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Control and Applications of Immiscible Liquids in Microchannels

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Liquids of the same or similar nature such as aqueous−aqueous solutions or hexadecane−hexadecane (HD) solutions exhibit stable laminar flow inside microchannels.[1] This liquid behavior has been successfully used in microfluidic diffusion-based separation and detection, fabrication of various microstructures, and patterning surface free energies inside microchannels.[2−6] Few studies have been reported on the flow behavior of immiscible liquids at the microscale. Owing to the different viscosities, densities, and interfacial free energies between liquids, the flow behavior of immiscible liquids was observed to be different from liquids of the same or similar nature.[7−9] Control of the flow is nontrivial, and separation of immiscible liquids is difficult once they are in contact. In a previous publication,[6] we described a method to pattern surface free energies inside microchannels to control gas−liquid interfaces using self-assembled monolayers (SAMs) in combination with either multistream laminar flow or photolithography. In this communication, we report on a strategy to control the flow of immiscible liquids in microchannels by patterning surface free energies; the application of this method to the fabrication of a semipermeable membrane is also demonstrated.

The channels used here were made from "Piranha"-treated glass slides and cover slips, and were coated with a photocleavable SAM of 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoro-1-octyl 4-(11-trichlorosilyl-1-oxoundecyloxy methyl)-3-nitrobenzoate (F-SAM).[10] A photomask and UV light were employed to pattern surface free energies (Figure 1a).[10] Upon exposure to UV irradiation, the *o*-nitrobenzyl−oxygen bond in F-SAM is cleaved, and the surface becomes hydrophilic. Aqueous solutions introduced to the surface-patterned channel flow only along the hydrophilic pathway when the pressure is maintained below a critical value (Figure 1b). However, organic liquids such as HD are not confined to either the hydrophilic or hydrophobic regions. The lack of confinement is consistent with the fact that the advancing contact angles of these organic liquids in air ($\theta_{\mathrm{org/air}}$) on both hydrophobic and hydrophilic regions are smaller than 90°.[10] By first introducing an aqueous solution in the hydrophilic region, we have discovered that HD and some other organic liquids subsequently introduced are confined to the hydrophobic region while the aqueous solution is confined to the hydrophilic region, provided the pressures are maintained below critical values (Figure 1c,d). Since organic liquids are not confined to the hydrophobic region without an aqueous solution first filling the hydrophilic region, we refer to the organic liquids as being confined by liquid walls.

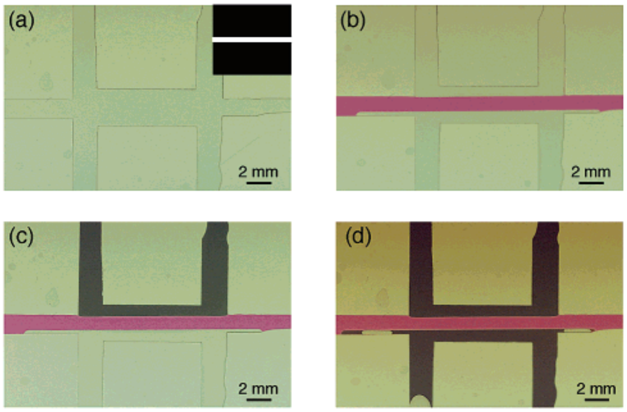

Figure 1. Images of (a) the channel and the photomask used in photopatterning, (b) an aqueous liquid flowing in the hydrophilic region, and (c, d) organic liquids confined to the hydrophobic regions. The aqueous liquid (red) is a solution of Rhodamine B dye (0.057 w/w %) in deionized water. The organic liquid (dark green) is a solution of diphenylthiocarbazone in xylenes (0.031 w/w %).

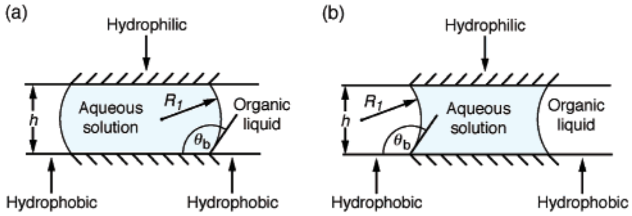

Figure 2. Angle of curvature θ_b when a pressure is applied to the aqueous solution (a) and to the organic phase (b). Here $h = 180\ \mu$m.

The interface of H_2O and organic liquid is pinned precisely at the boundary between the hydrophilic and hydrophobic surface patterns. If a pressure is applied to H_2O, the interface will curve toward the organic phase (Figure 2a), and vice versa (Figure 2b).[11] Critical conditions for liquid wall rupture will occur when the angle of curvature, θ_b, equals the advancing contact angle of H_2O on the hydrophobic surface covered in the organic liquid ($\theta_{\mathrm{water/org}}$) (if the pressure is applied to H_2O) or the advancing contact angle of the organic liquid on the hydrophilic surface covered in water ($\theta_{\mathrm{org/water}}$) (if the pressure is applied to the organic phase). When a liquid−liquid interface is curved, there is a pressure drop across the interface. This is described by the Young−Laplace equation, $\Delta P = \gamma(1/R_1 + 1/R_2)$,[12] where ΔP is the pressure difference, γ is the liquid−liquid interfacial tension, and R_1 and R_2 are the radii of curvature in directions vertical and parallel to the liquid stream. For a straight stream, the equation is simplified to $\Delta P = \gamma/R_1$, and since R_1 can be expressed by the equation $R_1 = h/[2\sin(\theta_b - 90°)]$, where h is the channel depth (~180 μm), the maximum pressures that liquid walls can sustain in a straight stream are $P_{\mathrm{water/org}} = (2\gamma/h)\sin(\theta_{\mathrm{water/org}} - 90°)$ above which H_2O flows into the hydrophobic region and $P_{\mathrm{org/water}} = (2\gamma/h)\sin(\theta_{\mathrm{org/water}} - 90°)$ above which the organic liquid flows into the hydrophilic region.

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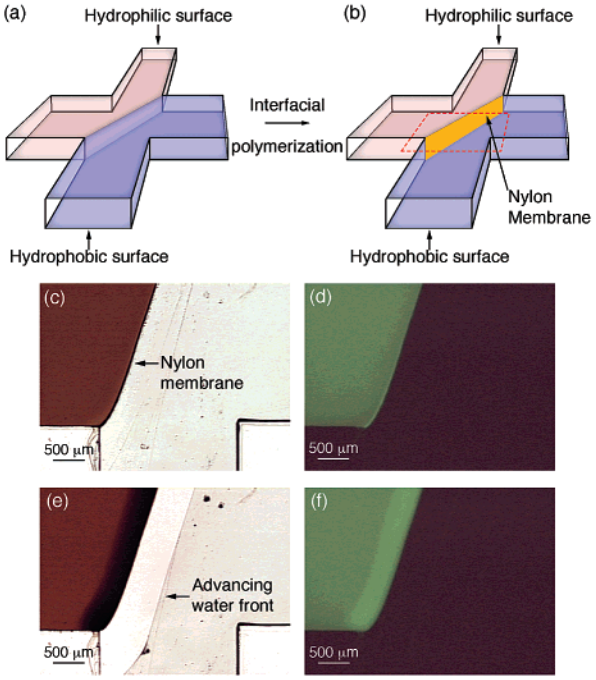

Figure 3. Fabrication and permeability study of a semipermeable polyamide membrane. (a) Schematic illustration of a surface-patterned channel. (b) Schematic illustration of a polymer membrane fabricated inside the channel by interfacial polymerization. The red border indicates the region where images (c), (d), (e), and (f) were recorded. Optical micrograph (c) and fluorescent image (d) of an aqueous suspension of 0.2 μm fluorescent microspheres confined to the hydrophilic region by the membrane. Optical micrograph (e) and fluorescent image (f) of the aqueous suspension of 0.2 μm microspheres when a pressure is applied. An advancing water front free of microspheres can be seen passing through the membrane.

Obviously, $\theta_{\text{water/org}}$ and $\theta_{\text{org/water}}$ must be greater than 90° to confine H_2O in the hydrophilic region and organic liquids in the hydrophobic region. We have measured $\theta_{\text{water/org}}$ on a F-SAM and $\theta_{\text{org/water}}$ on a UV-irradiated F-SAM. The experimentally determined maximum pressures that liquid walls can withstand are generally in good agreement with the calculated values by use of the independently measured values of $\theta_{\text{water/org}}$ and $\theta_{\text{org/water}}$ and the liquid−liquid interfacial tensions.[10]

In comparison to multistream laminar flow, the ability to confine organic liquids to hydrophobic regions and aqueous solutions to hydrophilic regions makes it practical to manipulate immiscible liquids inside microchannels. For example, one liquid can remain static while the other liquid is flowing and the boundary remains constant. Moreover, we have shown that immiscible liquids flowing in the same direction (concurrent flow) or in the opposite directions (countercurrent flow) also maintain a stable, stationary boundary. In contrast to laminar flow, the width ratio of two streams is not determined by the relative volumetric flow velocities but rather by the width ratio of hydrophobic and hydrophilic pathways provided the pressure is subcritical. We should point out that countercurrent flow is widely adopted in nature for efficient mass transfer such as gas exchange between air and blood in bird lungs and between water and blood in fish gills.[13] Here we utilize liquid walls to conduct an interfacial polymerization in a surface-patterned channel to fabricate a semipermeable membrane.

A F-SAM coated channel was photopatterned as illustrated in Figure 3a. An aqueous solution containing hexamethylenediamine (62.5 mM) was brought into the hydrophilic region followed by introduction of a solution of adipoyl chloride in xylenes (46.9 mM) into the hydrophobic region. Interfacial polymerization occurred immediately when the two phases made contact producing a polymer film at the hydrophilic−hydrophobic boundary (Figure 3b,c). The polymerization proceeded at room temperature for 8 min at which point the organic solution was flushed out of the channel with xylenes and the aqueous solution was flushed out of the channel with methanol. Both sides of the membrane were then rinsed with 10 mL of methanol and dried with nitrogen. Membrane permeability was studied on an Olympus fluorescent microscope BX 60 using an aqueous suspension of 0.2 μm fluorescent microspheres.[14] The suspension was injected into the hydrophilic region and was retained by the membrane under ambient conditions (Figure 3c,d). When a pressure was applied to the suspension, water gradually passed through the membrane while microspheres remained behind and became concentrated in the vicinity of the membrane (Figure 3e,f). This study indicated that the membrane's pore size is below 200 nm.

In conclusion, controlling the boundary between immiscible liquids has been achieved by patterning surfaces inside microchannels. The maximum pressures that liquid walls can sustain were derived analytically and studied experimentally. The ability to confine immiscible liquids in specified regions inside microchannels opens a wide range of opportunities in microfluidic systems, as exemplified here by fabrication of semipermeable membranes via interfacial polymerization.

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Supporting Information Available: Synthesis of F-SAM; photopatterning procedures; substrate preparation and microchannel fabrication; measurement of maximum pressures and $\theta_{\text{water/org}}$ and $\theta_{\text{org/water}}$; experimental results on maximum pressures and advancing contact angles (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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