Electronic Supplementary Material (ESI) for Polymer Chemistry.

Radical-Disulfide Exchange from Thiol-Ene-Disulfidation Polymerizations

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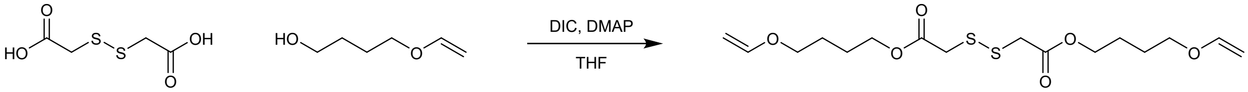
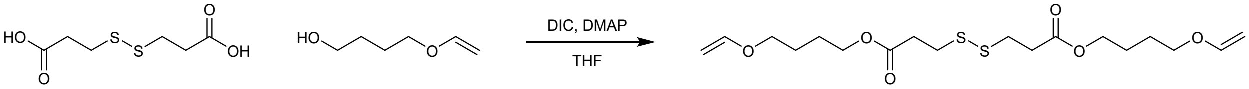
Appendix 1: Synthetic Procedures:

Dithioglycolate dinvinyl ether (DTG):



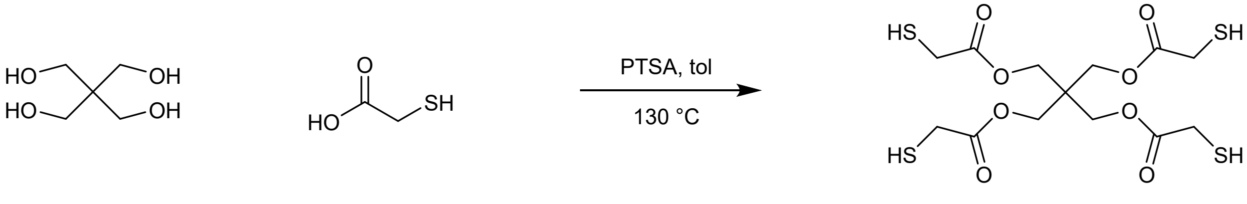
To a rapidly stirring solution of dithioglycolic (27.48mmol, 1 equivalence) in dry THF (0.11M) was added 1,4-butanediol vinyl ether (82.43mmol, 3 equivalences). Following, diisopropylcarbodiimide (DIC, 68.69mmol, 2.5 equivalences) was added in one portion along with 4-dimethylaminopyridine (DMAP, 4.12mmol, 0.15 equivalents). The mixture was allowed to stir at room temperature for 72 hours before the mixture was filtered over a pad of celite and washed with THF. The solution was then concentrated, and the crude mixture is purified by column chromatography (100% DCM). After the column, trace amounts of DIC starting material was further removed on a high pressure vacuum. Clear light yellow oil. 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) **δ** 6.45 (q, 2H), 4.13-4.21 (m, 6H), 3.96-4.00 (dd, 2H), 3.69 (m, 4H), 3.57 (s, 4H), 1.69-1.82 (m, 8H).

Di(3-mercaptopropionate) divinyl ether (DMP):



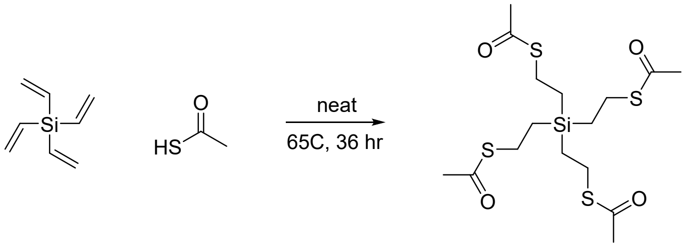
To a rapidly stirring solution of 3,3'-dithiodipropionic acid (27.5 mmol, 1 equiv.) in dry THF (0.11 M) was added 1,4-butanediol vinyl ether (82.43 mmol, 3 equiv.). Following, diisopropylcarbodiimide (DIC, 68.7 mmol, 2.5 equiv.) was added in one portion along with 4-dimethylaminopyridine (DMAP, 4.12 mmol, 0.15 equiv.). The mixture was allowed to stir at room temperature for 72 hours before the mixture was filtered over a pad of celite and washed with THF. The solution was then concentrated, and the crude mixture is purified by column chromatography (100% DCM). After the column, trace amounts of DIC starting material is further removed on a high pressure vacuum. Clear yellow oil. 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.46 (dd, *J* = 14.4, 6.8 Hz, 2H), 4.21 – 4.08 (m, 6H), 3.99 (dd, *J* = 6.8, 2.0 Hz, 2H), 3.75 – 3.65 (m, 4H), 3.00 – 2.85 (m, 4H), 2.74 (t, *J* = 7.0 Hz, 4H), 1.82 – 1.67 (m, 8H).

Pentaerythritol tetrakis(2-mercaptoacetate) (PETMA):

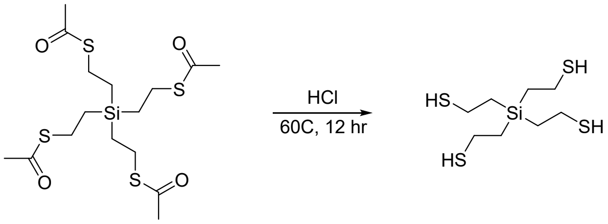


Pentaerythritol (36 mmol, 1 equiv.) was added to toluene (0.3 M), followed by para-toluene sulfonic acid (1.83 mmol, 0.5 equiv.). Following, thioglycolic acid (257 mmol, 7 equiv.) and reflux the mixture at 130 °C overnight. The solution was concentrated and the crude mixture was directly purified with column chromatography (gradient of 0 – 10% MeOH in DCM, 14 column volumes). Clear oil. 85% yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.23 (d, J = 9.4 Hz, 9H), 3.29 (d, J = 8.4, 1.1 Hz, 8H), 2.03 (t, J = 8.4, 0.8 Hz, 4H).

Silane tetrathiol (SiTSH):



Step 1 - SiTTE: Thioacetic acid (190 mmol, 5.2 equiv.) was added dropwise to tetravinylsilane (5 g, 36.7 mmol) in an ice bath. The mixture was then heated to 40 °C and the AIBN was added slowly over the course of 30 minutes to the mixture, with a reflux apparatus being placed over the flask in between additions. The mixture was then slowly heated to 65°C until reflux, then allowed to react for 36 hours. Care should be taken during this step as N_2 gas is also produced as AIBN initiates and the overall exothermic character of this react can cause the thioacetic acid to boil rapidly. Excess thioacteic acid was removed by vacuum distillation at 65°C to a yellow oil. This oil was dissolved in 2-3x it's volume in methanol, placed in the freezer and allowed to recrystallize for 5-6, then stirred and the solids broken up to be left in the freezer overnight. The solids were then vacuum filtered and rinsed with cold hexanes. 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.97 – 2.90 (m, 8H), 2.32 (s, 12H), 1.08 – 1.02 (m, 8H).



Step 2 - SiTSH: SiTTE was suspended in 50 mL of methanol and 30 mL of 12 mL HCl, heated to 60 °C and allowed to stir overnight. The product was concentrated to remove methanol. This crude product was mixed with equal volumes of DCM and water, then neutralized with saturated sodium bicarbonate to pH = 4-5 in the aqueous layer. The organic layer from the neutralization was then extracted one time with water. The aqueous layer from the neutralization was extracted 2 times with DCM. The organic layerd we combined and dried with brine, then sodium sulfate, then concentrated. The product was then subjected to column chromatography (DCM:Hexanes, 1:2 → 2:1). 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.65 – 2.56 (m, 8H), 1.58 (t, J = 6.9 Hz, 4H), 1.09 – 1.02 (m, 8H).

Appendix 2: Determining the Thiol-ene Rate Limiting Step for Thiol Monomers

The rate limiting step for the thiol-ene reaction using PETMP, PETTG, and SiTSH was determined to better understand what radicals are going to predominate during the polymerization. This was done using FTIR between salt plates for three different stoichiometric mixtures of each thiol with tri(ethylene glycol) divinyl ether (TEG): 2:1, 1:1, and 1:2 ratios of thiol to alkene. Mixtures were prepared at the each stoichiometry with 0.1 wt% TPO photoinitiator (405 nm), mixed well for 30 seconds, and subjected to FTIR in triplicate. Samples were irradiated with 405 nm light at 5 mW/cm^2 to initiate the polymerization.

The polymerization rate was determined from the rate of reaction of the limiting reagent of each stoichiometry: the vinyl ether for 2:1 and 1:1, and the thiol for the 1:2. The plots of conversion over time are provided in **Figure S3.** The rate was taken for a conversion of the limiting reagent from ~10-40% conversion.

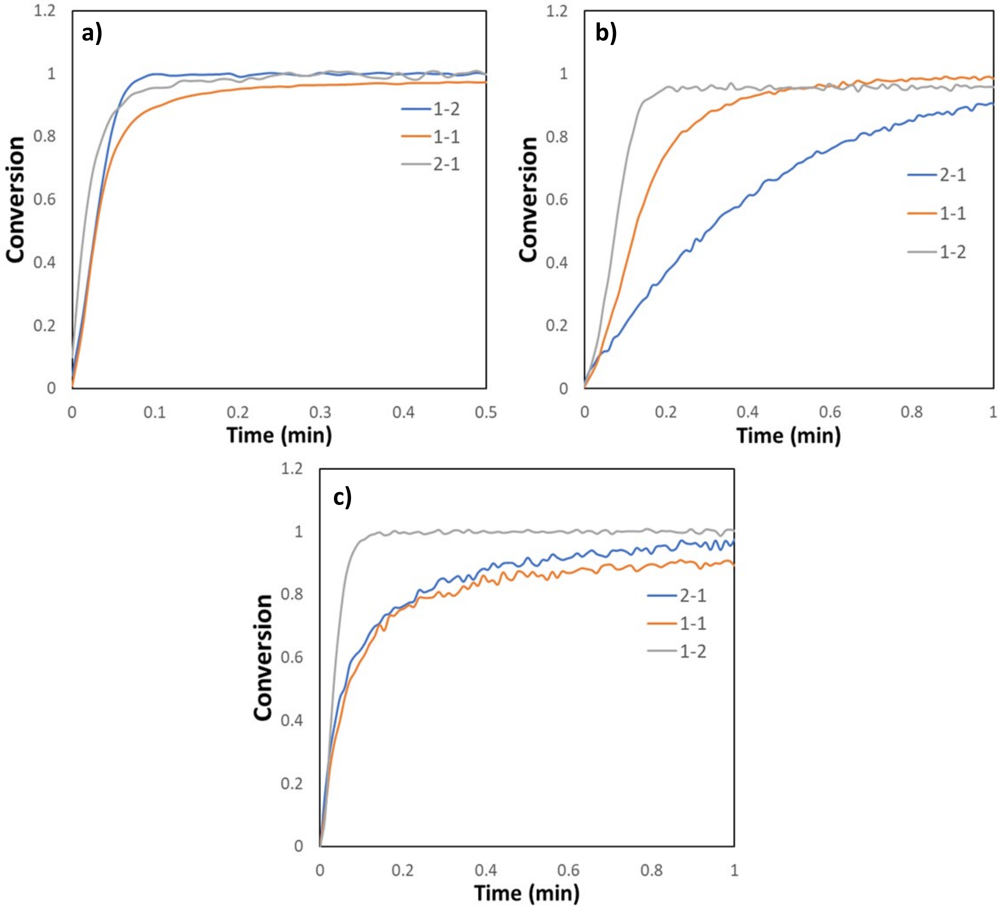


Figure S1: Conversion over time for a) PETMP, b) PETTG, and c) SiTSH with 0.1 wt% TPO at three stoichiometries used to determine the rate limiting step. The rate was determined from by taking the slope of the curve from 10-40% conversion of the limiting reactant for each stoichiometry: the vinyl ether for 2-1 and 1-1, and the thiol for 1-2.

The rate limiting step with PETMP was determined to be chain transfer, which aligned with the literature, because the fastest polymerization rate was observed with an excess of thiol, which appears only in the chain transfer step between a thiol and a carbon-centered radical. For PETTG and SiTSH, propagation was the rate limiting step because the fastest rates occurred for an excess of alkene, which appears only in the propagation between a thiyl radical and an alkene.

Unexpected behavior appeared during the initial testing using SiTSH, for which subsequent replicates taken immediately after mixing showed a progressively faster rate of polymerization, often times reaching a plateau by the third replicate, shown for the 1:1 stoichiometry in **Figure S4a**. This trend did not occur for PETMP or or PETTG, and no polymerization occurred in that time before the light was turned on. Introduction of a small amount of radical inhibitor (10 mol% relative to TPO of butylated hydroxytoluene (BHT)) only slowed the reaction, but did not result in an inhibition period or elimination of the increases in reaction rate for subsequent replicates (**Figure S4b**). However, the replicates became quite consistent when the SiTSH/TEG mixture was allowed to equilibrate for 10 minutes before FTIR analysis (**Figure S4c**). We hypothesize that this is because silanes such as SiTSH are known to have high concentrations of dissolved oxygen compared to other organic molecules (such as PETMP and PETTG in this case). Upon mixing with TEG, the overall affinity for dissolved oxygen likely lower than a simple average of the concentration for each monomer and it takes some time for the oxygen concentration to decrease and equilibrate with the air. Such a difference in oxygen concentration is not typically considered at normal initiation conditions (1-2 wt% TPO and 20 mW/cm^2 light intensity) for thiol-ene reactions. But at mild conditions, a significant increase in oxygen concentration compared to standard monomer mixtures coupled with the need to equilibrate that oxygen concentration could result in the changing kinetics over time observed here. Further investigation is required to fully assess the origin of this behavior but

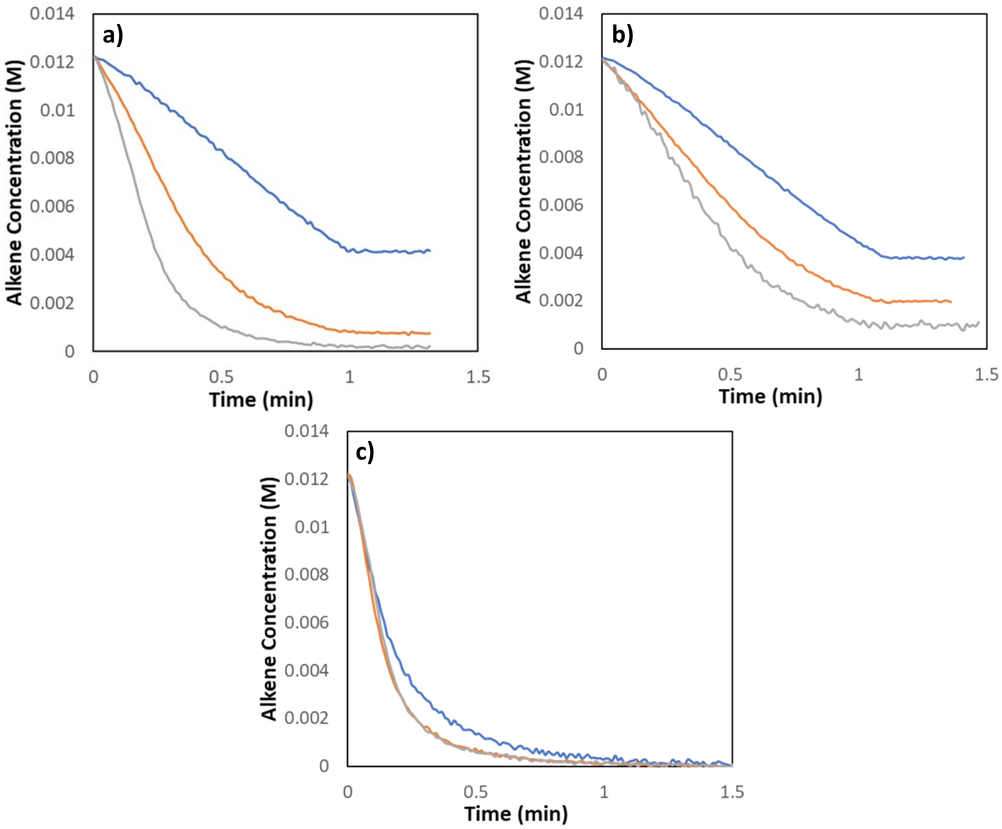


Figure S2: Alkene Concentration over time for SiTSH and TEG in a 1:1 ratio of thiol to alkene for: a) A freshly mixed initial resin without inhibitor, b) a freshly mixed initial resin with 10 mol% BHT relative to TPO, and c) A resin mixture without inhibitor that was allowed to rest for 10 minutes before testing. For each plot, blue was the first replicate, orange is the second, and grey is the third.

allowing the mixture to equilibrate before FTIR analysis enabled consisted measurement of conversion over time and it sufficient for this study.

Appendix 3: Additional Supplementary Figures:

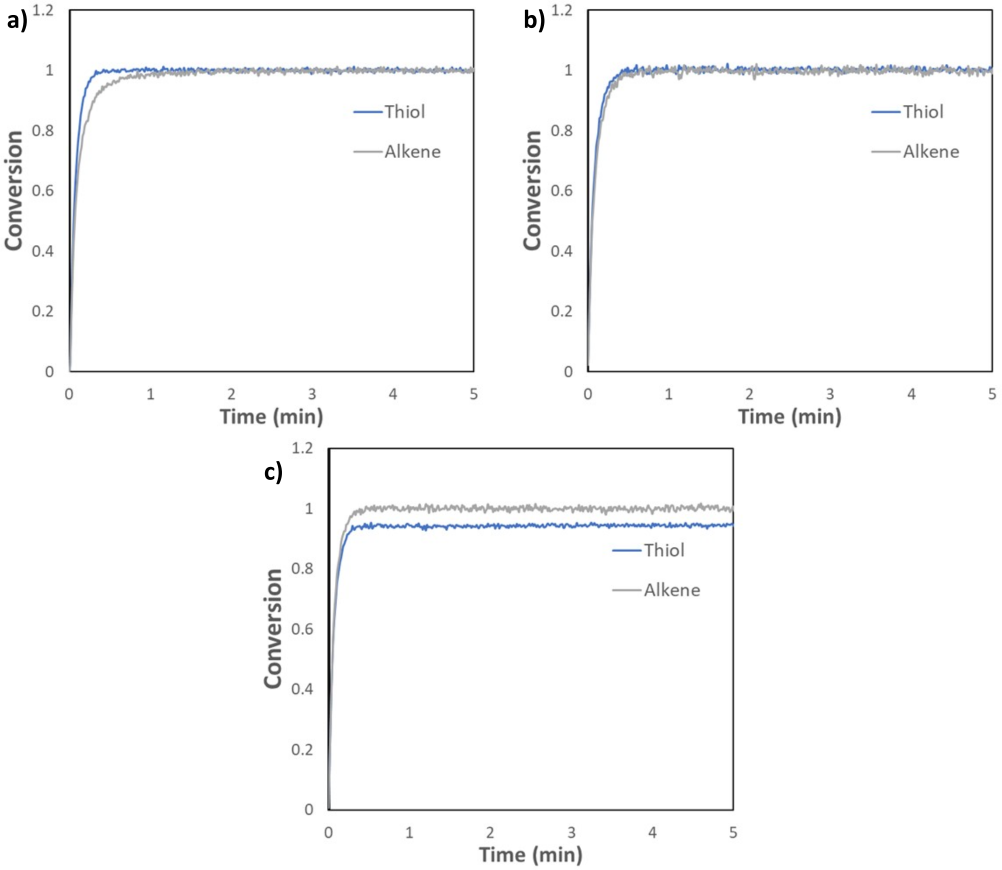


Figure S3: Thiol and alkene conversion over time PETMP and DSDVE at various thiol-to-alkene ratios a) 0.9:1, b) 1:1, and c) 1.1:1

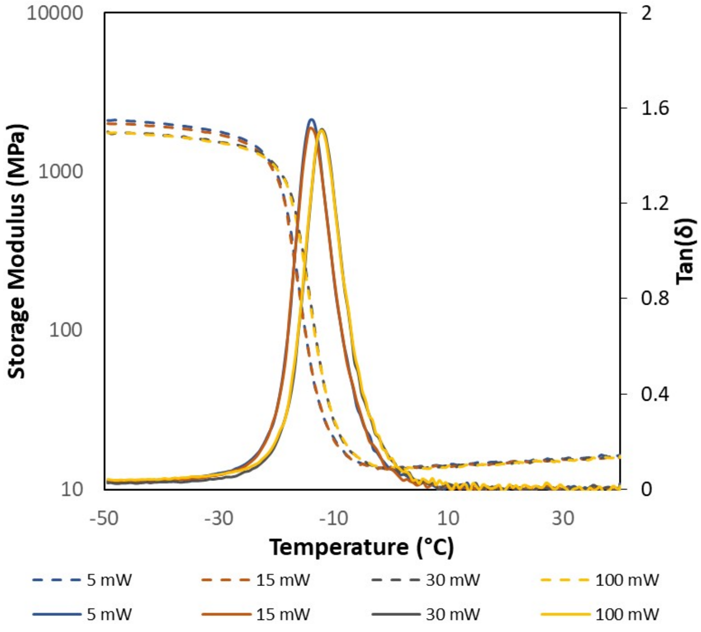


Figure S4: Dynamic Mechanical Analysis for PETMP and DTG at 0.5:1 ratio of thiol to alkene cured at various light intensities.

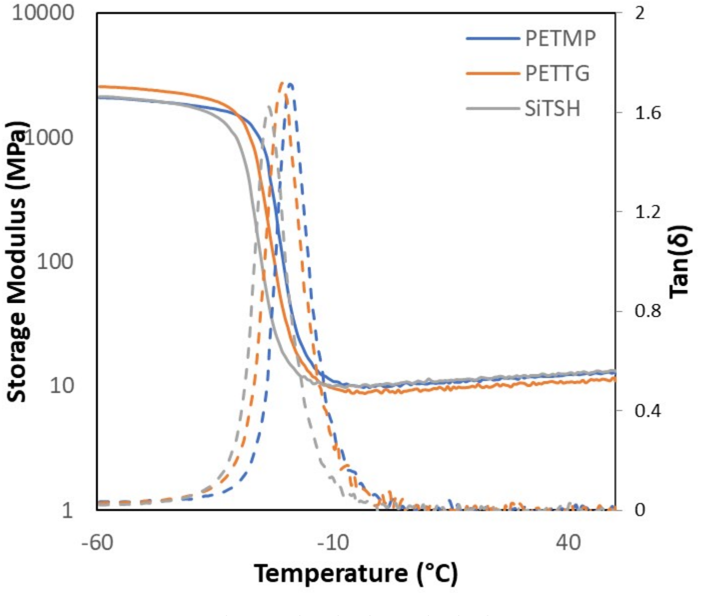
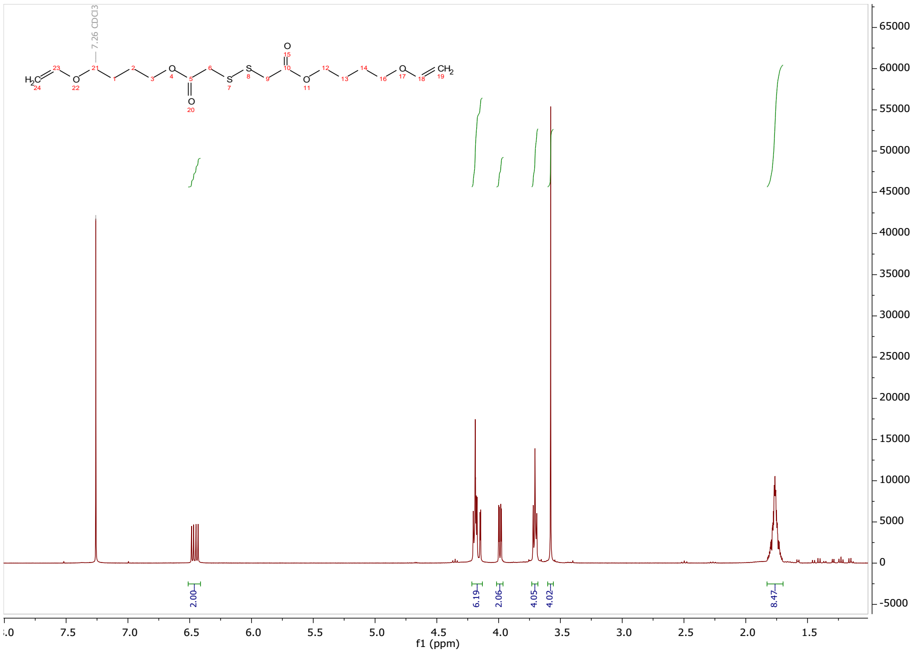


Figure S5: Dynamic Mechanical Analysis for DMP at 0.5:1 ratio of thiol-to-alkene with various thiols. Samples were cured with 1 wt% TPO and 405 nm light at 20 mW/cm^2 for 5 minutes on each side.

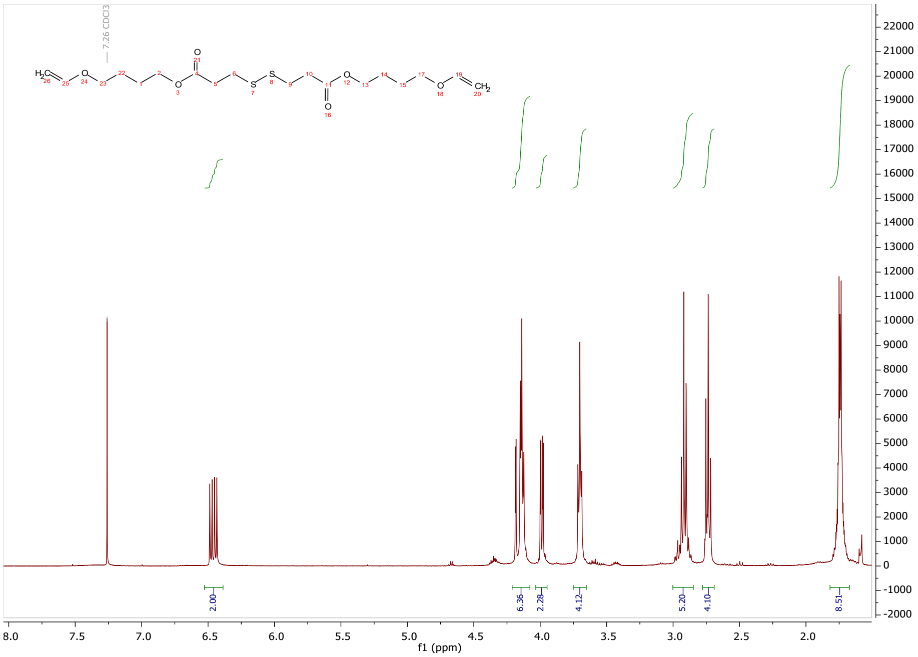
Table S1: Compilation of the glass transition temperatures and storage moduli for materials in this work.

Sample		T_g (°C)	Storage Modulus (MPa, 20 °C)
PETMP:DTG	0.9:1	-26	12
	1:1	-28	10.5
	1.1:1	-30	7.5
PETTG:DTG	1.1:1	-23	11
DTG (0.5:1)	PETMP	-19	13
	PETTG	-22	14
	SiTSH	-17	12.5
DMP (0.5:1)	PETMP	-19	11
	PETTG	-20	10
	SiTSH	-23	11

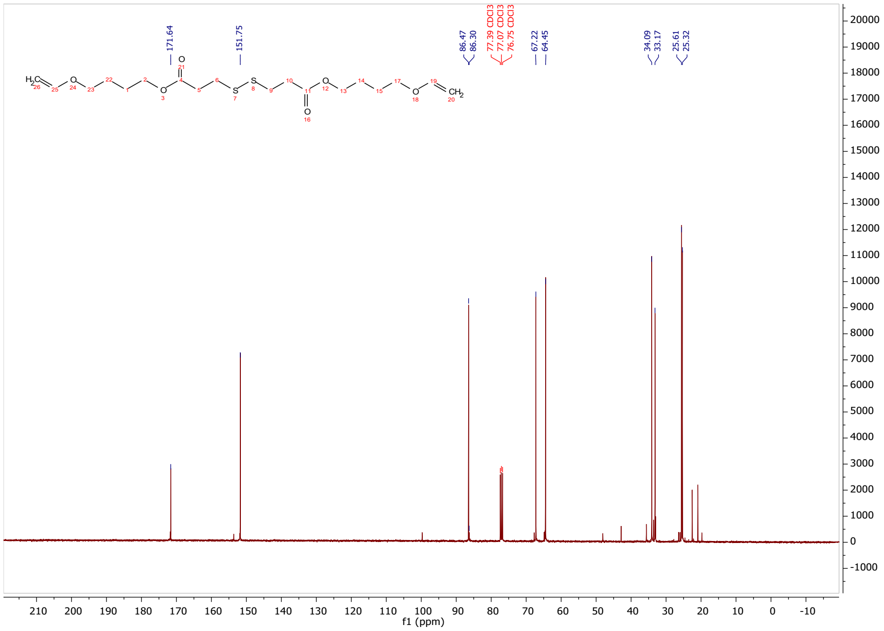
Appendix 4: NMR of Synthesized Species:



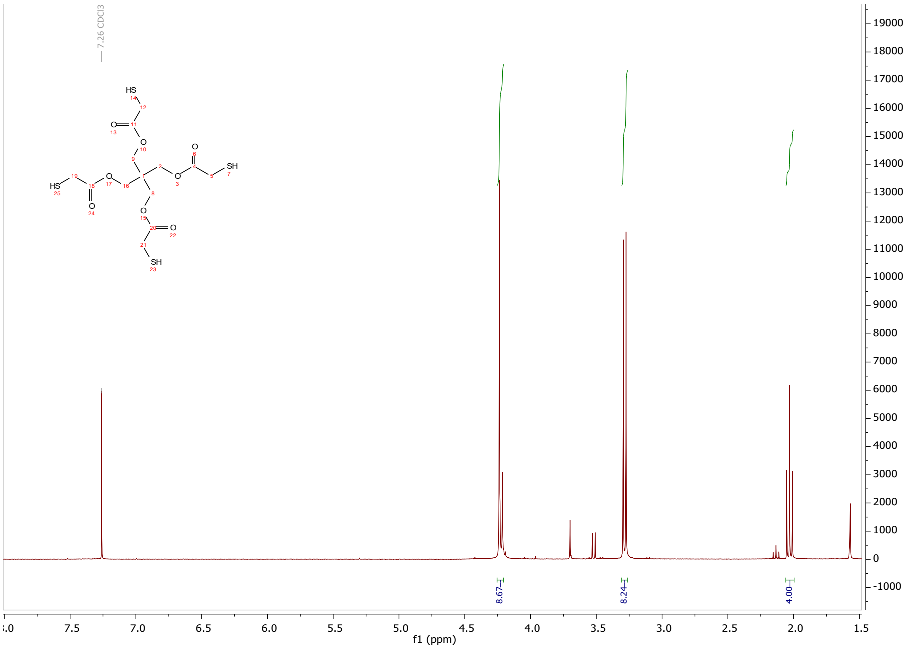
H^1-NMR, DTG



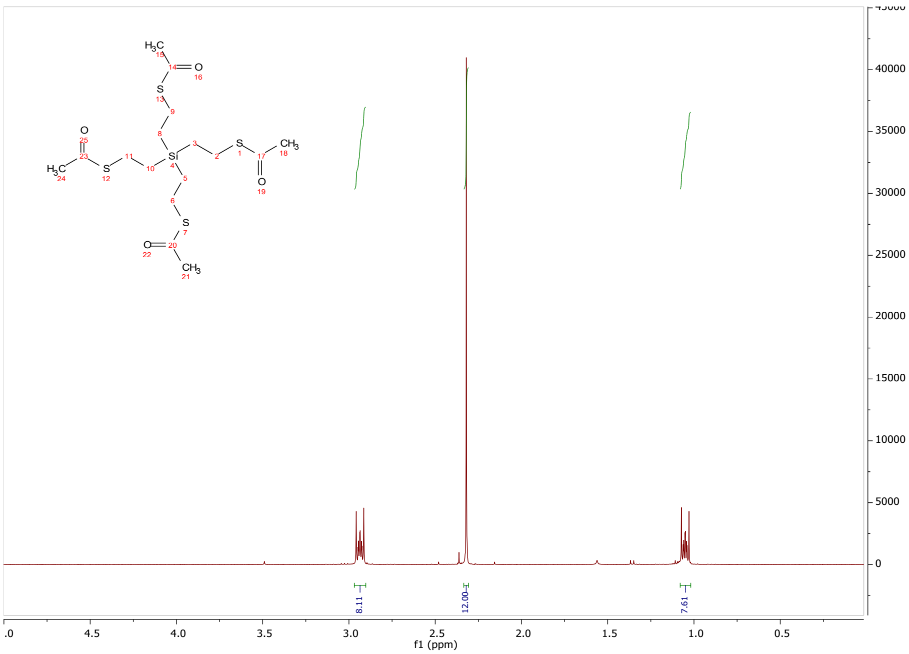
H1-NMR, DMP



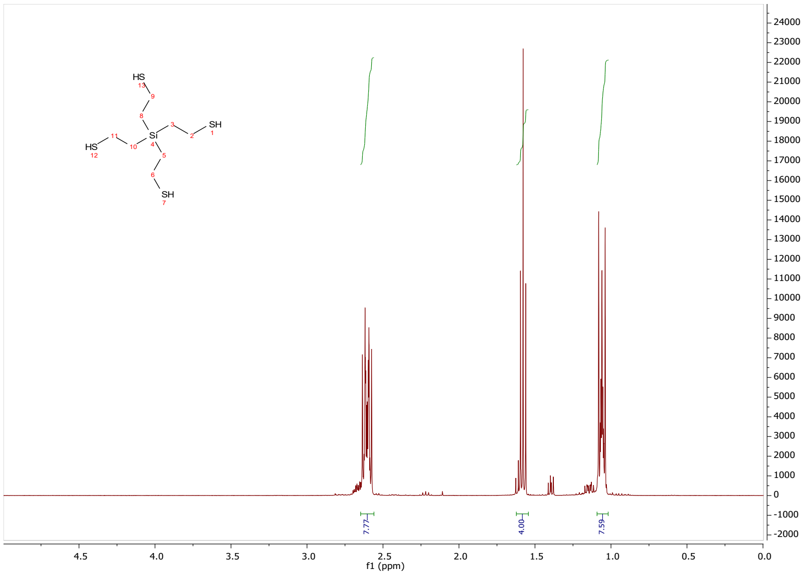
C13-NMR, DMP



H¹-NMR, PETMA



H¹-NMR, SiTTE



HS
13
9
8
Si
4
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2
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HS
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3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

H^1-NMR, SiTSH