PHOTOLITHOGRAPHIC STRUCTURING OF HIGHLY FLUORINATED POLYMERS FOR THE FABRICATION OF MICROFLUIDIC CHIPS  
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ABSTRACT  
This paper reports the fabrication of structured microfluidic chips from highly fluorinated polymers by photolithography. 2,2,3,3,4,4,5,5-octafluoro-1,6-hexanediol dimethacrylate (F8HDMA, see Figure 1) was synthesized from 2,2,3,3,4,4,5,5-octafluoro-1,6-hexanediol and polymerized by selective application of UV-light through a photomask inside a coated polycarbonate chamber (see Figure 2) to give a highly fluorinated thermoset chip for microfluidic applications (see Figure 3). The highly fluorinated polymer displays excellent stability against swelling in organic solvents such as DMF, toluene, THF and n-heptane (see Figure 4).

KEYWORDS: fluorinated polymers, photolithography, chip fabrication

INTRODUCTION  
PDMS is the standard material for the fabrication of microfluidic devices, due to its simple processing procedures, optical clarity and biocompatibility [1]. However, PDMS has some severe disadvantages. Most notably it swells considerably in numerous organic solvents such as in toluene, THF and n-heptane. PDMS swells after 24 h immersion in these solvents by 31\%, 38\% and 34\%, respectively [2]. Also, its low elastic modulus leads to problems with high-pressure microfluidic setups and its high gas permeability results in the loss of solvents due to evaporation.

THEORY  
Highly fluorinated polymers are of keen interest in microfluidics because they display low swelling in organic solvents, possess low surface energies and thus low wetting properties. Furthermore, they are optically highly transparent and have low refractive indices of around 1.3, matching with water. The most widespread fluorinated materials in microfluidics are amorphous, elastic perfluoropolyethers which may be polymerized and photostructured by the introduction of terminal methacrylate groups. These materials were first reported by Rolland \textit{et al.}[3] and are well known under the term “liquid teflon”. The perfluoropolyether technology was commercialized by the Fluorolink® product line of solvay plastics.

RESULTS AND DISCUSSION  
We have tested the commonly available Fluorolink® MD700 perfluoropolyether for its swelling properties in several solvents and found that the material swells less than PDMS but still considerably after 24 h immersion in organic solvents such as DMF, and THF, increasing the size of polymer blocks by 5.5\% and 6.5\%, respectively. We therefore developed a new highly crosslinked fluorinated compound, 2,2,3,3,4,4,5,5-octafluoro-1,6-hexanediol dimethacrylate (F8HDMA, see Figure 1) that shows superior swelling properties in DMF and THF of only 2.8\% and 1\%, respectively. We have constructed a microfluidic channel with F8HDMA fluoropolymer (see Figure 3) by polymerizing F8HDMA monomer in a methacrylate-silane coated polycarbonate HybriWell chamber (see Figure 2) by direct structuring with a photomask. Exposure of 370 nm light for only 30 seconds resulted in a clean channel. The polymer possesses high optical clarity (see Figure 3 and 5), low swelling properties in organic solvents and a high elastic modulus. that makes it an interesting material for high-pressure microfluidic devices.
Figure 1: Structure of highly fluorinated thermoset made from 2,2,3,3,4,4,5,5-Octafluoro-1,6-hexanediol dimethacrylate monomer (F8HDMA).

Figure 2: Fabrication of fluorinated polymer chip with microfluidic channels by photolithography.

Figure 3: F8HDMA microfluidic channel unfilled (left) and filled (right). The excellent clarity of the F8HDMA polymer is also visible.

Figure 4: Swelling properties of F8HDMA compared to commercially available perfluorinated polyether Fluorolink® MD700. *indicates that the material disintegrated by developing tension cracks on the surface.
CONCLUSION

The reported F8HDMA fluoropolymer can be easily structured by photolithography and is a promising polymer for microfluidic applications due to its high optical clarity, low swelling properties in organic solvents and high elastic modulus.

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