ADVANCED MATERIALS

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Highly Versatile and Robust Materials for Soft Imprint Lithography Based on Thiol-ene Click Chemistry**

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The drive towards miniaturization and high throughput processing in a wide variety of technologically relevant areas has led to the development of techniques for the rapid fabrication of nanoscale patterns,[1,2] including imprint lithography using hard[3] and soft[4] patterned substrates. Soft imprint lithography is among the most promising for large scale patterning of nano/microstructures on surfaces and its attractiveness is further enhanced by its simplicity.[5] Although a wide variety of materials have been examined for soft imprint lithography, many of them suffer from resolution and fidelity issues with synthetic challenges due to thermal expansion mismatch and/or oxygen sensitivity.[6–12] For example, the most widely used formulation is based on a thermally cross-linked poly(dimethyl siloxane) (PDMS, Sylgard 184^{TM}). While this material is capable of patterning microstructures, the poor mechanical properties (Young's modulus, *E*, ca. 2 MPa), poor solvent resistance, and thermal curing process[10] leads to complications at dimensions below 1 μm and for high aspect ratio systems. To overcome these issues, materials with higher cross-linking densities have been examined, which give rise to hard-PDMS having a modulus of ca. 9 MPa. However, a composite stamp with soft PDMS as a flexible backing layer is required, which complicates the fabrication process and the mechanical properties are still not sufficient for many demanding applications.[7,13,14] More recently, DeSimone[15] and Rogers[12] have introduced photocurable perfluoropolyether (PFPE) derivatives in a variety of soft lithographic techniques leading to significant improvements in feature fidelity, solvent resistance, and chemical robustness. These (meth)acrylate based systems suffer from high cost, limited structural variability, and oxygen inhibition, leading to prolonged processing times. In order to overcome these issues, we have focused on developing a tunable materials platform based on robust and orthogonal chemistry with controlled gelation that is photo- or thermocurable, insensitive to oxygen, while also being inexpensive and highly modular in nature. Such a robust material offers tunability of chemical and mechanical properties under simplified processing conditions, which further decreases the barrier to exploiting soft imprint lithography while increasing the range of possible applications.

The enabling feature of this approach is thiol-ene chemistry, a robust and user-friendly radical-based reaction that offers versatility through the incorporation of a plethora of cross-linkers coupled with the ease of rapid photocuring in the presence of oxygen.[6,16,17] In the tradition of Click chemistry,[18,19] this allows low-cost commercially available materials to be formulated to yield high fidelity cross-linked materials in a fast and reliable fashion. The cross-linking of thiol-ene based systems can be triggered photochemically or thermally and is propagated by steps A and B, in Scheme 1,[16] without the oxygen inhibition typically associated with other radical-based systems.[10,12] In the case where homopolymerizable groups are employed, such as (meth)acrylates, mixed mechanisms are generally observed,[20] as shown in Scheme 1 (Homopropagation). By simplifying both the chemistry and the technique, the manufacturing of multiple soft stamps in a short period of time (1–2 minutes) can be accomplished for parallel printing over large areas at very low cost. This manuscript describes the development of both polysiloxane and poly(ethylene glycol), PEG, based materials that are photochemically cross-linked at ambient conditions with a variety of small molecule and oligomeric compounds to tune both the chemical and mechanical properties of the films. Robust soft stamps are prepared, which permit the fabrication of micrometer and sub-100 nm features with high fidelity.

For a concrete demonstration of the versatility and high performance of thiol-ene based soft imprint lithography stamps, fabrication of nanostructures from two very dissimilar materials, poly(siloxane) and poly(ethylene glycol) was examined. In considering poly(siloxane) based materials, to take advantage of the physical and mechanical properties of PDMS-based materials and allow comparison with other systems,[6] poly[(mercaptopropyl)methylsiloxane] (PMMS) was chosen as the base component for the siloxane based

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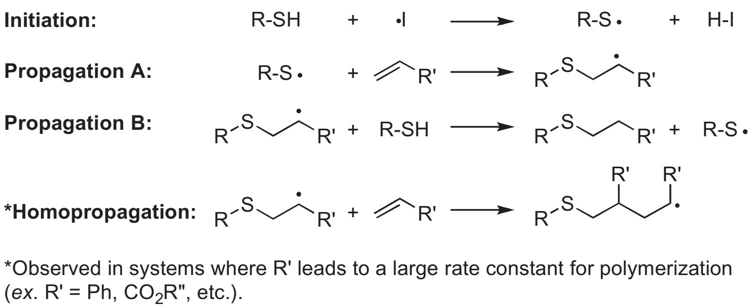
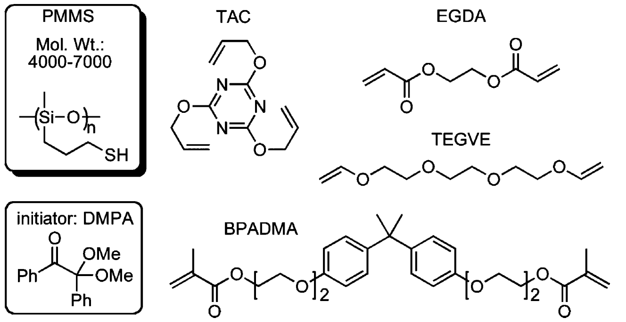


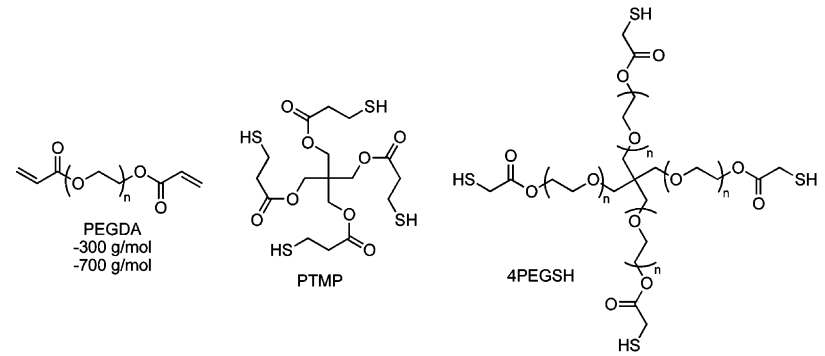
Scheme 1. Thiol-ene mechanism (I· is the radical initiator).

systems. The presence of a thiol group at each repeating unit along the backbone (ca. 99% functionalization) allows for a high degree of cross-linking, while the polymeric nature (M.W. ca. 4–7 kg mol^{-1}) eliminates odor problems traditionally associated with thiols. Similarly, the building block nature of this strategy is evident in the PEG-based systems, which take advantage of the commercial availability of tri- and tetra-thiols, namely pentaerythritol tetrakis(3-mercaptopropionate) (PTMP) and four-arm PEG star polymers. In selecting the alkene cross-linkers, a wide variety of conjugated and non-conjugated systems were examined in a high throughput strategy with representative formulations shown in Table 1 and the structures shown in Schemes 2 and 3.

The properties of the materials were optimized by screening blends of the cross-linkers with the respective thiols at various weight ratios in the presence of <0.1 wt % of 2,2-dimethoxy-2-phenylacetophenone (DMPA) as the photoinitiator. Due to the high throughput nature of thiol-ene chemistry, and the resulting mixed-mode polymerization (Scheme 1), weight ratios were optimized instead of tuning the alkene-to-thiol ratios, which, in all cases varied from 1.0 to 1.3 (mol alkene/mol thiol). Within the siloxane based systems, photocuring of sample blend 1 (**SB1**), composed of PMMS and triallyl cyanurate (TAC), resulted in a stiff highly cross-linked material with a high modulus of 47.3 MPa (Table 1). As a demonstration of the modularity[21] of these systems, incorporation of the diacrylate of ethoxylated bisphenol A (BPADMA; **SB2**) led to a significant decrease in modulus to 24.2 MPa. Similarly, modifying the blend ratios and addition of ethylene glycol diacrylate (EGDA), a small and flexible cross-linker, led to a material having a modulus of 15.6 MPa (**SB3**). Finally, the softest material, E = 5.0 MPa, was achieved by blending tetraethyleneglycol divinyl ether (TEGVE) with PMMS (SB4). Significantly, multicomponent materials incorporating 2 or more different cross-linkers can also be easily prepared, which allows further tuning



Scheme 2. Chemical structures of the alkene cross-linkers and the radical initiator employed for the polysiloxane-based patternable films.



Scheme 3. Chemical structures of the cross-linkers employed for the PEG-based patternable films.

Table 1. Composition of the sample blends (SB) with their respective elastic modulus and water contact angle.

Sample Blend [SB][a]	Equivalents by Weight	Young's Modulus [MPa]	Water Contact Angle [°]
1: PMMS/TAC	3/2	47.3 ± 1.36	71
2: PMMS/TAC/BPADMA	6/4/1	24.2 ± 0.66	75
3: PMMS/TAC/BPADMA/EGDA	7/2/1/2	15.6 ± 1.21	76
4: PMMS/TEGVE	1/1	5.0 ± 0.31	67
5: PTMP/PEGDA300	2/3	8.3 ± 0.33	57
6: PTMP/PEGDA700	2/7	7.1 ± 0.42	60
7: 4PEGSH/PEGDA700	9/8	4.8 ± 0.14	56

[a] All SBs include <0.1 wt % of DMPA.

of the physical, chemical, and mechanical properties. The surface properties of the cross-linker films are also important for soft imprint-lithographic applications, and the hydrophilic/hydrophobic character was determined by the water contact angle. The values for the various PMMS based materials vary between 67° and 76°, while the PEG-systems are more hydrophilic with values ranging from 50° to 60°. Interestingly, even for the hydrophilic PEG systems, low adhesion to hydrophilic surfaces is observed with minimal peeling resistance experienced for films cured between untreated glass plates.

In order to evaluate the performance of these materials for soft imprint lithography, stamps were prepared by drop casting onto patterned hard masters, followed by curing with a 365 nm lamp (intensity ca. 4.6 mw cm^{-2}) for 2 minutes under ambient conditions (Fig. 1). Two types of hard masters were examined, patterned silicon wafers with 200 nm features and highly-ordered porous aluminum oxide (PAO) templates with ca. 50 nm features.[22] The high performance of the thiol-ene based siloxane-based systems was evident in the lack of adhesion: the stamps were removed by straightforward peeling. As a result, the simplicity and generality of the process highlighted here allows for high throughput screening of materials with multiple stamp arrays being fabricated without advanced instrumentation or highly specialized facilities.[23] The performance of these new materials can be visually appreciated in Figure 2, which shows the scanning electron microscope (SEM) image of the original silicon master (Fig. 2A). While the high modulus TAC based system-**SB1** performed extremely well in replicating the features of the master, this material lacks mechanical flexibility at film thicknesses of 0.5 mm and above. This complicates the fabrication process when peeling such stiff polymeric materials from the master and increased the risk of breaking the master during stamp removal. In contrast, the intermediate modulus blend-**SB2** exhibited remarkable pattern replication (see Fig. 2B), while maintaining mechanical flexibility. The SEM image shows that the sub-micrometer features of the master are completely replicated in the stamp without the use of external pressure, and that adhesion to and wetting of the master is not an issue. The low modulus materials were also capable of replicating the master, however the posts were more rounded indicating a slight loss of fidelity.

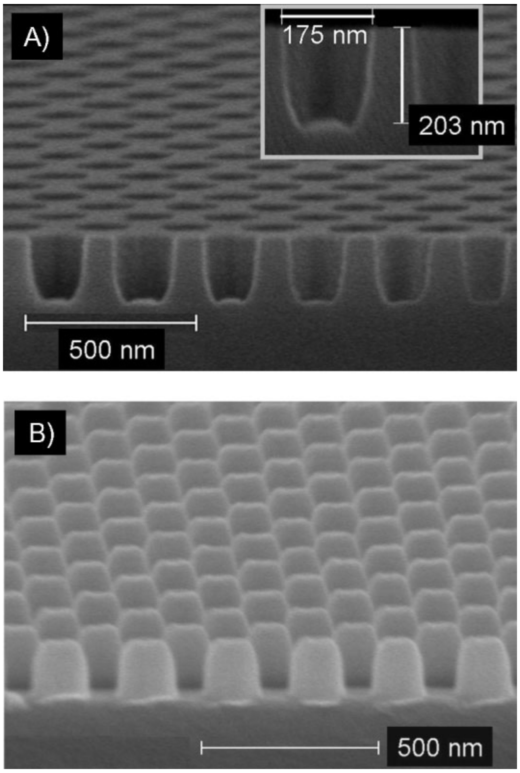


Figure 2. SEM images of: A) the hard master (holes: width ca. 175, height ca. 200 nm, period ca. 250 nm); B) the soft stamp cast on the master mold composed of **SB2** (posts: height ca. 200 nm, width ca. 170 nm, period ca. 250 nm.

Having demonstrated the ability to pattern 200 nm features, a much greater challenge is to reliably achieve fabrication of sub-100 nm features, especially since prior work has shown that mechanical properties and the ability of the liquid precursors to completely wet the molds becomes critical at these small dimensions. This challenge comes with significant opportunity and potential in a range of next-generation devices.[5,11] For example, McGehee and co-workers have recently employed an attractive approach taking advantage of the facile fabrication of porous aluminum oxide (PAO) templates, which can be used as molds to make

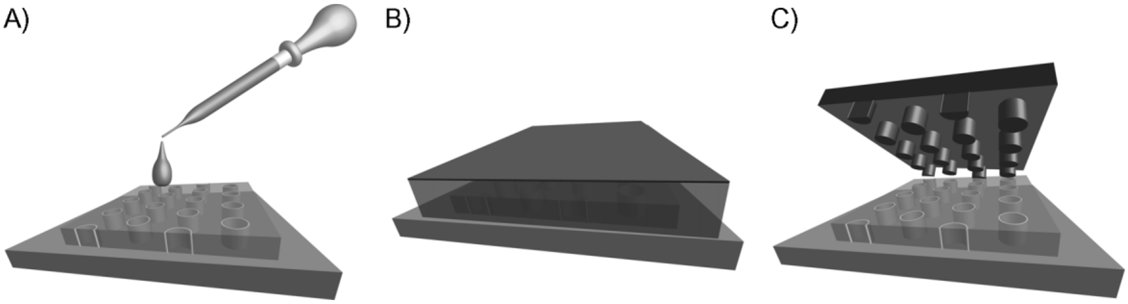


Figure 1. Process for making PMMS stamps: A) cast thiol-ene mixture onto patterned hard master; B) photocure with 365 nm light; C) remove the patterned soft stamp.

stamps for imprint lithography.[24] However, in their multi-step approach, the templates were destroyed in order to recover the newly patterned polymer-based structures and these composite films were prone to feature collapse. In order to test the performance limits of these thiol-ene based siloxane materials, PAO templates with ca. 50 nm features were prepared, and the ability to efficiently form soft stamps with high fidelity features without destroying the master was examined.

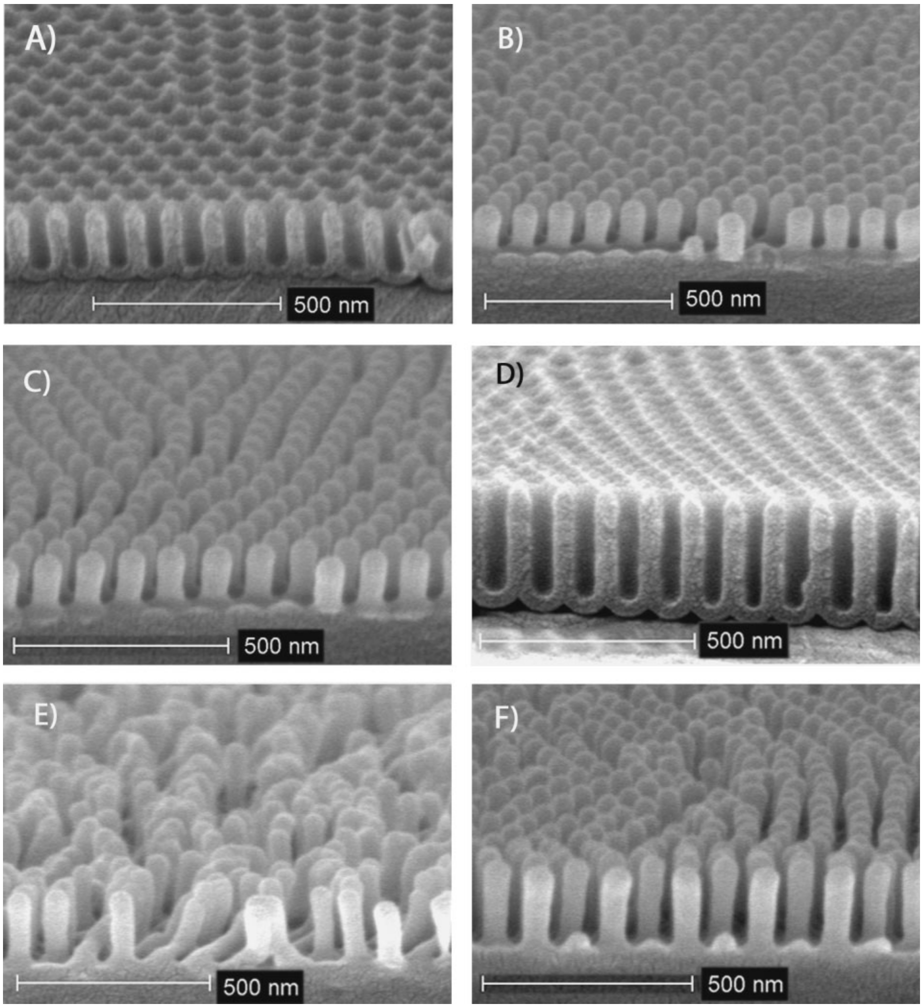


Figure 3. SEM images of: A) the master alumina mold (pore dimensions: height ca. 180 nm, width ca. 55 nm); B) **SB2** on A (height ca. 150 nm, width ca. 60 nm at the base), C) **SB1** on A (height ca. 170 nm, width ca. 60 nm at the base); D) the master alumina mold (pore dimensions: height ca. 280 nm, width ca. 55 nm); E) **SB2** on D (collapsed, width ca. 60 nm); F) **SB1** on D (height ca. 220 nm, width ca. 60 nm).

Porous aluminum oxide templates were fabricated by previously published procedures[21] to achieve pores having a diameter ca. 55 nm, and heights of ca. 180 nm and 280 nm (aspect ratio of ca. 3:1 and 5:1; Fig. 3A and D, respectively). As with the silicon master, the intermediate modulus resist, **SB2**, was cast onto the alumina template, pre-treated with a fluorinating agent, and photocured. Interestingly, the soft stamp was removed from the master with minimal resistance and stable features were obtained with a slight reduction in the height of the posts compared to the PAO template (150 nm vs. 180 nm; Fig. 3B). Examination of the higher modulus polymeric stamp, **SB1**, resulted in similar performance though with increased fidelity and feature heights of ca. 170 nm were obtained. Both of these results are noteworthy given that no external pressure was applied to force the liquid photocurable blend into the pores of the alumina template, which is typically required for other materials.[11,23] Furthermore, the alumina template remained intact and could be used multiple times. We must note that in this case, the higher modulus material worked well for the processing given that the alumina template has the added advantage of being more flexible than the silicon master counterpart. As a result, the stamp was capable of being peeled from the PAO template without the potential of breaking the master. For the higher aspect ratio masters, significant collapse was observed when using the intermediate modulus material, **SB2**, while for **SB1** no collapse was observed and high fidelity features obtained even for structures with aspect ratios of approximately 5.0 and diameters of 55 nm (Fig. 3D–F). This superior performance for **SB1** is in contrast to the 200 nm features and again demonstrates the potential for a robust materials platform with tunable properties.

As soft lithography is rapidly moving towards reaching features within the scale of single walled carbon nanotubes (SWCNTs),[12] we further analyzed the ability of a PMMS system to replicate relief features in the order of 10 nm. To achieve the structured patterning of such dimensions, the patterns (ca. 10 nm) in the PAO templates located at the interface of the aluminum substrate with the porous Al_2O_3 were exploited. To fabricate the master template of the inverse-PAO (iPAO) nanostructures, the aluminum substrate (Al) was selectively etched with an aqueous solution of $CuCl_2$/HCl, after attaching the face of the alumina to glass using an epoxy resin (Fig. 4A). This method revealed the bottom of the alumina pores and the SB2 was cured on the iPAO substrate to reveal the surface relief patterns that infiltrated the trenches of the master template. The surface topography of the iPAO master and the replicated SB2 stamp were characterized by atomic force microscopy (AFM, Fig. 4B and C, respectively).

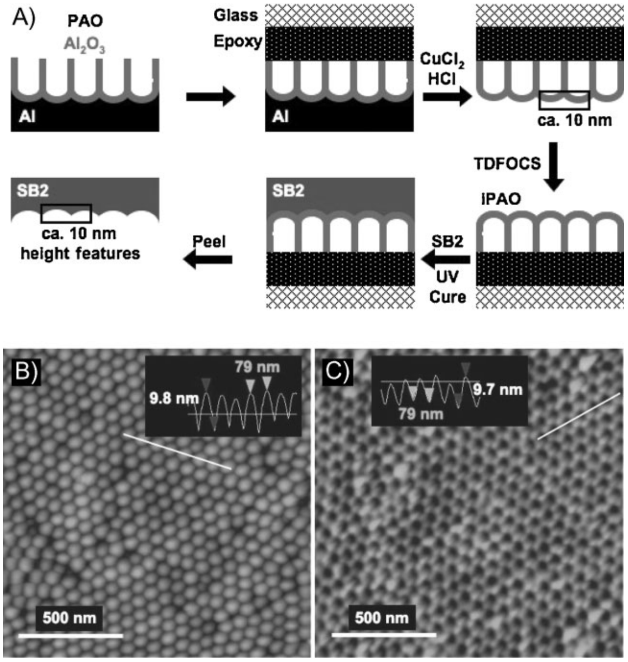


Figure 4. A) Process for fabricating the inverse-PAO (iPAO) master template and the patterned soft stamp based on SB2. B) Surface AFM image of the iPAO master. C) Surface AFM image of the SB2 soft stamp cured on the iPAO master.

The results suggest that the relief features of the soft stamp, measuring ca. 10 nm in height, are in accord with the features of the master with high fidelity.

A further demonstration of the capability of thiol-ene based systems is the development of patternable materials based on biocompatible hydrogels for applications involving the spatial differentiation of proteins, cells, and other biomolecules.[25,26] While (meth)acrylate-based and PDMS-based systems have been explored, these materials lack suitable mechanical properties as well as chemical orthogonality to serve as a reliable imprint platform for biological substrates. In this regard, thiol-ene chemistry using PEG-based systems has exhibited great potential for biomaterials applications[20,27,28] and to take advantage of the facile processability and chemistry of thiol-ene blends,[16] the PEG-derivatives shown in Scheme 3 were explored due to their varying molecular weight, PEG content, and ability to form well-defined networks with superior mechanical stability.

Given that micrometer features are generally employed for imprint lithography to produce microwell arrays of cells using biocompatible materials,[25,29] the capability to fabricate 5 µm thick lines and 10 µm hydrogel squares was initially investigated. In all cases, **SB5–SB7** were capable of reproducing high fidelity features as shown by the SEM images in Figure 5 with the cured stamps displaying only minimal resistance when peeling. In contrast, pattern replication of 200 nm features using the silicon master in Figure 2A was unsuccessful for the low modulus blends **SB6** and **SB7**, while the higher modulus **SB5**, displays high fidelity features under a wide variety of conditions and retain hydrogel character.[30]

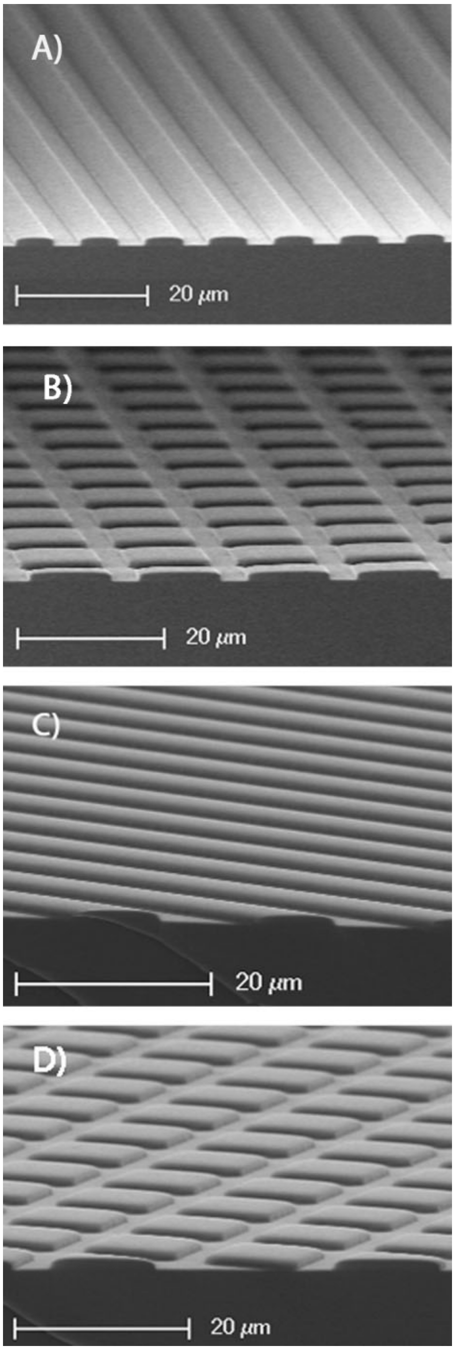


Figure 5. SEM images of the unhydrated, PEG-based sample blends (SBs) A) **SB5** (lines ca. 5 µm wide, ca. 1.5 µm high); B) **SB5** (squares ca. 10 µm × 10 5 µm, ca. 1.5 µm high). C) **SB7** (lines ca. 5 µm wide, ca. 1.5 µm high); D) **SB7** (squares ca. 10 µm × 10 5 µm, ca. 1.5 µm high). Note that the SEM images of **SB6** appear in the Supporting Information (Fig. S2).

Due to the variable nature of the molecular weight and composition of the cross-linkers in **SB5–SB7**, unpatterned PEG-based materials were characterized with respect to water uptake by mass. Samples of ca. 1 cm^2 by 0.5 mm thick were immersed in water over a period of 3 days. **SB5** showed the lowest water uptake at ca. 5 wt %, following by **SB6** at ca.

40 wt %, and **SB7** at 55 wt % with similar dimensional changes being observed for the micropatterned features. Furthermore, the elastic modulus, E, was also measured in their hydrated form to yield values of 8.5 MPa (**SB5**), 5.1 MPa (**SB6**), and 3.7 MPa (**SB7**). These results are in accord with the molecular weight of the cross-linkers employed.

In summary, thiol-ene chemistry has been exploited as a robust, efficient and orthogonal reaction for the fabrication of tunable PEG- and polysiloxane-based cross-linked materials. These materials are based on inexpensive starting materials and show great promise for imprint lithography applications. The facile cross-linking of polyfunctional thiols and alkenes with UV light can be carried out in the presence of oxygen in only 2 minutes which greatly increases the user-friendliness of this strategy.[31] In addition, the modular nature allows the physical and mechanical properties of the features to be tuned by selecting starting materials from a plethora of cross-linkers containing double bonds and/or thiols with distinctly different siloxane and hydrogel systems being demonstrated. Importantly, molding of the stamps was performed without the use of specialized equipment and high aspect ratio, sub-100-nm features were fabricated with high fidelity.

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