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Rate Mechanisms of a Novel Thiol-ene Photopolymerization Reaction

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Summary: A novel thiol-ene photopolymerization reaction involving copolymerization of tetrathiol monomer with vinyl silazane is experimentally characterized and is modeled successfully. The overall polymerization rate is found to be controlled by the ratio of the propagation to chain transfer kinetic parameters. The polymerization rate of this mixture, in the presence of added photoinitiator, is approximately first order in ene functionality and is independent of thiol functional group concentration. Initiation rates in this system, when cured utilizing a light centered around 365 nm light, and in the presence of no added photoinitiator, are shown to be proportional to the ene monomer concentration. When the mixture is polymerized utilizing light centered at 254 nm light, and without photoinitiator, the initiation rates are proportional to the thiol monomer concentrations. This novel reaction scheme is further utilized to form ultra rapidly polymerizable polymer derived ceramic structures with high aspect ratios.

Keywords: ceramics; crosslinking; initiatorless; modeling; thiol-ene

Introduction

The photopolymerization field has been one of the most rapidly growing industries in the past decade. Currently, this exciting field is dominated by acrylic photopolymerizations. However, thiol-ene systems exhibit several unique properties associated with their curing kinetics and material properties, making them a primary focus of recent research. Thiol-ene photopolymerizations exhibit desirable properties similar to acrylic polymerizations including solventless processing, spatial and temporal control of the polymerization, and good mechanical properties.[1-6] Further, these systems exhibit distinct advantages over acrylic systems like

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insensitiveness to oxygen inhibition[2,7-9], delayed gelation[3], and rapid curing in the presence of little or no added photoinitiator.[8,10,11] However, for commercial applications, thiol-ene systems have achieved limited utilizaton as compared to acrylates owing to their dark intsability over extended periods of time and the odor associated with the thiol monomer. Presently, extensive studies are being conducted in our lab to improve the dark stability and odor of the thiol-ene monomer mixtures.

Thiol-ene photopolymerizations are step growth radical polymerizations based on the addition of a thiol to a vinyl functional group. The step growth propagation mechanism of the thiol-ene photopolymerization was first proposed by Kharasch in 1938.[12] As outlined below, the reaction proceeds via propagation of a thiyl radical (or sulfenyl radical) through the vinyl functional group. The propagation step is followed by chain transfer of the radical to the thiol functional group, regenerating a thiyl radical. These successive steps of propagation and chain transfer serve as the basis for the thiol-ene photopolymerization reaction. The final material properties of a thiol-ene cured system are highly influenced by the monomer formulation. Highly crosslinked polymer networks result when multifunctional monomers with an average functionality greater than two are utilized.

Propagation $RS\bullet + R'CH = CH_2 \xrightarrow{k_{pSC}} R'C\bullet H - CH_2SR$ step 1

Chain Transfer $R'C\bullet H - CH_2SR + RSH \xrightarrow{k_{CT}} R'CH_2 - CH_2SR + RS\bullet$ step 2

The molecular weight and microstructural evolution encompassed in the step growth polymerization are quite distinct from those observed in chain growth acrylic polymerizations. In chain growth polymerizations, even at low double bond conversions, high molecular weight polymers are present along with uncured residual monomers, leading to low gel point conversion and the formation of a heterogeneous structure. On the other hand, in step growth polymerizations, the molecular weight builds up much more slowly, leading to higher gel point conversion and the formation of a homogenous network.[3,13] In network forming acrylic photopolymerization reactions, the study of polymerization kinetics is often complicated by early gel point conversions and diffusion limited reactions. However, the high gel point conversions and the delayed onset of the diffusion limited reactions in thiol-ene systems render the study of polymerization kinetics much more facile.

Thiol-ene photopolymerizations also exhibit a great versatility in their chemistry. A wide variety of vinyl and thiol chemistries are radically curable via a thiol-ene mechanism, thereby imparting specific material properties to the final cured product.[11] The unique advantages of thiol-ene curable systems coupled with their chemical versatility make them attractive for various applications.

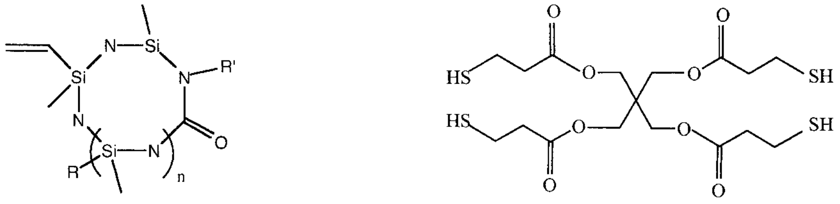
As a specific example of chemical versatility, a novel polymerization scheme based on the thiol-ene photopolymerization was used to form rapidly polymerizable polymer derived ceramic structures with high aspect ratios. Although polymers, glass, and silicon are commonly used materials for making MEMS devices, these materials cannot be used for applications that require high temperature or other harsh environmental resistance. Ceramics, which have superior chemical and high temperature resistance, are an excellent candidate for these types of applications, which include micro combustors, optical MEMS, and heat exchangers.

A considerable number of investigations have been conducted on thiol-ene photopolymerizations.[1-3,10,12] However, the various aspects of these polymerizations including overall reaction order[1-3,10,14], dependence of polymerization rate on monomer concentrations, initiatorless polymerization[8,10,11], and dark reaction[15-18] are not well understood. This work attempts to enhance the current understanding of the fundamental thiol-ene photopolymerization mechanism. We explore the dependence of polymerization rate on monomer concentration and overall reaction order for thiol-vinyl silazane systems both in the presence and in the absence of added photoinitiator molecules. The mechanistic study of this exciting novel thiol-ene polymerization is further supplemented with a novel route to form polymer derived ceramic structures.

Experimental

Materials

The monomers, pentaerythritol tetra-(3-mercaptopropionate) (tetrathiol) and VL20 (vinyl silazane), were donated by Bruno Bock (Marschacht, Germany) and Kion International (Columbus, OH), respectively. The photoinitiator, 2,2-dimethoxy-2-phenylacetophenone (DMPA), was purchased from Ciba-Geigy (Hawthorne, NY). All monomers and the photoinitiator were used as received. Monomer structures used in this study are indicated in Figure 1.



(a) vinyl silazane (n = 1 – 20) (b) thiol

Figure 1. Chemical structures of monomers utilized in this work (a) VL20, and (b) tetrathiol.

Methods

FTIR studies were conducted using a Nicolet 750 Magna FTIR spectrometer with a KBr beamsplitter and an MCT/A detector. Series scans were recorded, taking spectra at the rate of approximately 2 scans per second. The FTIR sample chamber was continuously purged with dry air. Samples were illuminated until the reaction is completed, as indicated by the functional group absorption peaks remaining constant. Thiol functional group conversion was monitored using the S-H absorption peak at 2570 cm^{-1}. Vinyl silazane conversion was monitored by using the double bond absorption peaks at 1593 cm^{-1}.

Monomer samples were laminated between NaCl salt crystals in an horizontal transmission apparatus.[19] Polymerizations with 365 nm light were initiated with a EXFO Acticure light source (EXFO, Mississauga, Ontario) with a 320-500 nm filter. Polymerizations with 254 nm were initiated with a PenRay 5.5 watt low pressure mercury arc lamp (Ultra-Violet Products, Upland, CA) with primary output at 254 nm. Irradiation intensities were measured with an International Light, Inc. Model IL1400A radiometer (Newburyport, MA).

Photopatterned microstructures were made utilizing contact lithography. In contact lithography, the monomer solution is exposed to UV illumination through a mask placed in contact with the monomer solution, thereby limiting diffraction. Photomasks were designed using DW-2000^{TM} layout editor software (www.designw.com), and the designs were printed on transparencies using a high resolution printer. A thin layer of Teflon was coated on the photomask to facilitate easy removal of the patterned structures from the mask after exposure. [20]

Results and Discussion

A model, based on the fundamental thiol-ene photopolymerization scheme, was developed for better understanding and prediction of thiol-ene photopolymerizations under various cure conditions. This model, based on fundamental polymerization steps like initiation, propagation, and termination, also assists in determining the relative importance of various kinetics parameters. Initiation rate is governed by equation 1, and is calculated based on standard values for DMPA(f - efficiency, ε - molar absorptivity =150 L/mol-cm for 365nm light, [I] - initiator concentration, I_O - light intensity, λ - wavelength, N_{AV} - Avogadro's number, h - Planck's constant, c - speed of light).[13,21] A mass balance was performed on the four reacting specie in the system. While thiol and vinyl monomer concentrations are accounted for by equations 2 and 3, the radical balances are presented in equations 4 and 5. Equation 2 represents the thiol monomer balance, wherein the thiol monomer is consumed via the chain transfer of carbon radical to thiol monomer. The ene monomer balance, which is governed by equation 3, accounts for consumption of the monomer by propagation through thiyl radicals. The thiyl and vinyl radical balances take into consideration the initiation and termination, as well as generation or consumption of radicals due to chain transfer and propagation. During the initiation step wherein the DMPA cleaves into two primary radicals, it is assumed that the primary radicals are equally likely to react to form either a carbon radical or a thiyl radical. Thiol-acrylate photopolymerizations also can be modeled (equation 6) by accounting for the ene homopolymerization in the ene monomer balance. In the monomer balance equations, consumption of monomers by initiation is assumed negligible.

$$R_i = -\frac{d[I]}{dt} = \frac{2.303 f\varepsilon[I]I_0\lambda}{N_{AV}hc} \qquad (1)$$

$$\frac{d[SH]}{dt} = -k_{CT}[SH][C\bullet] \qquad (2)$$

$$\frac{d[C=C]}{dt} = -k_p[C=C][S\bullet] \tag{3}$$

$$\frac{d[S\bullet]}{dt} = R_i - R_t(S\bullet) + k_{CT}[SH][C\bullet] - k_p[C=C][S\bullet] \tag{4}$$

$$\frac{d[C\bullet]}{dt} = R_i - R_t(C\bullet) - k_{CT}[SH][C\bullet] + k_p[C=C][S\bullet] \tag{5}$$

$$\frac{d[C=C]}{dt} = -k_{pSC}[C=C][S\bullet] - k_{pCC}[C=C][C\bullet] \tag{6}$$

$$R_t(S\bullet) = 2k_{t1}[S\bullet]^2 + k_{t2}[S\bullet][C\bullet] \tag{7}$$

$$R_t(C\bullet) = k_{t2}[S\bullet][C\bullet] + 2k_{t3}[C\bullet]^2 \tag{8}$$

Termination of these radical species is assumed to be by radical-radical bimolecular termination and are given by equations 7 and 8. All the radicals are assumed equally likely to terminate, and hence the termination kinetic constants for all radical-radical recombination are taken to be equal. The kinetic constants in all the model equations are assumed to remain constant throughout the polymerization. In traditional acrylic chain polymerizations, diffusion limited kinetics and early gel point conversions cause a dramatic change in kinetic constants.[23,24] However, as diffusion limited reactions dominate only at high conversions in step-growth, thiol-ene polymerizations, an assumption of constant rate constants is well-founded. Using the pseudo steady-sate assumption, the model equations for the thiol-ene system were solved analytically to obtain an expression for the polymerization rate.

$$R_p = \sqrt{\frac{R_i}{2k_t}}\frac{1}{\sqrt{\frac{1}{\left(k_{pS-C}[C=C]\right)^2} + \frac{1}{\left(k_{CT}[SH]\right)^2} + \frac{1}{\left(k_{pS-C}k_{CT}[C=C][SH]\right)}}} \tag{9}$$

Examination of the analytical expression clearly demonstrates that the polymerization rate and reaction order dependence are greatly influenced by $K_{pS-C}[C{=}C]/K_{CT}[SH]$, which is the product of the ratio of vinyl to thiol monomer concentrations with the ratio of propagation to chain transfer kinetic parameters. For a given thiol-ene system, (maintaining a constant K_{pS-C}/K_{pC-C}), manipulation of [CC]/[SH] leads to change in the polymerization rate. The magnitude of this change in polymerization rate with changes in monomer concentration yields estimate of the relative importance of propagation to chain transfer kinetic parameters. Here, two limiting cases are presented to illustrate reaction order dependence on the ratio of propagation to chain transfer kinetic parameters. In case 1, where the propagation kinetic parameter is very large compared to the chain transfer kinetic parameter, the polymerization rate simplifies to be dependent only on thiol concentration and is independent of the ene concentration (equation 10). For this case, the normalized polymerization rate of the thiol functionaility is completely independent of monomer concentrations, while the normalized polymerization rate of vinyl functionality is dependent on the concentrations of the monomers (equation 11). The thiol group and vinyl group conversions are represented by X_{SH} and X_{CC}, respectively. In case 2, for much greater values of chain transfer parameter than the propagation kinetic parameter, the overall polymerization rate transforms such that the rate is nearly independent of thiol monomer concentration and is proportional to the ene monomer concentration (equation 12). In this case, while the normalized polymerization rates of the thiol monomer are independent of the monomer concentration, the normalized polymerizaion rates of the ene monomer are independent of monomer concentrations (equation 13). Specifically, the rate equation transforms such that chain transfer is the rate limiting step when the propagation kinetic parameter is large compared to the chain transfer parameter. Similarly, when the chain transfer coefficient is much greater than the propagation coefficient, propagation is the rate limiting step.

$$R_p = \sqrt{\frac{R_i}{2k_t}}k_{CT}[SH] \qquad \text{for } k_{pSC} \gg k_{CT} \qquad (10)$$

$$\text{i.e.,} \quad \frac{dX_{SH}}{dt} = \sqrt{\frac{R_i}{2k_t}}k_{CT}(1 - X_{SH}) \quad \text{and} \quad \frac{dX_{cc}}{dt} = \sqrt{\frac{R_i}{2k_t}}k_{CT}\left(\frac{[SH]_0}{[C=C]_0} - X_{CC}\right) \qquad (11)$$

$$R_p = \sqrt{\frac{R_i}{2k_t}}k_{pSC}[C=C] \qquad \text{for } k_{CT} \gg k_{pSC} \qquad (12)$$

$$\text{i.e.,} \quad \frac{dX_{SH}}{dt} = \sqrt{\frac{R_i}{2k_t}}k_{pS\text{-}C}\left(\frac{[C=C]_0}{[SH]_0} - X_{SH}\right) \quad \text{and} \quad \frac{dX_{cc}}{dt} = \sqrt{\frac{R_i}{2k_t}}k_{pS\text{-}C}(1 - X_{CC}) \qquad (13)$$

In previous work, experiments were conducted utilizing a tetrathiol monomer with a variety of vinyl chemistries to determine the overall reaction order of the system and the dependence of rate on individual monomer concentrations. [24,25] Vinyl ether, allyl ether, norbornene, and acrylate monomers were polymerized with tetrathiol monomer with initially 1:1, 1:2 ,and 2:1 stoichiometric ratios of thiol to ene functional groups. Kinetic features of these systems were accurately predicted by fitting the ratio of propagation to chain transfer kinetic parameters. The absolute polymerization rates were then fit to the experimental rates by changing the propagation and chain transfer kinetic parameters and keeping $K_{pS\text{-}C}/K_{pC\text{-}C}$ constant.

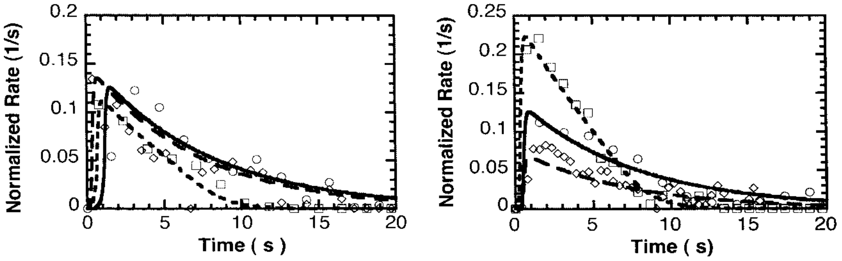
In previous work, [24,25] the ratio of propagation to chain transfer parameters, and the reaction order dependence on monomer concentrations for thiol-vinyl ether, thiol-allyl ether, thiol-norbornene, and thiol-acrylate polymerizations were obtained. Results are presented in Table 1. For the thiol-vinyl ether and thiol-norbornene systems, the polymerization rate is nearly equivalently affected by both the thiol and ene functional group concentrations, with the polymerization rate scaling to one half power in both concentrations. In the thiol-allyl ether system, chain transfer is the rate limiting step, and the rate is proportional to the thiol monomer concentration. The polymerization rate in thiol-acrylate polymerizations scales with the 2/5 power in thiol concentration and the 3/5 power in double bond concentration.

Table 1. Ratio of propagation to chain transfer kinetic parameters, and polymerization rate dependence on thiol and ene functional group concentrations for acrylate, allyl ether, vinyl ether, and norbornene polymerized with tetrathiol. Values for polymerization rate scaling are only valid for stoichiometric systems.

		$R_p \propto [SH]^a[C=C]^b$	
Functional Group	k_p/k_{CT}	a	b
acrylate	13	0.4	0.6
allyl ether	10	1	0
vinyl ether	1.2	0.5	0.5
norbornene	1	0.5	0.5

Here, we present experimental polymerization rates and model predictions for a thiol-vinyl silazane system (Figure 2). Vinyl silazane is a preceramic monomer, which is extensively utilized to form polymer derived ceramics.[20,28,29] Later in the paper, the thiol-vinyl silazane system is shown to be a vastly superior system to form polymer derived ceramics, primarily because of the unique advantages afforded by the step growth thiol-ene mechanism. Observation of polymerization rates of thiol-vinyl silazane copolymerization clearly indicates that the polymerization rate of vinyl silizane monomer is unaffected by the change in stoichiometric concentrations of monomers; however, changes in the monomer concentrations significantly affect the normalized polymerization rates of the thiol functional group.

The observed normalized polymerization rates for the thiol-vinyl silazane system compare well with those observed in case 2 (equation 12 and 13), demonstrating that propagation is the rate limiting step in this system. Here, the overall rate is proportional to ene monomer concentration, that is $R_p \;\alpha\; [SH]^0[C=C]^1$. The experimentally observed rates in this system were predicted accurately by modeling the ratio of propagation to chain transfer parameter as 0.2.



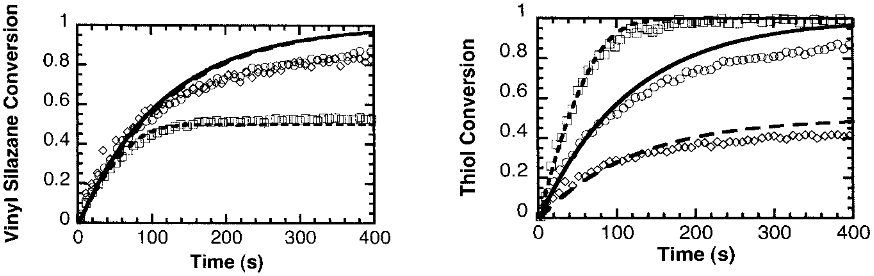
(a) vinyl silazane (b) thiol

Figure 2. Model predictions and experimental data for normalized polymerization rates (s^{-1}) of tetrathiol and vinyl silazane photopolymerizations. (a) Vinyl silazane normalized polymerization rates for initially 1:1 (2.35 mol/L) (O,—), 2:1 (3.84:1.92 mol/L) (◊,– –), and 1:2 (1.33:2.65 mol/L) (□,---) ratios of thiol to vinyl silazane functional groups. (b) Thiol functional group polymerization rates (s^{-1}) for the same polymerizations (initially 1:1 (O,—), 2:1 (◊,– –), and 1:2 (□,---) ratios of functional groups). Samples contain 0.1 wt% DMPA and are irradiated at 2.0 mW/cm^2. Kinetic parameters for modeling are k_p=5.0x10^4 L/mol-s, k_{CT}=2.5x10^5 L/mol-s, k_{t1}, k_{t2}, k_{t3}= 1x10^6 L/mol-s.

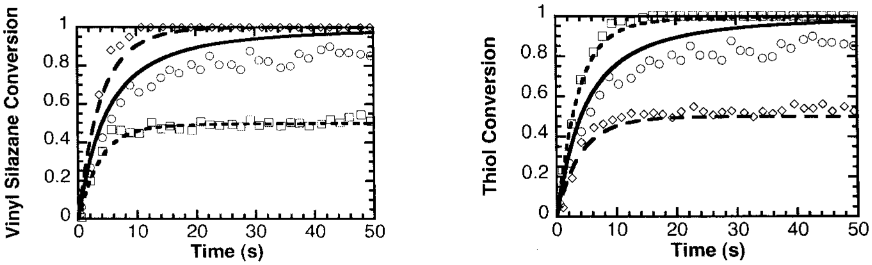
Rate Mechanism for Initiatorless Polymerization

Further, experiments were performed to investigate the self-initiation mechanism of the novel thiol-vinyl silazane system in the absence of added photoinitiator molecules. The monomer system was irradiated with UV light centered around both 365 nm and 254 nm. Polymerization studies were conducted on mixtures initially having 1:1, 2:1, and 1:2 stoichiometric ratios of thiol to ene functionalities, but containing no initiator. Results of the polymerization kinetic studies and the modeling predictions for this system are presented in Figure 3.

In the system polymerized with 365 nm light, kinetic rates are well predicted by assuming the initiation rate is proportional to the ene functional group concentration. Earlier in this article, the rate in thiol-vinyl silazane systems was shown to be dependent only on the ene functional group



(a) Irradiated with 365 nm light (b) Irradiated with 365 nm light



(c) Irradiation at 254 nm Light (d) Irradiation at 254 nm light

Figure 3. Model predictions and experimental data for tetrathiol and vinyl silazane mixtures irradiated using 365 nm light (a) and (b) at an intensity of 50 mW/cm^2 , and at 254 nm light (c) and (d) with an irradiation intensity of 0.05 mW/cm^2. (a) and (c) Functional group conversion as a function of time of vinyl silazane for initially 1:1 (2.35 mol/L) (O,—), 2:1 (3.84:1.92 mol/L) (◊,– –), and 1:2 (1.33:2.65 mol/L) (□ ,---) ratios of thiol to vinyl silazane functional groups. (b) and (d) Thiol functional group conversion versus time for initially 1:1 (O,—), 2:1 (◊,– –), and 1:2 (□ ,---) ratios of functional groups. While, model predictions for monomers irradiated with 365 nm light are obtained by setting the initiation rate proportional to ene monomer concentration, the model predictions for the mixtures illuminated at 254 nm light are based on initiation rates being proportional to the thiol functional group concentrations. Kinetic parameters for modeling are similar to those used in system with initiator, i.e., k_p=5.0x10^4 L/mol-s, k_{CT}=2.5x10^5 L/mol-s, k_{t1}, k_{t2}, k_{t3}= 1x10^6 L/mol-s.

concentration, i.e., $R_p \; \alpha \; [C=C]$. Values of the propagation, chain transfer, and termination kinetic parameters that were employed to predict polymerization kinetic behavior in systems having added photoinitiator were utilized in modeling systems having no added photoinitiator. The model accurately predicts experimental initiatorless polymerization kinetics by setting $R_p \; \alpha \; [C=C]$. The overall initiatorless polymerization rate is independent of thiol monomer concentration, and is given by $R_p \; \alpha \; [C=C]^{\frac{3}{2}}$.

In the system illuminated with 254 nm light, experimental rates are consistent with model predictions when the initiation rate is assumed to be proportional to the thiol monomer concentration. The overall initiatorless kinetics are proportional to the thiol monomer concentration to the half power and the ene monomer has a first order dependence, i.e., $R_p \alpha [C=C][SH]^{\frac{1}{2}}$. This dependence of the initiation rates on the ene and thiol monomer concentrations at 365 nm and 254 nm light, respectively, has been previously observed for other thiol-ene systems.[26] For irradiation with 365 nm light, it is hypothesized that the excitation of ene monomers followed by interaction with thiol functional groups leads to generation of radical centers. The mechanism of initiation at 254 nm light is attributed to direct cleavage of thiol functionalities, giving rise to radical centers. These systems cure extremely rapidly in the presence of 254 nm light as compared to when initiated by a 365 nm light.

Polymer Derived Ceramics

The chemical versatility of thiol-ene polymerization chemistry coupled with the unique properties associated with their mechanism is utilized to form polymer derived ceramic structures with high aspect ratios and with controlled shape and structure.[27] Photopolymerization is a rapid, relatively inexpensive route to form highly crosslinked structures from liquid monomers. It also offers spatial and temporal control of the polymerization. Photopolymerization further enables the use of photolithography to form complex three-dimensional structures.

Formation of polymer microstructures using photopolymerization of preceramic vinyl monomers, followed by its pyrolysis has been shown to form ceramic structures.[20,28,29] However, this reaction is extremely inefficient relative to typical radical photopolymerizations.[27] Even in the presence of large amounts of added photoinitiator, these systems cure very slowly relative to typical acrylic or methacrylic photopolymerizations. The presence of photoinitiators in large quantities, which are necessary for appreciable speeds of polymerization, severely limits the attainable curing depths, due to light attenuation by the photoinitiator molecules.

As thiol-ene systems cure rapidly even in the presence of small amounts of photoinitiators, the limitations of slow cure speeds, high initiator concentration, and high cure depths are overcome by utilizing this novel reaction scheme. To demonstrate these results, photopolymerization experiments were carried out with vinyl silazane monomer in the presence of the radical photoinitiator DMPA. These polymerizations are compared to photopolymerization of thiol-vinyl silazane systems. The amount of photoinitiator used, cure time, and final double bond conversion of the bulk vinyl silazane monomer and of the thiol-vinyl silazane system are presented in Table 2. Addition of thiol monomer to the vinyl silazane monomer increased the polymerization rates by several orders of magnitude. The addition of a thiol monomer to the vinyl preceramic monomers changes the predominant polymerization behavior from a pure chain growth mechanism to a thiol-ene step growth mechanism, thereby leading to an increased rate and reduction in the necessary photoinitiator concentration. Photoinitiators are primarily responsible for light attenuation in photopolymerization reactions. Hence, lower photoinitiator concentrations, which are afforded by the thiol-vinyl silazane systems, lead to higher optical transparency of the system and hence greater achievable cure depths.

The polymer structures formed from this novel reaction were pyrolysed in a nitrogen atmosphere to convert the polymer into the ceramic, a silicon carbon nitride (SICN) material. In the pyrolysis procedure, the polymer sample is heated at a rate of 10 ^{0}C /min to 400 ^{0}C, and held constant for one hour. The sample is then heated at a rate of 1^{0}C /min to 700 ^{0}C and held at 700 ^{0}C for one hour. Finally, the sample is heated at a rate of 1 ^{0}C /min to 1000 ^{0}C , and held at this temperature for four hours. The sample is then cooled at a rate of 1 ^{0}C /min to ambient temperature.

Table 2. Final double bond conversion, cure time, and amount of photoinitiator used in pure preceramic monomer and thiol-ene polymerization mixture containing a 1 : 5 weight ratio of thiol : preceramic monomer. Samples were irradiated at 57 mW/cm^2.

	Cure Time (s)	Double Bond Conversion	Wt% photoinitiator (DMPA) used
Bulk VL20	1200	40 %	6.0
Tetrathiol-VL20 (weight ratio 1:5)	2	55 %	0.02

Figure 4 shows a structure made from tetrathiol-VL20, before and after pyrolysis. In the pyrolysis step, the structures formed through this novel reaction scheme exhibit similar shrinkage and mass loss values as displayed by those made from pure vinyl silazane monomers. Further, the addition of thiol monomers does not appear to cause any apparent degradation of the final ceramic properties.

(a) (b)

Figure 4. Ceramic structures formed by the pyrolysis of polymer structures made from tetrathiol and VL20 (1 : 5 weight ratio), with 0.02 wt% DMPA (a) Polymer structure before pyrolysis and (b) Ceramic structure after pyrolysis. The polymer structure has channel dimensions of 600 microns, and the channels are dyed for purposes of clarity.

Conclusion

Thiol-ene photopolymerization kinetics and the rate limiting step for the thiol-vinyl silazane system and experimentally characterized and successfully modeled. The overall polymerization rate for this system is found to be proportional to the ene monomer concentration, and independent of the thiol monomer concentration, i.e., $R_p \;\; \alpha \;\; [C = C]$. The observed kinetic behavior is predicted by using propagation as the rate limiting step, which is modeled by setting the ratio of the propagation to the chain transfer parameters equal to 0.2. Polymerization kinetics of thiol-vinyl silazane mixtures without added photoinitiator were also studied, utilizing light centered at 365nm light and 254 nm light. For curing under 365 nm light, model predictions were consistent with the experimental kinetics when the initiation rate is assumed to be proportional to the ene functional group concentration, and for 254 nm light the model predicted the initiation rates to be proportional to the thiol monomer concentration. The novel properties afforded by this system are exploited for a novel application to high aspect ratio polymer derived ceramics.

Acknowledgments

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