobility values were used as reported before.34 The resistance \( R \) was calculated from the inverse of the slopes of the curves of Figure 7(b). A nonlinear relation was observed between calculated length and the molarity of KCl solution as shown in Figure 8.

If we assume the electric field to be constant across the channel we can write it in terms of the length of the channel, \( L \) and the applied bias \( \phi \) as \( E = -\phi / L \). On the other hand, the electro-osmotic flow mobility \( \mu_{EO} \) of the ions through the channels can be calculated from \( \mu_{EO} = V_{EO} / E \) where \( V_{EO} \) is the flow velocity. These two equations lead to \( \mu_{EO} \propto -L \).

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where walls increasing The low mobility (at higher molarity) can thus be attributed to n
The calculations for the pore length included A
Then, for a constant R
KCl is the number of ions of KCl and L
PDMS channels show the same trends with respect to ionic mobility.

5. CONCLUSION
This work demonstrated the use of bench-top techniques for the fabrication of PDMS channels and membranes. Several parameters like polymerization temperature, nano/micro particle properties and magnetic strength characterize the physical dimension of the channels. The channels were formed using hydrophilic beads and nanoparticles. This can also be extended to other materials.

Owing to their excellent biological, physical, chemical and mechanical properties, PDMS membranes can be used for biological filtration of cells, protein and as dialyzer membranes. There is possibility of making cylindrical or spherical membranes that are useful for in vivo studies, e.g., for making synthetic alveoli in lungs or drug delivery particles. Perforated membrane coatings on biomedical implants can also offer better tissue growth with increased surface area. Fabrication of single micropore can be used to study cell movement across the PDMS membrane for biomechanical studies.

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References and Notes


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