

Supplementary Information

for

Microfluidic Channels Fabricated from Poly(vinylmethyloxane)

Networks that Resist Swelling by Organic Solvents

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Experimental

We synthesized hydroxyl-terminated PVMS by two methods, both of which have been previously reported in the literature.¹⁻² Step-growth polymerization¹ involves the reaction of short chain siloxanes with hydroxyl end groups (Dow Corning PJ Fluid) with lithium hydroxide (Sigma-Aldrich) dissolved in water. The reaction vessel was heated above 100°C to evaporate water, which is formed as a by-product. Typically, the reaction vessel maintained a temperature of 115°C ±5°C with 500 mL of short-chain siloxanes and 30 ppm LiOH for 4 or more hours under constant nitrogen flux and vigorous stirring, until the mixture became viscous. The viscosity increase over time indicated the approximate molecular weight of the polymer, with a targeted molecular weight of roughly ≈35 kDa. The addition of dry ice terminated the reaction, resulting in PVMS with hydroxyl end groups. This material was then purified by passing the material through a Celite® filter cake, followed by two extractions in methanol.

Alternatively, one-pot anionic ring opening polymerization (ROP)¹⁻² produced hydroxyl terminated PVMS. First, catalyst synthesis involved the procedure for making dilithium diphenylsilanolate reported elsewhere³ using diphenyl silane diol (Sigma-Aldrich) and n-butyl lithium (Sigma-Aldrich) as starting materials. Distilled cyclic vinyl methyl siloxane (Dow Corning) was added to dry THF in a reaction vessel and kept under argon while reacting with the dilithium initiator. A typical reaction would consist of 30 mmol vinyl methyl siloxane cycles, 0.3 mmol initiator, and 10 mL of dry THF. The reactions proceeded quickly, reaching full molecular weight in less than an hour. The reaction terminated with the addition of acetic acid, resulting in hydroxyl end groups on the polymers. The resulting polymer was purified twice in methanol before using. GPC determined the molecular weight of the materials, all of which were between 20 and 45 kDa.

A tin catalyst (tin(II) 2-ethylhexanoate, Sigma Aldrich) diluted in tetrahydrofuran (THF) (ratio of 1:9 v/v of tin to THF) and a short chain crosslinker of poly(vinylmethoxysiloxane) (PVMES; Gelest VMM-010) mixed with PVMS formed the crosslinked PVMS networks.^{1,4} The amount of crosslinker varied according to the molecular weight of the polymer; a typical network consisted of 10 g PVMS, 0.48 g PVMES, and 0.1 g tin/THF solution (a mole ratio of approximately 1.3 mol PVMES: 1 mol PVMS: 0.042 mol tin catalyst), which after degassing cured in a 60°C oven for an hour against a mold. We made PDMS microfluidic channels with both the standard commercial Sylgard-184 kit (prepared with 10:1 ratio of resin to hardener, as specified by the manufacturer) and an unfilled silanol terminated PDMS (Gelest, DMS-S35-100gm). Network formation with the silanol-terminated PDMS followed the same method as with PVMS; that is, with the tin catalyst and a methoxy crosslinker. All networks cured in an oven at 60°C for an hour (or more) until needed for microchannel fabrication.

Replica molding the polymers against a fluorosilane-treated master mold (SU-8 patterned lithographically on a silicon wafer) produced a molded microfluidic channel.⁵ After treating the channels for 20 seconds with oxygen (air) plasma, a molded sheet and flat sheet of siloxane sealed together with the application of gentle pressure. PVMS channels can also be sealed to a glass slide using the same technique with oxygen plasma.

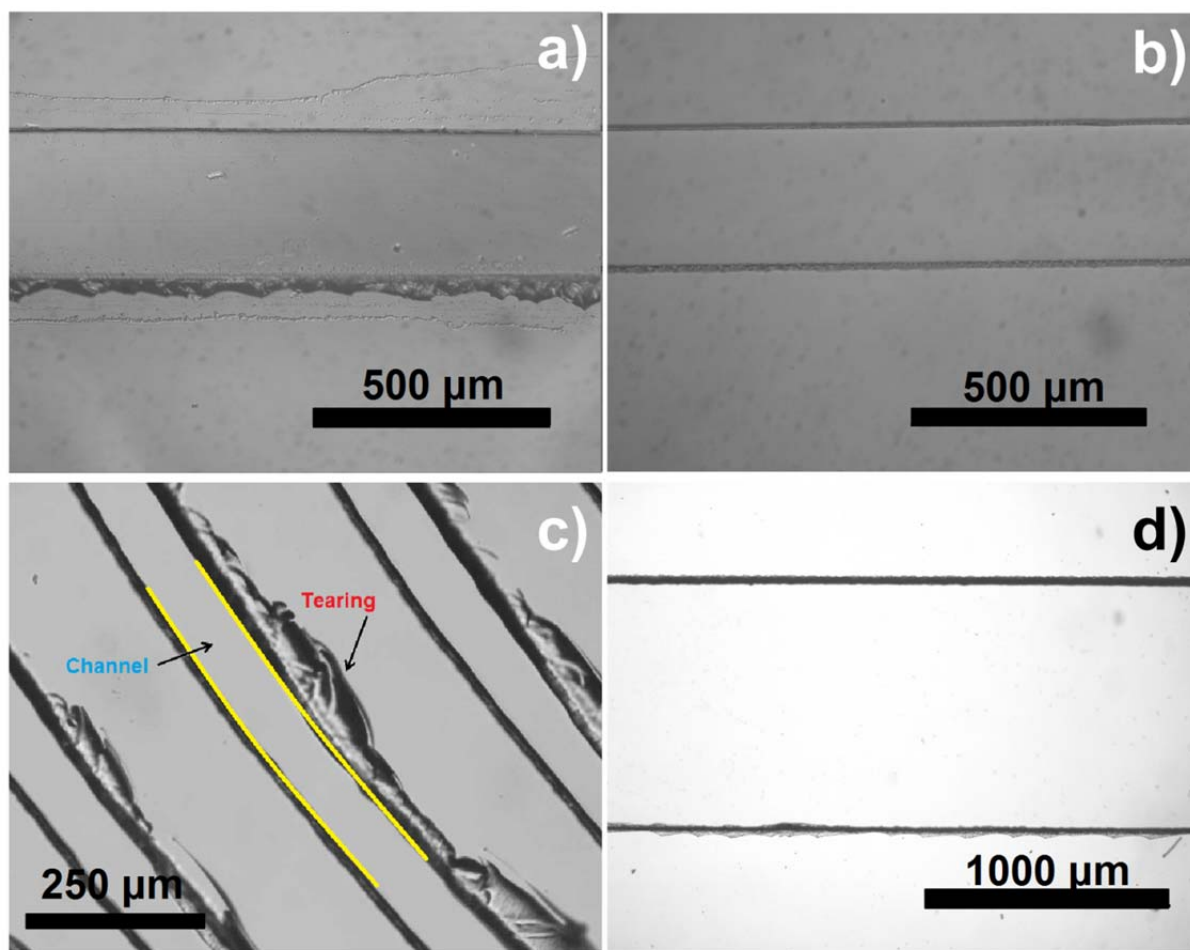
An FTA1000B goniometer determined the contact angles of deionized water and toluene. We recorded at least three contact angles for each sample, and averaged multiple samples for all CA values reported. The drops were 5-6 μL in volume.

A 400W metal halide lamp (Uvitron IntelliRay 400) provided a source of UV light for post-assembly modification of the channels. The lamp used emits primarily at 365 nm, though no optical filter was used to remove other wavelengths (a range of wavelengths are produced

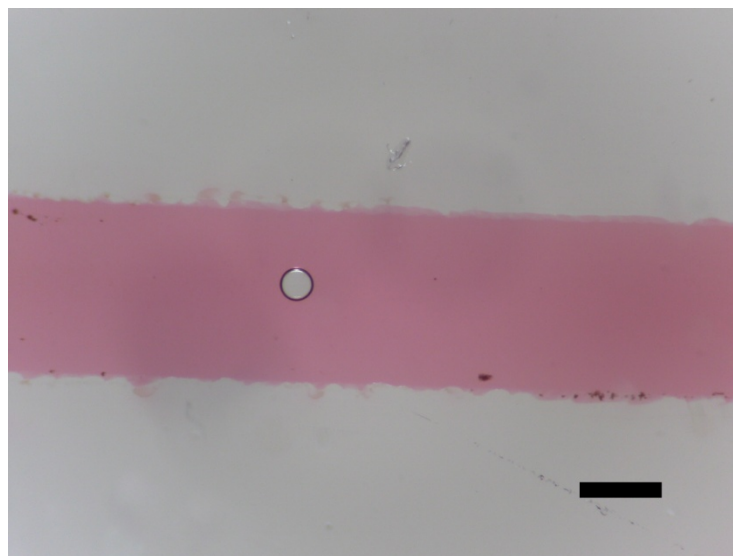
between 250 nm and 450 nm). Networks soaked in a solution of photoinitiator (2-hydroxy-2-methylpropiophenone, VWR International) 10 wt% in ethanol (Sigma-Aldrich) for 30-60 minutes before treating with UV light. For microchannels, the solution flowed through the channel for 30 to 60 min at a rate of 1 mL/hr. This process allowed the photoinitiator to diffuse slowly into the channel walls⁶ and the time of exposure controls the amount of photoinitiator added. While UV doses varied from 60 s to 30 min for the purposes of characterization (corresponding to an intensity of 3,500 to 107,000 mJ/cm²); the more typical exposure doses used in the microchannels were between 18,000 to 36,000 mJ/cm² (5-10 min).

We used several analytical techniques to characterize the surface of the siloxane networks. Fourier transform infrared spectroscopy in the attenuated total reflection mode (FTIR-ATR) was employed to characterize chemical changes using a Nicolet 6700 spectrometer equipped with germanium ATR crystal (Ge-ATR). For each sample, 256 scans were collected under constant nitrogen flux.

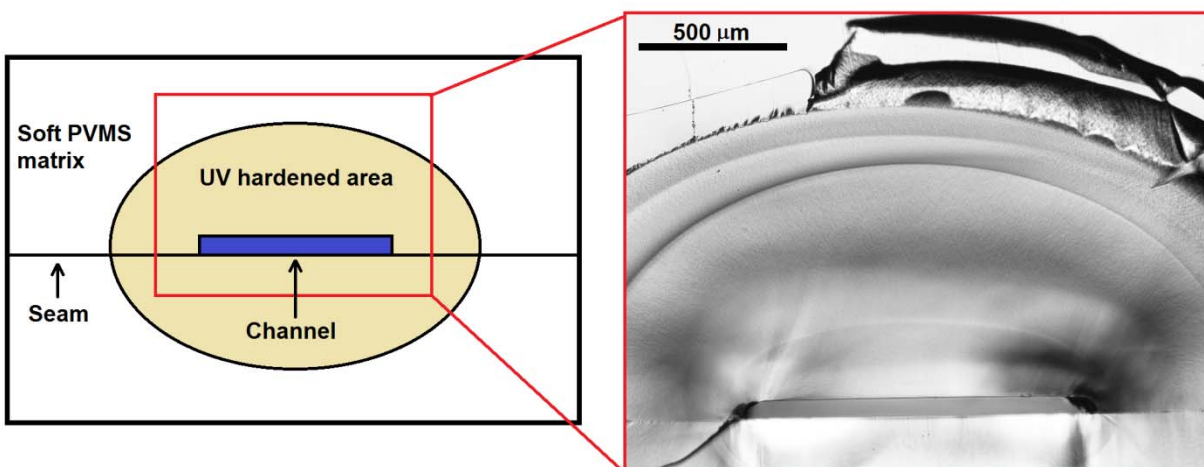
Dynamic mechanical analysis (Rheometric Scientific, model DMTA-IV) determined the material stiffness with varying UV treatment times. Flat PVMS networks (1mm thick) cut into 20mm×10mm rectangles were immersed in a solution of photoinitiator and ethanol for 30-60 min (the same time as the exposure in microchannels). After drying, the samples were UV treated with varying exposure times (corresponding to an intensity of 3,500 to 107,000 mJ/cm²). Storage modulus (E'), loss modulus (E''), and loss tangent ($\tan \delta$) were recorded over frequency range from 1-100 rad/s with 5 points collected per decade at a strain of 0.1% in tensile mode, all within the rubbery plateau region. We collected all data at room temperature (23°C).



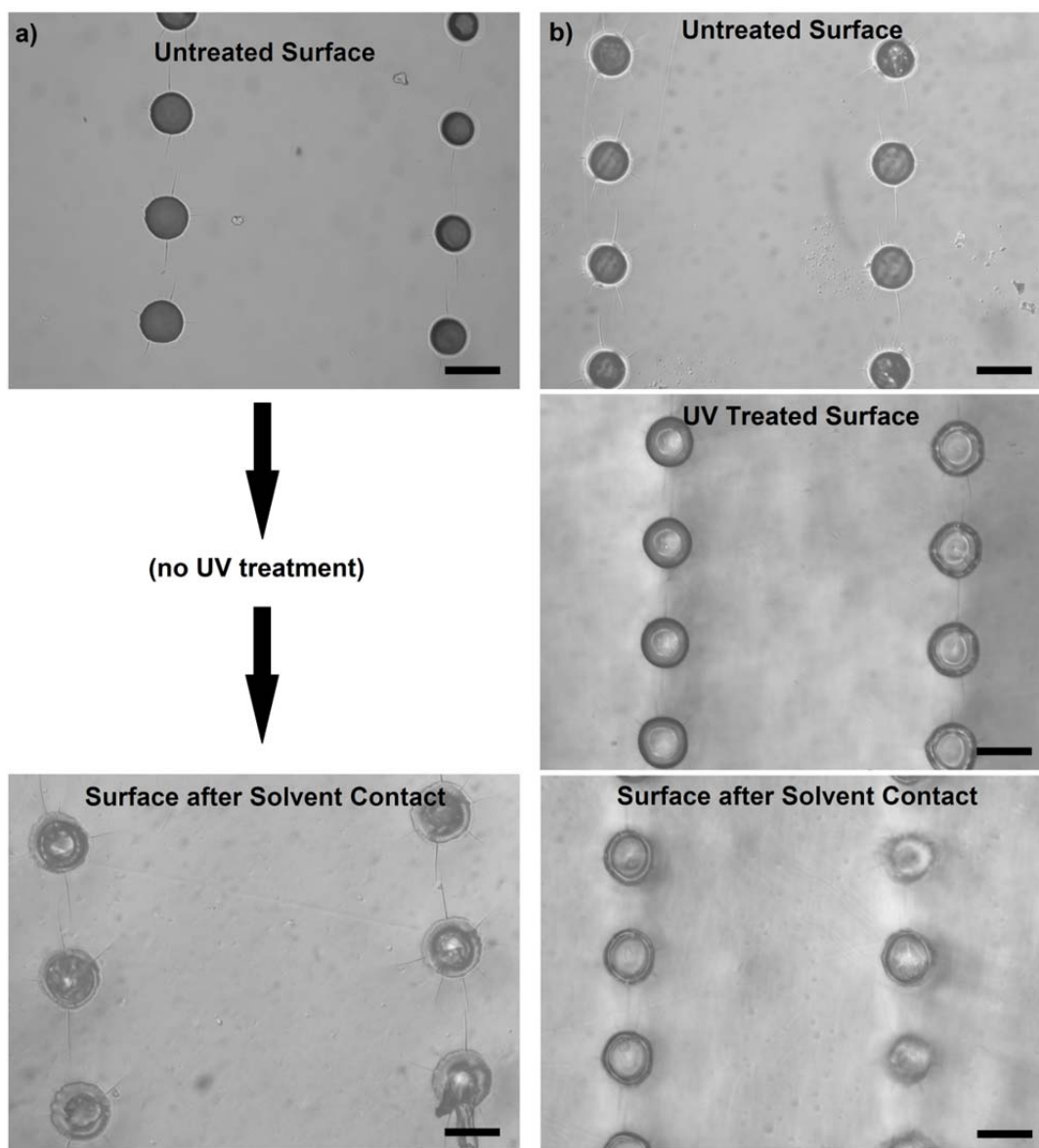
Supplemental Figure 1: Various degrees of tearing in pure PVMS, pure PDMS, and Sylgard-184 channels. Microchannel composed of A) PDMS (no fillers) and B) PVMS (no fillers). C) Tearing on a PVMS channel. Edges of the channel are highlighted with yellow lines. Significant tearing can be seen outside the channel walls. D) Sylgard-184 channel with some tearing on the edges.



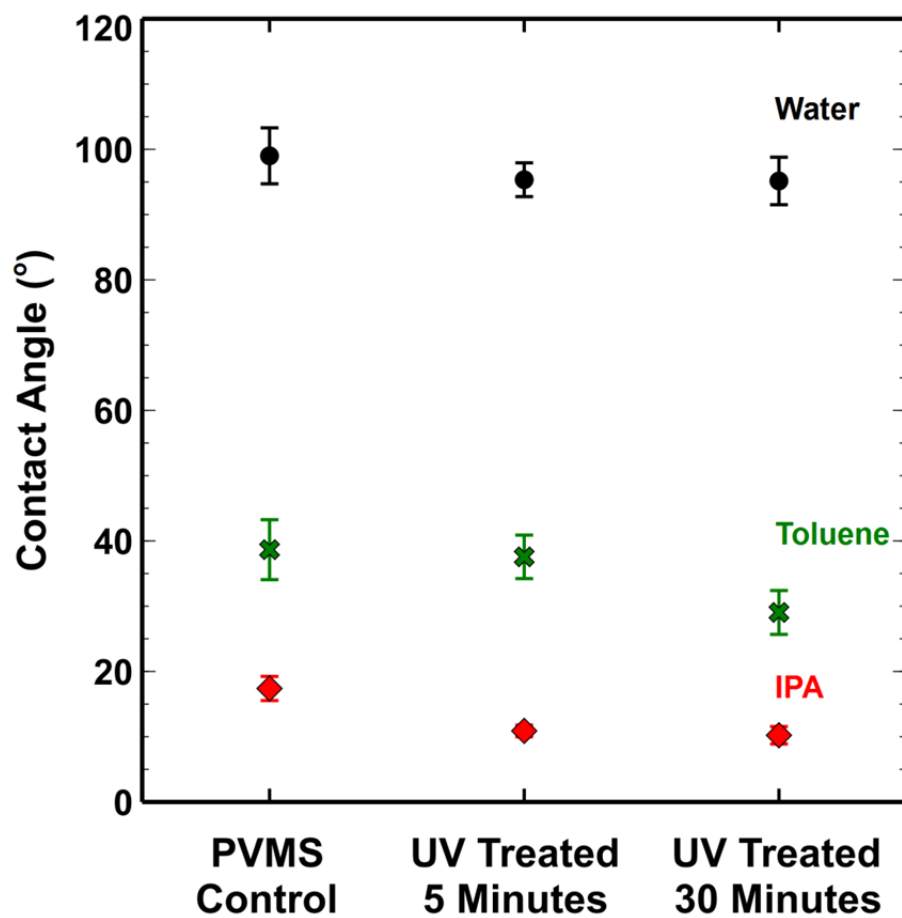
Supplemental Figure 2: PVMS channel after two hours of exposure to toluene/red dye mixture. Scale bar 500 μm .



Supplemental Figure 3: Cross-section of UV treated channel prepared by cutting a channel with a razor blade.



Supplemental Figure 4: Microwells swelling and deforming with exposure to toluene. Scale bar 100 μm . A) PDMS wells before exposure to solvent (top) and after swollen with toluene (bottom). Swelling shown is approximately 200% by volume. B) Untreated PVMS wells (top), UV treated PVMS wells before exposure to solvent (middle) and after exposure to toluene (bottom). The UV treatment results in the change in appearance of PVMS seen in B) moving from the top to the middle image.



Supplemental Figure 5: Static contact angles using DI water (black circles), toluene (green crosses), and IPA (red diamonds) on pristine PVMS and UV-treated PVMS .

References

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