Bio-Based Thiol-ene Network Thermosets from Isosorbide and Terpenes

Emily A. Prebihalo,[a] Melody Johnson,[b] Theresa M. Reineke[a]*

[a]Department of Chemistry, University of Minnesota, 207 Pleasant St. SE, Minneapolis, MN 55455, USA.

[b]Department of Chemistry and Biochemistry, North Dakota State University, 1231 Albrecht Blvd, Fargo, ND 58102, USA.

Corresponding author: treineke@umn.edu

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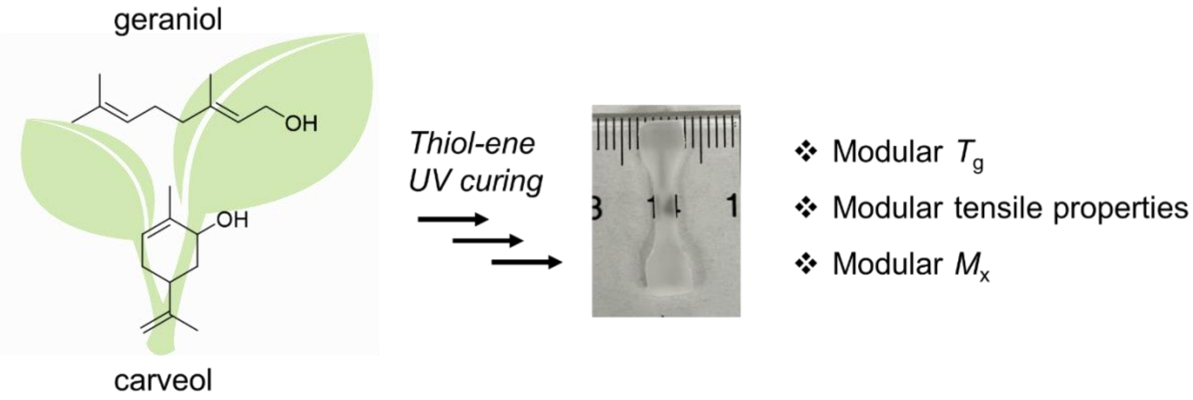

Abstract

Thermoset networks are chemically crosslinked materials that exhibit high heat resistance and mechanical strength; however, the permanently crosslinked system makes end-of-life degradation difficult. Thermosets that are inherently degradable and made from renewably-derived starting materials are an underexplored area in sustainable polymer chemistry. Here, we report the synthesis of novel sugar- and terpene-based monomers as the enes in thiol-ene network formation. The resulting networks showed varied mechanical properties depending on the thiol used during crosslinking, ranging from strain-at-breaks of 12-200%. Networks with carveol or an isosorbide-based thiol incorporated showed plastic deformation under tensile stress testing, while geraniol-containing networks demonstrated linear stress-strain behavior. The storage modulus at the rubbery plateau was highly dependent on the thiol crosslinker, showing an order of magnitude difference between commercial PETMP, DTT, and synthesized Iso2MC. Thermal degradation temperatures were low for the networks, primarily below 200 °C, and the T_g values ranged from -17 to 31 °C. Networks were rapidly degraded under basic conditions, showing complete degradation after 2 days for nearly all synthesized thermosets. This library demonstrates the range of thermal and mechanical properties that can be targeted using monomers from sugars and terpenes and expands the field of renewably-derived and degradable thermoset network materials.

Introduction

Thermosets account for nearly 18% of the world production of polymers, come primarily from petroleum-based sources, and tend to be non-degradable.[1] The enhanced thermal and mechanical properties as a result of the chemical crosslinks enable use in a wide variety of applications such as coatings,[2,3] adhesives,[4,5] 3D printing,[6] and hydrogels.[7,8] However, the tradeoff of these desirable properties is difficult recycling or degradation of the material at the end of its life. As the field of polymer chemistry has become increasingly attentive to the environmental impacts of plastics, research into bio-based and degradable polymers has expanded in scope and urgency. While thermoset networks derived from natural sources have been reported for systems such as polyesters,[9] epoxies,[10,11] and acrylics,[12] one particularly exciting area of research is thiol-ene networks, useful due to the efficient and well-established click chemistry. Thiol-ene chemistry has been demonstrated across a wide array of applications in both thermoplastics and thermosets[7,13–16] and typically yields low reaction times with high crosslinking density. Thiol-ene networks made from bio-based materials has been a growing field, particularly focused on naturally-sourced enes crosslinked with standard commercial thiols.[17–23] Examples of renewably-derived thiols for these networks are fewer,[24–26] highlighting the need for further exploration into alternative thiols and their mechanical properties as well as end-of-life degradation.

A common source for safe, bio-based enes is terpenes and terpenoids, a class of non-toxic natural products found in many plant oils and used in flavors and fragrances.[27] Terpenes have been investigated for polymerization ability, ranging in applications from coatings to 3D printing.[28–30] The structural diversity of monoterpenes allows for a range of properties to be studied; of particular interest here are the aliphatic geraniol and the cycloaliphatic carveol due to their structural differences and easy availability. In previous terpene reports, geraniol-based networks show softer mechanical properties while the presence of a cycloaliphatic group, such as in limonene, confers higher T_g and plastic deformation under strain in thiol-ene networks.[17,28] Weems *et al.* crosslinked unfunctionalized terpenes into networks with a standard tetrathiol crosslinker to investigate 3D printing applications.[28] Those materials were not degradable at the end-of-life and that studied library was limited to unfunctionalized terpenes and a commercial thiol. Inspired by that work, we sought to incorporate the use of the sugar isosorbide with terpenes to further modulate mechanical and thermal properties. Isosorbide can be obtained from starch and is a useful platform chemical due to its and two free alcohols serving as synthetic handles and rigid bicyclic structure, expected to confer higher T_g and mechanical properties. It has been incorporated into network materials through various methods, primarily in the form of polyesters[9,31–33] as well as thiol-ene networks.[2,24,25,34,35] Herein, we describe thiol-ene thermosets from a family of isosorbide- and terpene monomers crosslinked with commercial and bio-based thiols. In particular, we compare traditional commercial thiol pentaerythritol tetrakis(3-mercaptopropionate) (PETMP) with bio-based thiol dithiothreitol (DTT) and an isosorbide-based thiol (Iso2MC). This work represents an expansion of the library of renewably-derived thiols and enes for thiol-ene thermoset networks and investigates modular thermal and mechanical properties based on identity and ratio of the crosslinking thiol.

Isosorbide functionalized with geraniol and carveol was synthesized in two steps by utilizing carbodiimidazole (CDI) to install a carbonate linkage to the desired terpene at each alcohol of isosorbide, yielding isosorbide-geraniol-carbonate (IGC) and isosorbide-carveol-carbonate (ICC) (Figure 1a). The corresponding terpene-only monomers were synthesized using the same CDI route to yield dimerized di-geraniol-carbonate (DGC) or di-carveol-carbonate (DCC) (Figure 1b). In line with the environmental considerations of the networks, we endeavored to use greener reaction conditions during synthesis. To that end, acetone was used as a green solvent, and literature standard DBU was replaced with potassium carbonate as a greener base. Purification was only required on the final product, minimizing excess solvent and material usage. Isosorbide-based thiol (Iso2MC) was used alongside DTT and commercial PETMP as multifunctional thiol crosslinkers (Figure 1d).

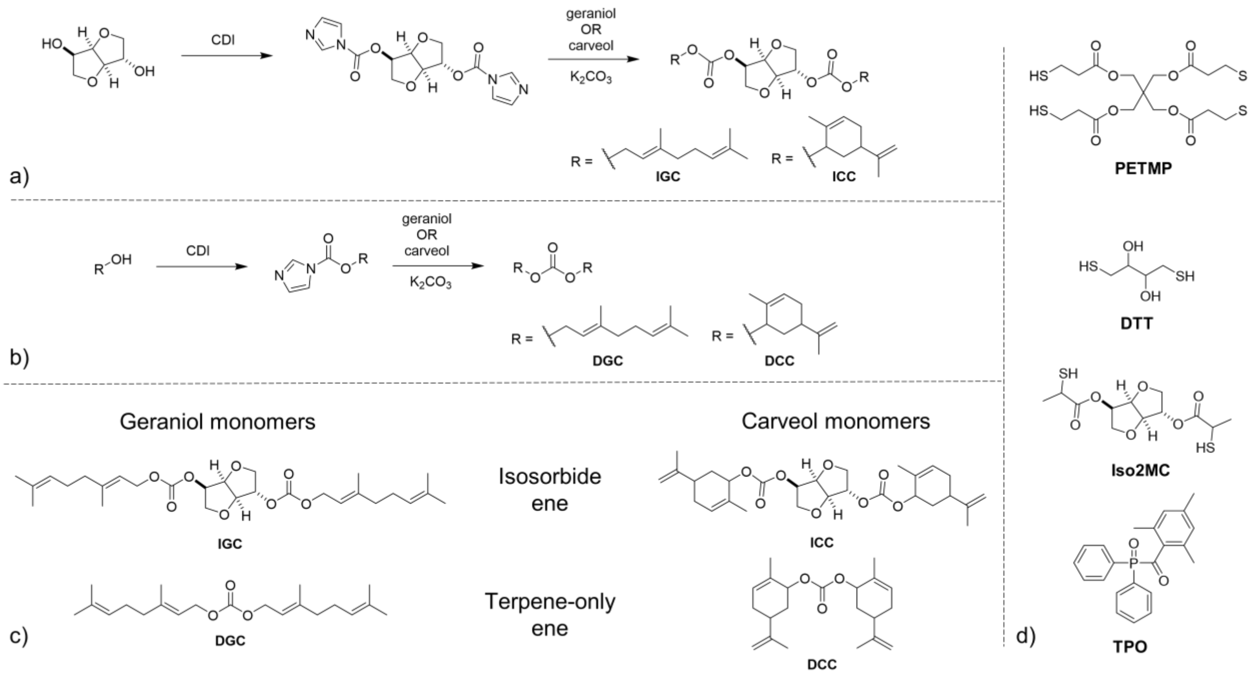

Figure 1. a) Synthesis of isosorbide and terpene ene monomers b) Synthesis of terpene-only ene monomers c) Full structures of ene monomers organized by geraniol/carveol and isosorbide/terpene-only d) Structure of thiols and photoinitiator used

Based on the highly substituted nature of the enes in geraniol and carveol, thiol-ene kinetics are expected to be significantly slower than for terminal allyl enes,[36–38] confirmed by a lack of gelation after 40 minutes of UV irradiation. Therefore, UV exposure was conducted overnight via a MelodySusie® 36 W UV Nail Dryer, and after a screening of photoinitiators, diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO) was selected due to the lack of yellowing and efficiency of crosslinking (Figure 1d). Initial crosslinking used ethoxylated trimethylolpropane tri(3-mercapto-propionate) (ETTMP) as a polymeric trithiol control, however, the resulting networks were consistently too soft to work with, due to the flexible aliphatic arms of the polymeric thiol as well as aliphatic geraniol. Thus the thiol library was limited to PETMP, DTT, and Iso2MC. All crosslinked networks showed no coloration beyond a varying degree of cloudiness. Acetone was used to solubilize formulation components and was removed by heating samples at 40 °C under vacuum after crosslinking. IGC, ICC, and DCC networks formed easy-to-handle solids and easily removed from the silicone molds. DGC networks were soft and sticky, complicating the replication of data; this is attributed to the aliphatic DGC monomer lacking rigid structure.

The extent of crosslinking was investigated and confirmed by IR spectroscopy. Crosslinked networks showed no residual -SH stretch at 2670 cm^{-1}, however a small alkene stretch at 1666 cm^{-1} indicates some unreacted enes (Figure 2a). Examination of the fingerprint region did not reveal any significant S-S stretch, indicating that all of the thiols from DTT or PETMP reacted with enes before forming dithiols.

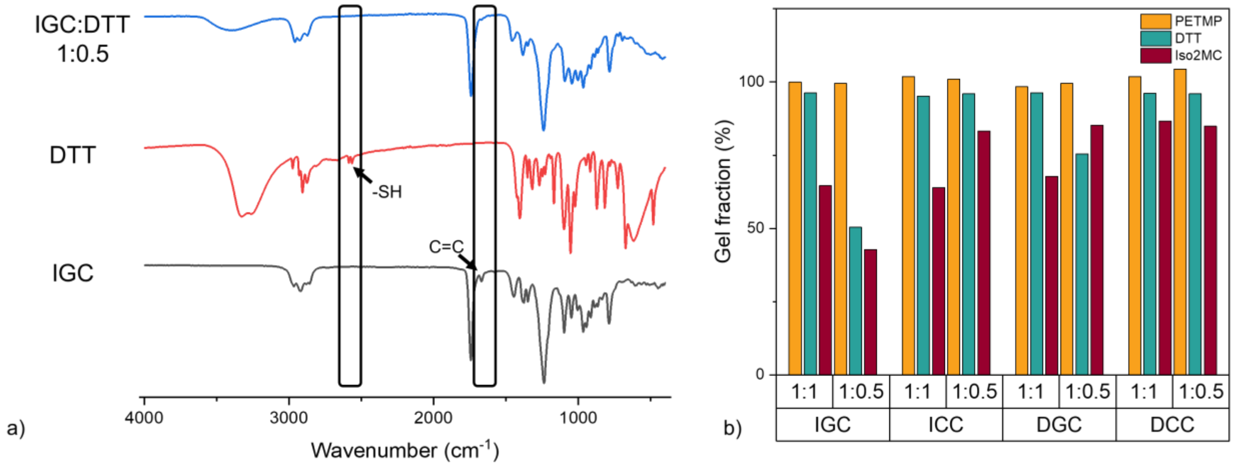

Figure 2. a) IR spectra of IGC:DTT 1:0.5 network (top), DTT monomer (middle), IGC monomer (bottom), b) gel fraction of crosslinked networks

To evaluate the gel content networks were left to swell in acetone overnight, followed by drying under vacuum. Gel content of networks with PETMP and DTT varied between 95-100% for most formulations, indicating near complete network formation (Figure 2b). A notable exception was IGC:DTT 1:0.5 and DGC:DTT 1:0.5, which showed gel fractions of 50 and 75%, respectively. This was attributed to lower mobility of the smaller DTT and lower reactivity of trisubstituted geraniol-based enes. Networks with isosorbide-based Iso2MC thiol showed lower gel fractions, ranging from 43-87%, indicating that the bulkiness of the isosorbide core and branched side chain hinder mobility, particularly with less reactive terpene alkenes.

The thermal characteristics of networks were tested using thermogravimetric analysis (TGA) to investigate the thermal decomposition. Interestingly, samples all showed multi-step decompositions, uncharacteristic of thermoset network materials but previously noted for terpene-containing networks.[28,39,40] (Figure 3). Iso2MC as the thiol crosslinker showed higher thermal stability, as expected by the increased isosorbide content in the networks. The $T_{d,5\%}$ is shown in Table 1, indicating the temperature at which 5% mass had been lost. Networks showed 5% decomposition at temperatures under 200 °C, hypothesized to be due to leftover unsaturation in the network from slow reactivity of tri-substituted enes not fully converted during thiol-ene crosslinking,[41] with the exception of a few DGC networks that showed $T_{d, 5\%}$ values up to 230 °C. Networks with DTT showed consistently lower onset of thermal degradation followed by gradual mass loss. Investigation using TGA-MS indicated that carbon dioxide was lost during significant mass loss events but was unable to identify specific fragments. Particularly in networks with DTT, FTIR coupled with thermal degradation showed the presence of small molecule organics during mass loss events, likely due to free hydroxyls in DTT back-biting into the network.

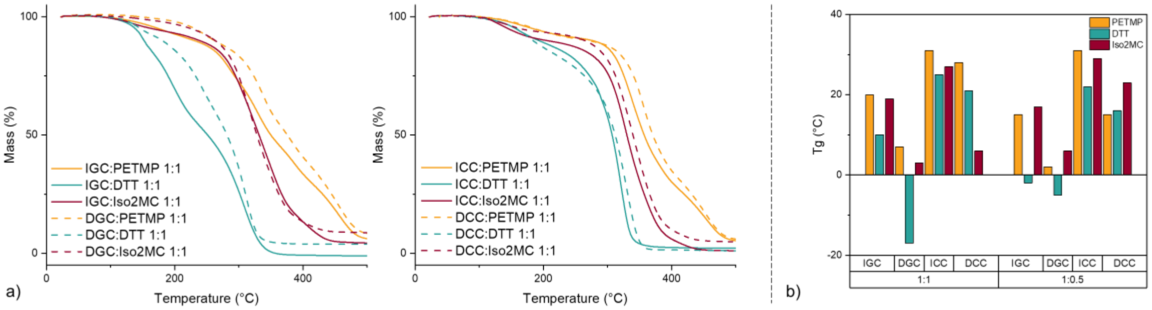

Figure 3. a) TGA curves for 1:1 ene:thiol networks (See Supplementary Information for specific values and 1:0.5 ratio curves) b) T_g values as measured by DSC

The thermal behavior was investigated using differential scanning calorimetry (DSC), with networks showing low T_g values between -17 and 31 °C, modulated by thiol functionality and presence of incorporated isosorbide in the network. Samples crosslinked with DTT tended to show a lower T_g than those with PETMP across the ene monomers (Figure 3b, Table S1). Direct comparisons of isosorbide-containing ene monomers to dimerized the terpene-based ene monomers show a decrease in T_g when isosorbide is not present, as expected. When Iso2MC was used as the crosslinker, there a wider difference in T_g value is observed between 1:1 and 1:0.5 ratio samples, indicating the strong effect isosorbide has on the thermal behavior of the network.

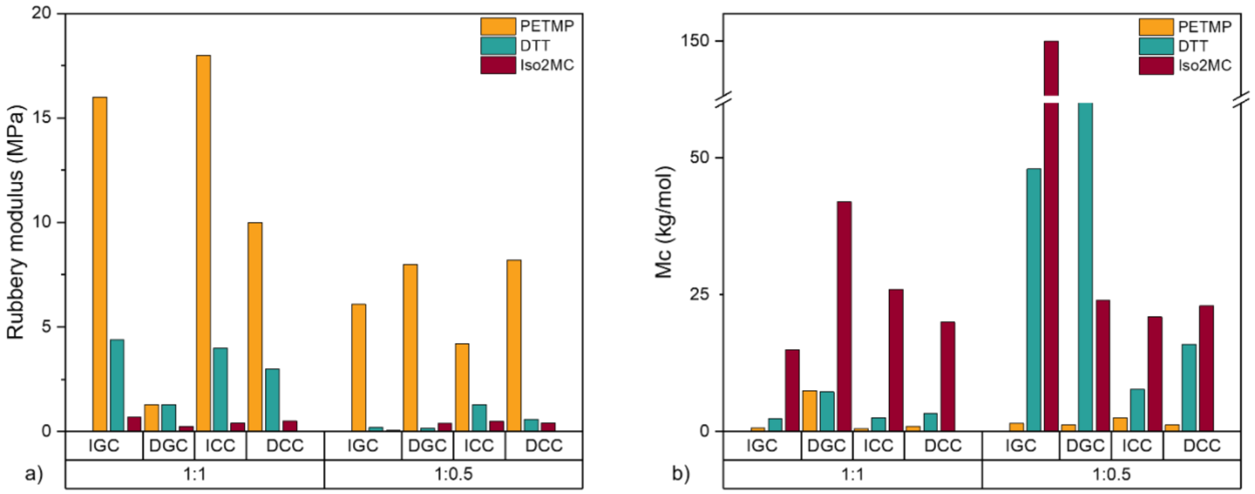

Figure 4. a) Rubbery modulus as measured by DMA b) Molar mass between crosslinked calculated from plateau rubbery modulus

The thermomechanical properties of the networks were also investigated by dynamic mechanical analysis (DMA) to probe the moduli of the formed networks. Several networks showed a bimodal tan (delta) curve, indicating inhomogeneities in the crosslinked structure. This is hypothesized to be due to slower reactivity of internal enes[37] in terpene monomers and limited mobility of dithiol crosslinkers. The storage modulus at the rubbery plateau was used to calculate the crosslinking density for each system (Figure 4, See Supplemental Information for curves and specific values). Within networks with a 1:1 ene:thiol ratio the storage modulus at rubbery plateau decreases by an order of magnitude from PETMP to DTT to Iso2MC as the thiol crosslinker, regardless of the ene monomer used with the exception of DGC. The rigidity of thiol crosslinker is thought to hinder mobility across chains during slow thiol-ene kinetics, leading to looser networks and therefore lower moduli. Within 1:0.5 ene:thiol ratio networks a similar trend can be seen for isosorbide-containing enes IGC and ICC. Both terpene-only enes DGC and DCC show a smaller difference in rubbery modulus between DTT and Iso2MC as the thiol crosslinker. The crosslink density as reflected in the molecular weight between crosslinks ranges from 0.6 to 48 kg/mol across types and ratios of monomers, indicating loose crosslinking particularly in the networks with a difunctional thiol and trisubstituted geraniol alkenes.

Tensile testing was used to investigate the stress-strain behavior of the networks (Figure 5). General trends showed an increase in strain at break and decrease in maximum stress as the thiol crosslinker changed from PETMP to DTT to Iso2MC. ICC showed brittle behavior, hypothesized to be due to the rigid multi-cyclic nature of ICC particularly with the bicyclic Iso2MC at the 1:1 ratio. Networks with a 1:0.5 ene:thiol ratio showed higher strain at breaks and lower maximum stress, with the exception of the DGC networks that were extremely soft and sticky, making repeatable data difficult to obtain. In comparison of carveol-containing vs. geraniol-containing samples the carveol-containing monomers showed a yield point followed by plastic deformation. This has been noted in cyclic terpene networks previously[28] and is most pronounced in ICC samples. While DCC networks exhibit a less pronounced yield point, plastic deformation still extends up to 120% strain-at-break. Geraniol-containing formulations show more linear stress-strain behavior, with the exception of Iso2MC-containing IGC samples that again show a yield point and deformation.

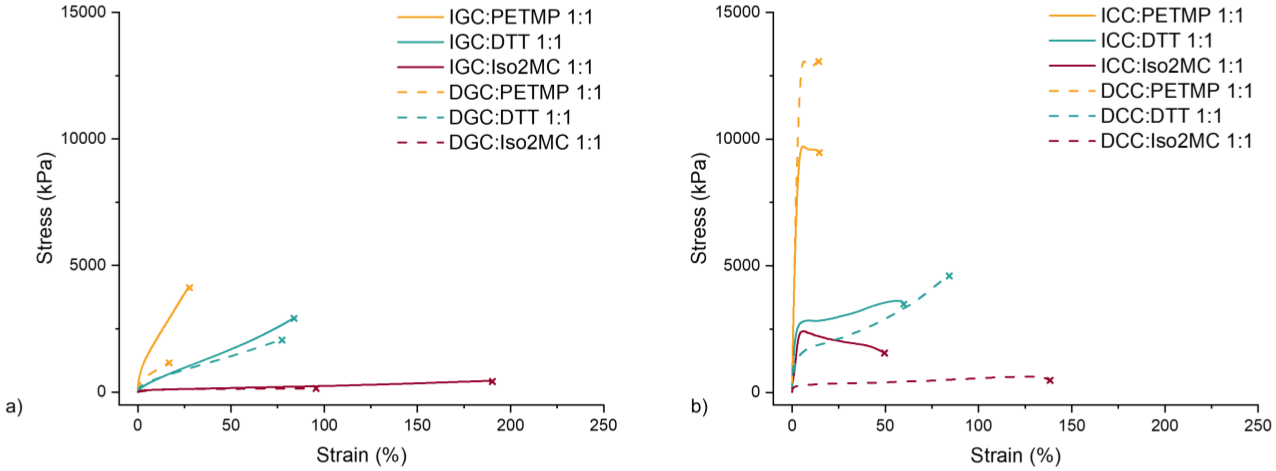

Figure 5. Representative stress-strain curves of a) Geraniol-containing networks IGC and DGC, and b) Carveol-containing networks ICC and DCC with PETMP, DTT, and Iso2MC at 1:1 ene:thiol ratio (See Figure S11 for 1:0.5 ratio curves).

Finally, the end-of-life of the crosslinked networks was studied. Initial screening of acidic, neutral, and basic conditions showed NaOH as the most effective degradation medium. Upon further testing, 1 M NaOH was doped with acetone to increase the wettability of the sample and after two days nearly all of the samples had fully degraded as measured by mass loss of solid networks, with the exception of DCC:PETMP 1:1, DCC:DTT 1:1 and 1:0.5, and IGC:PETMP 1:1 (Figure S12). This is markedly faster degradation than previously reported isosorbide carbonate networks,[42] and shows the potential for material management at the end-of-life.

In conclusion, thermoset networks from isosorbide- and terpene-based monomers were synthesized using thiol-ene chemistry. All networks showed thermal stabilities under 300 °C, likely due to lower crosslink density from slow thiol-ene kinetics and inherent thermal stabilities of terpenes. The mechanical properties of the resulting networks can be varied for a particular ene monomer based on the corresponding thiol crosslinker. In particular, difunctional and renewably-derived thiols DTT and Iso2MC showed softer and more linear tensile behavior across all enes used. The inclusion of cycloaliphatic carveol in the network materials introduced yield and plastic deformation during tensile testing, while aliphatic geraniol-based monomers resulted in softer and stickier networks. These networks demonstrate the utility of safe and renewably-derived monomers using sugars and terpenes and displayed rapid degradation under basic conditions, indicating end-of-life management possibilities. As the plastic crisis continues, expanding work on renewably-derived and readily-degradable materials will only increase in importance as we move toward a more circular and sustainable economy of plastics.

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Supporting Information.

Supporting figures, experimental details, and relevant spectra.

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