Supporting Information

Vapor deposition of cross-linked fluoropolymer barrier coatings onto pre-assembled microfluidic devices

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Experimental

Standard photolithography was used to create an SU-8 50 photoresist (MicroChem) mold on a silicon wafer using an emulsion transparency (CAD/Art Services, Inc.). Poly(dimethylsiloxane) (PDMS) channels were fabricated by casting a 2 mm thick layer of Sylgard® 182 (10:1 base:crosslinker ratio) onto the mold and curing in an oven at 65°C for 4 hours. The channel used for the absorption and swelling experiments had a depth of 450 µm, the channel width at the three-branched inlet was 200 µm, and the main channel width was 1000 µm. 2 mm diameter holes were punched at the inlets to the channels. The channels were assembled by treating the slab with the channel imprint and another 2 mm thick slab of cured PDMS with a corona generator (Electro-Technic Products, Inc.) and curing in the oven at 65°C for 4 hours.[i]

The pre-assembled microfluidic devices were modified in a custom-designed iCVD chamber (GVD Corporation). The reactor pressure was 125 mTorr, the stage temperature was 35°C, and the filament temperature was 200°C. The initiator, di-*tert*-butyl peroxide (DTBP) (98%, Sigma), monomer, 1*H*,1*H*,2*H*,2*H*-perfluorodecyl acrylate (97%, Sigma), and cross-linker, ethylene glycol diacrylate (90%, Sigma), were used as received. Table 1 shows the flow rates of DTBP, PFDA, and EGDA.

A 1 mM solution of Rhodamine B (Alfa Aesar) in water was continuously flown through the channels at 700 µL hr^{-1}. Fluorescence images were captured each hour with an 800 ms exposure and the epifluorescent illumination was turned off between imaging. The fluorescence intensity at a given distance was plotted as an average over the length of a 550 µm segment. Hexane droplets were formed in a continuous aqueous phase (dyed orange), driven by a syringe pump at 9 mL hr^{-1}, and observed as they flowed down the length of the channel. The length of each droplet was measured at the T-junction (i.e. the point of droplet formation) and at the end of the channel. Contact angle goniometry (Ramé-hart Model 290-F1) was used to study the surface energy of the coatings on a reference silicon wafer.

Dimensions of the Microfluidic Devices

The devices used for the absorption and swelling experiments had channels with 200 and 1000 µm widths and a height of 450 µm (see Figure 1b in the communication for an image of the channel geometry). We tested the ability to coat smaller channels with poly(PFDA-*co*-EGDA) using the reaction conditions for Sample C1 described in Table 1. Devices with the same channel widths as the experimentally tested device and a decreased height of 200 µm are represented in Figure S1a. Aditionally, we coated devices where the channel width was 200 µm througout the device and the channel heights were 230, 95, and 50 µm as pictured in Figure S1b-d. After 40 minutes of deposition, there is a continuous film deposited in the unmasked region of the silicon wafer for heights greater than 50 µm whereas there is no coating in the center of the main channel when the height is 50 µm. Film thicknesses on silicon were measured by profilometry on at least three separate samples for each geometry (Dektak IIA). (Table S1).

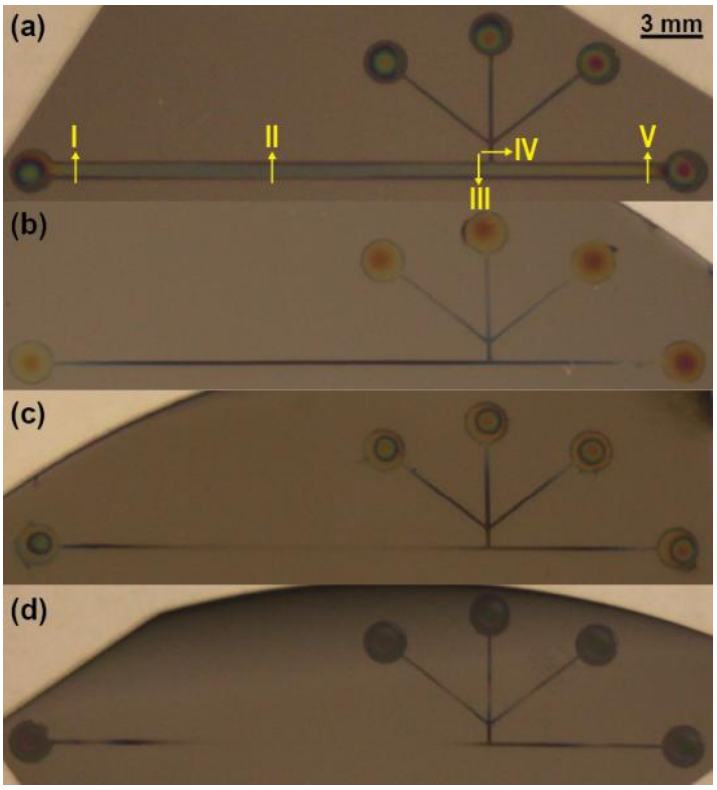

Figure S1. Silicon wafers with a deposited poly(PFDA-*co*-EGDA) coating in (a) a channel with 200 and 1000 µm wide sections and a height of 200 µm and channels with a constant width of 200 µm and heights of (b) 230 µm, (c) 100 µm, and (d) 50 µm

	main channel width (µm)	channel height (µm)	film thickness (nm±10%)				
			I	(center) II	III	IV	V
(a)	1000	200	350	225	300	310	350
(b)	200	230	150	100	120	150	160
(c)	200	95	130	45	55	65	130
(d)	200	50	100	0	40	60	100

Table S1. The thicknesses measured by profilometry of the poly(PFDA-*co*-EGDA) coatings at different locations of the channels as a function of the channel width and height.

SEM Analysis

Scanning electron microscopy images were used to examine the cross section of a channel (200 µm width, 230 µm height) before and after coating as seen in Figure S2a,b. The coating clearly does not impede the channel or alter its geometry. Figure S2c shows that the film is relatively smooth and has a roughness of less than one micron. Figure S2d shows that the coating is continuous in the channel, including at the edges, throughout the micrograph. This is representative of the entire channel.

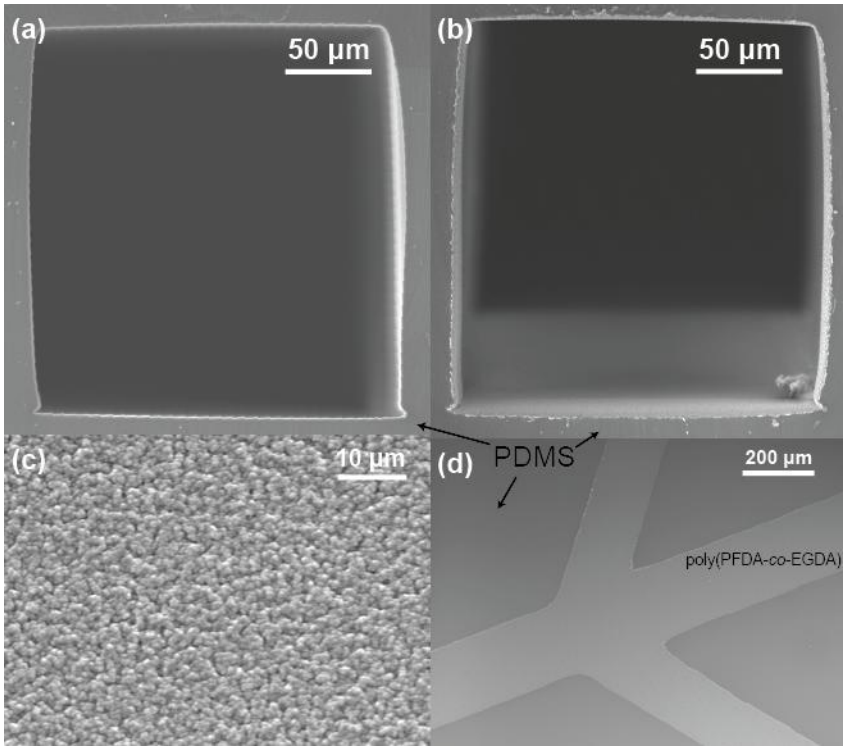

Figure S2. SEM micrographs of cross-sectional view of microchannel (a) before and (b) after coating, (c) the poly(PFDA-*co*-EGDA) film on PDMS, and (d) poly(PFDA-*co*-EGDA) deposition within the PDMS channel.

[i] K. Haubert, T. Drier, and D. Beebe, *Lab Chip*, 2006, **6**, 1548-1549.