



## Cross-Linked Networks that Selectively and Controllably Disassemble On-Demand via Cascading Bond Cleavage

Journal:	<i>Materials Horizons</i>
Manuscript ID	MH-COM-01-2018-000117.R1
Article Type:	Communication
Date Submitted by the Author:	20-May-2018
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**Conceptual Insights:****Cross-Linked Networks that Selectively and Controllably Disassemble On-Demand via Cascading Bond Cleavage**

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Here we demonstrate the first cross-linked polymeric networks, polyurethane thermosets, which disassemble in multiple directions via cascading bond cleavage. Materials that can disassemble via cascading bond cleavage are advantageous because multiple bonds are broken with a single reagent, thus generating smaller and more mobile molecules that facilitate access of additional reagents and lead to increased network disassembly. In contrast to previous degradable thermosets, where covalent bonds and linkages are cleaved uncontrollably, the cascading bond cleavage described herein allows the time of disassembly to be controlled, thereby imparting tunable properties to the cross-linked network. Furthermore, we demonstrate that disassembly is initiated with a selective, mild, and relatively benign chemical stimulus, which is desirable because cross-linked networks are usually degraded and disassembled using environmentally toxic and harsh chemical treatments. The stimuli-responsive technology in this communication could pave the way for new cross-linked smart materials with controllable, on-demand features, such as selectively degradable coatings and composites for the aerospace, automotive, and electronics industry, time-dependent degradation of medical implants, and consumer products with recyclable components.



Journal Name

COMMUNICATION

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Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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**Cross-linked polymeric networks are found in numerous consumer, medical, and industrial materials. However, these materials require harsh chemical treatments to degrade their covalently bonded and tangled matrix of chains, often leading to environmental and safety issues. Herein, we describe the first networks, silyl-containing polyurethanes, which are highly cross-linked, rigid, and possess good thermal stability, yet will disassemble in multiple directions via cascading bond cleavage upon exposure to a selective chemical stimulus. These materials are formed from aliphatic polyisocyanates and synthesized silyldiols with varying electrophilicity and chain lengths, and disassembly is initiated by reaction with mild fluoride ion to release small molecules via slightly different mechanisms, which enables the time of disassembly to be controlled. These silyl-containing polyurethanes are resistant to disassembly with strong acid and base, which demonstrates their selectivity and robustness compared to other degradable cross-linked materials.**

### Introduction

Chemical cross-linking of molecules leads to stable and irreversible three-dimensional networks that cannot be dissolved. These networks are found in numerous materials, such as hydrogels,<sup>1</sup> foams,<sup>2</sup> coatings,<sup>3</sup> and composites,<sup>4</sup> where gels possess limited cross-links and the others are more extensively cross-linked. Materials that possess significant cross-links are often referred to as thermosets, as they cannot be heated and reshaped once formed, which makes them extremely useful for applications where thermal, chemical, mechanical, and ultraviolet (UV) light stability are required.<sup>5</sup> For instance, polyurethane thermosets, which are formed from the reaction of hydroxyl- and isocyanate-functional molecules

to generate carbamate (urethane) linkages, offer unique properties that enable their use in electrical housing panels, rigid foams, and high-performance coatings.<sup>6-7</sup> However, like all cross-linked networks, the chemical bonds and polymeric chains in polyurethane thermosets are difficult to degrade and destroy unless toxic and harsh chemical treatments, abrasive materials, or incineration, are utilized. Specifically, polyurethane coatings used on commercial and military aircraft are often removed with environmentally hazardous and potentially carcinogenic chemicals, such as dichloromethane, due to its rapid and thorough stripping action, and a benign alternative with similar effectiveness continues to remain elusive.<sup>8-9</sup>

Prior research on chemically degradable thermosets has focused on designing networks with cleavable bonds or linkages that are equivalent to the number of cross-links. For example, olefinic bonds in epoxy-functional components were cleaved with potassium permanganate in acetic acid when used in epoxy/amine thermosets.<sup>10</sup> Acetal groups in cycloaliphatic epoxy components were cleaved by heating with a solution of phosphoric acid when used in anhydride-cured thermosets, whereas tertiary carbamate groups in epoxy/amine thermosets were cleaved with heated solutions of mineral acids.<sup>10,11</sup> Recently, poly(hexahydrotriazine) (PHT) thermosets formed from aromatic diamines and paraformaldehyde under thermal conditions were disassembled by reversing to the diamines with a solution (pH = 0) of sulfuric acid.<sup>12</sup> In all of these cases, highly acidic conditions were required to facilitate bond cleavage, each cleavage was essentially stoichiometric with regard to the reagent, meaning that one cleavage did not promote subsequent cleavages within the thermoset, and disassembly was uncontrollable. While these concepts were viable for their respective systems, they are not feasible for the majority of conventional thermosets, especially polyurethanes, where mechanical properties and acid stability are required, and where thermosets cannot be degraded or destroyed by exposing to a hazardous chemical solution.

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† Electronic Supplementary Information (ESI) available: Experimental procedures, NMR data, HRMS data, XPS spectra, ATR-FTIR spectra, static contact angle measurements, swelling data, TGA-MS thermograms, and glass transition temperature bar graphs. See DOI: 10.1039/x0xx00000x

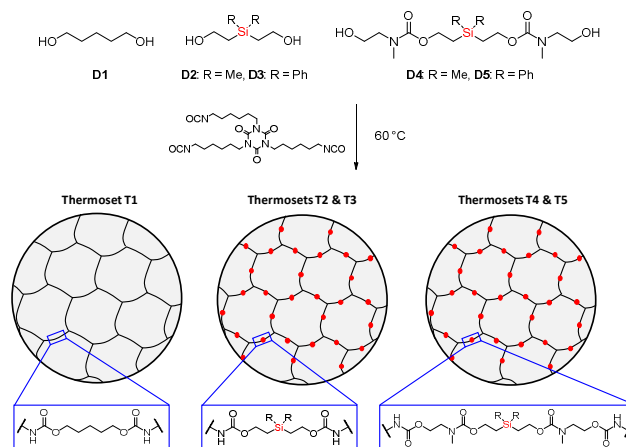
To design a material with chemical bonds and hydrocarbon chains that resembled those of a practical thermoset, while also possessing the ability to completely disassemble upon treatment with a chemical reagent, we envisioned that a thermoset should possess the following features: 1) unique chemical bonds (i.e., triggers) that are cleavable with a selective chemical reagent (i.e., stimulus), 2) the ability for subsequent and multiple bond cleavages to occur upon activation of the triggers, 3) multi-directional bond cleavage, and 4) the ability for bond cleavage to occur through the cross-links and into adjoining regions of the thermoset. To accomplish this, we utilized the concept of cascading bond cleavage found in self-immolative thermoplastic polymers and adhesives.<sup>13-18</sup> However, instead of utilizing linear or branched aromatic polymers (e.g., poly(benzyl ethers)) that possess a terminal chemical trigger and disassemble from head-to-tail, we used aliphatic molecules that contained a centralized difunctional silyl trigger to enable bond cleavage in two opposing directions. Furthermore, these aliphatic molecules possessed terminal functionality for forming highly cross-linked networks with glass transition temperatures ( $T_g$ s) above room temperature. Herein, we report the first thermosets, silyl-containing polyurethanes, with the ability to disassemble on-demand via cascading bond cleavage when treated with a selective chemical stimulus.

## Results and Discussion

### Synthesis and Characterization of Thermosets

Silyl-diols (**D2-D3**) and extended chain silyl-diols (**D4-D5**) were synthesized for use as the aliphatic trigger-containing molecules with terminal reactive groups (see Scheme S1, ESI<sup>†</sup>). These molecules were selected based on earlier work from our group where we demonstrated that different rates of disassembly for silyl-terminated ethoxycarbonyls could be achieved by modifying the electrophilicity of silicon and the structure of the appended aliphatic chain.<sup>19</sup> However, unlike those molecules, the silyl-centered diols (**D2-D5**) herein contain two aliphatic chains that can both undergo cascading bond breakage, and it was envisioned that the variations of composition and chain length could provide different degrees of disassembly when incorporated into a thermoset.

Scheme 1 shows the reaction of diols **D1-D5** with an aliphatic polyisocyanate trimer to form polyurethane thermosets **T1-T5**. Pentane-1,5-diol (**D1**) was selected to form a control thermoset because it did not contain silicon-carbon bonds, yet possessed a similar aliphatic structure to the silyl-diols. All thermosets were clear rigid films of about 2 mm thickness (Fig. S1, ESI<sup>†</sup>), and confirmation of thermoset formation was determined by spectroscopic and bulk analysis. Attenuated total reflection fourier transform infrared (ATR-FTIR) spectroscopy showed that no isocyanate peaks remained, signifying complete reaction of the hydroxyl and isocyanate groups, and gel fraction calculations of all films were greater than 0.92, which is indicative of highly cross-linked networks (Table 1). Thermogravimetric analysis (TGA)



**Scheme 1.** Formation of thermosets **T1-T5** by reacting a non-silyl-diol (**D1**), silyl-diols (**D2-D3**), and extended chain silyl-diols (**D4-D5**) with an aliphatic polyisocyanate (pure trimer). The silicon atom of the trigger-containing linkages in thermosets **T2-T5** are highlighted in red, whereas the blue expansion boxes show the linkages and newly formed carbamate bonds.

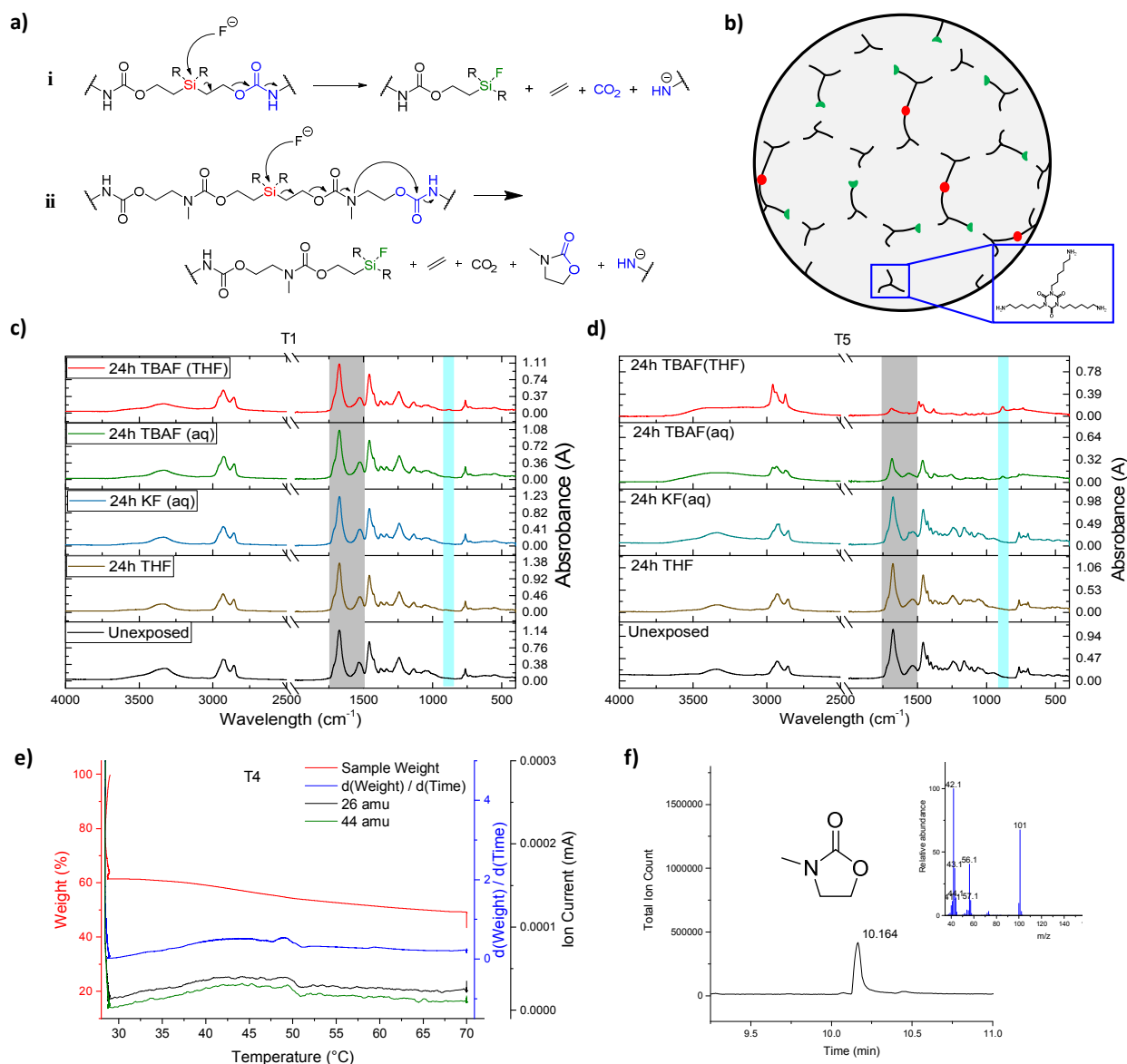
of the silyl-containing thermosets (**T2-T5**) revealed onset degradation temperatures and thermal degradation profiles that were similar to the non-silyl-containing thermoset (**T1**), thereby confirming formation of cross-linked systems with excellent thermal stability (Fig. S2, ESI<sup>†</sup>). X-ray photoelectron spectroscopy (XPS) was utilized to detect silicon on the surface of thermosets **T2-T5**, thereby confirming silyl-diol incorporation, whereas silicon was not present in the control (**T1**) (Fig. S3, ESI<sup>†</sup>).

### Exposure of Thermosets to Selective Chemical Stimuli

Solutions of fluoride salts were chosen as the selective chemical stimuli for evaluation of thermoset disassembly due to their mild reactivity and benign nature compared to strong acids and bases, the ability of fluorine to form strong covalent bonds with silicon, and the inability of fluoride ion to cleave linear aliphatic carbamate groups at room temperature.<sup>20</sup> As shown in Fig. 1a, we envisioned that fluoride ion would react with the silyl-triggers of thermosets **T2-T5** to cleave the Si-C bond. This would be followed by a cascading reaction of bond cleavages that would eliminate ethylene and carbon dioxide, and in several cases cyclic molecules, including breaking the carbamate groups within the cross-links to disassemble the thermosets. Disassembly of the remaining aliphatic chain would occur upon trigger activation with a second fluoride ion,

**Table 1** Numerical designation of polyurethane thermosets and comparison of gel fraction and thermal properties

Designation	Gel Fraction	$T_g$ (°C)	Onset Degradation Temperature (°C)
<b>T1</b>	0.97	40.7	320
<b>T2</b>	0.92	68.1	298
<b>T3</b>	0.97	40.6	291
<b>T4</b>	1.00	45.0	286
<b>T5</b>	0.99	51.6	289



**Fig. 1.** Thermoset disassembly and analysis after exposure: a) Proposed mechanisms of chain disassembly within thermosets (i) **T2** and **T3** and (ii) **T4** and **T5** upon reaction with fluoride ion, where green highlights Si-F bond formations and blue highlights bond breakage and small molecule formation as disassembly occurs within the carbamate groups, b) illustration of a partially disassembled thermoset upon treatment with fluoride ion, where green indicates activated triggers, red indicates non-activated triggers, and amine trimers are shown as all black, c) ATR-FTIR spectra of **T1** (control) before and after 24 hour exposures, where the grey area encompasses amide I and amide II peaks and the light blue area indicates the Si-F stretching region, d) ATR-FTIR spectra of **T5** before and after 24 hour exposures, e) TGA-MS of exposed **T4** showing ethylene (black, 26 amu (secondary fragment)) and CO<sub>2</sub> (green, 44 amu) emitting from the thermoset and matching the derivative of the weight over time (blue) as the temperature increases from room temperature to 70 °C, and where the sample weight (red) loss is partially due to evaporation of THF, and f) GC chromatogram and corresponding MS spectrum of extract from 24 hour exposed **T4** indicating loss of 3-methyloxazolidin-2-one ( $m/z = 101$ ) during disassembly.

which should increase the potential for thermoset fragmentation and complete disassembly. We presumed that disassembly would occur throughout the thermoset until only amine-terminated aliphatic trimers remained. An illustration of a partially disassembled thermoset upon reaction with fluoride ion is shown in Fig. 1b.

All thermosets were immersed in room temperature solutions of 1 M aqueous (aq) potassium fluoride (KF), 1 M

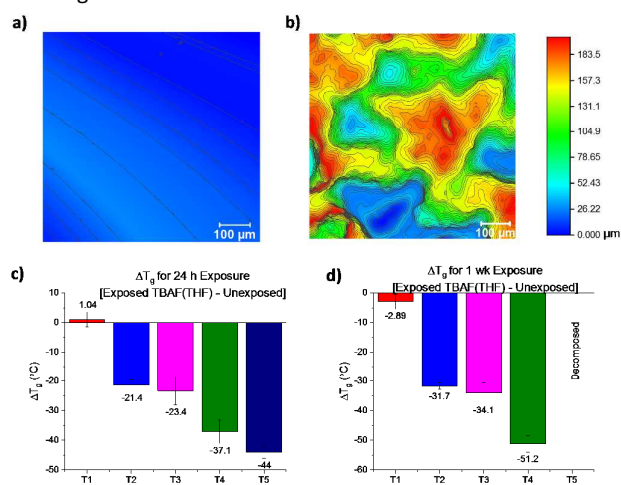
aqueous tetrabutylammonium fluoride (TBAF), 1 M TBAF in tetrahydrofuran (THF), and neat THF for 24 hours without stirring in order to prevent introduction of added stress on the thermosets. Following exposure and drying, ATR-FTIR analysis indicated no change in peaks for any of the thermosets when exposed to THF and KF (aq) for 24 hours compared to the unexposed thermosets (Fig. 1c and 1d; Fig. S4, ESI<sup>†</sup>). For thermosets **T2** thru **T5**, exposure to 1M TBAF (aq) revealed a

new peak at  $881\text{ cm}^{-1}$ , which is indicative of Si-F bond formation resulting from fluoride ion attack on the silyl-trigger.<sup>21</sup> A decrease in the amide I peak at  $1676\text{ cm}^{-1}$  and amide II peak at  $1535\text{ cm}^{-1}$ , as well as subsequent peak broadening in the NH peak at  $3338\text{ cm}^{-1}$ , provided conformation for loss of carbamate groups. However, these decreases were small, indicating that limited fragmentation had occurred. Consequently, when the same thermosets were exposed to 1 M TBAF (THF), a large decrease in the amide I and amide II peaks, along with increased peak growth of the Si-F band and further broadening of the NH peak, were observed. The larger decreases in both the amide I and amide II peaks also signified increased loss of the carbamate groups compared to thermoset exposure in aqueous TBAF. The marked difference in the IR spectra between TBAF (aq) and TBAF (THF) is due to THF providing greater wetting and swelling of the polymer networks compared to water (Fig. S5 and S6, ESI†), which allows for increased fluoride ion penetration and attack of silyl-groups below the surface. A change from the dimethyl groups on silicon in **T2** to the diphenyl groups in **T3** resulted in a small increase in the reduction of the amide I and amide II peaks, likely due to silicon's increased electrophilicity, and hence increased reactivity with fluoride ion. However, thermosets **T4** and **T5**, which were formed from longer chain silyl-diols (i.e., **D4** and **D5**), showed the largest reductions in their amide I and amide II peaks, indicating an increased ability to disassemble due to inclusion of more cleavable bonds and a greater reaction entropy.

Although ATR-FTIR revealed chemical changes for thermosets **T2-T5**, the proposed mechanisms of disassembly were evaluated using thermogravimetric analysis / mass spectrometry (TGA-MS). Initial tests performed on **T1** (control) showed only the emission of THF when exposed to 1 M TBAF (THF) (Fig. S7, ESI†). However, for all other thermosets, THF, ethylene, and carbon dioxide were detected leaving the films after exposure to 1 M TBAF (THF) for 120 min., followed by heating to  $70\text{ }^{\circ}\text{C}$  (Fig. 1e; Fig. S8-S10, ESI†). The matching profile of the derivative of weight over time with respect to ethylene and carbon dioxide is shown for all silyl-containing thermosets, which illustrates that the weight loss is due to off-gassing.<sup>22,23</sup> The detection of ethylene and carbon dioxide alongside the matching derivative curves also supports the proposed mechanisms of disassembly for **T2-T5** as shown in Fig. 1a. Further confirmation for the proposed mechanisms of disassembly for **T4** and **T5** was determined by gas chromatography / mass spectrometry (GC-MS) analysis of extracts from 24 hour exposed samples, which were found to contain cyclic molecule 3-methyloxazolidin-2-one (Fig. 1f).

Confirmation of disassembly on the surface of the thermosets was confirmed through confocal microscopy measurements. Analysis of unexposed thermosets revealed a smooth surface with small (i.e., tenths of microns) height differences over the length of the observed area (Fig. 2a). Exposure to THF and 1 M KF (aq) showed only minor changes in the topography of the thermosets, remaining in the tenths of microns range (Fig. S11, ESI†). However, for thermosets **T2-**

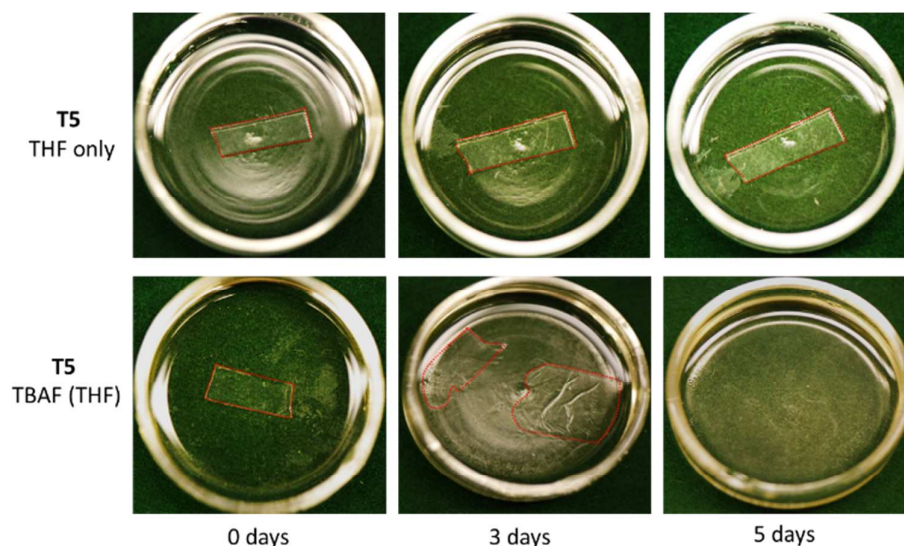
**T5**, exposure to 1 M TBAF (aq) revealed that pits and valleys had begun to form. Increased features were observed from



**Fig. 2.** Surface and bulk analysis of thermoset disassembly: a) Topographic map of unexposed thermoset **T5**, b) topographic map of **T5** after 24 hours exposure in 1 M TBAF (THF), c) change ( $\Delta$ ) in glass transition temperatures ( $T_g$ s) of thermosets **T1-T5** after exposed to 1 M TBAF (THF) for 24 hours, d) change ( $\Delta$ ) in  $T_g$ s of thermosets **T1-T5** after exposed to 1 M TBAF (THF) for 1 week.

exposure to 1 M TBAF (THF), with height changes in the hundreds of microns revealing large pits and valleys (Fig. 2b). The changes in surface topography support the ATR-FTIR results, thereby providing a visual conformation of thermoset disassembly.

The glass transition temperature ( $T_g$ ) of all thermosets were determined by differential scanning calorimetry (DSC) both before and after 24 hour exposures to the fluoride salt solutions. A decrease in a thermoset's  $T_g$  can result from reduced cross-links, which would indicate bond breakage.<sup>24,25</sup> Exposure of thermoset **T1** (control) to THF and all fluoride salt solutions for 24 hours resulted in a 1-3  $^{\circ}\text{C}$  change ( $\Delta$ ) in the  $T_g$ s, showing the control was unaffected (Fig. 2c; Fig. S12-S14, ESI†). Exposure of thermosets **T2-T5** in THF, 1 M KF (aq), and 1 M TBAF (aq) solutions for 24 hours resulted in a 0.2-10.4  $^{\circ}\text{C}$  change in the  $T_g$ s, which indicated either polymer rearrangement or limited degradation. However, when **T2-T5** were exposed to 1 M TBAF (THF) for 24 hours the  $T_g$ s decreased by 21-44  $^{\circ}\text{C}$  compared to the unexposed samples (Fig. 2c). The larger changes in these  $T_g$ s confirmed that degradation observed on the surface with ATR-FTIR and confocal microscopy had also occurred within the thermoset. The decrease in  $T_g$  depended on the hydrocarbon group attached to silicon and the chain length of the silyl-diol used in the thermoset. In general, smaller changes were observed utilizing dimethyl groups on silicon compared to diphenyl groups, whereas larger changes were observed upon inclusion of more cleavable bonds in the aliphatic chains. The results also indicate that increased bond breakage within the thermoset can increase the potential for the entire material to disassemble.



**Fig. 3.** Visual analysis of thermoset disassembly in non-stirred liquids: Time-lapse images of thermoset **T5** exposed in THF (top) and 1 M TBAF in THF (bottom) at room temperature, showing that **T5** was unaffected by THF, yet completely disassembled within 5 days of exposure to the fluoride ion stimulus. The thermoset is outlined in red for visual indication.

All thermosets remained exposed to the non-stirred THF solvent and fluoride salt solutions for a total of 1 week. At this point, all thermosets, except for **T1**, demonstrated even greater decreases in their  $T_g$ s compared to the 24 hour immersions (Fig. 2d; Fig. S12-S14, ESI†). Further reductions of the amide I and amide II peaks for **T2-T5** were also observed via ATR-FTIR (Fig. S15, ESI†). Immersion in 1 M TBAF (THF) provided the largest change in  $T_g$  for **T2-T5** (see Fig. 2d), indicating that additional bond cleavage had occurred between 24 hours and 1 week. Thermosets **T2-T4**, when removed from solutions, were now flimsy and gel-like materials. However, after only 5 days of immersion in non-stirred 1 M TBAF (THF), thermoset **T5** showed no visible pieces remaining in solution, apparently due to complete, or near complete, disassembly (Fig. 3). Evaporation of the THF and drying of this solution produced a slightly viscous residue with a non-detectable  $T_g$ . Attempts to purify the residue were unsuccessful due to the large amount of TBAF present. However, FTIR showed the presence of mainly hydrocarbons, likely from the hexamethylene groups of the remaining amine-functional trimers. This indicated that the majority of cleavable bonds in the thermoset had been broken and that disassembly had occurred through the carbamate linkages and into adjoining regions of the thermoset. Immersion of **T5** in a stirred solution of 1 M TBAF (THF) led to complete disassembly in less than 24 hours, which can be attributed to increased swelling of the network, increased collisions between the stimuli and triggers, and increased mobility of the disassembled molecules.

Characteristics of increased degradation were consistently observed for thermosets **T4** and **T5** compared to **T2** and **T3**. Although changing the pendant hydrocarbon groups on silicon led to small increases in disassembly, the ability of thermoset **T4** and **T5** to additionally eliminate 3-methyloxazolidin-2-one provided for the greater increase in disassembly. This explains

the more pronounced visual,  $T_g$ , and FTIR changes for **T4** and **T5**, and demonstrates that thermosets with increased bond breakage have a more pronounced effect on the ability and time for disassembly to occur. As observed in the surface topography images of **T4** and **T5**, the generation of small and volatile molecules, coupled with increased bond breakage and the generation of liquid cyclic molecules, appears to have increased polymer chain mobility and pore formation by allowing THF and fluoride ions to continuously penetrate the thermoset's matrix and access the underlying triggers.

Thermosets **T1-T5** were immersed in 1 M HCl and 1 M NaOH for a period of 1 week to evaluate their stability to dangerous and corrosive chemical stimuli. The ATR-FTIR spectra of all thermosets after 24 hours and 1 week of exposure indicated no changes in chemical bonds (Fig. S16, ESI†), unlike when exposed to 1 M TBAF in THF, and the  $T_g$ s changed minimally even after 1 week of immersion (Fig. S17 and S18, ESI†). The stability of thermosets **T2-T5** in these strong acid and base solutions is likely due to water's insufficient surface wetting and minimal swelling of the polymer networks (Fig. S5 and S6, ESI†), in addition to the lack of fluoride ion to initiate Si-C bond cleavage. These results demonstrate that the silyl-containing thermosets possess high chemical stability and robustness compared to previously reported degradable thermosets.

## Conclusions

In summary, we demonstrate that highly cross-linked and rigid networks can be synthesized and selectively triggered with a chemical stimulus to disassemble on-demand via cascading bond cleavage. The silyl-containing polyurethane thermosets showed good thermal stability with degradation beginning around 300 °C, which is typical for a cross-linked polymeric

material. Exposure of the silyl-containing thermosets to THF, strong acid, and strong base resulted in zero to minor changes in chemical structure and thermal properties, whereas these changes were pronounced when exposed to TBAF. The silyl triggers within the thermosets were susceptible to nucleophilic attack by fluoride ion to initiate cascading bond breakage in two opposing directions, thus enabling multi-directional disassembly and the formation of small liquid and volatile molecules. The generation of these mobile molecules also increased network disassembly by facilitating pore formation and access to the underlying triggers. In addition, the time of disassembly was proven to be reduced, and was thus controlled, by changing the electrophilicity and aliphatic chain structure of the silyl-diol. This modification resulted in complete disassembly of a thermoset material, even when the stimulus solution was not stirred.

Cross-linked networks that can selectively disassemble on-demand via cascading bond cleavage have numerous potential uses in today's society. Applications include coatings that are removed with benign chemical stimuli to eliminate the use of hazardous dichloromethane, recyclable composites and packaging, and biomaterials for tissue engineering and drug delivery.

### Conflicts of interest

There are no conflicts to declare.

### Acknowledgements

This research was supported by the U.S. Naval Research Laboratory Base Program. The authors declare no competing financial interests. E. C. would like to thank financial support from the American Society for Engineering Education (ASEE). All authors contributed equally to this work.

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## Table of Contents Entry

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Silyl-containing polyurethane thermosets disassemble in multiple directions via cascading bond cleavage when exposed to a fluoride ion stimulus.

