ACS APPLIED MATERIALS & INTERFACES

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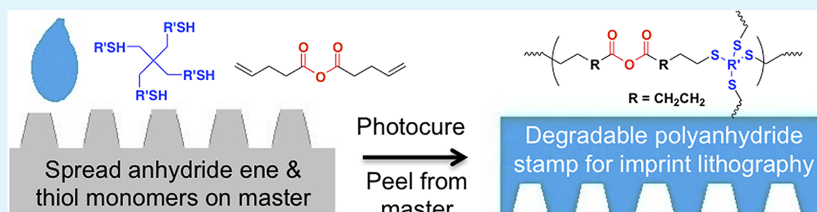
Imprint Lithography with Degradable Elastomeric Polyanhydrides

Qin Lou and Devon A. Shipp*

Department of Chemistry and Biomolecular Science and Center for Advanced Materials Processing, Clarkson University, Potsdam, New York 13699-5810, United States

Ⓢ Supporting Information



ABSTRACT: A photocurable, degradable polyanhydride cross-linked elastomer that can be used as a stamp in imprint lithography applications has been developed. The degradable stamp materials are based on polyanhydrides synthesized using thiol−ene polymerization. In this study, curing the monomers 4-pentenoic anhydride and pentaerythritol tetrakis(3-mercaptopropionate) on a master mold yields low modulus, elastomeric, degradable polyanhydride polymer stamps that are a negative of the master. These stamps can be then used as a sacrificial template during the fabrication of a replica of the master, and can be readily degraded away from the replica using water. The resultant imprinted materials exhibited excellent uniformity over a large area. Compared with other conventional imprint lithography stamp materials, the thiol−ene polymerized polyanhydrides are degradable, master mold safe, show great release properties, have fast cure rates, are relatively low cost, and can be fabricated onto variety of substrates and materials.

KEYWORDS: *soft imprint lithography, degradable network polymer, polyanhydride, patterning, degradable stamp, thiol−ene polymerization*

INTRODUCTION

Imprint lithography, or nanoimprint lithography (NIL), has been demonstrated as a high resolution and cost-effective patterning technique with submicrometer resolution, and as such NIL has many applications, ranging from medical device production to printing of integrated circuitry.[1−8] The mold (also called "stamp" in soft imprint lithography[6,9] and in step-and-flash imprint lithography[10,11]) is the most important part for NIL and usually fabricated on stiff materials, such as silicon or silica substrates.[12,13] The most commonly used stamp material in imprint lithography is commercially available poly(dimethylsiloxane) (PDMS),[14] such as Sylgard 184 PDMS.[6,15] Before the PDMS is cured on the master substrate, an anti-adhesion layer is coated onto the master to prevent the PDMS partially adhering to it during the de-molding process. Once the PDMS stamp is cured, a fluorinated silane compound is coated on the stamp to prevent the imprint material sticking. Thus, for conventional imprint lithography, anti-adhesion layers are necessary between the master mold and stamps, and the stamp and final imprinted product, for better release.[8]

Despite these anti-adhesion layers, adhesion always occurs to some extent during imprint lithography, and as a result defects are left on master mold, stamp or imprinted materials.[16] Furthermore, once a defect has occurred on the master mold, the master is no longer perfect and will result in defective stamps, which then passes these defects onto the imprinted materials.

To overcome these defect issues, we have developed a degradable stamp that no longer contaminates the master mold because it can be fully degraded and removed if imperfect demolding occurs, thus leaving material behind on the master mold. The degradable contaminations that remain on the master substrate can be removed by simply immersing the contaminated master into water. Thus, the master substrate is saved and can be reused for creating another degradable stamp. Moreover, the degradable stamp no longer needs an anti-adhesion coating because the stamp becomes a one-time-use device. Alternatively, these new materials could be used solely as an anti-adhesion layer in conjunction with conventional imprint lithography materials. It also eliminates dust accumulation during repeated use, as may occur when using conventional PDMS stamps, hence ensuring the patterns on the master are flawlessly transferred into the imprint materials every time.

The degradable stamp materials are based on our recently developed method of synthesizing polyanhydrides, a class of polymer that undergoes degradation when exposed to water, using thiol−ene polymerization.[17,18] This discovery opens up a wide range of uses for these materials because previous methods of polyanhydride synthesis precluded the use of

Received: July 12, 2012
Accepted: August 20, 2012
Published: August 20, 2012

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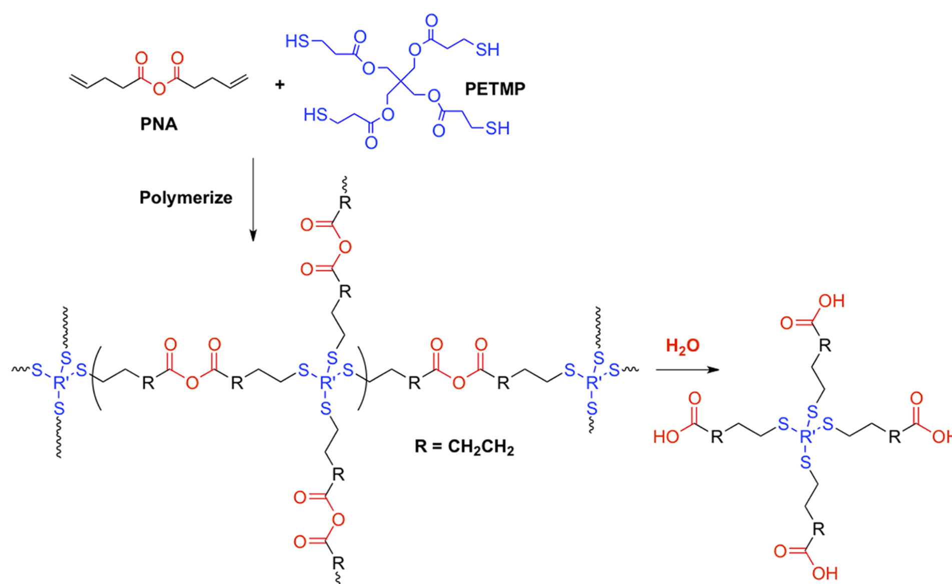
Scheme 1. Outline of the Synthesis of Polyanhydrides Using Thiol−ene Polymerization, and Their Subsequent Degradation via Hydrolysis



photoinitiation (they were condensation polymerizations)[19] or needed monomers that are not commercially available.[20] The chemistry involved in the thiol−ene polymerization approach to polyanhydrides is shown in Scheme 1. Typically, a diene monomer that contains an anhydride moiety is used. The thiol-containing compound may be di, tri-, tetra-functional, or even higher. We have studied the system of 4-pentenoic anhydride (PNA) and pentaerythritol tetrakis(3-mercaptopropionate) (PETMP), which results in a low modulus elastomer (Young's modulus of ∼5-10 MPa) that degrades via surface erosion (as compared with bulk erosion often seen in polyester materials) in a matter of hours-to-days, depending on the degradation conditions.[17,18] Such easily (photo)cured elastomers make excellent candidates for stamps in imprint lithography, and their degradation behavior allows for their use as a one-time-use stamp that would reduce or even eliminate any defects in both the master mold and the imprinted product.

Hawker et al.[21,22] have recently espoused the use of thiol−ene polymerizations for the production of soft lithography stamps. They have shown that thiol−ene polymerization, a type of Click chemistry,[23−27] may be used in the simple production of stamps that contain many favorable attributes. In particular, the properties of the thiol−ene based stamps can be tuned by addition of a wide-range of available monomers. For example, it was shown that both PDMS and poly(ethylene glycol) materials can be cured using thiol−ene polymerizations.[21] The materials can be photopolymerized, allowing for use in step-and-flash NIL. Molecular weight growth in thiol−ene polymerization follows a step-growth mechanism, which results in low-stress materials, high crosslinking density and narrow glass transition temperatures. Furthermore, thiol−ene polymerizations are less sensitive to oxygen compared the acrylic polymerizations, and are very efficient (high monomer conversions) and very quick, with films needing only seconds-to-minutes to reach full cure.[28,29] Thus, thiol−ene chemistry provides a robust and modular framework for the production of stamps that can be used in soft NIL, as shown in the recent application of this approach in the synthesis of arrays of ZnO nanoposts.[30]

EXPERIMENTAL SECTION

Preparation of PGMA Master Mold. Poly(glycidyl methacrylate) (PGMA, 4.0 wt %, M_n = 13 100; PDI = 1.43) and Irgacure 250 photo acid generator (PAG, 1 wt %) were dissolved in THF and spin coated onto a Si substrate at 2,000 rpm for 1 minute. The PGMA resist film was then cover with TEM grid and exposure under 365 nm light for 2 minutes. The UV light source for photolithography was an Oriel Instruments, model 68811, 500 W mercury xenon arc lamp (intensity ∼90mW/cm^2, as measured by a Dymax Corp. Accu-Cal-30 intensity meter). After exposure, the PGMA film was immersed into THF solution for 10 seconds to remove unreacted PGMA resist.

Preparation of Polyanhydride Imprint Stamp Materials. 4-Pentenoic anhydride (PNA, 0.96 ml), pentaerythritol tetrakis(3-mercaptopropionate) (PETMP, 1.0 ml) and 1-hydroxycyclohexyl-phenyl ketone (photoinitiator, 40 mg) were mixed together and placed onto surface of the master substrate then cured under 365 nm UV light for 1 min. After curing, the degradable polyanhydride stamp was peeled from the master surface and ready for the imprint lithography process.

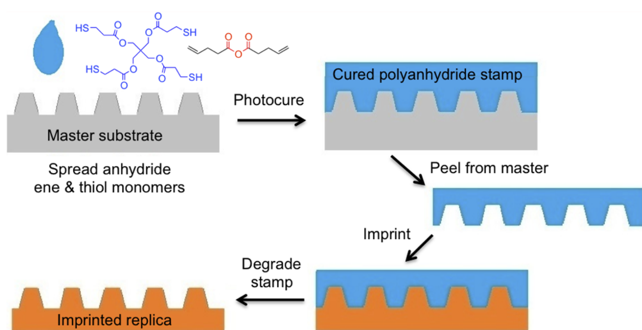
Preparation of PGMA Imprint Material Using Polyanhydride Stamp. Poly(glycidyl methacrylate) (PGMA, 10 wt.%) and Irgacure 250 photoacid generator (PAG, 1 wt %) were dissolved in THF and a drop of this solution was placed onto the polyanhydride stamp surface and cured under UV light for 10 minutes. Once cured, the polyanhydride stamp and PGMA film were placed into a NaOH aqueous solution (3.3 wt.%) for 30 minutes to partially degrade the polyanhydride stamp surface. Once this was done, the cured PGMA film was easily peeled from the surface of polyanhydride stamp.

RESULTS AND DISCUSSION

The procedure for imprint lithography using a degradable stamp is shown in Scheme 2. The degradable polyanhydride is cured on master substrate by 365 nm UV light. This is typically only for a matter of minutes. The cured polyanhydride stamp is peeled from the master substrate, and then the imprint material is then placed onto the stamp and cured. The imprint materials could be a wide range of materials, such a siloxanes, acrylics, etc., and cured using methods such as thermal or redox techniques. The cured imprint materials on the polyanhydride stamp are then placed into the water to allow full degradation of polyanhydride stamp and leave only the imprinted film.

dx.doi.org/10.1021/am301312n | ACS Appl. Mater. Interfaces 2012, 4, 4457−4460

Scheme 2. Imprint Lithography Process Using Degradable Stamps Made from Polyanhydride Materials



As an example of this new approach and to determine the quality of the cross-linked polyanhydride stamp, the imprint behavior of the polyanhydride stamp was tested via photocurable imprint studies. In our experiments, a master was made of a cross-linked poly(glycidyl methacrylate) (PGMA) homopolymer.[31,32] Briefly, the master was prepared by dissolving the PGMA, along with a photo acid generator (PAG, Irgacure 250), in tetrahydrofuran (THF) and this solution spin-coated onto a silicon substrate. Exposure of the film through a simple 60 μm × 60 μm electron microscope grid cross-linked the PGMA so that upon developing (by simply rinsing with THF) 60 μm × 60 μm PGMA squares resulted (approximately 0.5 μm thick). This was used as the master mold, but other molds can also be used. Scanning electron microscope (SEM) images of the PGMA master molds are shown in Figure 1.

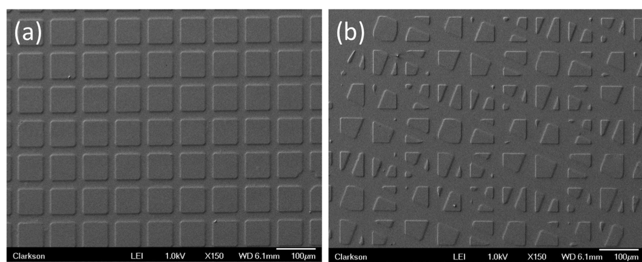


Figure 1. SEM images of a master mold fabricated by photolithography onto a Si substrate with (a) 60 μm × 60 μm squares and (b) smaller features.

The polyanhydride monomer system, which consisted of PNA, PETMP and 1-hydroxycyclohexylphenyl ketone (as photoinitiator) was then added to the PGMA master by placing a drop of the solution to the up-turned master. Exposing the film to 365 nm UV light for 10 minutes then produced the polyanhydride stamp. Images of the negative duplicated polyanhydride stamp surfaces are shown Figure 2. The successful negative 60 μm × 60 μm squares and micrometer patterns from the PGMA master is evident.

Finally, the polyanhydride stamp was used to imprint a copy of the original PGMA master, using photoinitiated cross-linking of PGMA. A THF solution of PGMA (10 wt %) and PAG was placed onto polyanhydride stamp surface and cured under UV light for 10 mins. Once cured, the polyanhydride stamp and PGMA film were placed into a NaOH aqueous solution (3.3 wt %) for 30 min to partially degrade the polyanhydride stamp (longer times can fully degrade the stamp if desired). After the

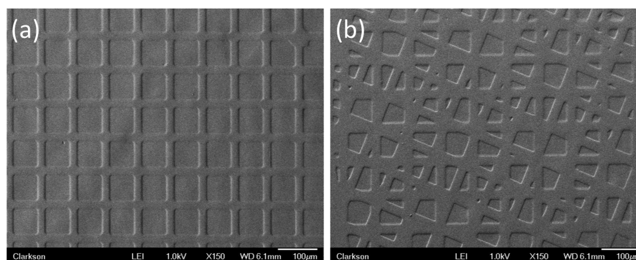


Figure 2. SEM results of surface morphology for polyanhydride degradable stamp transferred from master substrate with (a) 60 μm × 60 μm squares and (b) micrometer features.

partial degradation, the cured PGMA film can be easily peeled off the surface of polyanhydride stamp. The imprinted PGMA film can be seen in the SEM images shown in Figure 3. The

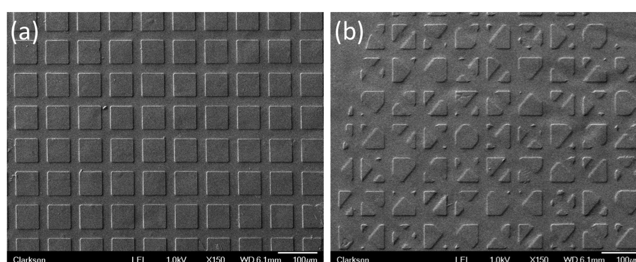


Figure 3. SEM results show the PGMA surface imprinted by the degradable polyanhydride stamp with (a) 60 μm × 60 μm squares and (b) micrometer features.

final imprinted patterns are observed to be identical in size to those on the polyanhydride stamp and PGMA master mold. As can be seen in these SEM images, excellent imprint uniformity was observed.

There have been previous reports of using degradable polymers in NIL based on acetal and hindered ester dimethacrylate crosslinkers in the imprint resist material (i.e., a stamp). Palmeiri et al.[33] showed that excellent reproduction of micrometer-sized features if the formulation of the resist material was adjusted to provide optimum mechanical and wetting characteristics. Degradation of the hindered ester materials was achieved using concentrated sulfuric acid at 100°C for 1 minute, followed by dissolution in acetone, while the acetal-based materials were degraded using 10% trifluoroacetic acid in 4-methyl-2-pentanone solutions over 5 minutes at room temperature. These are harsh conditions compared to our polyahydride system. The same authors also examined a degradation pathway that only involved heating by designing di(meth)acrylate crosslinkers containing a Diels-Alder or urethane-oxime linkages.[34] While these degrade under less stringent conditions, the synthesis of these crosslinkers was not routine. Lin et al.[35] used a photoreversible crosslinker based on coumarin, but these systems took several hours of irradiation to become soluble, and selective wavelengths are needed in order to avoid re-cross-linking the resist.

An obvious drawback of the thiol−ene-based polyanhydrides is that they will not have a significant shelf life at ambient conditions as moisture will lead to degradation and hence loss of fidelity. This could be overcome by ensuring the polyanhydride stamp is used soon after production. Another option is to use the polyanhydride as a dewetting/release layer only, and using more traditional materials for the production of

the stamp. The polyanhydride layer would then be easily removed from either the stamp or the master, thus removing any potential defects from either device. Work exploring this avenue is currently underway in our laboratories.

■ CONCLUSIONS

In summary, we have developed a photocurable, degradable polyanhydride cross-linked polymer network system that can be used in imprint lithography applications. We have shown that the fabrication of these degradable polyanhydride polymer stamps is easy, and the resultant imprinted materials exhibit excellent uniformity over a large area. Compared with other conventional imprint lithography stamp materials, the thiol−ene polymerized polyanhydrides are degradable, master mold safe, have fast cure rates, are relatively low cost, and can be fabricated onto variety of substrates and materials. They show great promise as a one-time-use device that reduces defects in master and imprint copies, thus may find use in manufacturing of micrometer and potentially submicrometer-sized devices and structures, such as microelectromechanical systems (MEMS), microfluidics, integrated circuits, and semi-conductor manufacturing.

■ ASSOCIATED CONTENT

Supporting Information

Optical images and profiles of imprint master and replica. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: +1-315-268-2393. Fax: +1-315-268-6610. E-mail: dshipp@clarkson.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the Department of Chemistry and Biomolecular Science, and the Center for Advanced Materials Processing (a New York State Center for Advanced Technology) at Clarkson University for support.

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