



Recyclable and Repolymerizable Thiol-X Photopolymers

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Conceptual Insights

Cross-linked photopolymers are typically prepared from liquid monomers with as little as a second of light exposure with the accompanying formation of desired 3D shapes, features, and material behaviors. However, the crosslinks which form these networks prohibits them from being remolded, reshaped, or repurposed. Herein, we demonstrate a class of rapidly photopolymerizable thiol-ene networks that incorporate thioester functional groups, which allow complete degradation of the network into oligomers by thiol-thioester exchange reactions. The degraded oligomers can subsequently be repolymerized into a nearly indistinguishable material with no change in material behavior through multiple cycles. Both the original and the recycled materials yield optically clear photopolymers with tunable mechanical properties, and have rapid polymerization kinetics. The recycling and subsequent polymerization processes are highly reproducible and consistent at each round of recycling. Adding to the benefits afforded from a photo-curing processes, such as on-demand formation and spatial initiation, fully recyclable coatings, optical devices, and 3D printed products could be readily realized utilizing this method.



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Recyclable and Repolymerizable Thiol-X Photopolymers

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We demonstrate a class of rapidly photopolymerizable step-growth cross-linked networks that incorporate thioesters into the backbone. The thioester functional groups enable complete degradation of the network into oligomers that can subsequently be recycled into a nearly indistinguishable material with no change in material behavior.

From elastomers to fibers to photopolymers, polymer thermosets have stood as ubiquitous materials with diverse applications for more than a century. For instance, the annual consumption of photopolymers in North America alone is above 100,000 metric tons.^[1] As the main component in coatings, adhesives, dental restorative materials, and stereolithographic 3D printed materials, crosslinked photopolymers are typically generated from reactive liquid monomers upon irradiation.^[2] Such free-flowing liquid resins facilitate storage, handling, and application of the resins, while their resulting cured polymer networks are mechanically robust and solvent/heat resistant. Processing time is generally rapid, requiring as little as a fraction of a second of irradiation. In free-radical chain-growth photopolymers, multifunctional monomers are implemented to enable rapid curing kinetics, which ultimately leads to highly crosslinked materials.^[3] However, the crosslinks which form these networks prohibits them from being remolded, reshaped, or repurposed. Therefore, photopolymers generally cannot be recovered but are typically turned into waste after the product's lifetime.

By incorporating dynamic covalent bonds throughout the network, several classes of polymer networks are capable of adjusting their molecular topologies.^[4] Many dynamic covalent

chemistries have been introduced to network polymers; some examples include the Diels-Alder reaction, disulfide exchange, free-radical reversible addition-fragmentation transfer (RAFT), transesterification, and the boronic acid-ester exchange.^[5] In these systems, such dynamic reactions shuffle the network building blocks, usually upon the onset/offset of an external stimuli. Currently, very few implementations of such dynamic linkages have been reported in photopolymers^[2] and recyclability has yet to be achieved. It is worth noting that true "recyclability" would allow for replicable reuse of the recovered material in the same manner as the original material with little or no changes in methods for handling or polymerization.^[6]

Here, we employ a bi-functional reactive group, which productively engages in the polymerization and subsequent dynamic exchange reactions. The exchanged product, in this case, is in the form of degraded oligomers, which are capable to undergo polymerization again, and thus enabling the reclamation of the pristine polymer. Step-growth photopolymers are ideal candidates as they possess uniform and highly tunable network structures.^[9] We sought to examine thiols due to their well-studied reactivity in both photopolymerizations and dynamic covalent reactions, including a series of thiol-X polymerization reactions^[10] and the thiol-thioester exchange (transthioesterification) reaction^[11], respectively. Though the thiol-thioester exchange reaction has been well-studied in biochemistry, it has only recently been utilized in organic media and network polymers.^[12] Herein, we investigate the combination of the thiol-ene photopolymerization reaction and thiol-thioester exchange reaction as a strategy to create a robust, recyclable, and repolymerizable photopolymer network.

Stoichiometric thiol-ene polymerizations between a tetra-thiol (PETMP) and a di-ene (TEDAE) monomers are used for the preparation of pristine polymers with a catalytic amount of photoinitiator (2,2-dimethoxy-2-phenylacetophenone, DMPA)

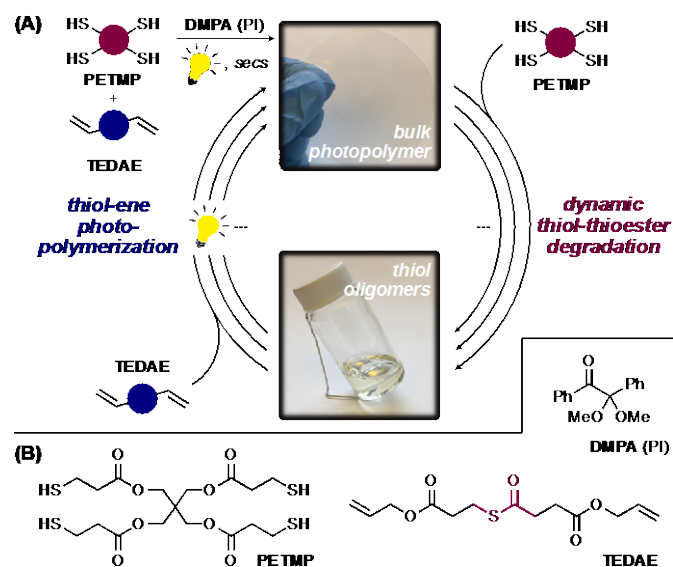
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added prior to UV light exposure. As expected, the free-radical thiol-ene polymerization was noted to proceed rapidly and



Scheme 1. (A) Reaction scheme for recycling and repolymerizing cross-linked photopolymers by a free radical thiol-ene polymerization and an anionic thiol-thioester dynamic degradation. In particular, the pristine polymer is initially prepared by photo-initiated thiol-ene polymerization between a stoichiometric ratio of a tetra-thiol and a thioester-containing diallyl ether. The bulk photopolymer is degraded into thiol oligomers by thiol-thioester exchange with a defined amount of a tetra-thiol under basic condition. Subsequently, these oligomers are polymerized with a thioester-containing diallyl ether by a photo-initiated thiol-ene reaction. Three complete cycles of this procedure is demonstrated here to indicate the capacity for full recovery of the initial polymer. (B) Monomers employed in this study.

generated an optically clear, colorless, and tack-free film after just seconds of irradiation. As illustrated in **Scheme 1**, the crosslinked polythioether contains a thioester linkage in each of its repeating units, which is quite stable in neutral or slightly acidic conditions.^[13] However, upon the addition of excess PETMP (5, 7 and 9 equivalencies to the polymerized moieties, as listed in Table 1) and a mild organic base triethylamine (TEA), the thiol-thioester exchange reaction occurs rapidly. Acetone (equivalent mass to the sum of polymer and additional PETMP) is added to improve the mass transfer of solid/liquid phases. Under these “exchange conditions” the film was noted to disappear completely within 3 hours to yield a colorless non-viscous solution of dissolved oligomers. It is worth noting that the degradation time is tunable with respect to either the thiol-thioester exchange reaction rate and/or the diffusivity of the thiolates. Concentration of this solution gave a viscous liquid, to which a stoichiometric (thiol:ene, 1:1) amount of TEDAE was added (with additional DMPA), thoroughly mixed, and directly repolymerized by a subsequent thiol-ene photoinitiated reaction. Three rounds of this operation was conducted without noticeable changes in any detectable property of the either the

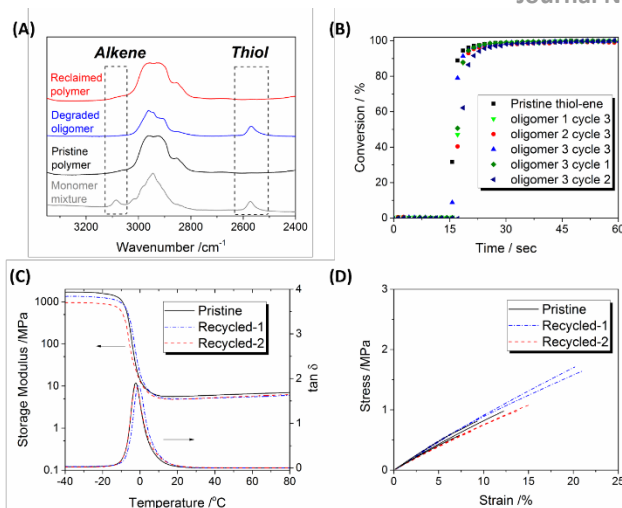


Figure 1. Chemical and mechanical characterizations of pristine PETMP-TEDAE polymer and recycled polymers. Reclaimed polymers are obtained from oligomer 2 (listed in **Table 1**) and TEDAE. Degradation condition: five, seven or nine equivalencies of additional PETMP, 50 mol% TEA with respect to the thioester functional group, acetone, 3 h. Irradiation Conditions: 2 wt% DMPA, UV light (5 mW/cm² @ 365 nm), continuous irradiation starts at 15 sec. (A) FT-IR of the PETMP-TEDAE monomer mixture (pre-polymerization, pristine polymer, degraded oligomer, and reclaimed polymer). (B) Reaction kinetics profiles (thiol groups) of the pristine monomer mixtures and various oligomers (listed in **Table 1**) with TEDAE. (C) Dynamic mechanical analysis (DMA) of pristine and reclaimed polymers. The glass transition temperatures overlay at -2 °C. (D) Tensile stress-strain curves of pristine and reclaimed polymers. The tensile Young's modulus overlay at 8 MPa.

oligomers or polymers. In particular, as shown in **Figure 1A-B**, the full conversions of both the pristine and reclaimed polymers, as confirmed by the complete disappearances of both thiol and alkene groups in Fourier transform infrared spectra (FT-IR) was noted. Moreover, **Figure 1C** shows invariable thermomechanical properties whereby the pristine and reclaimed polymers have a consistent glass transition temperature of -2 °C, as well as a rubbery modulus of 6 MPa. Tensile test shows that both pristine and reclaimed polymers break at ~15% strain on average with a Young's modulus of ~8 MPa, as shown in **Figure 1D**. In addition, both the pristine and recycled polymers obtained a high transparency in the visible range (Figure S1), and a refractive index of 1.54 (measured on a Metricon 2010/M prism coupler at a wavelength of 633 nm).

Since the TEDAE is a thioester derived from a mercaptopropionate, the exchange between the PETMP-TEDAE polymer and excess PETMP results in a thiol and thioester product nearly identical in structure/reactivity as the starting material, implying a near-zero net free energy change. Based on the Flory-Stockmayer equation, network polymers can be formed from tetra-thiol/di-ene monomers with no higher than two molar equivalents of excess thiol functionality (i.e., the off-stoichiometric ratio r must be no less than 0.333). To avoid oligomers that are too viscous to handle, we designed a series

of formulations with five, seven and nine molar equivalents of thiol, in which the ene:thiol stoichiometric ratios are 0.167, 0.125, and 0.100, respectively, as listed in **Table 1**. In each round of degradation, the polymer samples disappeared within three hours and once the solvent/volatile components were removed the oligomers were of consistent viscosities. As can be noted from oligomers 1, 2, and 3, the larger off-stoichiometric

Table 1. Formulations consisting of recycled thioester containing thiol oligomers formed by degrading PETMP-TEDAE polymers with additional PETMP. Oligomer 1, 2 and 3 were obtained from degrading the polymers with five, seven and nine equivalencies of additional PETMP. The oligomers were purified by the complete removal of the volatiles (TEA and acetone) before viscosity measurements.

Entry	Stoichiometric number (ene:thiol)	Functionality ratio (thiol:thioester)	oligomer viscosity /Pa-s
Oligomer 1	0.167	10	3.2±0.2
Oligomer 2	0.125	14	2.2±0.2
Oligomer 3	0.100	18	1.2±0.1

ratio leads to lower molecular weight oligomeric mixtures which exhibits decreased viscosities ranging from 3.2, 2.2, and 1.2 Pa-s, respectively. Further, the chemical structures are consistent between rounds of recycling, which was confirmed by ¹H NMR (**Figure S2**). It is worth noting that the expected Flory distribution is observed for the oligomers (gel permeation chromatography, **Figure S3**), where the fraction of higher molecular weight components decreases exponentially, as expected for step-growth polymers/oligomers formed at relatively low conversions.

Within the constraints of appropriate safety concerns, a reaction rate as high as possible is generally favored in photocuring applications. When photopolymerization is integrated as part of a process, such as in stereolithographic 3D printing, it is expected to be a highly robust and reproducible. **Figure 1B** shows the reaction kinetics by monitoring the decrease of the thiol peak centered at 2570 cm⁻¹ in real-time FT-IR. Under mild irradiation conditions (5mW/cm² @ 365 nm) the thiol-allyl ether polymerizations occur very rapidly. More than 90% conversion was achieved within 3-5 seconds under these initiation conditions. Interestingly, a kinetic profile was observed by overlaying many oligomer formulations (as listed in **Table 1**) together with the pristine sample, which indicated the consistency in reaction rates with no lapse in activity of the thiol-ene reaction even after several rounds of recycling. The PETMP-TEDAE system produces rubbery materials, thus the absence of vitrification allows constant reaction rate, even from monomers with various viscosities. Given that the chemical composition and reactivity of the recycled oligomers were consistent in each round of the recycling, we believe such recyclability can readily be continuously achieved beyond the three rounds, although at some point any issues with initiators

and catalysts and their decomposition products would need to be addressed.

PETMP and TEDAE are both aliphatic ester based monomers, which, when reacted yield generally hydrophobic polymers. While thioesters are more prone to hydrolytic degradation than esters, significantly, we did not observe a notable difference in stability between a structurally similar polythioester and polyester films. Diallyl adipate is structurally nearly identical to TEDAE with the notable exclusion of the thioester group. In a water uptake test, we observed less than 1% weight gain in both the polythioester and the control films over the course of one week, indicating the durability of recyclable thioester containing polymers (details in **Table S1**). In theory, the thioester-based films, due to their lower electron density on the oxygen of the carbonyl groups, when compared to similar ester-based films, would likely have improved stability in acidic media and decompose more rapidly in basic media^[13] than their analogous ester-containing networks. Furthermore, for both the polythioester and the polyester control films thermogravimetric analysis (TGA) showed little weight loss up

Table 2. Formulations of recyclable polymers that are prepared by various thiol monomers with TEDAE. Degradation conditions: the respective thiol monomers with a particular stoichiometric number were added with triethylamine (50 mol% to thioester groups) and acetone (equal in mass to the non-volatile compounds), 3h at ambient.

Thiol monomers	Tg /°C	Rubbery modulus /MPa	Recycling stoichiometry ratio ene:thiol	Recycled oligomer viscosity /Pa-s
TMPTMP ^{a)}	-4	3.5	0.25	4.1±0.2
TEMPIC ^{a)}	6	1.7	0.25	108±4
ETTMP700 ^{a)}	-22	1.8	0.25	1.4±0.1
ETTMP1300 ^{a)}	-28	1.3	0.25	1.8±0.1
PETMP ^{b)}	-2	6.0	0.167	11±1
PCL4MP ^{b)}	-23	2.4	0.167	3.8±0.1
Di-PETMP ^{c)}	7	8.6	0.1	32±2

^{a)} Tri-thiol; ^{b)} Tetra-thiols; ^{c)} Hexa-thiols.

to 320 °C under N₂, as shown in **Figure S4**. Though the polythioester films are extremely dynamic when placed under exchange conditions, the thioester functional group evidently does not effect the solvent/heat stabilities of the network polymers.

In step-growth reactions, the network structure is readily adjustable by simple changes in the structure of the monomer, and thus, material properties are precisely tunable. We therefore studied the tunability of the recyclable thiol-ene photopolymers by incorporating various thiol monomers with stoichiometric TEDAE, as listed in **Table 2** (chemical structures of monomers are shown in **Figure S5**). Notably, both chemical structure and functionality of the thiol monomers affected the properties of the polymer. Structurally similar tri-thiol (TMPTMP), tetra-thiol (PETMP) and hexa-thiol (Di-PETMP) monomers generated polymers with small increases in their

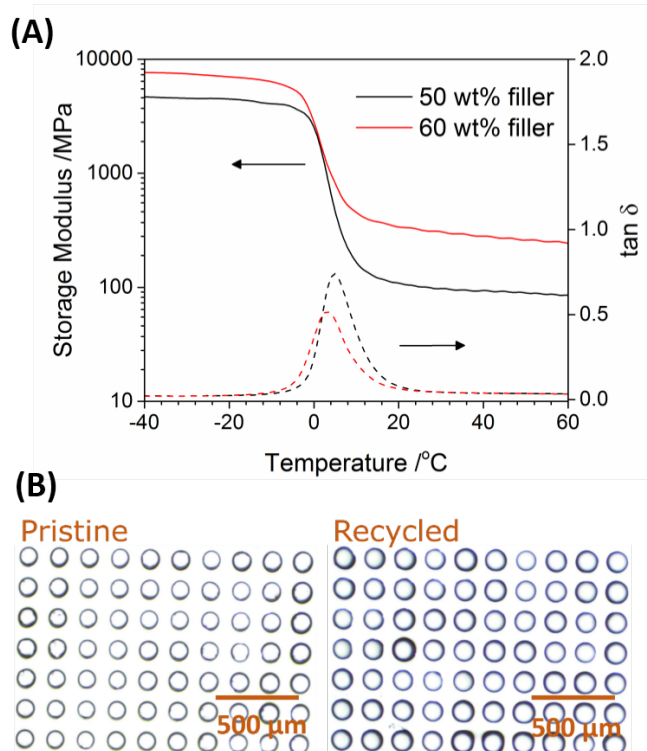


Figure 2. (A) Dynamic mechanical analysis of silica particle filled composite materials. Two samples with 50 wt% and 60 wt% silica particles in PETMP-TEDAE matrices were polymerized with 2 wt% DMPA under irradiation of 8 mW/cm² @ 365 nm for 5 mins. (B) Images of contact liquid photolithography of pristine and reclaimed PETMP-TEDAE polymers. Both pristine and reclaimed samples consist of stoichiometric PETMP-TEDAE monomers with 0.5 wt% I184 and 0.3 wt% methylhydroquinone with respective to polymerizable components. Photomasks are comprised of 100 μm circles separated by 100 μm screening gaps. Collimated UV light (50 mW/cm² @ 365 nm) was exposed for 120 sec on the pristine samples and for 80 sec on the recycled samples.

respective glass transitions (T_g) from -4°C, to -2°C, to 7°C, respectively, with rubbery modulus of 3.5, 6.0, and 8.6 MPa, respectively. Also, the tri-thiol which contains a stiff ring-structured core (TEMPIC) offers an increased T_g as compared to that of the structurally dissimilar tri-thiol TMPTMP (6°C vs. -4°C), while the flexible polyethylene glycol based thiols (ETTMP 700 and 1300) form softer materials (-22°C and -28°C,

respectively). The viscosities of these oligomers are in good agreement with the monomer structures. For example, the TEMPIC oligomer has a viscosity of 108 Pa·s while the viscosity of ETTMP oligomers is merely 1-2 Pa·s. Even with the relatively small number of thiol monomers used here, simply altering one of the two reactive components, we are able to design recyclable thiol-ene polymers with robustly tunable thermomechanical properties.

Filler-reinforced composites are commonly employed for photopolymers to obtain enhanced mechanical properties, including tensile modulus. Photopolymers loaded with various amount of silica particles (diameter: 0.4 μm) were prepared simply by dispersing un-functionalized particles into a PETMP-TEDAE mixture and subsequently curing with UV light. The obtained composites were translucent, indicating good compatibility of silica particles with the polymer matrix. Interestingly, the rubbery modulus of 50 wt% and 60 wt% particle loading composites are 94 MPa and 282 MPa, respectively, both of which are significantly higher than the pure PETMP-TEDAE polymer (6 MPa), as shown in **Figure 2A**. The particle loadings were confirmed by TGA analysis, in particular, samples that are loaded with 50 wt% and 60 wt% particles show weight losses of 50 % and 40 %, respectively (**Figure S6**). The composites degraded completely under our exchange conditions with excess thiol, base and acetone, and both silica particles and thiol oligomers were recovered by simple centrifugation and subsequent drying under vacuum.

After consistent reaction kinetics and material properties were noted in these recyclable materials, we implemented such polymerizations in contact liquid photolithography. As shown in **Figure 2B**, both pristine and recycled PETMP-TEDAE polymers were polymerized into cylinders ~100 μm in diameter and 80 μm in height on glass slides. A free-radical inhibitor (methylhydroquinone) was used to mitigate the migration of radical species and thus improve spatial resolution. Of note, the reclaimed samples require less curing time than that of the pristine samples as a result of the increased viscosity. Both of the surface features were found to be degradable under similar conditions to the abovementioned unfilled systems. This implementation in photolithography, though primitive, is potentially useful in fabricating degradable and recyclable materials with functionalized surfaces, and stereolithographic 3D objects.

Conclusions

Here, a truly recyclable photopolymer was achieved by incorporating thioester moieties into thiol-ene polymerization reactions with great tunability and variability of the mechanochemical behavior of the polymers formed. Various stoichiometric ratios between thiol and thioesters were studied for degrading polymers into thiol-laden oligomers that can be readily repolymerized to achieve the native polymer network behavior. Specifically, up to three rounds of recycling was carried out, in which the reclaimed polymers were discovered to have identical mechanical properties and polymerization kinetics as the original monomers. Mechanical properties are readily tunable by selection of the polymerization system, thiol monomers, and complementary monomers. Applications in composite materials and photolithography were also demonstrated. Future work will concentrate on optimizing the reaction conditions, comprehensively understanding the degradation/stability behaviors of such photopolymers, and

implementing this recycling scheme to materials with a wide range of properties for specific photopolymer applications.

Conflicts of interest

A full patent regarding this work has been filed by the Technology Transfer office at the University of Colorado at Boulder. Worrell, B. T.; McBride, M. K.; Lyon, G. B.; Wang, C.; Bowman, C. N. *Thioesters in Network Polymers*, U.S. Patent 62/378,447, 2018, *filed*.

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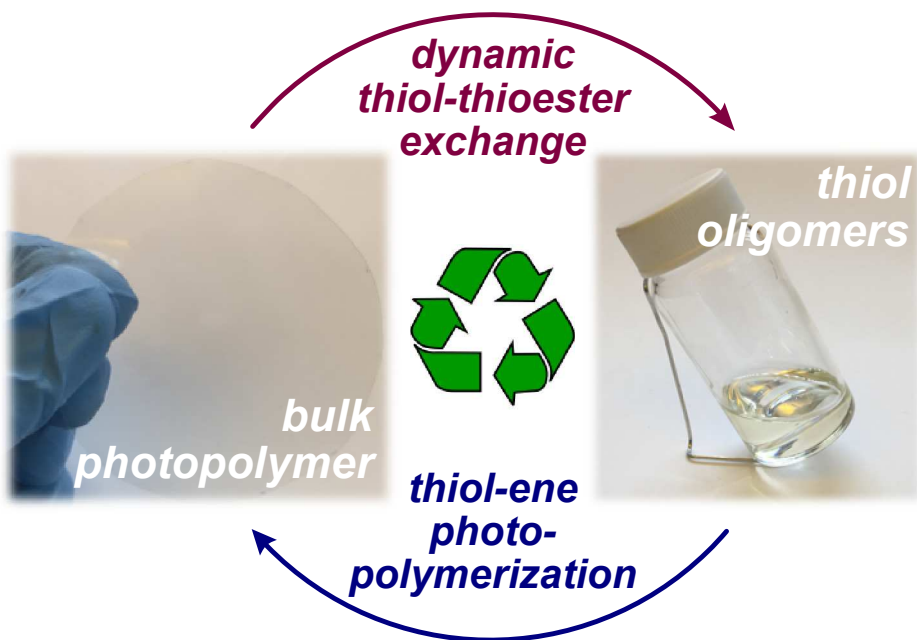
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† Electronic Supplementary Information (ESI) available: Experimental details and characterization methods. See DOI: 10.1039/b000000x/

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Truly recyclable and repolymerizable photopolymers were achieved by utilizing thiol-ene polymerization and thiol-thioester exchange reactions.