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Complete List of Authors:	Bongiardina, Nicholas; University of Colorado Boulder College of Engineering and Applied Science, Materials Science and Engineering Soars, Shafer; University of Colorado Boulder, Chemistry Podgórski, Maciej; MCS University, Polymer Chemistry Bowman, Christopher; University of Colorado at Boulder, Chemical and Biological Engineering

Radical-Disulfide Exchange in Thiol-Ene-Disulfidation Polymerizations

Nicholas J. Bongiardina[1], Shafer M. Soars[2], Maciej Podgorski[3,4], Christopher N. Bowman[1,4,*]

[1]*Material Science and Engineering Program, University of Colorado, Boulder, Colorado 80309, United States.*

[2]*Department of Chemistry, University of Colorado, Boulder Colorado 80309*

[3]*Department of Polymer Chemistry, Institute of Chemical Sciences, Faculty of Chemistry, Maria Curie-Sklodowska University, M. Curie-Sklodowska Sq. 5, Lublin 20-031, Poland*

[4]*Department of Chemical and Biological Engineering, University of Colorado at Boulder, Colorado 80309, United States.*

* Corresponding author: christopher.bowman@colorado.edu

ABSTRACT

Radical-disulfide exchange reactions in thiol-ene-disulfide networks were evaluated for several structurally distinct thiol and disulfide containing monomers. A new dimercaptopropionate disulfide monomer was introduced to assess how different disulfide moieties affect the exchange process and how the dynamic exchange impacts polymerization. The stress relaxation rate for the disulfides studied herein was highly tunable over a narrow range of network compositions, ranging from 50% relaxation over 10 minutes to complete relaxation over a few seconds, by changing the thiol-disulfide stoichiometry or the disulfide type in the monomer. The thiol/disulfide monomer pair was shown to have significant influence on how radical-disulfide exchange impacts the polymerization rate, where pairing a more stable radical forming thiol (e.g. an alkyl thiol) with a less stable radical-forming disulfide (e.g. a dithioglycolate disulfide) reduces the rate of the thiol-ene reaction by over an order of magnitude compared to the case where those two radicals are of the same type. The variations in rates of radical-disulfide exchange with dithioglycolate and dimercaptopropionate disulfides had a significant impact on stress relaxation and polymerization stress, where the stress due to polymerization for the final dimercaptopropionate network was about 20% of the stress in the equivalent dithiogylcolate network under the same conditions. These

studies provide a fundamental understanding of this polymerization scheme and enable its implementation in materials design.

INTRODUCTION

Polymer networks containing dynamic bonds are a growing class of smart and responsive materials known as covalent adaptable networks (CANs)[1, 2]. A diverse and continually expanding set of applicable chemistries and dynamic bonds enable unprecedented development of materials with the viscoelastic characteristics of thermoplastics with the material properties and performance of thermosets. This vast array of dynamic bonds provides the tools to control the rheological behavior of polymer networks by tuning the particular functional groups, catalysts, and their respective concentrations, thereby determining rates of bond reconfiguration.

Disulfides, considered as one of the most common type of dynamic bonds and having been used in industrial polymer processing since the invention of vulcanized rubbers[3-5], play a crucial role in protein folding[6] and have been a known class of reconfigurable bonds since the 1950's[7]. Disulfides are responsive to a variety of stimuli and reactants including heat, light, the presence of base or nucleophiles, or free radicals which enables a host of dynamic pathways, including metathesis[8] (**Figure 1a**), reversible addition when radicals are generated through the homolytic cleavage and recombination of disulfides[9] (**Figure 1b**), reversible exchange when there are

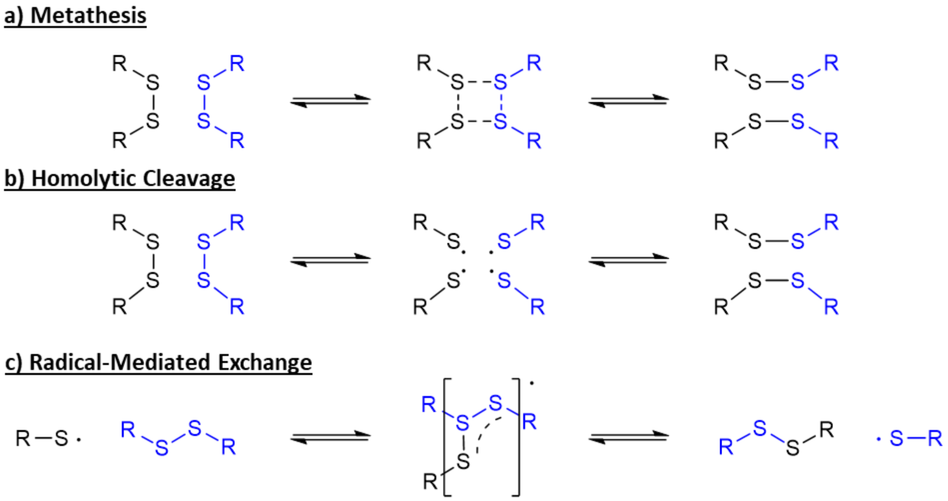

Figure 1: Schematic of several dynamic mechanisms of disulfide bonds: a) metatheses, b) reversible addition via homolytic cleavage and recombination of disulfide bonds, and c) radical-mediated reversible exchange between thiyl radicals and disulfides.

persistent thiyl radicals to facilitate bond exchange[10] (**Figure 1c**) or through thiolate mediated pathways[7].

Numerous types of disulfide-based CANs have been fabricated, e.g. aromatic disulfide-containing polyurethane networks[8, 11], photoadaptable hydrogels[10], and epoxy resins[12]. Recently, however, a variety of disulfides have been investigated for their participation in disulfide-ene reactions in which the disulfide reacts with norbornenes[13] or vinyl ethers[14] via a step growth mechanism analogous to the thiol-ene reaction. Disulfide-ene reactions with cyclic,[15, 16] and certain linear disulfides,[14, 17] are efficient crosslinking chemistries that generate thioacetal linkages rather than the thioethers associated with thiol-ene, doubling the number of bonds formed per alkene. In addition, thiol-ene and disulfide-ene are highly compatible reactions. Both reactions share a propagation step during which a thiyl radical adds into the alkene to form a carbon centered radical. The mechanism then diverges to thiol-ene or disulfide-ene depending on whether the carbon radical chain transfers to a thiol or to a disulfide, respectively (**Figure 2**).

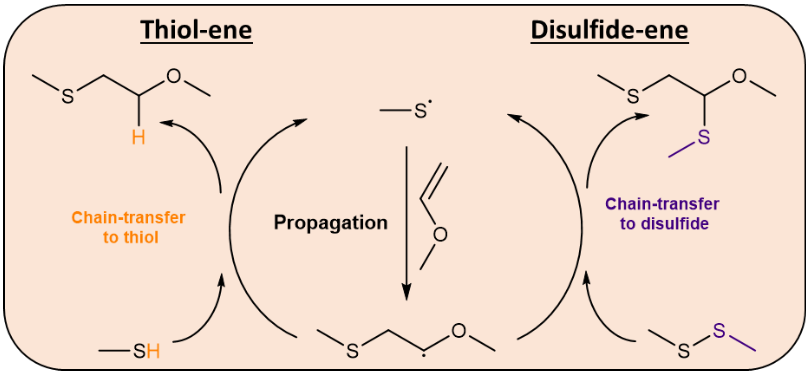

Figure 2: Mechanism of thiol-ene disulfidation polymerization, where both reactions share a propagation step but have distinct chain transfer pathways.

It has been demonstrated that these two reactions are effectively sequential, where the thiols are consumed about 30 times more rapidly than the disulfides. This behavior has been attributed to increased steric hindrance during the chain-transfer step associated with a disulfide compared to a thiol.[17] Combining thiol-ene/disulfide-ene enables spatial and temporal control over network architecture by sequentially forming a thioether network via thiol-ene followed by an increase in crosslinking via thioacetal formation from disulfide-ene (**Figure 3**). This approach enables consumption of the disulfides to form additional crosslinks or leaves them available for bond exchange by manipulating the initial stoichiometry and/or the curing conditions.

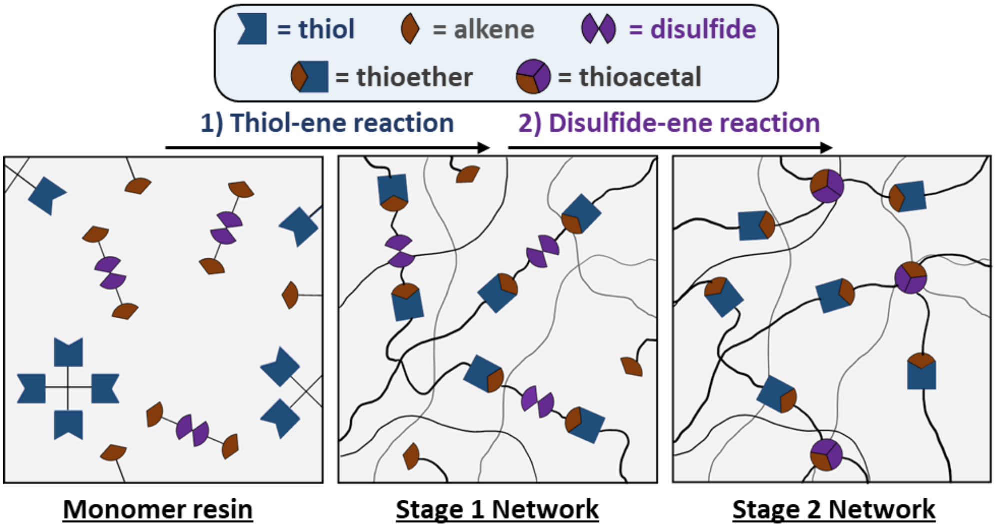

Figure 3: Schematic of the thiol-ene-disulfide polymerization for a multifunctional thiol with a disulfide containing divinyl ether (alkene). Polymerization proceeds, beginning with a monomer resin mixture to form a primarily thiol-ene stage 1 network made up of thioether bonds, then through the disulfide-ene reaction to form the thioacetal bonds in the stage 2 network.

Radical-disulfide exchange is an intrinsic feature of this polymerization because thiyl radicals and disulfides are integral to both stages of the polymerization. In their study of the kinetics of the thiol-ene-disulfidation, Soars *et al*. also demonstrated that a mix of different thiyl radicals can impact the rate of polymerization during the thiol-ene stage[17]. In their work, a divinyl ether monomer containing a thioglycolate disulfide core was co-reacted with two different thiols to elucidate whether a more stable thiyl radical should emerge after disulfide exchange events. That exchange process is expected to impact the rate of the thiol-ene polymerization. Therefore, further investigation of the impact of radical-disulfide exchange for these and similarly structured disulfides is needed to understand the impact of bond exchange both during polymerization and during post-polymerization testing.

In this work, a combined thiol-ene/disulfide-ene approach to forming radically active CANs was investigated to provide a fundamental basis for materials design using linear disulfides for dynamic polymer networks. First, stress relaxation during photoinitiated radical-disulfide exchange was measured for networks of various thiol content of the initial resin to probe structure-property relationships between the disulfide content of the final network, crosslinking, and the ability to relax stress. In addition, the disulfide-ene polymerization has relatively slow reaction rates compared to thiol-ene and the majority of the crosslinks form during the second stage of the polymerization. Stress relaxation experiments during the second stage of the polymerization were performed to probe the effectiveness of the disulfide exchange to reduce polymerization stress, and any effects on the final network structure were characterized by dynamic mechanical analysis.

Next, the impact of radical-disulfide exchange that arises from different thiol/disulfide pairs was investigated. Two divinyl ether monomers with different disulfide cores were polymerized with three multifunctional monomers yielding thiyl radicals of varied stabilities. This experimental approach elucidates how the disulfide impacts radical-disulfide exchange during thiol-ene and subsequent disulfide-ene , and how varying the relative thiyl radical stability of specific thiol/disulfide pairs affects disulfide exchange during polymerization.

MATERIALS AND METHODS

Materials: Pentaerythritol tetrakis(3-mercaptopropionate) (PETMP), diphenyl(2,4,6-trimethylbenzoyl) phosphine oxide (TPO), 2,2-dimethoxy-2-phenylacetophenone (DMPA), tri(ethylene glycol) divinyl ether (TEG), and butyl vinyl ether (BVE) were all purchased from general suppliers (Sigma Aldrich) and used as delivered. Dithioglycolate divinyl ether (DTG), di(3-mercaptoprionate) divinyl ether (DMP), pentaerythritol tetrakis(2-mercaptoacetate) (PETTG), and silane tetrathiol (SiTSH) were synthesized via the procedures provided in the supplementary information (**Figures S1 and S2**).

Dynamic Mechanical Analysis (DMA): Dynamic mechanical analysis was performed on an RSA-G2 (TA Instruments). Samples of approximate dimensions 20mm x 5mm x 0.25mm were cut, and measurements were taken using a temperature ramp rate of 3 °C/min at frequency of 1 Hz to measure the storage modulus, loss modulus, and tan(δ). The glass transition temperature (T_g) was taken to be the peak of the tan(δ) during the second temperature sweep.

DMA Stress Relaxation (SR): Stress relaxation was performed on a RSA-G2 (TA Instruments). Samples of approximate dimensions 20mm x 5mm x 0.25mm (LxWxH) were cut, and an 8% strain was applied while measuring the relaxation modulus. Samples were irradiated using a mercury-lamp (Acticure 4000) with a 400-500 nm or a 365 nm band gap filter to trigger the appropriate photoinitiator for the specific stress relaxation experiment.

Fourier Transform Infrared (FT-IR) Spectroscopy: Functional group conversion during two stage polymerizations was monitored using a FTIR spectrometer (Nicolet 8700) to monitor realtime functional group conversions. Monomer resin was placed between two NaCl plates and placed into a horizontal transmission apparatus. Samples were irradiated using a mercury-lamp (Acticure 4000) with a 400-500 nm band gap filter to initiate the polymerization. The light intensity was measured by an THORLABS PM100D radiometer. Conversion of the alkene and thiol were measured by monitoring the peak area at 3100-3135 cm^{-1} and 2520-2620 cm^{-1}, respectively. Conversion was also monitored for associated stress relaxation experiments using the ATR configuration for this spectrometer, and the alkene peak at 860 cm^{-1} was monitored to determine the cure time needed to reach a plateau in alkene conversion.

RESULTS AND DISCUSSION

Radical-mediated Stress Relaxation

The structures of the monomers used in this study are provided in **Figure 4**. The disulfide monomer, DTG, was chosen because of the relatively high reaction rates of its disulfide with vinyl ethers[14]. In addition, DTG can be effectively copolymerized with PETMP, which is a widely used and commercially available multifunctional thiol.

Previously, the dynamic behavior of thioglycolate disulfides in bulk films has been inferred based on the known behavior of disulfides when radicals are present. To study exchange with this specific disulfide directly, networks were designed such that a large number of disulfides remain to undergo bond exchange post polymerization at complete thiol and alkene conversion. Three stoichiometries were selected that vary both the amount of disulfide present and the overall structure of the network: 0.9:1, 1:1, and 1.1:1 ratios of thiol to alkene were studied.

The 0.9:1 ratio was selected such that 10% of the disulfides would be consumed after the thiol-ene stage of the polymerization resulting in complete vinyl conversions. This network is the most crosslinked of the three stoichiometries due to the formation of additional crosslinks via the disulfide-ene reaction, and therefore leaving the fewest disulfide bonds available for exchange.

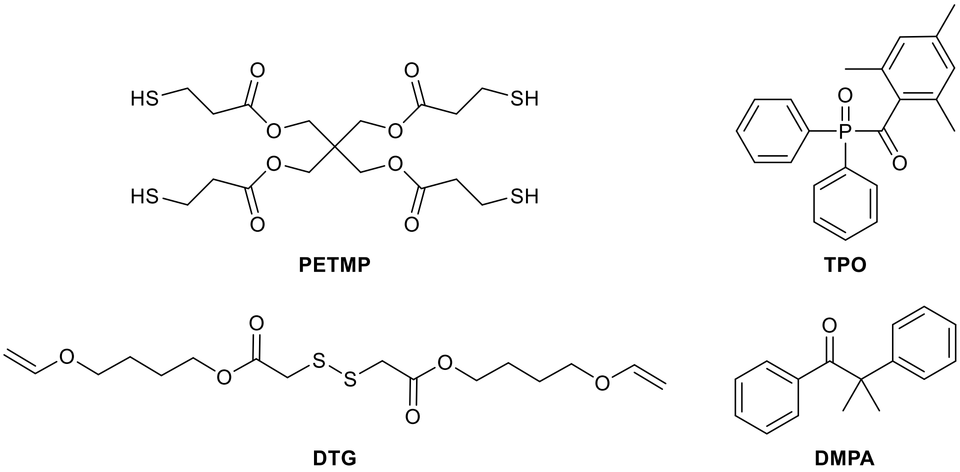

Figure 4: Monomers (PETMP and DTG) and photoinitiators (TPO and DMPA) used to study stress relaxation in thiol-ene disulfide networks. TPO is initiated by visible light at 405 nm and DMPA is initiated by UV light at 365 nm.

The 1:1 ratio was chosen such that essentially all of the vinyl groups are consumed by all of the thiols with little disulfide-ene reaction. The resulting network has the maximum possible number of disulfides available for exchange but is slightly less crosslinked than the 0.9:1 stoichiometry. Lastly, the 1.1:1 ratio was selected such that 10% of the thiols remain unreacted at complete vinyl conversion. This network is the least crosslinked and the unreacted thiols can participate in the exchange process. It should be noted that the structural and compositional changes of the final networks cannot be modulated independently because the initial ratio of alkene-to-disulfide is fixed at 2:1 by the disulfide monomer structure.

Each stoichiometry was cured using 1.5 wt% TPO photoinitiator using 405 nm light at an intensity of 20 mW/cm^2 for 10 minutes (5 minutes on each side of a 250 μm thick sample) at ambient conditions. In addition, 3.5 wt% DMPA was included as a UV photoinitiator to induce stress relaxation post-polymerization. This two-initiator system ensures that a known amount of the UV sensitive photoinitiator (DMPA) is present for stress relaxation experiments because it remains largely unconsumed during the visible light induced polymerization. Each formulation was cured using FT-IR to monitor and confirm the thiol and vinyl ether conversion which were found to match well the theoretical values (supplementary information, **Figure S3**). Dynamic mechanical analysis (DMA) was also performed on each formulation (**Figure 5a**). As expected, there was a small decrease in the glass transition temperature (T_g) as the ratio of thiol to alkene

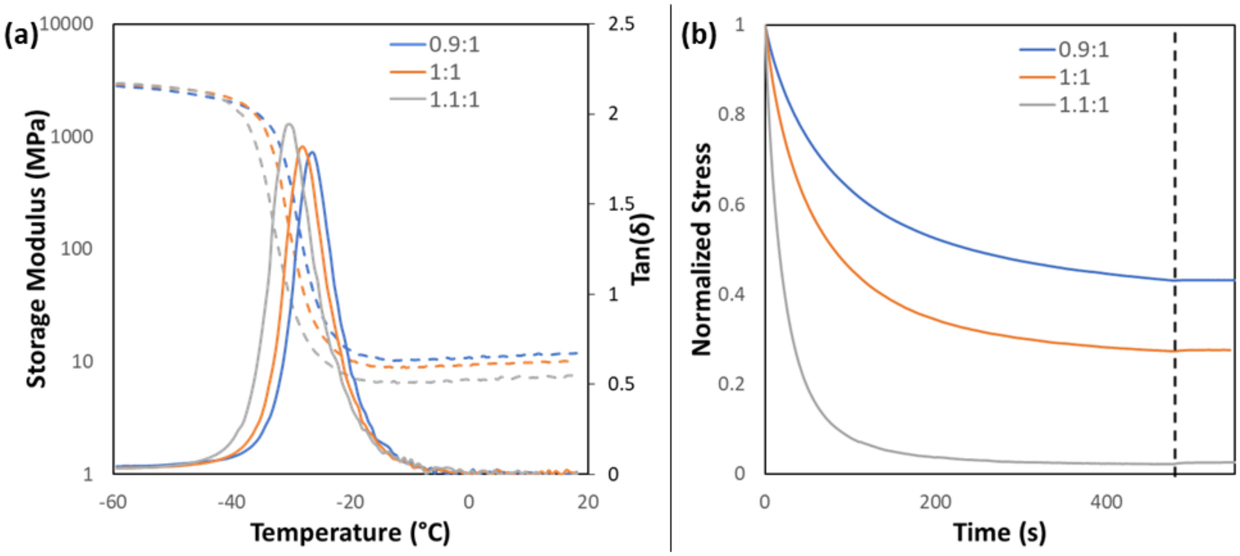

Figure 5: a) Dynamic mechanical analysis of the 0.9:1, 1:1, and 1.1:1 stoichiometry networks. The tan(δ) is shown as a solid line and the storage modulus is shown as a dashed line for each formation, and b) the normalized stress over time, for 0.9:1, 1:1, and 1.1:1 ratios of thiol to alkene with 3.5wt% DMPA as a UV photoinitiator at 15 mW/cm^2. The vertical dashed line indicates the time at which the light was turned off during the experiment.

increased, where the 0.9:1, 1:1, and 1.1:1 networks had T_g's of -27°C, -29°C, and -31°C, respectively. Likewise, a small decrease in the rubbery storage modulus was observed, showing a small but measurable decrease in crosslinking as the thiol content is increased.

Stress relaxation was performed on samples at each of these stoichiometries to demonstrate bond exchange as well as its dependence on the network composition. Rectangular samples (n = 3) were subjected to 8% strain for 30 seconds, then a 365 nm light of 30 mW/cm^2 was turned on for 10 minutes to induce stress relaxation (**Figure 5b**). Overall, both the rate and total amount of relaxation increased with increasing thiol-content in the initial resin, where the 0.9:1 thiol to alkene ratio relaxed the most slowly and reached a final normalized stress of 43 ± 5%, followed by the 1:1 ratio which reached 27 ± 2%, then the 1.1:1 ratio which reached nearly 100% relaxation, likely near the sensitivity level of the instrument (2.5 ± 0.6%). The final normalized stress was taken after the light was turned off and the sample was allowed to equilibrate to room temperature. No cooling effect was observed at this light intensity.

The increase in relaxation with relative thiol content of the initial resin is likely due to both the decrease in crosslinking and the increase in the content of functional groups that can participate in bond exchange. The relative contributions of crosslinking and functional group content are likely different for the increase in stress relaxation for the 0.9:1 to the 1:1 formulations, which showed an increase of 16% total relaxation, relative to the increase when comparing the 1:1 to the 1.1:1 formulations, which showed a larger increase of 25% total relaxation.

First, the structural changes for each pair of formulations were considered. In the disulfide-ene reaction, two bonds are formed for each disulfide bond that is broken. For the 0.9:1 ratio, in which the preferred reactive thiol group is limited, 10% of the alkenes necessarily react with disulfides to form additional crosslinks. Compared to the case where all of the alkenes react with thiols, this approach results in a net gain of one bond per reacted disulfide that contributes to the overall crosslinking density. For the 1:1 stoichiometry, all of the unreacted functional groups, namely the disulfides, still contribute to the overall crosslinking of the network. Conversely, the 10% unreacted thiols for the 1.1:1 network don’t contribute to crosslinking and instead are dangling chain ends.

Next, the role of the reactive functional groups that are present in each formulation was considered. The number of disulfides available for stress relaxation increases for the 1:1 compared to the 0.9:1 ratio because all of the disulfides are available in the 1:1 formulation but not the 0.9:1 formulation. However, every disulfide is available in both the 1:1 and 1.1:1 formulations, but 10% of thiols are unreacted for the 1.1:1 formulation and may also participate directly in thiol-disulfide exchange. Thiyl radicals should form more readily from a thiol than a disulfide due to reduced steric hinderance associated with abstracting a hydrogen compared to that same initiator fragment reacting with a disulfide bond. In addition, free thiols may also facilitate reaction mediated diffusion by which the thiyl radicals effectively diffuse through the network through repeated hydrogen abstraction reactions. Therefore, the effect of free thiols is likely to have a greater impact on stress relaxation than increasing the number of disulfides available for bond exchange, all else being equal. The relative importance of these structural and chemical effects is further explored later in this work.

Overall, the thioglycolate disulfides effectively induce stress relaxation. The relaxation rate is readily manipulated by small changes in the initial stoichiometry, likely due to some combination of changes in crosslinking density and whether free thiols are present to participate in the exchange reaction.

Exchange During Disulfide-ene Polymerization

An important feature of this polymerization scheme is that radical-disulfide exchange is active throughout both stages of the polymerization. It is well documented that polymerizations in the presence of allyl sulfides or trithiocarbonates reduce the buildup of polymerization stress through addition-fragmentation, which is a similar radical-mediated mechanism to radical-disulfide exchange[18-20]. The impact of disulfide exchange during this polymerization is distinct for two reasons. First, the disulfides are direct participants in both the second phase of the polymerization and the exchange process itself rather than serving as an additive designed to induce bond exchange. Second, the disulfide-ene reaction is far slower than the thiol-ene reaction, so the polymerization rate may have an outsized impact on the final polymerization stress due to the rapid radical-disulfide exchange rate.

To examine the stress buildup during the second stage of the polymerization, PETMP and DTG were used in a 0.5:1 ratio of thiol to alkene, such that 100% conversion of all functional groups is possible. A 250 µm film was cured using 3 wt% TPO at 14 mW/cm^2 for approximately 40 seconds at ambient conditions such that the film was cured just enough to consume all thiols. Approximately 50% of the alkenes were reacted. A single photoinitiator, TPO, was used to better

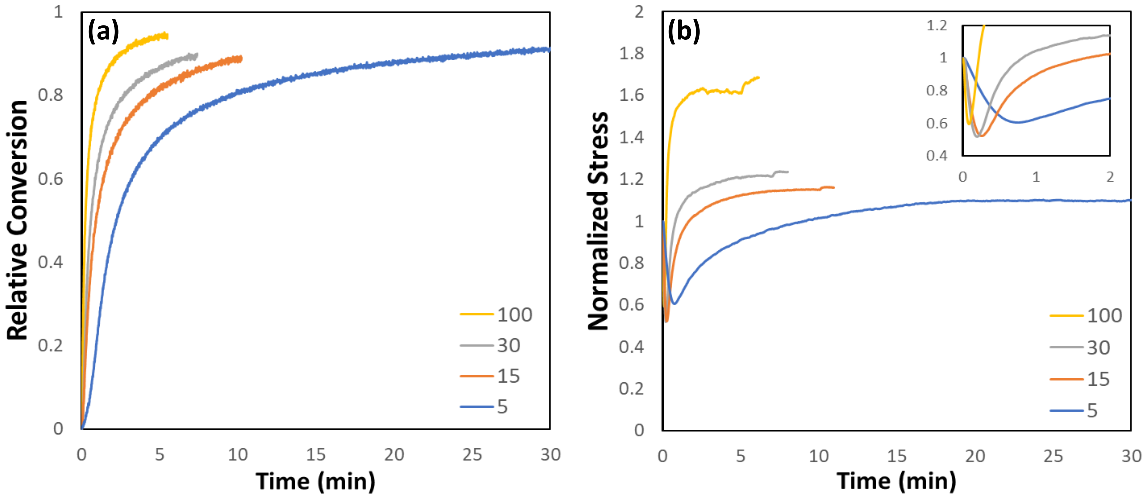

Figure 6: For PETMP-DTG with a 0.5:1 ratio of thiol to alkene, , a) relative conversion of alkene over time at various light intensities (mW/cm^2), where zero conversion corresponds to the initial conversion reached after the first stage thiol-ene reaction, and b) the normalized stress during the disulfide-ene polymerization for samples cured through the disulfide-ene reaction at various light intensities (mW/cm^2). The inset highlights the initial drop instress for each light intensity. Samples were first cured using 14 mW/cm^2 405 nm light until the film was just cured enough to cut and handle

reflect the initiator concentration in a sample that is continuously cured to full conversion. All samples were cut from this single film to ensure that the initial vinyl ether conversion was consistent across all samples at each wavelength. Infrared spectroscopy (ATR configuration) was used to first compare the "relative conversion" over time for 5, 15, 30, and 100 mW/cm^2 light intensities (**Figure 6a**).

"Zero conversion" for this data corresponds to the alkene conversion achieved after the first stage thiol-ene polymerization. At each intensity, the sample was irradiated until the conversion had largely plateaued due to consumption of the disulfides and/or photoinitiator to provide a baseline to compare the final stress between intensities. The irradiation times established during FTIR experiments were subsequently used to measure stress during polymerization on samples of identical thickness. Samples at all four light intensities (5, 15, 30, and 100 mW/cm^2) reach relative conversions of approximately 90% after reacting for 30 min, 10 min, 7 min, and 5 min, respectively. In reality, 90% relative conversion corresponds to around 95% total alkene conversion because at least 50% of the alkenes were consumed during the thiol-ene stage of the polymerization. The highest light intensity, 100 mW/cm^2, reached the highest conversion overall due to the rapid polymerization rate at high light intensity.

To test the buildup of stress during the disulfide-ene step of the polymerization, samples cured through the thiol-ene stage were subjected to a constant 8% strain and irradiated at 5, 15, 30, or 100 mW/cm^2 for 30, 10, 7, or 5 min, respectively (**Figure 6b**). The results are summarized in **Table 1**.

Table 1: Summarized values for the irradiation time, minimum stress, and maximum stress during stress relaxation experiments

Intensity (mW/cm^2)	Irradiation time (min)	Stress Min (% of initial stress)	Final Stress (% of initial Stress)
5	30	63 ± 3	107 ± 4
15	10	57 ± 4	110 ± 10
30	7	56 ± 3	130 ± 30
100	5	58 ± 4	180 ± 40

After the light was turned on, the normalized stress initially decreased, reached a minimum, then increased as the polymerization continued, reaching a plateau as the functional groups and photoinitiator were consumed. Initially, any buildup of stress due to polymerization was offset by disulfide cleavage and exchange to reduce the stress below the initially applied stress. However, as the reaction proceeded, the disulfides converted to thioacetals and the rate of shrinkage stress development outpaced the rate at which disulfide exchange could relax that stress, leading to final stresses above the applied stress in this experiment regardless of light intensity.

The minimum stress decreased only slightly as the light intensity increased and was statistically indistinguishable between the 15, 30, and 100 mW/cm^2, as highlighted in the inset of **Figure 6b**. This behavior is only possible in a dynamic system because additional post-gelation polymerization in a non-dynamic network would be expected to generate significant additional stress. This behavior is advantageous for generating low-stress dual-cure materials because of the delay in gelation associated with step growth polymers and reduction in stress buildup during this stage of the polymerization due to disulfide exchange.

An increase in the final stress as light intensity increased was also observed. There was also a clear heating effect after the light was turned off due to thermal contraction. This effect is small but became more significant at higher light intensities due to faster reaction rates and direct heating from the light source. The increase in the final stress is due to more rapid consumption of the disulfides as the light intensity was increased, essentially decreasing the number of disulfide exchange events that occur before they are consumed by polymerization. This behavior is distinct from what is observed in typical addition-fragmentation systems, in which the dynamic functional group is not consumed as part of the desired polymerization (although they are subject to irreversible side reactions that may contribute to additional crosslinking). As previously mentioned, this final stress is expected to be far lower than for a comparable network structure without the capacity for bond-exchange, as evidenced by the initial decrease in stress due to bond exchange and the persistence of bond exchange throughout the polymerization.

To determine whether the difference in second stage light intensity has any impact on final network properties, DMA was performed on samples cured at all four light intensities, where 250 µm samples were irradiated for the same amount of time as the stress measurements, and each side of the sample was irradiated for half of that time. Only a small difference in the T_g was observed of 1-2 °C with virtually no difference in the storage modulus after two cycles run to 40 °C (supplementary information, Figure S4), indicating that the final network properties are largely unaffected by the rate of the second stage polymerization.

Overall, disulfide exchange during the disulfide-ene stage of the polymerization significantly reduced the polymerization stress. A non-dynamic network under the conditions tested here must experience an increase in the internal stress during polymerization. However, disulfide exchange initially reduces the stress until the disulfides are consumed an incorporated into the network faster than they can relax polymerization stress.

Effect of Thiol and Disulfide Type on Exchange

Radical-disulfide exchange is intrinsic to both the thiol-ene and disulfide-ene stages of the polymerization. When PETMP and DTG are polymerized, this exchange process has been shown to slow the thiol-ene step compared to the case where no disulfides are present in small molecule studies. This effect is exacerbated when the thiyl radical formed from hydrogen abstraction of the thiol is more stable than the radical formed by cleaving the disulfide[17]. It is hypothesized that the different thiol/disulfide pairs will impact the rates of both polymerization stages depending on the relative stability of the thiyl radicals that form the thiol and the disulfide.

Three monomers were synthesized to test the effect of relative radical stability. First, DMP was synthesized, containing a 3-mercaptopropionate disulfide core. The overall monomer structure is identical to DTG, except the disulfide is based on 3-mercpatopropionate rather than thioglycolate. In addition, two multifunctional thiol monomers were synthesized to vary the stability of the thiyl radicals: PETTG as the thioglycolate analogue of PETMP, and SiTSH which contains alkyl thiols. All five monomers are illustrated in **Figure 7a**. These two disulfides and three thiols enable a more thorough study of how disulfide exchange influences the polymerization. Specifically, measuring the conversion over time for each disulfide/thiol pair will elucidate whether disulfide exchange effects the thiol-ene polymerization under three different conditions: (1) when the radical formed by the thiol and disulfide are the same and therefore exchange cannot result in the formation of a different thiyl radical; (2) when the radical derived from the thiol is more stable than the disulfide radical and therefore little/no change in the type of thiyl radical present during thiol-ene should occur, and (3) when the disulfide radical is more stable than the thiol-derived radical and therefore asymmetric disulfides can form during the thiol-ene step, which may impact the rate of polymerization during the disulfide-ene step.

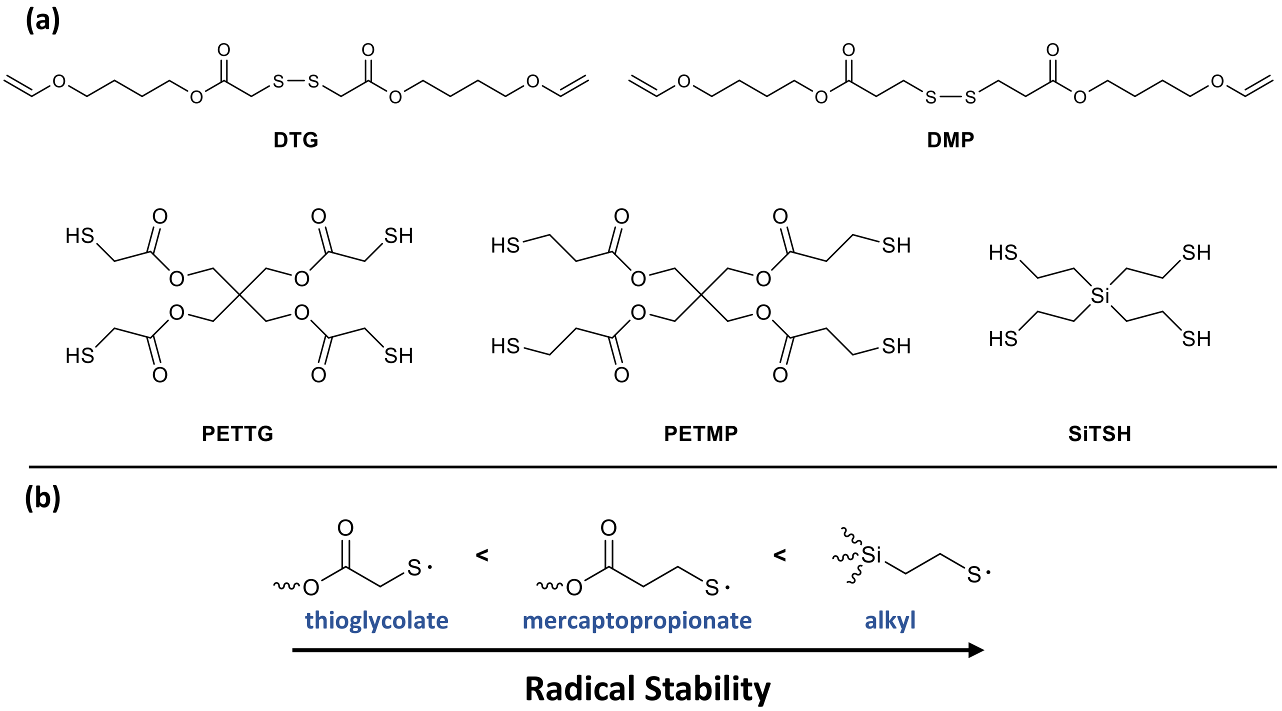

Figure 7: a) Monomers used to study the impact of different kinds of thiols and disulfides on thiol-ene-disulfide materials, and b) The stability of the thiyl radical derived from PETMA, PETMP, and SiTSH, respectively, going from left to right.

The relative stability of the thiyl radicals that form is shown in **Figure 7b**. The thioglycolate radical, formed from PETTG and DTG, is the most electron poor due to its proximity to the carbonyl carbon and is therefore the least stable. The next more stable is the mercaptopropionate radical, formed from PETMP and DMP, because this radical is slightly more electron rich due to the extra carbon spacer between the sulfur and the carbonyl carbon. The radicals formed by SiTSH are the most electron rich because there is no electron withdrawing group making this the most stable of the three radicals that form using this monomer scope. However, the relative stability of these radicals does not necessarily correlate with thiol-ene reaction rate because although increasing thiyl radical stability may tend to increase the chain transfer rate, increased thiyl radical stability will also tend to slow down the propagation step. Given that chain transfer is only mildly rate limiting for mercaptopropionates with vinyl ethers ($k_p/k_{ct} \approx 1.2$), changing the thiol to a thioglycolate or an alkyl thiol may also change the rate limiting step, which may in turn impact how disulfide exchange influences different thiol/disulfide pairs.

To the best of our knowledge, the rate limiting step has not been established for these two thiols with vinyl ethers. As such, a kinetic analysis using FTIR was performed to determine the rate limiting step for each of these monomers with tri(ethylene glycol) divinyl ether (TEG) at three ratios of thiol to alkene: 2:1, 1:1 and 1:2. The conversion over time for the limiting reactant for each stoichiometry as well as a more thorough explanation of the procedure adapted from Cramer et al.[21] is provided in the supplementary information (**Figure S1 and S2**), and the summary of the polymerization rate behavior is provided in Table 2. The rate limiting step for PETMP was chain transfer as previously reported[21], and the rate limiting step for both PETTG and SiTSH was propagation.

All six possible pairs of thiol/disulfide monomers were polymerized and their conversion over time measured using FTIR. Polymerization mixtures were prepared with 1.5 mol% TPO (relative to monomer present) and a 0.5:1 ratio of thiol to alkene, such that at full conversion 50%

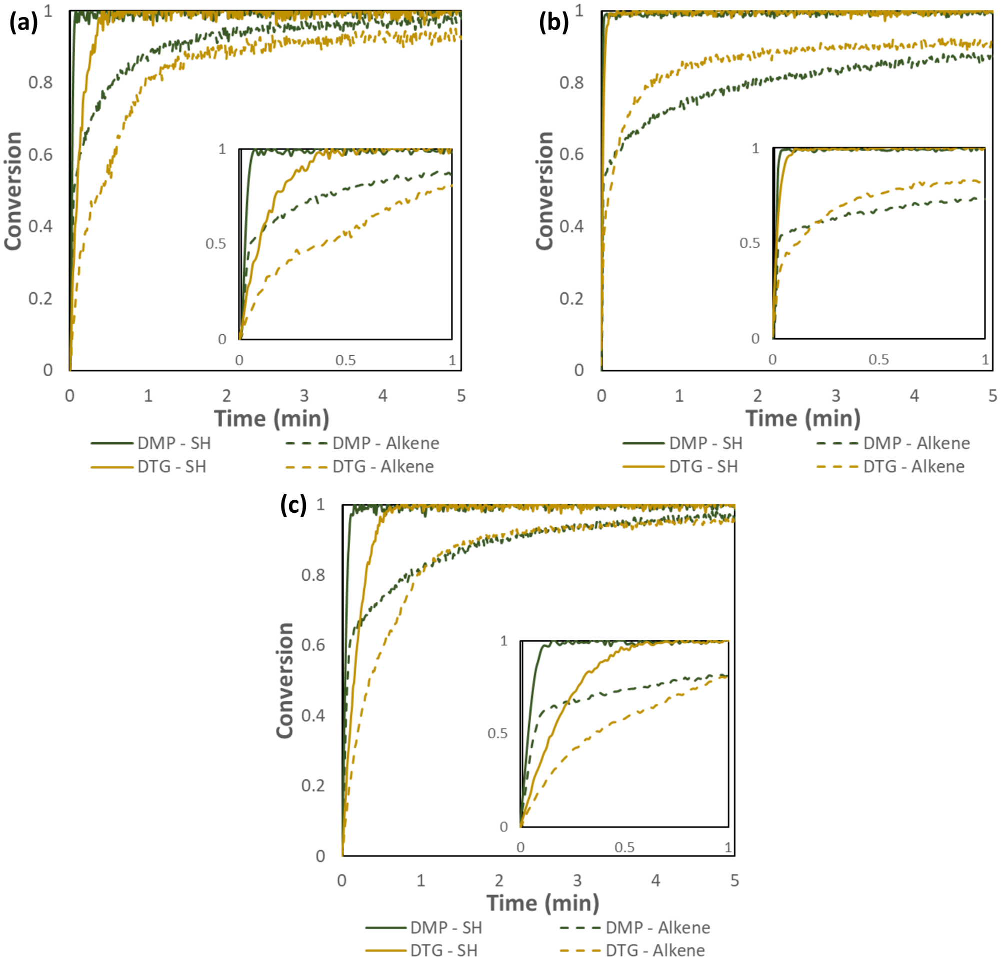

Figure 8: Thiol and vinyl conversion over time for the two disulfide-containing divinyl ether monomers copolymerized with thiols of different thiyl radical stability: a) PETMP, b) PETTG, and c) SiTSH. The insets show the first minute of the polymerization for each thiol to emphasize the difference in the thiol-ene rate for each thiol-disulfide pair.

of the alkenes are consumed by the thiols and the other 50% by the disulfides. Samples were irradiated with 405 nm light at 10 mW/cm^2 for 5 minutes.

The conversion over time is shown in **Figure 8**, comparing the reaction rate when polymerized with either DTG or DMP for all three thiol monomers. The first feature to note is that for all three thiols the disulfide-ene rate for both disulfides is roughly the same, reaching approximately the same final conversion after 5 minutes. This outcome differs from the small molecule studies performed by Kamps et al., where the mercaptopropionate disulfide reacted approximately 10 times slower than the thioglycolate disulfide[14]. Nevertheless, the fact that the disulfide-ene rate with DMP is comparable to DTG indicates that the scope of linear disulfides that can be effectively copolymerized with thiols is not limited by their reaction rates in model reactions. In addition, the relative rate of thiol-ene polymerization for each thiol monomer aligns with the relative rates observed in the control thiol-ene reactions at the same 1:2 ratio of thiol to alkene as found in **Table 2**: PETTG was the fastest, then PETMP, then SiTSH.

Table 2: For three different thiol to alkene stoichiometries, the rate of consumption of the limiting reactant for various thiol monomers, and which step, i.e., either chain transfer or propagation, is the rate limiting step. Samples were polymerized at 0.1 wt% TPO with 405 nm light at 5 mW/cm^2.

	Rate (mM/s)		
Thiol-Alkene Ratio	**PETMP**	**PETTG**	**SiTSH**
2-1	180 ± 30	80 ± 10	13 ± 4
1-1	180 ± 10	90 ± 20	55 ± 8
1-2	109 ± 4	130 ± 20	56 ± 6
Rate Limiting step	CT	Prop	Prop

As mentioned previously, significant retardation of the thiol-ene reaction has been observed with PETMP and DTG. This outcome was attributed to disulfide exchange during which the mercaptopropionate radical may add into the dithioglycolate disulfide, which then fragments preferentially to reform the same disulfide and thiyl radical. This effectively sequesters propagating radicals in a similar manner observed for additional fragmentation reactions of allyl sulfides and trithiocarbonates[22]. It was therefore hypothesized that with PETMP the thiol-ene step would be faster with DMP because both monomers would produce the same thiyl radical and reduce the slowing effect on the reaction.

Indeed, this trend was observed as shown in **Figure 8a**, where the alkene conversion reaches approximately 50% after a few seconds with DMP, but after 30 seconds with DTG. The initial 50% alkene conversion is almost completely attributed to the thiol-ene reaction because this conversion corresponds to complete consumption of the thiol. This is good evidence that the specific thiol/disulfide pair and the associated radical-disulfide exchange play important roles in the thiol-ene stage of the polymerization.

To test the importance of the thiol/disulfide pair further, PETTG (the thioglycolate analogue of PETMP) was copolymerized with both DMP and DTG (**Figure 8b**). In this case, the rates of thiol-ene are similar for both disulfides compared to the same polymerization with PETMP. However, the disulfide-ene rate with DMP is slower than with DTG. This difference is attributed to the varying thiyl radical stability for PETTG as compared to PETMP. It was hypothesized that because the thioglycolate radical is less stable, exchange events with DMP will preferentially fragment into a mercaptopropionate radical and an asymmetric disulfide. There is no such bias with PETMP to form asymmetric disulfides because the thiol itself forms the more stable radicals. This process does not result in a slower thiol-ene rate because mercaptopropionates are in fact more reactive in thiol-ene reactions than thioglycolates. However, the additional complexity of the resulting asymmetric disulfides would result in a slower disulfide-ene step compared to when DTG is used. This mechanism explains the relative polymerization rates for both PETMP and PETTG.

Lastly, SiTSH was used to probe this effect further. SiTSH forms the most stable radical of the three thiols investigated here and would therefore experience a reduced rate of thiol-ene with both disulfide monomers compared to the cases where the thiol and disulfide monomers match. Indeed, this is the case as shown in **Figure 8c**. The thiol-ene reaction is slower with DTG than for DMP, reaching 50% alkene conversion after about 25 and 4 seconds, respectively. Subsequently, the disulfide-ene step from both disulfide monomers reaches the same conversion after 5 minutes.

It should be noted that there was little difference in the material properties using these three thiols. DMA temperature sweeps of networks with PETMP, PETTG, and SiTSH copolymerized with DMP were performed and the T_g and storage moduli of all three networks were nearly identical (supplementary information, Figure S5). Using SiTSH was expected to increase the T_g

compared to the other two monomers due to the shorter chains between crosslinks, which has been observed previously in thiol-ene networks[23, 24]. The fact that SiTSH did not increase the T_g indicates that the T_g in these thiol-ene-disulfide networks is largely driven by the disulfide-ene step of the polymerization. This result is reasonable because, at these stoichiometric ratios, the disulfide-ene results in twice as many bonds formed compared to thiol-ene, and the molecular weight between crosslinks of the disulfide-ene step is largely unaffected by the identity of the multifunctional thiol monomer, provided that the number of thiols-per-monomer is the same. In fact, the rate of the thiol-ene step may be independent of the material properties of the final polymer when a significant number of crosslinks are formed by the disulfide-ene step, enabling tunability of the dual-cure rate for applications in optical materials and other fields by simply changing the thiol/disulfide pair. Alternative disulfide monomer structures may also be used to further tune the T_g and dynamic moduli.

Overall, the thiol-ene-disulfide reaction proceeds quite well with all three thiols, with the only exception being PETTG with DMP during the disulfide-ene stage because of the formation of asymmetric thiols. Furthermore, using DMP instead of DTG resulted in a faster thiol-ene polymerization with all three monomers, regardless of the rate limiting step of the thiol-ene reaction. Further investigation is needed to determine if other linear disulfide cores, such as purely alkyl or sulfonate ester disulfides, are also viable in this reaction scheme.

Impact of Structure and Functional Groups on Stress Relaxation

Decoupling the impact of network structure and chemical functionality on stress relaxation is crucial to understand and tune the relaxation rates in these dynamic networks. For example, it was shown in **Figure 5b** that stoichiometries with excess thiol significantly decrease the relaxation time as compared to a balanced ratio of thiol to alkene and when alkene is in excess and can react with a portion of the disulfides.

To probe the relative effect of the structural impact of changing stoichiometry versus the chemical impact of having excess thiols present to participate in bond exchange, a series of control stress relaxation experiments was performed on networks with excess thiol (1.1:1 ratio of thiol to alkene) and DTG as the disulfide monomer. First, 10 mol% butyl vinyl ether (BVE) was included to react with the excess thiols without changing the connectivity of the network, isolating the impact of the excess thiols on radical-disulfide exchange independent of the overall structure of the network. Second, controls were performed with PETTG instead of PETMP, both with and without 10 mol% BVE, to determine whether the type of thiol, specifically whether the mismatch between the mercaptopropionate radical associated with PETMP and the thioglycolate radical associated with DTG, impacts the rate of relaxation.

The DMA traces for these networks are shown in **Figure 9a.** Each network was initially cured with 1 wt% TPO and 405 nm light at 20 mW/cm^2 for 5 minutes on each side. For stress relaxation, 3.5 wt% DMPA was used with 365 nm light at 15 mW/cm^2 and 8 % strain. The PETMP networks with or without BVE have similar glass transition temperatures (within a degree or so), storage moduli, and molecular weight between crosslinks (1040 g/mol and 950 g/mol, respectively). The same is true for the PETTG networks with and without BVE (760 g/mol and 770 g/mol, respectively). These results indicate that BVE did not significantly impact the network structure for either thiol monomer, but the shorter chain length associated with PETTG compared to PETMP does increase the T_g and rubbery storage modulus.

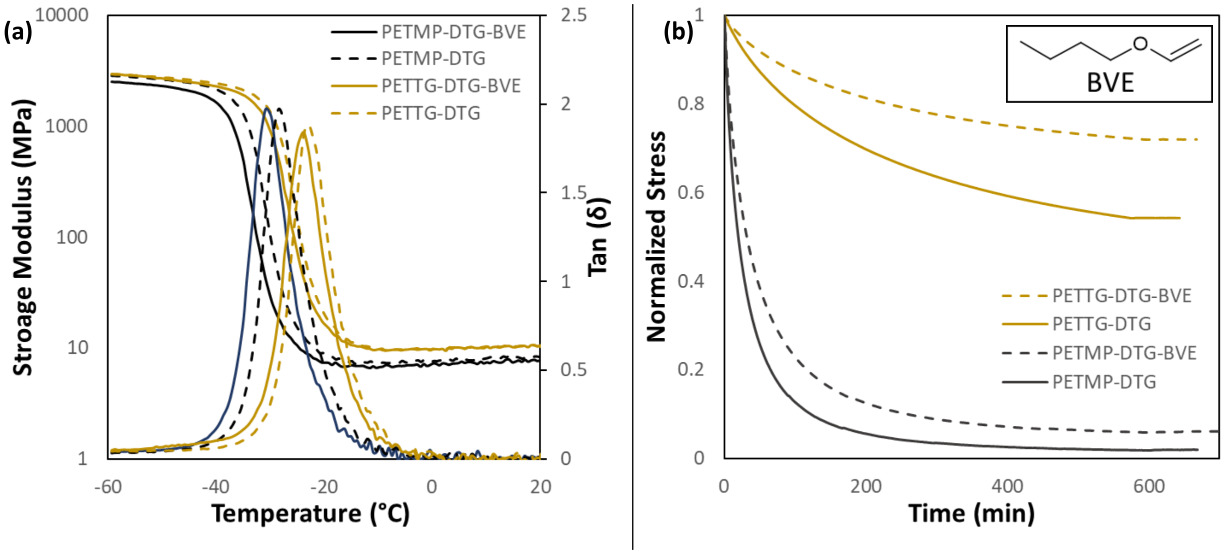

Figure 9: a) DMA trace and b) stress relaxation of each network, with butyl vinyl ether included in the top right. Each network was made with a 1.1:1 ratio of thiol to alkene and was cured into a 250 µm films with 1 wt% TPO irradiated with 405 nm light at 20 mW/cm^2 for 5 minutes on each side. Stress relaxation was done with 3.5 wt% DMPA and 365 nm light at 15 mW/cm^2 for 10 minutes at 8% strain.

Stress relaxation behavior for these four networks is shown in **Figure 9b**. As expected, reacting the excess thiols with BVE resulted in slower stress relaxation compared to when free thiols were present for both thiol monomers, but this effect was more pronounced for PETTG than PETMP. This result is not surprising because kinetic analysis indicates that little productive bond exchange occurs between mercaptopropionate radicals and thioglycolate disulfides[14], meaning excess thiols should impact relaxation more for PETTG than PETMP. Interestingly, the PETMP networks relaxed stress far more rapidly than PETTG both with and without BVE though they only differ in their molecular weight between crosslinks. This indicates that while both structure and presence of reactive groups play a role in the rate of stress relaxation, the network structure also has a significant impact on the stress relaxation rate.

Stress Relaxation with DMP

After demonstrating the viability of DMP in thiol-ene-disulfide polymerizations, the performance of the mercaptopropionate and thioglycolate disulfides was compared in stress relaxation experiments. Two of the stoichiometries tested before, namely 0.9:1 and 1.1:1 ratios of thiol to alkene, were used to determine the exchange characteristics with and without the excess thiol. The DMP films relaxed extremely rapidly compared to films made with DTG for both stoichiometries (**Figure 10**). For the 0.9:1 ratio, the DTG network is two orders of magnitude

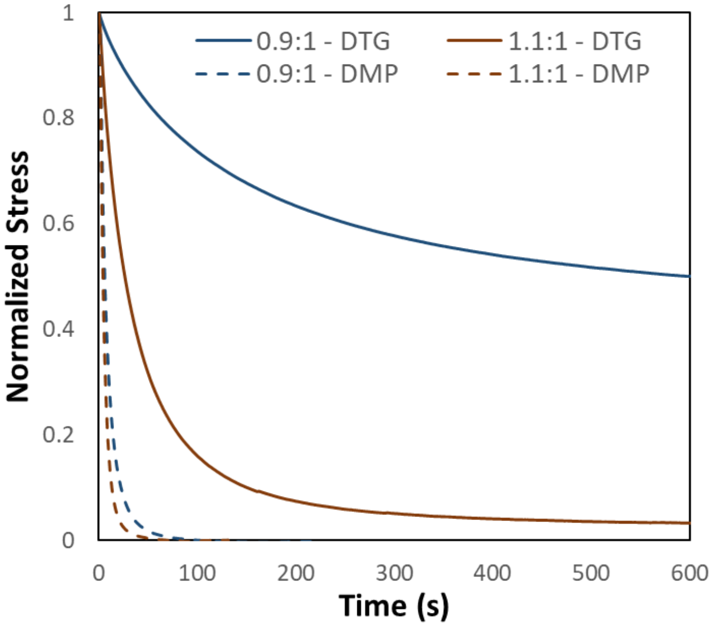

Figure 10: The normalized stress over time for for DTG (solid) and DMP (dashed) at two ratios of thiol to alkene. Samples were prepared with 3.5 wt% DMPA, stretch to 8% strain, and exposed to 15 mW/cm^2 365 nm light.

slower, only reaching about 50% relaxation in 10 minutes while the DMP network achieved 50% relaxation in about 5 seconds and 100% relaxation in 1.5 minutes. The difference is less stark in systems with abundant thiols, for which DTG reached nearly complete relaxation after 10 minutes compared to 1 minute with DMP. This difference of only one order of magnitude is likely because an excess of thiol will impact the slower exchange associated with the thioglycolate disulfide more than the already rapid exchange for the mercaptopropionate disulfide.

In addition, there was only a small difference in relaxation rate between the two networks with DMP with or without thiols to participate in exchange, which again is likely because the exchange rate of this disulfide is already quite fast and therefore is not substantially enhanced by an excess of thiol. These rapid exchange kinetics with DMP indicate that networks with far more crosslinking and fewer unreacted disulfides are possible while maintaining fast stress relaxation capability.

The fact that DMP shows much faster radical-disulfide exchange also has important implications for stress development during polymerization because faster exchange should result in lower volumetric shrinkage stress compared to DTG. To investigate any difference in stress development during polymerization, samples with a 0.5:1 ratio of thiol to alkene were prepared with PETMP, either DMP or DTG, and cured with 3 wt% TPO under 14 mW/cm^2 irradiation at 405 nm to the point where the thiol-ene reaction was complete and the samples were sufficiently polymerized to maintain integrity, i.e., 12 seconds and 40 seconds, respectively. It should be noted that the alkene conversion between these two samples is not coincident as these two networks experience different polymerization rates for the thiol-ene step, but in both cases very little disulfide-ene reaction occurs before appreciable amounts of disulfide react under these conditions. In addition, nearly all the stress that develops during polymerization should occur during the disulfide-ene step because gelation would occur at the later stages of the thiol-ene step.

Vinyl conversion over time was measured using FTIR in an ATR configuration for the disulfide-ene reaction, and was initiated using 5, 30, or 100 mW/cm^2 light intensity for 305 nm light (**Figure 11a**). The ATR configuration was used so variables such as sample thickness, and therefore light attenuation, would be identical between FTIR and stress relaxation experiments. Although the polymerization rate is slightly slower for DMP compared to DTG, both networks reach similar conversions over comparable time scales at a given light intensity. Photocured

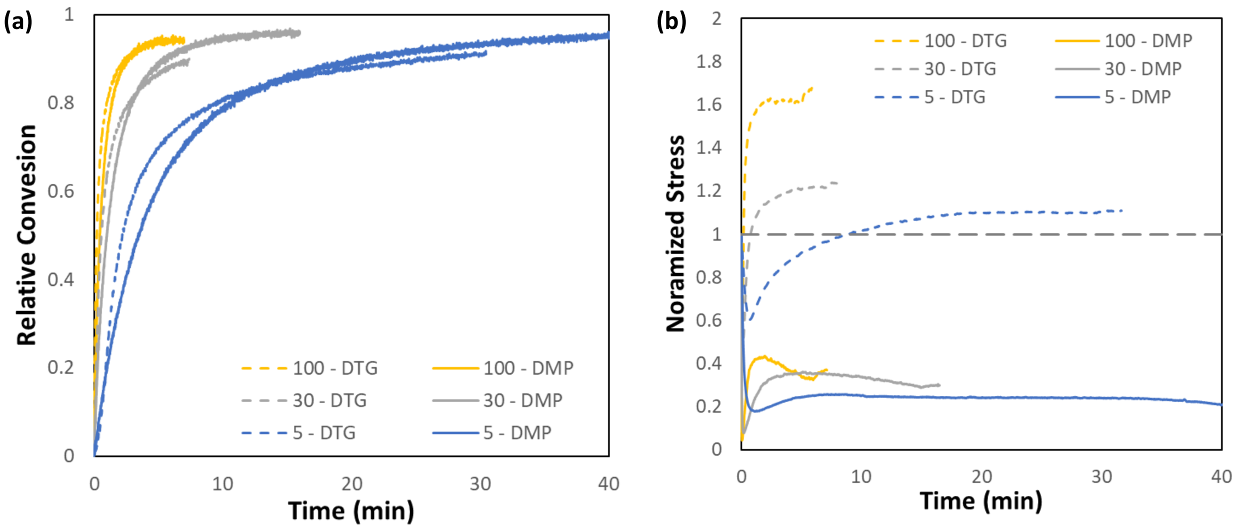

Figure 11: For samples of PETMP with either DTG (dashed) or DMP (solid) with a 0.5:1 ratio of thiol to alkene, a) relative conversion of alkene over time during the disulfide-ene polymerization at various light intensities (mW/cm^2), where zero conversion corresponds to the initial conversion reached after the first stage thiol-ene reaction, and b) the normalized stress during the disulfide-ene polymerization for samples cured through the disulfide-ene reaction at various light intensities (mW/cm^2). Samples were first cured using 14 mW/cm^2 405 nm light until the film was cured enough to cut and handle.

samples were then subjected to 8% strain and irradiated for the same durations as determined by ATR time-conversion analysis. The stress over time was measured, shown in **Figure 11b**, and the results comparing the two disulfide monomers are summarized in **Table 3**.

Table 3: Summarized values for the irradiation time, minimum stress, and maximum stress during stress relaxation experiment for DMP and DTG.

Intensity (mW/cm^2)	Disulfide Monomer	Irradiation time (min)	Stress Min (% of initial stress)	Final Stress (% of initial Stress)
5	DTG	30	63 ± 3	107 ± 4
	DMP	40	13 ± 6	18 ± 8
30	DTG	7	56 ± 3	130 ± 30
	DMP	15	6 ± 3	28 ± 6
100	DTG	5	58 ± 4	180 ± 40
	DMP	6	5.0 ± .7	37 ± 1

For all three light intensities, DMP both reached a lower minimum stress and a lower final stress despite reaching similar or higher alkene conversion compared to DTG. As seen previously, there is an initial drop in the stress as disulfide exchange relaxes the applied stress, followed by an increase in stress as disulfides convert to thioacetals and shrinkage stress develops. However, DMP proves to be far more effective at reducing stress buildup at all three light intensities. Using 5 mW/cm^2 as an example, the stress is reduced to about 13% of the initial value but remains well below the initial stress, plateauing at about 18% strain by the end of the experiment. This value is far lower than for DTG, where the initial stress only decreases to a minimum of 63% of the initial stress, but ultimately polymerization results in final stresses that are greater than the applied stress. The ultimate stress increases with light intensity for both disulfide monomers, though the final stress is far below the applied stress for DMP, while the final stress nearly doubles for DTG. This result agrees with the stress relaxation observed in **Figure 10**, showing that the rate of radical-disulfide exchange is faster for the mercaptopropionate-based disulfide compared to the thioglycolate-based disulfide.

Overall, thiol-ene-disulfide networks with either DTG or DMP were capable of relaxating stresses both during and after polymerization. However, under identical curing and stress relaxation conditions, the mercaptopropionate disulfide relaxed stress significantly faster than those based on thioglycolates with only small changes in the material properties. This provides tunability of the material properties that is largely decoupled from the dynamic behavior, in this case, the relaxation times, of these materials. The ability to tune the relative relaxation rates and the final material properties could prove useful for applications such as imprinting and holography in which independent control over the polymerization, relaxation, and material properties may be important to performance. A table containing the basic mechanical properties of the networks studied here is provided in Table S1.

CONCLUSIONS

Thiol-ene-disulfide networks were investigated to better understand the role of radical disulfide exchange during network formation and stress relaxation, improving the fundamental understanding of the relationship between the monomer selection, material properties, and relaxation behavior of thiol-ene-disulfide networks.

Disulfides derived from mercaptopropionates were found to be nearly as efficient for the disulfide-ene polymerization as those based on thioglycolates, despite showing significantly slower rates in previous model studies. Furthermore, the thiol-ene step of the polymerization using DMP was as fast or faster, and therefore less inhibited by disulfide exchange, than DTG regardless of the type of thiol comonomer. The disulfide-ene rate was largely unaffected by the thiol/disulfide pair when the thiyl radical formed by the thiol was more stable than the radical formed by the disulfide, but slower in the opposite scheme when asymmetric disulfides could form during the thiol-ene polymerization.

Both DMP and DTG induced stress relaxation both during polymerization and during post-polymerization. However, relaxation with DMP was significantly faster than for DTG in all cases. The type of disulfide did not however greatly impact the material properties of the final networks, which is advantageous for tunability of the exchange rate independently of the mechanical properties of the network.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website.

Synthetic procedures, dynamic mechanical analysis, NMR characterization.

AUTHOR INFORMATION

Corresponding author

Christopher Bowman – *Department of Chemical and Biological Engineering, Materials Science and Engineering Program, University of Colorado at Boulder, Colorado 80309, United States*. Email: christopher.bowman@colorado.edu

Authors

Nicholas J. Bongiardina - *Material Science and Engineering Program, University of Colorado, Boulder, Colorado 80309, United States.*

Shafer M. Soars - *Department of Chemistry, University of Colorado, Boulder Colorado 80309, United States.*

Maciej Podgórski - *Department of Chemical and Biological Engineering, University of Colorado at Boulder, Colorado 80309, United States.*

Department of Polymer Chemistry, Institute of Chemical Sciences, Faculty of Chemistry, Maria Curie-Sklodowska University, M. Curie-Sklodowska Sq. 5, Lublin 20-031, Poland

Notes

The authors declare no competing financial interest.

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