

Polymer-Derived Ceramic Materials from Thiol-ene Photopolymerizations

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A novel reaction scheme for rapidly fabricating polymer-derived ceramic structures with high aspect ratios and with controlled shape and structure is described. The reaction scheme is based largely upon a thiol-ene photopolymerization mechanism. Thiol-ene photopolymerizations offer unique advantages including high polymerization speed in the presence of little or no photoinitiator, the ability to delay gelation, and the ability to achieve high double bond conversions. The addition of thiols to polymerizable vinyl-containing ceramic precursors further enables the formation of thicker structures than traditionally achieved. Structures formed using this mechanism exhibit little warping, and upon pyrolysis the polymer structures are transformed into ceramic structures of a self-similar shape. In the pyrolysis step, structures formed using this novel mechanism exhibit shrinkage and mass loss values similar to those produced from typical ceramic precursors. Further, the photolithographic process described here is readily extendable to make complex three-dimensional ceramic microstructures and microdevices.

Introduction

The field of microelectromechanical systems (MEMS) is being heavily investigated for applications such as sensor and actuator systems, microfluidic devices, microcombustors, heat exchangers, and micro-optics systems. Polymers, silicon, and glass are all common materials for making MEMS devices, though many of these materials are not suitable for high temperature or other harsh environmental applications. Ceramics are an excellent candidate for these types of MEMS applications; however, they are limited by difficulties in forming microscale parts and structures.

Shaping and manufacturing for miniaturization of ceramic devices is currently a complex process. Thus, there is a great interest in developing new materials fabricated by cost-effective techniques. Powder sintering¹ is one such process for making ceramic MEMS. However, the dimensional tolerances of the resultant structures are dependent on the uniformity and purity of the powder packing, which is difficult to control in small-scale structures. A second ceramic MEMS technique is based upon chemical vapor deposition of silicon carbide followed by its micromachining.^{2,3} Slow deposi-

tion rates² (20–50 $\mu\text{m}/\text{h}$) of silicon carbide and complex micromachining³ make this process unsuitable for many applications.

In contrast, polymer-derived ceramics have excellent thermal and mechanical properties,⁴ while at the same time the polymer fabrication route is an excellent way to control the size and shape of devices, as well as material properties, through tailoring of the chemistry of the organic precursors.⁵

Photopolymerization is a rapid, inexpensive, and simple technique for producing free-standing structures from liquid precursors. It offers temporal and spatial control of the formation of these microstructures and allows for processing at ambient conditions. It also enables the utilization of photolithography, facilitating the formation of complex, three-dimensional structures.

Photopolymerization of vinyl-containing liquid pre-ceramic monomers, using free radical photoinitiators, has previously been used to form free-standing microstructures without requiring demolding.^{4,6,7} Unfortunately, even with large amounts of photoinitiator, the curing rates attainable during the formation of these structures are low, especially relative to other typical photopolymerizations, e.g., those of acrylates and meth-

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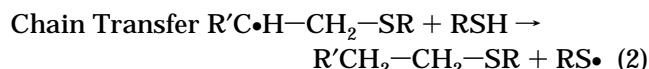
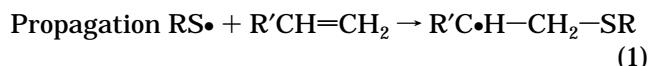
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acrylates. Higher initiator concentrations are required for appreciable polymerization rates, which leads to an inability to produce thick structures with high aspect ratios due to light absorption and attenuation by the photoinitiator molecules. Further, the final double bond conversion achieved in these systems is very low.

These limitations of low cure depth, slow polymerization rates, and low ultimate double bond conversion in vinyl-containing systems are overcome by the addition of a thiol comonomer to the system, thereby changing the predominant polymerization mechanism to that of a thiol-ene polymerization. Thiol-ene polymerizations are radical, step growth polymerization reactions that involve a multifunctional thiol and multivinyl monomer.^{8,9} These photopolymerizations exhibit several distinct advantages relative to typical chain growth vinyl photopolymerizations in that they are not inhibited by oxygen and rapidly polymerize in the presence of little or no added photoinitiator.^{8,10}

The thiol-ene polymerization reaction is based on the addition of a thiol to a vinyl functional group, which proceeds sequentially, via propagation of a thiyl radical through a vinyl functional group and subsequent chain transfer of hydrogen from the thiol, which regenerates the thiyl radical.^{8–15} This successive propagation/chain transfer mechanism is the basis for step growth thiol-ene polymerizations and is presented in the scheme below.



Here, this work utilizes a thiol-ene photopolymerization mechanism to form ceramic materials for MEMS and microfluidic devices. Photopolymerization of the liquid ceramic precursors via this unique reaction technique offers a novel alternative to the currently available technologies. The thiol-ene reaction scheme enables otherwise slowly reacting vinyl moieties to be rapidly polymerizable by a photoinitiated radical mechanism. For example, vinyl and allyl ethers that do not radically homopolymerize are polymerized readily by the addition of thiols to those systems.⁹

Experimental Section

The monomers utilized in this study are pentaerythritol tetra(3-mercaptopropionate) (tetrathiol) donated by Bruno

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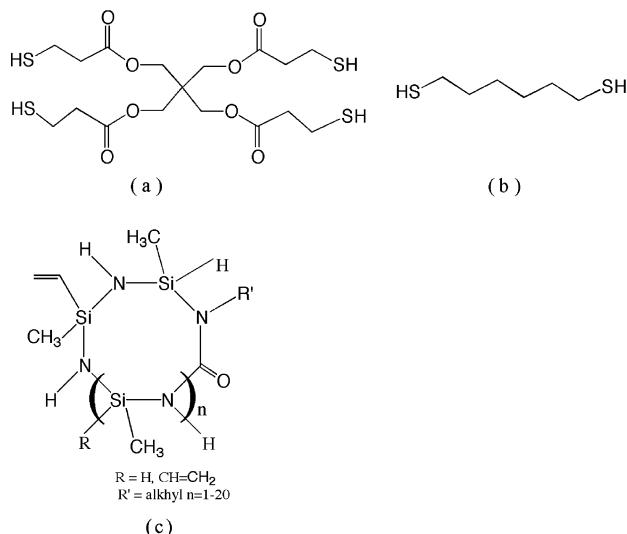


Figure 1. Chemical structures of monomers utilized in this work (a) tetrathiol, (b) dithiol, and (c) Ceraset. Both Ceraset and VL20 are produced by Kion Corporation. Ceraset is a polyureasilazane, whereas VL20 is a polysisilazane which does not contain the urea groups. Additional information on the structure of VL20 is not available.

Bock (Marschacht, Germany), 1,6-hexanedithiol (dithiol) purchased from Aldrich (Milwaukee, WI), and vinyl-containing ceramic precursor monomers, VL20 and Ceraset, donated by Kion Corporation (New York, NY). The photoinitiator 2,2-dimethoxy-2-phenyl acetophenone (DMPA) was purchased from Ciba-Geigy (Hawthorne, NY). All monomers and the photoinitiator were used as received, and the structures of the monomers used are shown in Figure 1.

FTIR studies were conducted using a Nicolet 750 Magna FTIR spectrometer with a KBr beam splitter and an MCT/A detector. Series scans were recorded, taking spectra at the rate of approximately 5 scans per second while the FTIR sample chamber was continuously purged with dry air. Samples were irradiated until the reaction was complete, as indicated by the double bond and thiol peak absorptions remaining constant. Thiol functional group conversion was monitored using the S-H absorption peak at 2570 cm^{-1} , while vinyl conversions were monitored using the carbon–carbon double bond absorption peak at 1593 cm^{-1} . A representative FTIR spectrum of the tetrathiol-VL20 system before and after polymerization is shown in Figure 2. Conversions were calculated using the ratio of peak areas to the peak area prior to polymerization. Analyses and apparatus for FTIR experiments were previously discussed in great detail.^{16,17}

For kinetic studies, monomer samples were placed between NaCl crystals in a horizontal transmission apparatus.¹⁶ Photopolymerizations were initiated via an EXFO Acticure light source (EXFO, Mississauga, ON) with a 320–500-nm filter. Irradiation intensities were measured with an International Light, Inc. model IL1400A radiometer (Newburyport, MA). All reactions were performed under ambient conditions.

Contact lithography was employed in the fabrication of the photopatterned polymer structures. Contact printing, where the solution is exposed to UV through a mask placed directly on the photopolymerizable monomers, limits diffraction effects from the UV light exiting the mask. Thus, the resolution of contact printing is higher than most other optical lithography processes.¹⁸ The maximum resolution of these microstructures is limited by diffraction during the photolithographic step. Theoretically, a resolution of 1 micrometer is possible with

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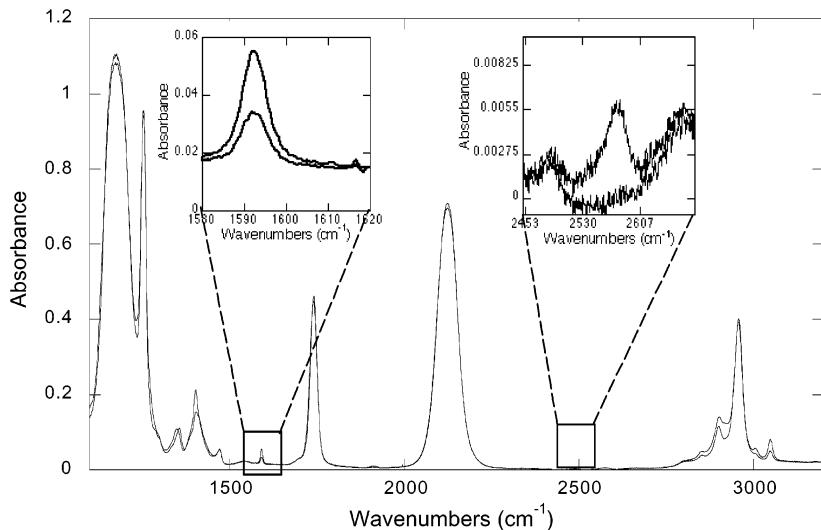


Figure 2. FTIR spectrum before and after polymerization. The initial and final area of the thiol (2570 cm^{-1}) and ene (1593 cm^{-1}) peaks are utilized to calculate conversions.

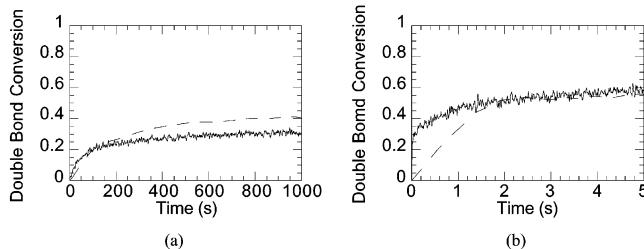


Figure 3. Double bond conversion versus time for (a) polymerization of bulk Ceraset (—) and bulk VL20 (---) and (b) 1:1 weight fraction of tetrathiol in Ceraset (—) and 1:5 weight fraction of tetrathiol in VL20 (---). VL20 samples irradiated at 57 mW/cm^2 using 6 wt % DMPA for bulk VL20 polymerization and 0.02 wt % DMPA for tetrathiol-VL20 polymerization. Ceraset samples irradiated at 20 mW/cm^2 using 1.3 wt % DMPA for bulk Ceraset and 0.7 wt % DMPA for thiol-Ceraset.

Table 1. Final Double Bond Conversion, Thiol Conversion, and Initial Polymerization Rate in Four Mixtures Having Varying Weight Ratios of VL20/Tetrathiol^a

weight ratio of VL20/Tetrathiol	final double bond conversion (%)	final thiol conversion (%)	initial polymerization rate (1/s)
8:1	34	100	0.014
5:1	55	100	0.035
2.7:1	100	100	0.041
1:0	0	—	0.00

^aPolymerization kinetics of these mixtures were studied under identical conditions: 0.02 wt % of photoinitiator (DMPA) and irradiation at 2 nW/cm^2 . Under these curing conditions, no double bond conversion was observed in pure VL20 system even after exposure for 1 hour.

contact lithography,¹⁸ however, factors such as mask quality, debris between the mask and substrate, and development conditions decrease the practical resolution. This processing route for SiCN is well-suited for low-cost, large-scale fabrication of MEMS. Photomasks for lithography were designed using DW-2000 layout editor software (www.designnw.com). The designs were then printed on transparencies using a high-resolution printer. A thin layer of Teflon was coated on the photomask to facilitate easy removal of patterned structures from the mask after the exposure.⁷

The polymer structures were pyrolyzed in a nitrogen atmosphere to convert the polymer into the ceramic, a silicon

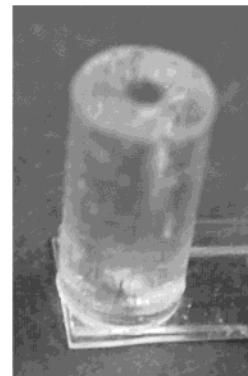


Figure 4. Side view of photopolymerized cylindrical structure 6 mm long with an outside diameter of 3.2 mm. Structure was made from a 1:5 weight ratio of tetrathiol and VL20 and 0.02 wt % DMPA, with curing from the top.

carbon nitride (SiCN) material. The pyrolysis procedure consisted of heating the polymer sample at a rate of $10\text{ }^\circ\text{C}/\text{min}$ to $400\text{ }^\circ\text{C}$, holding at $400\text{ }^\circ\text{C}$ for 1 h, further heating at a rate of $1\text{ }^\circ\text{C}/\text{min}$ to $700\text{ }^\circ\text{C}$ and holding at $700\text{ }^\circ\text{C}$ for 4 h, and, finally, heating at a rate of $1\text{ }^\circ\text{C}/\text{min}$ to $1000\text{ }^\circ\text{C}$ and holding at $1000\text{ }^\circ\text{C}$ for 4 h. The sample was then cooled at a rate of $1\text{ }^\circ\text{C}/\text{min}$ to ambient temperature.

Results and Discussion

We have polymerized both dithiol and tetrathiol monomers with the vinyl-containing preceramic monomers VL20 and Ceraset. Photopolymerization of these preceramic monomers via a thiol-ene mechanism drastically improves the polymerization kinetics without any apparent degradation of the final ceramic properties. Increased polymerization rate and reduced photoinitiator concentrations are due to changing photopolymerization mechanism from homopolymerization of relatively unreactive vinyl moieties to a very reactive thiol-ene step growth mechanism.

To demonstrate these results, VL20 and Ceraset monomers were photopolymerized with the radical photoinitiator DMPA, and the observed polymerization kinetics are presented in Figure 3. It was found that the addition of thiol monomers to VL20 and Ceraset increases the polymerization rate by several orders of

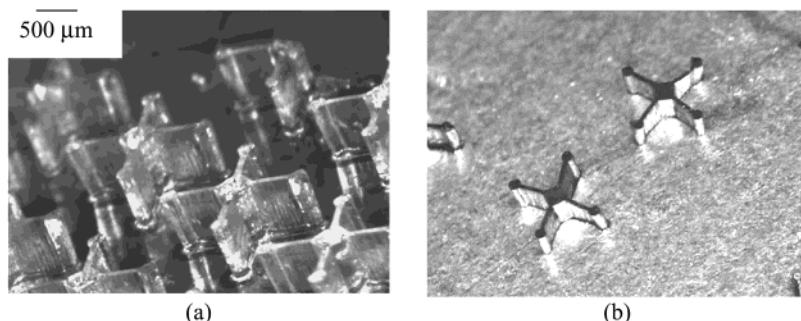


Figure 5. Photopolymerized electrostatic actuator structures from 15 wt % dithiol in Ceraset with 0.2 wt % DMPA: (a) polymer structures and (b) structures after pyrolysis. An aspect ratio of 15:1 was obtained in these structures.

magnitude. Without the thiol, the bulk VL20 monomer with 6 wt % added photoinitiator reaches 35% conversion in approximately 400 s, with the final conversion being 40% after 1200 s of exposure. However, with the addition of only 16 wt % tetrathiol monomer to the bulk VL20 system and in the presence of only 0.02 wt % DMPA, 55% double bond conversion is attained in approximately 2 s. This mixture represents a stoichiometric ratio of 1.85:1 of vinyl to thiol functional groups. The initial polymerization rate, and final conversion of thiol and ene functionalities achieved in these thiol-VL20 systems for varying ratios of thiol:VL20 are presented in Table 1. In contrast, Ceraset with 1.3 wt % added photoinitiator and without thiol requires nearly 300 s to achieve 25% conversion, with the final conversion being 34% after 1200 s. With the addition of 50 wt % tetrathiol monomer to the system, 50% conversion is attained in approximately 2 s utilizing only 0.7 wt % DMPA.

In photopolymerizations, the absorption of irradiating light is primarily due to the photoinitiator molecule, and thus the photoinitiator concentration is the primary factor influencing achievable curing depths.¹⁹ As seen in Figure 3, very low photoinitiator concentrations in thiol-ene systems still result in very high cure rates. Thus, these systems have a very high optical transparency, which facilitates the formation of thick structures. For example, a masked and photocured tetrathiol-VL20 system with 0.02 wt % DMPA was successfully performed, maintaining the masked pattern in a sample with a thickness of 6 mm as shown in Figure 4.

The high cure depths in thiol-ene systems also facilitate achievement of higher aspect ratios. The largest cure depth obtained from the bulk Ceraset and 5 wt % DMPA solution has been observed to be approximately 700 micrometers. In contrast, a cure depth of 1200 μ m was achieved for a device 80 μ m wide from the dithiol-Ceraset solution with 0.2 wt % DMPA, having an aspect ratio of 15:1, as shown in Figure 5. The photopolymerized structures were made on a silicon wafer and later transferred onto a graphite foil for the pyrolysis step.

Mass loss and volume shrinkage for the tetrathiol-VL20 and homopolymerized VL20 systems are indicated in Table 2. Polymer structures made from thiol-ene reactions exhibit similar shrinkage and slightly higher mass loss during the pyrolysis step, relative to that of bulk VL20 or Ceraset structures. The presence of thiol

Table 2. Average Mass Loss and Linear Shrinkage Measurements (relative to the sizes and masses of the structures immediately after photopolymerization) for VL20 and Tetrathiol-VL20 Systems, during Pyrolysis

	Tetrathiol-VL20	VL20
mass loss	$39.1\% \pm 1.0\%$	$34.2\% \pm 1.8\%$
linear shrinkage	$32.6\% \pm 1.6\%$	$34.9\% \pm 2.2\%$

^a The Tetrathiol-VL20 system was cured with 0.02 wt % DMPA, whereas the VL20 system was cured with 6 wt % DMPA. Values are an average for measurements on six test samples.

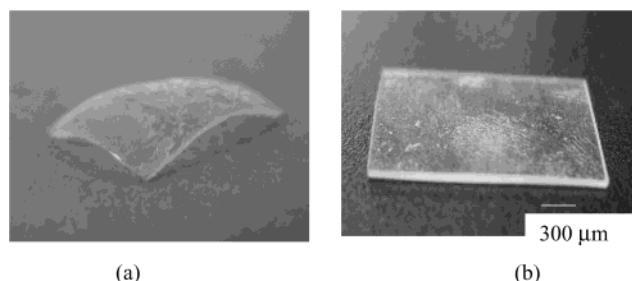


Figure 6. Image showing warping of polymer films formed from (a) VL20 and (b) 1:5 weight ratio of thiol-VL20 mixture. 6 wt % of DMPA was used in curing of pure polysilazane, whereas 0.02 wt % DMPA was used in curing the thiol-VL20 system.

in the thiol-VL20 system might cause one to expect a higher weight loss in these systems. The smaller than expected difference in the overall ceramic yield is due to a larger amount of uncured monomers being present in polymers formed from the polymerization of pure preceramic monomers. Enhanced mass loss occurs because of evaporation of residual uncured monomers and small-molecular-weight oligomers during pyrolysis. The step growth mechanism results in a lower concentration of residual monomers and oligomers both due to the step growth mechanism and higher conversion, leading to a reduction in mass loss. Comparable shrinkage and slightly higher mass loss indicates the thiol-VL20 system has a greater reduction in its density as compared to those formed from the pure VL20 system. Interestingly, the mechanical properties do not appear to be negatively impacted.

In addition to improved kinetics, utilizing a thiol-ene polymerization results in the ability to make structures that do not warp. Structures from photopolymerization of pure polysilazane monomers (both VL20 and Ceraset) exhibit significant warping.⁴ Figure 6 compares the shape of similar films formed by homopolymerization of VL20 and by polymerization of VL20 with 16 wt % tetrathiol. The structure made from thiol-VL20 is flat

relative to the bulk polymerized VL20 structures. Due to their step growth mechanism and the concomitant gel point delay, thiol-ene systems exhibit significantly less stress development as compared to traditional vinyl homopolymerization systems. The lowered stress in thiol-ene systems results in reduced warping in the polymer structures. Elimination of warping in these devices is obviously highly desirable for integration of these structures into other microstructures or devices.

Conclusions

The polymerization rate of vinyl-containing preceramic monomers VL20 and Ceraset is increased by several orders of magnitude upon addition of thiol monomers to the system. Increased polymerization rates are due to involvement of these monomers in a thiol-ene step-growth radical polymerization mechanism rather than a radical chain growth mechanism. The very

low initiator concentrations required for polymerization of these systems facilitate the formation of thick structures with high aspect ratios. Warping, which has been observed in the structures formed through photopolymerization of pure ceramic precursors, is largely eliminated by copolymerization with thiol monomers. In the pyrolysis step, mass loss and linear shrinkage of the structures formed using this novel reaction scheme are similar to those observed in structures made from pure polysilazane systems.

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