

# Effects of Modulus and Surface Chemistry of Thiol-Ene Photopolymers in Nanoimprinting

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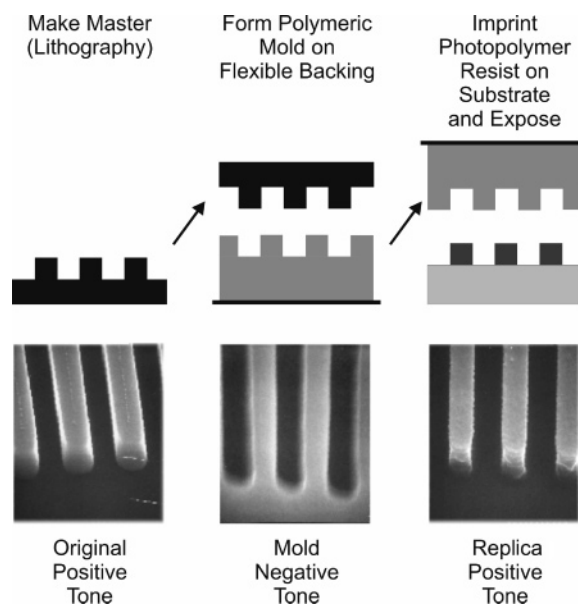
## ABSTRACT

Thiol-ene photopolymers were studied as patternable resins for nanocontact molding imprint lithography. Photopolymerizable thiol and ene monomer mixtures were used, and after molding, patterned thiol-ene polymer features the size and shape of the original molds were replicated. Adhesion and release were examined and controlled by manipulating the surface chemistry of the substrate and mold. A direct correlation between cured thiol-ene polymer modulus and pattern fidelity was observed.

The preparation of complex sub-micrometer patterns in polymer films has been widely explored by classic photolithographic techniques<sup>1,2</sup> as well as newer methods such as microcontact printing ( $\mu$ CP) of self-assembled monolayers, polymer brushes, block copolymer self-assembly, and a variety of imprint techniques which have been reviewed.<sup>3</sup>

Over the past several years we have developed a nanocontact molding (NCM) imprint lithographic technique for the replication of nanometer-scale features using functional cross-linked polymeric materials.<sup>4,5</sup> Figure 1 gives an overview of the NCM process where a transparent polymeric patterned mold is placed into contact with a thin layer of a photopolymerizable resin and is exposed to UV radiation while in contact, resulting in the curing of the photopolymer. After exposure, the mold is released leaving patterns dictated by the mold. The NCM process offers many advantages over other imprint lithographic processes including the ability to utilize inexpensive templates, excellent control of the chemistry of the molded polymer, and the ability to perform surface transformations via the incorporation of reactive functionality into patterned cross-linked polymers.<sup>6,7</sup>

The NCM process relies on the use of photopolymerizable monomer compositions, both for the creation of the mold template and for the patterned replication layer. We have



**Figure 1.** Nanocontact molding (NCM) imprint lithographic process for pattern replication. From left to right, original master pattern to be replicated (left), polymeric mold cast from master (center), and imprinted replica (right). The features shown are 500 nm lines and spaces with a feature depth of 500 nm.

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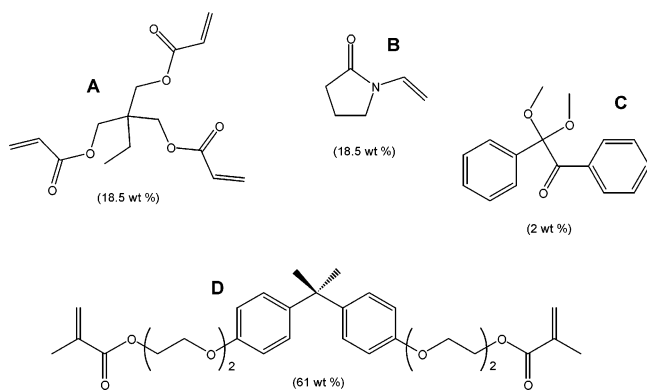
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relied predominately upon resin formulations consisting of meth-/acrylate monomer mixture that undergo a photoinitiated polymerization when exposed to 365 nm light (see Chart 1). The properties of these highly cross-linked acrylate-based

**Chart 1.** Meth-/acrylate Monomer Mixture Used in Nanocontact Molding<sup>7</sup>



resins can be controlled by the choice of the components. Unfortunately, this free radical polymerization is inhibited by ambient oxygen. The required exclusion of oxygen from the working environment increases the complexity of the imprint process. The use of the photocurable perfluoropolyether (PFPE) elastomers in the NCM process has been reported.<sup>8</sup> The study demonstrated that molds based on PFPE fluoropolymers displayed a number of unique properties such as the ability to make conformal contact with surfaces, solvent resistance, and durability making them valuable in many soft lithographic techniques. While these PFPE-based materials were able to replicate sub-100-nm sized features, their photopolymerization is still inhibited by oxygen, and in much of our work, acrylate-based molds are preferred due to their known performance.

The addition of thiols to olefins yielding thioethers is a reaction that has been known since it was reported in 1905,<sup>9</sup> and the UV-initiated reaction was reported several decades later.<sup>10</sup> Thiol-ene polymers have a number of favorable properties, such as the reported lack of inhibition by oxygen and their ability to undergo initiator-free initiation,<sup>11</sup> that make them attractive polymers in NCM patterning processes. These reasons, coupled with the wide variety of available thiol and vinyl monomers,<sup>12</sup> have made the examination of these materials very attractive.

Two important considerations must be addressed during the development of any new resin for NCM, namely, adhesion of the cured resin to the substrate and release of the mold from the resin. It has long been known that various silane coupling agents can be used to modify the both adhesion and release properties of oxide surfaces.<sup>13,14</sup> Adhesion is facilitated through the use of appropriate silane coupling reagents.<sup>13</sup> A thin layer of (3-acryloxypropyl)trimethoxysilane was applied by soaking clean wafers in a 1% solution of (3-acryloxypropyl)trimethoxysilane in heated (90 °C) toluene. We have found this method of applying thin layers of functional siloxane to Si/SiO<sub>2</sub> surfaces to be quite effective.<sup>15</sup> A monomer solution consisting of a stoichiometric amount of pentaerythritol tetrakis(3-mercaptopropionate), PTMP, and 1,4-cyclohexanedimethanol divinyl ether, **E1**, was coated and photocured (365 nm UV exposure) on the silane-coated substrates. Films cured on (3-acryloxypropyl)trimethoxysilane functionalized surfaces

exhibited good adhesion to the surface, resisting abrasion with a razor blade and passing the classic “Scotch tape” qualitative adhesion test. Attempts to use untreated substrates gave inconsistent results and poor adhesion of the cured photopolymer layer.

Developing good release properties from mold surfaces is also quite important in imprint lithography, especially in processes that require the use of expensive quartz masters as molds. A significant amount of effort in developing release coatings has been reported.<sup>3,16,17</sup> Typically, the mold used in NCM is a meth-/acrylate based material which is fabricated by curing the resin in contact with a patterned Si/SiO<sub>2</sub> master. Though other mold materials have been investigated in the NCM process,<sup>8</sup> the acrylate-based molds used have consistently yielded excellent results due to their tough, cross-linked nature and negligible swelling by the monomers used in the NCM process.<sup>5,7</sup>

A considerable amount of effort was made to improve mold release from cured thiol-enes. 2,2,2-Trifluoroethyl methacrylate was added to the mold formulation with monomer weight percentages of up to 10%. The monomer components become immiscible at higher concentrations. Molds fabricated with the fluorinated monomer did provide some enhancement of release from molded thiol-ene surfaces though the separation time was long—tens of minutes. It was observed that molds that had aged in ambient conditions for 90 days displayed excellent release characteristics. Unfortunately, this aging process is quite inconvenient and attempts were made to duplicate the surface chemistry of aged molds.

Static water contact angle measurements can be used to quickly estimate changes in surface chemistry and surface energy and compare different surfaces. Measured water contact angles of newly prepared surfaces and aged surfaces were observed to increase from 45° to 69°. This indicated that the chemistry of the surface was changing over time. Therefore freshly prepared molds were subjected to a number of treatments to determine if the aging process could be mimicked in an accelerated process. Both contact angle and ease of release were measured following mold treatment.

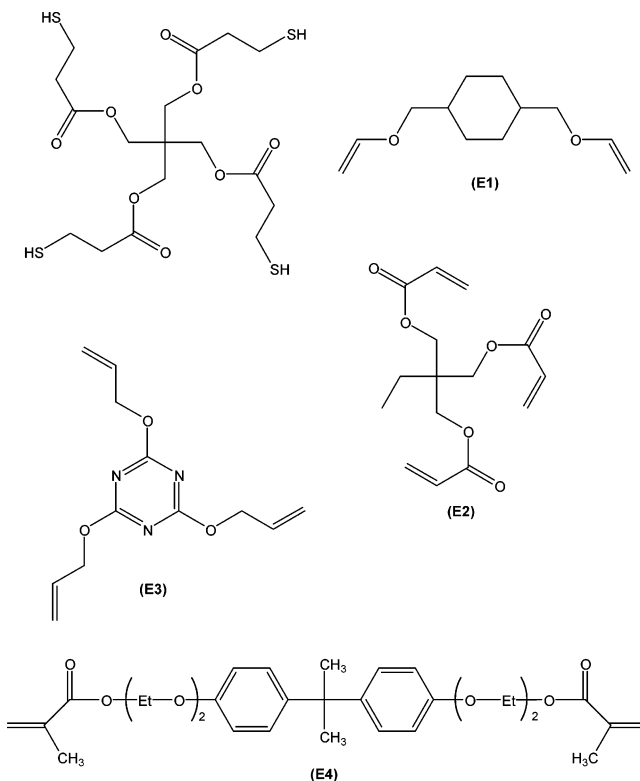
Molds that contained 10 wt % 2,2,2-trifluoroethyl methacrylate were heated at varying temperatures for specific times with hopes of facilitating the migration of CF<sub>3</sub> groups to the surface of the mold. These thermal treatments did alter the measured water contact angle, the value increasing to 65° after heating for 1 h at 120 °C, but no noticeable improvement in release was observed. Molds were subjected to overexposure with high-intensity UV radiation in air with hopes of oxidizing any residual carbon-carbon double bonds. No change in water contact angle was observed, and no improvement in release was observed. The molds were also systematically treated in a wide variety of solvent, acid, and base baths over a wide temperature range in order to mimic the surface of aged sample (Table 1). Only two of the surface treatments, exposure to chloroform and triethylamine, resulted in molds with enhanced release properties. Exposure to chloroform and triethylamine caused large changes in the surface energy of the mold surface with the halogenated solvent decreasing the contact angle to 35° and

**Table 1.** Static Water Contact Angles Measured for Various Treated Mold Surfaces.

contact angle	water contact angle (deg)
as prepared	45
boiling water (1 h)	52.5
boiling toluene (1 h)	49.5
boiling toluene (12 h)	57.7
ethylenediamine (2 h)	50.1
methanol (2 h)	56.3
hexane (2 h)	57
THF (2 h)	60.6
dipropylamine (2 h)	52.5
2-(2-aminoethylamino)ethanol (2 h)	54.7
NaOH	47.2
acetic acid	52.9
triethylamine	74.1
ammonium hydroxide	53.3
chloroform	37.9
90 days aging	69.4

the amine solvent increasing the contact angle to 74°. One valuable conclusion from these surface treatment studies was that the water contact angles, hence surface energy, did not necessarily correlate with the ease of release of the mold from cured thiol-ene photopolymer.

Surface analysis by X-ray photoelectron spectroscopy (XPS) proved useful in identifying the specific chemical changes of the mold surfaces that were responsible for release. XPS experimental conditions and data can be found in the Supporting Information. The theoretical surface atomic percentages of nitrogen were calculated and compared to the concentrations obtained from XPS from four sets of samples: freshly prepared samples, 30 days aged, 90 days aged, and molds extracted with chloroform. The freshly prepared molds had a higher than expected concentration of nitrogen at or near the surface than the amount predicted assuming a statistical distribution of monomers in the film. The level of surface nitrogen found in molds that were allowed to age for 30 days at ambient temperature was essentially unchanged. Significant changes were observed in the molds that were aged for 90 days with a decrease in the nitrogen concentration from 3.1% to 1.7%. Mold samples that were treated with chloroform had a measured decrease in the surface nitrogen concentration from 3.1% to 0.3%. The only source of nitrogen in the photopolymer was the *N*-vinyl pyrrolidinone (NVP), so we conclude that the elevated nitrogen concentration observed was due to uncured monomer at or near the surface. Samples that have been aged for 90 days show a significant depletion of uncured NVP, presumably due to slow evaporation and oxidation of NVP over time. Subjecting cured films to high vacuum did not appreciably change the surfaces, whereas extraction with chloroform was successfully employed to remove the residual NVP monomer. NVP-containing polymers have been shown to bind strongly to polar molecules, especially sulfur-containing materials. While we determined that chloroform treatments are required for good release, we are currently investigating mold formulations that do not contain NVP for NCM molding of thiol-enes.

**Chart 2.** Monomers Used To Formulate Thiol-ene Resins: Pentaerythritol Tetrakis-(2-mercapto)propionate (PTMP), 1,4-cyclohexanedimethanol Divinyl Ether (**E1**), 2,4,6-Trialloyloxy-1,3,5-triazine (**E2**), 2-Ethyl-2-(hydroxymethyl)-1,3-propanediol Triacrylate (**E3**), and Ethoxylated(2) Bisphenol-A Dimethacrylate (**E4**)

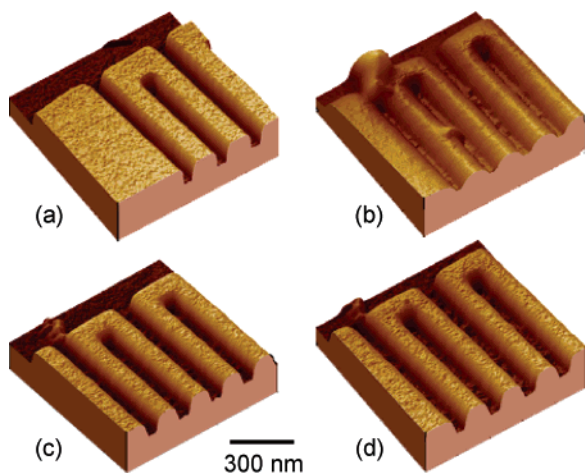
We next examined the performance of thiol-ene photopolymers in the NCM imprint process. The nature of the photopolymerization of thiol and ene monomers is fairly well understood.<sup>18</sup> In order to control the rate of photoinitiation, we added small amounts of photoinitiator, though prior studies have shown that the thioleues can photoinitiate in the absence of added initiator. In this study we only used one thiol monomer, pentaerythritol tetrakis-(2-mercapto)propionate (PTMP), and a variety of -ene monomers were examined. The ene components were chosen on the basis of structure–property relationships to give a range of mechanical properties upon curing. The ene components used were 1,4-cyclohexanedimethanol divinylether (**E1**), 2,4,6-trialloyloxy-1,3,5-triazine (**E2**), 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (**E3**), and ethoxylated(2) bisphenol A dimethacrylate (**E4**). The monomer structures are shown in Chart 2. In formulation of the resins, miscibility of the monomers was an important issue. All of the -ene monomers were completely miscible with PTMP except -ene **E4**. The -ene monomer **E4** could only be incorporated by utilizing mixed ene monomer systems. Miscible solutions containing up to 50% **E4** combined with any other -ene monomer could be made.

The various cured resins were studied by DMA to give a quantitative measure of their mechanical properties (see Table 2) and each was patterned using the NCM process. Atomic force microscopy (AFM) was used to assess the fidelity of the imprint process.<sup>8</sup> An AFM image of the original SiO<sub>2</sub>

**Table 2.** Elastic Moduli of Various Thiol-Ene Polymers<sup>a</sup>

sample	ene component	elastic modulus (25 °C), MPa
<b>T1</b>	1,4-cyclohexanedimethanol divinyl ether ( <b>E1</b> )	3
<b>T2</b>	2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate ( <b>E2</b> )	74
<b>T3</b>	2,4,6-triallyloxy-1,3,5-triazine ( <b>E3</b> )	1375
<b>T4</b>	[50%] <b>E1</b> + [50%] bisphenol ( <b>E4</b> )	460
<b>T5</b>	[50%] <b>E2</b> + [50%] bisphenol ( <b>E4</b> )	425
<b>T6</b>	[50%] <b>E3</b> + [50%] bisphenol ( <b>E4</b> )	1800

<sup>a</sup> Measured by dynamic mechanical analysis (DMA) of cured samples.

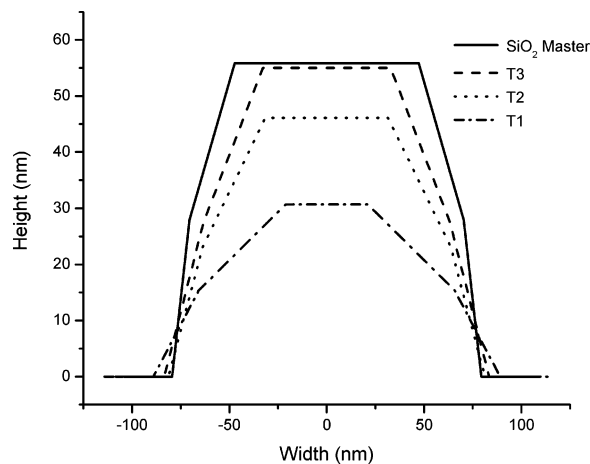


**Figure 2.** Atomic force microscopy (AFM) of 100 nm line and space patterns: (a) original silicon oxide master fabricated by e-beam lithography; (b) replicated pattern in ether-based thiol-ene **T1**; (c) replicated pattern in triacrylate-based thiol-ene **T2**, and (d) replicated pattern in triazine-based thiol-ene **T3**. The depth (Z) scale is the same for each plot, with the master having line heights of 55 nm.

master surface is shown in Figure 2. The height of the trenches is  $54 \pm 2$  nm, and the width at the bottom of each protrusion is  $164 \pm 2$  nm. A mold is cast from this master, and the mold is used to transfer the pattern into the various thiol-ene photopolymers.

The first resin examined was the thiol-ene **T1** formed by the photoinitiated reaction of PTMP and **E1**. The ether linkages in **T1** produce a thiol-ene polymer with a low  $T_g$  and modulus. DMA measurement gave a storage modulus of 2.9 MPa. An AFM image of the imprint patterned made using this thiol-ene is shown in Figure 2. The replicated pattern in this resin exhibited rounded features due to mechanical relaxation of the material upon release from the mold. The features of the imprinted layer were  $31 \pm 2$  nm in height and  $184 \pm 2$  nm in width, quite different from those of the SiO<sub>2</sub> master. The distortion is due to relaxation of cured polymer after release from the mold.

The thiol-ene photopolymer **T2** derived from **E2** and PTMP has a modulus of 74 MPa, and the AFM micrograph of this polymer after molding is shown in Figure 2. This higher modulus material exhibited much better pattern resolution with features  $45 \pm 2$  nm in height and  $168 \pm 2$  nm in width. These features also were much less rounded as compared to the lower modulus thiol-ene.



**Figure 3.** Plot of cross-sectional AFM data for the SiO<sub>2</sub> master and molded replicas **T1**, **T2**, and **T3**.

The triazine-based thiol-ene, **T3** had a storage modulus to 1400 MPa, and this resin exhibited dramatically improved patterning with excellent resolution, with features very close in size and shape of the original SiO<sub>2</sub> master. The patterned features were  $54 \pm 2$  nm in height and  $164 \pm 2$  nm in width. The plotted AFM surface data shown in Figure 2 show the excellent replication of the original SiO<sub>2</sub> master with nearly perpendicular side walls and tops. We performed a more rigorous analysis of the cross-sectional AFM data, tracking height and width of lines sampled over 15 independent points. Width at the baseline, width at half-height, and width and height at the top of the lines were measured. These data were averaged and plotted for the master and molded samples of **T1**, **T2**, and **T3** (Figure 3). The plots clearly support the assertion that pattern fidelity is strongly dependent upon the modulus of the cured polymer.

The modulus of the resin could be further modified by replacement of 50% of the ene component with ethoxylated-(2)bisphenol A dimethacrylate. Increased modulus values were observed for resins containing mixtures of each of the previously mentioned ene components with the bis-A derivative, with the mixture containing the triazine monomer (**E3**) having the highest modulus. At the time of this writing, no effective mold release treatment was found for these mixed ene systems.

In summary, we have successfully utilized thiol-ene photopolymers in a high-resolution imprint lithography process, nanocontact molding. These resins are not oxygen sensitive like conventional acrylate-based photopolymers and



can be used to generate sub-100-nm features. We addressed issues relating to adhesion of the thiol-enes to silicon surfaces and release of cured thiol-ene from the mold. Through a careful examination of how surface chemistry is related to release, we found that measurement of surface energy alone is not a good predictor of adhesion and release. Residual uncured monomer from polymeric molds is proposed to be the greatest contributor to poor release. We observed a correlation between cured thiol-ene resin modulus and fidelity of replicated pattern with harder resins creating better replicated patterns. Future studies will include the examination of the plasma etch properties of various thiol-ene resins and their usefulness in device patterning applications.

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**Supporting Information Available:** Experimental information and tables of XPS survey data and AFM cross

section data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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