

Solvent-Resistant Photocurable “Liquid Teflon” for Microfluidic Device Fabrication

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Supporting Information

Experimental

1. Materials: Poly(tetrafluoroethylene oxide-*co*-difluoromethylene oxide) α,ω diol (ZDOL, Average M_n ca. 3,800 g/mol, 95% Aldrich), 2-Isocyanatoethyl methacrylate (EIM, 99% Aldrich), 2,2-Dimethoxy-2-phenyl acetophenone (DMPA, 99% Aldrich), Dibutyltin diacetate (DBTDA, 99% Aldrich), and 1,1,2-trichlorotrifluoroethane (Freon 113, 99% Aldrich) were used as received.

2. Preparation of PFPE DMA: In a typical synthesis, ZDOL (5.7227g, 1.5 mmol) was added to a dry 50 mL round bottom flask and purged with argon for 15 minutes. EIM (0.43 mL, 3.0 mmol) was then added via syringe along with Freon 113 (2 mL), and DBTDA (50 μ L). The solution was immersed in an oil bath and allowed to stir at 50°C for 24h. The solution was then passed through a chromatographic column (alumina, Freon 113, 2x5 cm). Evaporation of the solvent yielded a clear, colorless, viscous oil which was further purified by passage through a .22 μ m polyethersulfone filter. ¹H-NMR (ppm): 2.1, s (3H); 3.7, q (2H); 4.4, t (2H); 4.7, t (2H); 5.3, m (1H); 5.8, s (1H); 6.3, s (1H).

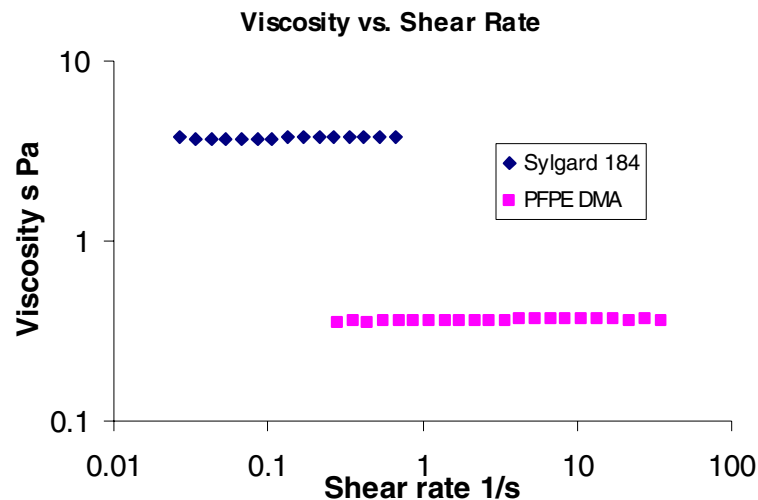
3. Photocuring of PFPE DMA: In a typical cure, 1 wt% of DMPA (0.05g, 2.0 mmol) was added to PFPE DMA (5g, 1.2 mmol) along with 2 mL Freon 113 until a clear solution was formed. After removal of the solvent, the cloudy viscous oil was passed through a .22 μ m polyethersulfone filter to remove any DMPA that did not disperse into the PFPE DMA. The filtered PFPE DMA was then irradiated with a UV source (Electrolite UVcuring chamber model no. 81432-ELC-500, $\lambda = 365$ nm) while under a nitrogen purge for 10 min. This resulted in a clear, slightly yellow, rubbery material.

4. Device Fabrication with PFPE DMA: In a typical fabrication, PFPE DMA containing photoinitiator (as described in section 3.) was spin coated to a thickness of 20 μ m (800 rpm) onto a Si wafer containing the desired photoresist pattern. This wafer was then placed into the UV curing chamber and irradiated for 6s. Separately, a thick layer

(~5 mm) of the material was produced by pouring the PFPE DMA containing photoinitiator into a mold surrounding the Si wafer containing the desired photoresist pattern. This wafer was irradiated with UV light for 1min. Following this, the thick layer was removed and inlet holes were carefully punched in specific areas of the device. The thick layer was then carefully placed on top of the thin layer such that the patterns in the two layers were precisely aligned, and then the entire device was irradiated for 10 min. Once complete, the entire device was peeled from the wafer with both layers adhered together. These curing times were determined to be the optimal exposure times to achieve a good balance between structure failure and proper adhesion of the two layers.

5. Swelling Experiments: Swelling experiments were performed by soaking fully cured PFPE DMA and fully cured Sylgard 184 (Dow Corning) in dichloromethane. % Swelling was determined using the following equation: $\% \text{ swelling} = 100\% * (W_t - W_0) / W_0$ where W_t is the weight of the material immediately after soaking in dichloromethane for time t and being patted dry with a kimwipe, and W_0 is the original weight of the material.

6. Rheometry: Viscosities of the two elastomer precursors (PFPE DMA and Sylgard 184) were measured on a TA Instruments AR2000 Rheometer. Measurements were taken on approximately 3-5 mL of material. Measurements on the Sylgard 184 precursors were taken immediately after mixing the two components. The shear rate for Sylgard 184 was varied from 0.03 s^{-1} to 0.70 s^{-1} and resulted in a constant viscosity at each shear rate. The shear rate for PFPE DMA was varied from 0.28 s^{-1} to 34.74 s^{-1} and also resulted in a constant viscosity regardless of the shear rate. Viscosities were obtained by taking an average of the viscosity values over all measured shear rates on a logarithmic plot. The raw data for these experiments is shown below.



7. Dynamic Mechanical Analysis (DMA): Modulus measurements were taken on a Perkin Elmer DMA 7e Dynamic Mechanical Analyzer. Samples were cut in to 4mm x 8mm x 0.5 mm (width x length x thickness) rectangles. The initial static force on each of the two samples was 5 mN and the load was increased at rate of 500 mN/min until the

sample ruptured or it reached 6400 mN. The tensile moduli were obtained from the initial slope (up to ~ 20 % strain) of the stress/strain curves.

8. Dynamic Mechanical Thermal Analysis: Thermal transitions of the two elastomers were obtained on a Seiko DMS 210 Dynamic Mechanical Thermal Analyzer. Samples were cut into 4mm x 20mm x 0.5 mm (width x length x thickness) rectangles. The following settings were used: $L_{amp}=10$, Min Tension/Compression force = 10.000g, Tension/Compression correction = 1.2 Force amplitude = 100. The temperature sweep ranged from -140°C to 50°C. Tg's were obtained from the corresponding temperature at the maxima in a plot of E'' (loss modulus) vs. temperature.

9. Contact Angle Measurements: Static contact angles were measured using a KSV Instruments LTD CAM 200 Optical Contact Angle Meter. Droplets were placed on each of the fully cured elastomers using a 250 μ L screw-top syringe.