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Solvent-Resistant Photocurable "Liquid Teflon" for Microfluidic Device Fabrication

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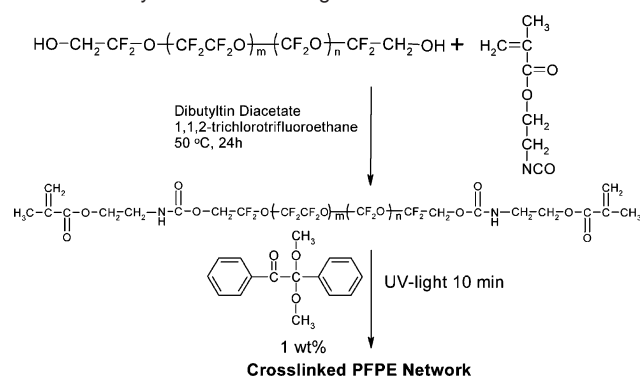
Microfluidic devices developed in the early 1990s were fabricated from silicon and glass using photolithography and etching techniques.^{1,2} These processes were costly, required clean-room conditions, were labor intensive, and posed several disadvantages from a materials standpoint. For these reasons, soft materials have emerged as excellent alternatives for microfluidic device fabrication. Soft materials make possible the easy manufacture and actuation of devices containing valves, pumps, and mixers.^{1–5} This has allowed microfluidics to explode into a ubiquitous technology that has found application in genome mapping, rapid separations, sensors, nanoscale reactions, ink-jet printing, and drug screening.^{1–6} It should be noted that an elegant system developed by Moore et al. allows for control over flow direction without mechanical valves.⁷

Poly(dimethylsiloxane) (PDMS) has rapidly become the material of choice for many microfluidic device applications.^{2–6} PDMS offers numerous attractive properties in relation to microfluidics. Upon cross-linking, it becomes an elastomeric material with a low Young's modulus of ~750 kPa.³ This enables it to conform to surfaces and form reversible seals. It has a low surface energy around 20 erg/cm² which usually facilitates easy release from molds after patterning.^{2,4} Another important feature of PDMS is its outstanding gas permeability. This allows for gas bubbles within channels to permeate out of the device and is also useful in sustaining cells and microorganisms inside the features. The nontoxic nature of silicones is also beneficial in this respect and allows for opportunities in the realm of medical implants.⁴

Many current PDMS devices are based on Sylgard 184 (Dow Corning) which cures thermally through a platinum-catalyzed hydrosilation reaction. With this material, complete curing can take up to 5 h. However, Rogers et al. have recently reported the synthesis of a photocurable PDMS material with mechanical properties similar to that of Sylgard 184 for use in soft lithography.⁸

Despite the advantages of PDMS for microfluidics technology, this material suffers from a serious drawback in that it swells in most organic solvents. Whitesides et al. have recently reported in detail on the limited compatibility of PDMS-based microfluidic devices with various organic solvents.⁹ Among those that greatly swell the material are hexanes, ethyl ether, toluene, dichloromethane, acetone, and acetonitrile.⁹ The swelling of PDMS-based devices makes it impossible for organic solvents to flow inside the channels. It has been proposed that those applications requiring the use of organic solvents will need to revert back to first-generation systems using glass and silicon.⁹ This approach is limited by the disadvantages outlined earlier.

Scheme 1. Synthesis and Curing of Photocurable PFPEs



Thus, an elastomer which exhibits the attractive properties of PDMS along with a resistance to swelling in common organic solvents would greatly extend the use of microfluidic devices to a wide variety of new chemical applications and other domains yet to be explored.

Our approach to this problem has been to replace PDMS with photocurable perfluoropolyethers (PFPEs). PFPEs are a unique class of fluoropolymers that are liquids at room temperature, exhibit low surface energy, low modulus, high gas permeability, and low toxicity with the added feature of being extremely chemically resistant like Teflon.¹⁰ DeSimone et al. have reported extensively on the synthesis and solubility of PFPEs in supercritical carbon dioxide.¹¹ Herein we report the first fabrication of a microfluidic device based on photocurable PFPEs.

Materials Synthesis and Characterization. The synthesis and photocuring of these materials (Scheme 1) is based on earlier work done by Bongiovanni et al.¹² The reaction involves the methacrylate-functionalization of a commercially available PFPE diol ($M_n = 3800$ g/mol) with isocyanatoethyl methacrylate. Subsequent photocuring of the material is accomplished through blending with 1 wt % of 2,2-dimethoxy-2-phenylacetophenone and exposure to UV radiation ($\lambda = 365$ nm).

To measure solvent resistance, tests using classical swelling measurements¹³ were performed on both the cross-linked PFPE DMA and Sylgard 184. Sample weight was compared before and after immersion in dichloromethane for several hours. The data show that after 94 h the PDMS network had swelled to 109% by weight, while the PFPE network showed negligible swelling (<3%).

The PDMS and PFPE precursor materials and the fully cured networks have similar processing and mechanical properties. Rheology experiments showed the viscosity of the uncured PFPE DMA at 25 °C to be 0.36 Pa·s which is significantly lower than that of 3.74 Pa·s for the uncured Sylgard 184. However, because

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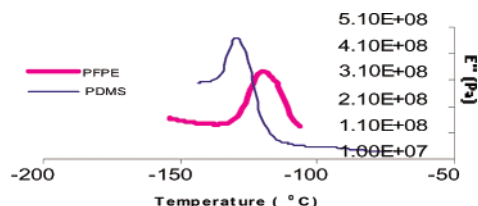


Figure 1. DMTA traces of crosslinked PDMS and PFPE materials showing maxima in the loss modulus as a function of temperature.

Table 1. Static Contact Angles^a (deg)

elastomer	water	methanol	toluene	dichloromethane
PFPE DMA	107	35	40	43
Sylgard 184	101	22	—	—

^a A (—) indicates that the solvent swelled the material and no accurate measurement could be taken.

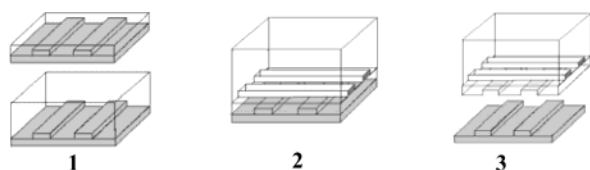


Figure 2. Device fabrication procedure. (1) A thin layer (20 μm) and a thick layer (5 mm) of PFPE DMA are partially cured. (2) The thick layer is peeled off its wafer, rotated 90°, and placed on top of the thin layer. The entire device is then fully cured to adhere the two layers together. (3) The device is peeled off the wafer.

both materials are viscous oils at room temperature, standard PDMS device fabrication methods were able to be employed.

Dynamic mechanical thermal analysis was performed on the fully cured materials. Both the PFPE and PDMS networks exhibited low-temperature transitions (−112 and −128 °C, respectively) as evidenced by maxima in the loss modulus E'' (Figure 1). This transition accounts for the similar elastic behavior of the two crosslinked materials at room temperature. Stress strain analysis shows that the tensile modulus of the fully cured PFPE-based elastomer is 3.9 MPa, similar to that measured for fully cured Sylgard 184 (2.4 MPa).

Static contact angle measurements were made on both the elastomers (Table 1). The PFPE DMA elastomer showed a higher contact angle than Sylgard 184 for water and methanol. Toluene and dichloromethane instantly swelled Sylgard 184 on contact, which prevented measurements to be taken. However, values for these solvents were obtained for the PFPE DMA material, as no swelling occurred.

Device fabrication was accomplished according to the procedure illustrated in Figure 2. Details are given in the Supporting Information. This method utilizes partial curing techniques to adhere the two layers without compromising feature sizes.³ The PFPE DMA material was easily spin-coated and molded using procedures designed for Sylgard 184.

To compare the solvent compatibility of devices made from the two materials, a dyed solution containing dichloromethane, acetonitrile, and methanol was introduced into both a PFPE and a PDMS channel by capillary action (Figure 3). The PFPE channels showed no evidence of swelling as the solution traveled easily through the channel. A pronounced reverse meniscus was observed, indicating good wetting behavior. In contrast, no solution entered the PDMS device because the channel was plugged shut when it made contact with the droplet. As a control, a dyed methanol solution was easily introduced in the PDMS channel in the same manner.

Actuation of the valves was accomplished by introducing pressurized air (~25 psi) to small holes that were punched through

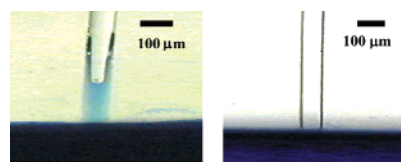


Figure 3. Dyed solution of dichloromethane, acetonitrile, and methanol entering PFPE device channel (left). No solution entered a PDMS channel of the same size due to swelling (right).

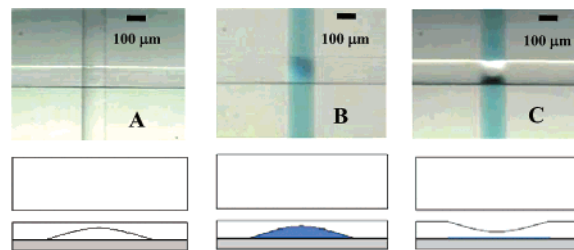


Figure 4. (A) Top-down view of channels containing no solvent. The channels on the thin layer (fluid) run vertically, while those on the thick layer (air) run horizontally. (B) Thin-layer channel filled with dyed solution of acetonitrile, dichloromethane, and methanol. (C) Valve actuation produced by introducing 25 psi of air into the thick-layer channel. Beneath each picture, a cartoon representation of the valve.

the thick layer at the beginning of the channels. When the solution was present in the channel, valve actuation was easily observed (Figure 4).

In summary, we present a novel solvent-resistant microfluidic device fabricated from PFPE-based elastomers. Photocuring decreases fabrication from several hours to a matter of minutes. The device showed a remarkable resistance to organic solvents. This work has the potential to expand the field of microfluidics to many novel applications. Current efforts to use a PFPE-based device in a novel approach to DNA synthesis are underway.

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Supporting Information Available: Device fabrication details (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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