

PTFE-LIKE/PDMS HYBRIDS: SYNTHESIS OF PHOTOCURABLE, HIGHLY CHEMICALLY RESISTANT POLYMERS AND THEIR APPLICATION IN MICROFLUIDICS

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ABSTRACT

Polydimethylsiloxane (PDMS) has been the preferred material for microfluidic devices since its introduction more than a decade ago. The material is attractive due to ease of processing (usually by means of two-component curing systems) and its elasticity paired with good biocompatibility. However, it has been repetitively criticized due its limited solvent resistance. In the past several other materials have been suggest for a potential use in microfluidics. Of increasing interest have been fluorinated polymers which exhibit a number of advantages including high chemical resistance. A disadvantage of using these materials is the fact that the curing mechanism and the mechanical properties are different from PDMS. In order to combine certain advantages inherent to PDMS (such as elasticity) and of fluorinated polymers (such as high chemical resistance) we have been working on synthesis protocols to create hybrid materials consisting of PTFE (polytetrafluoroethylene) like and PDMS like monomers. These materials may be a useful alternative to conventional PDMS microfluidics and commercially available fluorinated polymers.

KEYWORDS: Chip Material, Resists, Fluorinated Polymer, Microfluidics

INTRODUCTION

Polymers are the most widely used materials for microfluidics with PDMS still being the most commonly used material, since its first suggestion by the Whitesides group [1]. The main advantages of PDMS are high optical transparency, ease of manufacturing and low critical surface tensions. However, the material is of limited use in applications that require organic solvents such as xylene, chloroform, toluene or similar substances [2]. Typical applications include solid phase extraction or synthesis on chip. For these applications fluorinated polymers are an interesting alternative as they feature high chemical resistance, low to none solvent induced swelling, low critical surface tensions, high hydrophobicity as well as low refractive indices. The most commonly used fluorinated polymers are materials that are commercially available. These typically include polymers such as PTFE, fluorinated ethylene propylene (FEP) which are for the most part thermoplastic materials. In order to structure these materials replication technology (such as hot embossing or injection molding) or direct mechanical structuring (by milling, drilling, or similar techniques) is usually required. In this paper we describe a different approach by using a synthesis that creates a radically curable fluorinated monomer which can be turned to its polymer by means of exposure to UV or to heat. One of the most convenient substances to use for such syntheses are perfluorinated polyethers (PFPE). The earliest report about a polymer synthesized with this material was presented by Priola et al. [3] with subsequent work by Rolland et al. [4] who described these materials for microfluidics.

THEORY

We have taken up the original synthesis by Priola et al. and modified it to allow the use of other modifiers and substrates. Two photocurable monomers were synthesized: PFPE-diethylmethacrylurethan (PFPE-DEMAU) and PFPE-divinylurethan (PFPE-DVU). The reaction involves the formation of urethanes by reaction of isocyanate groups with the hydroxyl groups of the PFPE. The reaction scheme is shown in fig. 1. For this reaction, PFPE is brought in solution under reflux (around 50°C, refluxed using a fluorinated solvent, such as trichlorotrifluoroethane). Subsequently the modifier (in this case a curable isocyanate) is dripped into the solution over a period of 30 minutes. Substrate and modifier are used in equimolar ratio (potentially with a 5-10 % excess of the modifier). The reaction is continued for 12 hours over night. After this period, a mixture of water and acetone (ratio 1:1), is poured into the cooled reaction mixture. After phase separation, the lower phase of the 2-phase system is extracted and the solvent evaporated leaving the pure monomer as transparent viscous liquid.

Using this reaction PFPE can be turned into a monomer by reaction with isocyanatoethyl methacrylate (resulting in PFPE-DEMAU) or with vinyl isocyanate (resulting in PFPE-DVU). There are alternative techniques to using isocyanates (which come with a number of disadvantages such as the fact that they need to be handled by a trained specialist) but we have found this technique to be extremely useful and easily adaptable.

RESULTS AND DISCUSSIONS

The monomers have been polymerized by mixing with dimethoxy phenylacetophenone (1-4 %wt) and exposure to light (365 nm, approximately 5 seconds). The liquid monomers were characterized by means of FTIR and ¹H-NMR to verify the

synthesis whereas the cured polymers were characterized by XPS in order to check for the overall fluorination (see fig. 2). We have found that the PFPE-DEUMA exhibits an increased fluorination (see table 1) compared to the published literature on PFPE polymers. We have successfully used these materials for the creation of microfluidic structures, e.g., for droplet microfluidic applications (see fig. 3).

CONCLUSION

We think that in order to make these materials suitable for microfluidics, two main drawbacks of the materials have to be overcome: the high oxidation stability (which does not allow for plasma based bonding processes which are commonly used with PDMS) and the high stiffness (which makes these materials unsuitable for the creation of commonly used mechanical microvalves). Therefore we modified the synthesis procedure in order to create PDMS based photocurable monomers (see fig. 4) resulting in PFPE/PDMS hybrid materials by blending the two monomers. This will allow for a versatile adjustment of chemical as well as mechanical properties of the cured polymers by blending the monomers in various ratios.

We will describe the detailed synthesis of the PDMS as well as of PFPE monomers and their respective polymers as well as the polymers created from the blend. Having such a hybrid materials will allow a number of techniques that have commonly be used for PDMS (such as plasma based bonding) to also be usable for such fluorinated materials.

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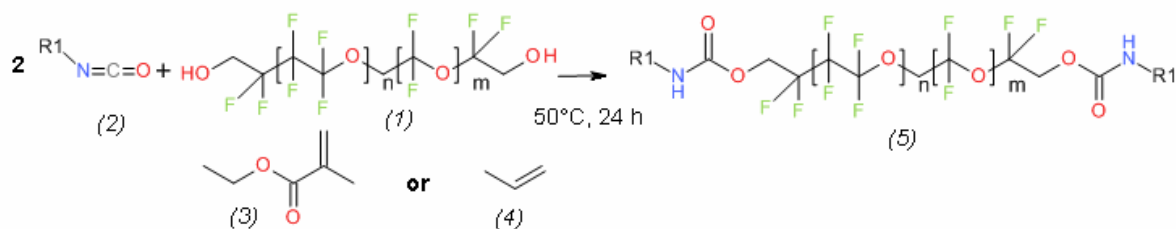


Figure 1 – Schematic of the employed synthesis chemistry. A PFPE diol (1) is treated with an isocyanate containing modifier (2, typically in solvent with the help of a catalyst) such as isocyanatoethyl methacrylate (3) or vinyl isocyanate (4). The result is a fluorinated monomer (5) that can be cross-linked to a polymer.

Polymer	C1	N1	O1	F1
PFPE-DEMAU	32.3	0.9	18.0	48.8
PFPE-DVU	29.9	0.8	17.8	51.6
PTFE (theor. values)	33.3	0	0	66.7

Table 1. XPS results for the synthesized monomers. As can be seen the synthesized PFPE-DVU monomer yields polymers with higher overall fluorination as the currently published state of literature (Priola et al.[3] described the synthesis of PFPE-DEMAU), hydrogen cannot be detected by XPS

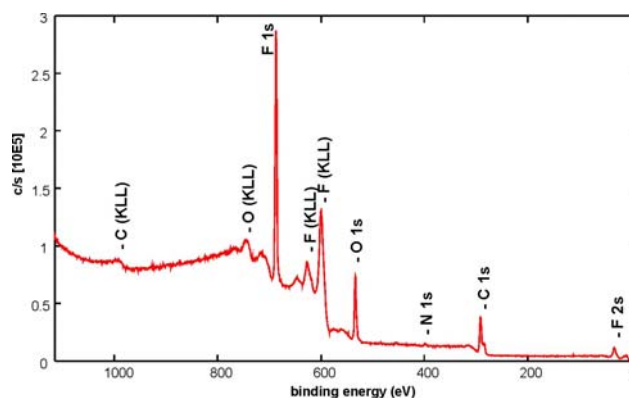


Figure 2 – X-ray photoelectron spectroscopy (XPS) of cured PFPE-DVU, the atomic concentrations of the different elements on the polymer is calculated by the intensities of elemental lines (see also table 1).

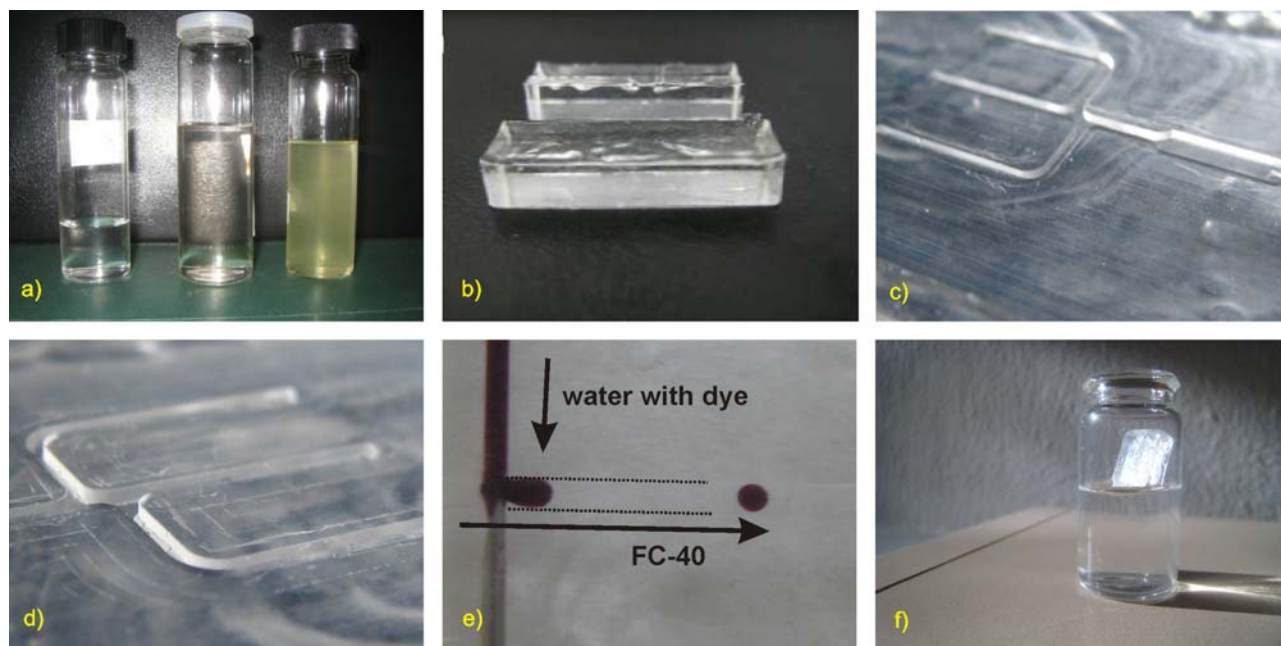


Figure 3 – Synthesized monomers and polymeric structures created from them. a) Synthesized PFPE based monomers, b) cured block of PFPE-DEMAU, c/d) microfluidic channel structures created in PFPE-DVU, e) droplet microfluidic application: creating droplets of water (with dye) in fluorinated oil FC-40 at a T-junction (channel width 800 μm), f) block of cured PFPE-DEMAU immersed in water – due to the matching refractive indices of water and the polymer (approx. 1.34) the block seems almost invisible.

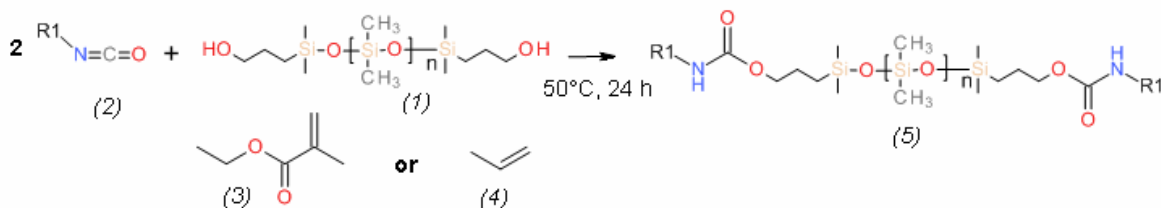


Figure 4 – Schematic of the modified synthesis for the creation of a PDMS based monomer. Here a PDMS diol (1) is treated with the isocyanate modifier (2), such as isocyanatoethyl methacrylate (3) or vinyl isocyanate (4). The result is a PDMS monomer (5) that can again be cross-linked.