End-of-life upcycling of polyurethanes using a room temperature, mechanism-based degradation

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Abstract

A major challenge in developing recyclable polymeric materials is the inherent conflict between the properties required during and after its life span. In particular, materials must be strong and durable when in use, but undergo complete and rapid degradation ideally under mild conditions upon end-of-life. We report a mechanism for degrading polymers called CyclizAtion-Triggered CHain (CATCH) cleavage that achieves this duality. CATCH cleavage features a simple glycerol-based acyclic acetal unit as a kinetic and thermodynamic trap for gated chain-shattering. Thus, an organic acid induces transient chain breaks with oxocarbenium ion formation and subsequent intramolecular cyclization to fully depolymerize the polymer backbone at room temperature. With minimal chemical modification, the resulting degradation products from a polyurethane elastomer can be repurposed into strong adhesives and photochromic coatings, demonstrating the potential for upcycling. The CATCH cleavage strategy for low-energy input breakdown and subsequent upcycling may be generalizable to a broader range of synthetic polymers and their end-of-life waste streams.

Introduction

The global effort to reduce polymeric waste entering oceans and landfills has become more urgent as the scale of problem has come into focus.[1,2] Of the many approaches to make polymeric materials more sustainable, closed loop recycling, where depolymerization produces the original monomer, has been especially promising.[3,4] The process can be quite efficient for some materials; however others, especially thermosets, require harsh conditions and most often the breakdown is insufficiently clean and too energy intensive to be practical.[5] Dynamic covalent chemistry[6] offers one promising strategy to make entirely new polymeric materials that contain chemical linkages that are easily broken.[7,8] A complementary approach uses existing polymer chemistry but new degradation processes to generate either the original monomers for recycling or alternative breakdown products for upcycling applications.[3-5] In this regard, a particularly challenging class of polymers is polyurethanes.

The widespread commercial success of polyurethanes is attributable to both their ease of synthesis via polyaddition polymerization of multifunctional alcohol and isocyanate monomers as well as their superior material properties.[9] Monomer structures and polymerization conditions can be adapted for the generation of bulk materials with a wide range of potential applications. This tunability allows polyurethanes to be used in a multitude of consumer products from durable foams, rubbers, and adhesives to hard plastics and coatings. The high stability of the urethane linkages provides outstanding durability during the material's lifetime, but also limits opportunities for energy efficient polyurethane recycling.[3] As a result, polyurethane waste frequently ends up in landfills, leading to a myriad of environmental hazards.[10] Methods have been developed recently wherein polyurethanes can be chemically recycled with carbamate exchange catalysts and elevated reprocessing temperatures. This approach is a very promising direction, particularly for existing post-consumer polyurethane materials,[11] but these methods can require a moderately high energy input and there is a need for alternative methods, especially in the area of upcycling. Given the low reactivity of the urethane linkage under mild conditions, one degradation strategy is to integrate a more readily cleavable bond into either the isocyanate or alcohol monomer. However, a key property of polyurethanes is their hydrophobicity, making hydrolysis significantly more challenging. For example, a polyurethane containing ketal groups was reported to be resistant to hydrolysis even at pH 1 and elevated temperature for two weeks (Fig. 1a).[12] These studies underscore the central paradox of the plastic recycling problem.[13] Having stable physical, mechanical, and chemical properties for the life-span of the material is at odds with the desire for a rapid and complete degradation under the mild conditions sought for end-of-life disposal and possible recycling or upcycling. Herein we report one strategy to achieve these conflicting properties with a gated polyurethane that responds to two signals with transient polymer chain breaks that are kinetically trapped, leading to full breakdown. Further, we show the upcycling of the degradation products into strong adhesives and coatings.

Results and Discussion

Design of gated, CATCH-degradable polyurethanes. Ring-chain equilibria have proven a useful strategy for depolymerizing suitable condensation polymers.[14] Clever tuning of the monomer structure can produce high molecular weight polymers with useful properties that can be repeatedly cycled between monomer and polymer.[15] Our design was also influenced by stimuli-responsive degradable polymers that undergo chain cleavage through iterative cyclization processes.[16-19] Thus, we envisioned the need for water being obviated by pendant alcohol groups proximal to an acetal (see **1**) that might undergo cyclization upon induction of transient oxocarbenium ion chain breaks (**2a** to **2b**, see Fig. 1c,d). The resulting cyclic acetal (**3**) would serve as a kinetic and thermodynamic trap for chain cleavage in a process we refer to as CATCH cleavage. As outlined in Fig. 1b, we further envisioned a gated system that would avoid premature breakdown. Thus, aqueous acid would be unable to permeate the hydrophobic polymeric network but a combination of organic solvent and organic acid (AND gate) might permeabilize the polyurethane, allowing oxocarbenium ion formation and CATCH cleavage. We describe here a simple acetal-containing polyol (**5**, Fig. 2) that reacts with common industrial diisocyanates to form robust polyurethanes (**1**) that are capable of undergoing this type of gated CATCH cleavage degradation to **3** with the derived polyol **4** capable of upcycling into higher value polyurethane materials. Thus, polyurethanes derived from **5** are robust but can be degraded with minimal energy input and given a useful second life through repurposing.

Polyol synthesis and mechanistic verification in a model. The synthesis of tetrol **5** was accomplished in two steps using a preparation that was conveniently performed on a 50 g scale. Thus, butyraldehyde and allyl alcohol reacted to form the corresponding acetal, which underwent Upjohn dihydroxylation (Fig. 2a). To test the potential for the CATCH cleavage mechanism in a model system, **5** was reacted with butylisocyanate to give **6** (Fig. 2b). A small amount of product from reaction at a secondary alcohol group was observed, and this was removed during purification. With ^{1}H NMR monitoring, a solution of **6** with 10 mol% *p*-toluenesulfonic acid in anhydrous acetonitrile-d_3 was shown to transform smoothly at room temperature over a 3.5 h period ($t_{1/2} < 30$ min, Extended Data Fig. 1), producing two major new species. The ^{1}H NMR and MS were fully consistent with formation of cyclic acetal **7** and diol **8**, the former a mixture of diastereomers. In addition to supporting the Fig. 1c,d cleavage mechanism, the small molecule model demonstrated the significantly greater reactivity of the primary vs. secondary alcohol with alkyl isocyanates. To further investigate the degradation mechanism, we performed a Hammett analysis using three aromatic acetals containing electron-donating or electron-withdrawing groups. ^{1}H NMR-monitored degradation studies gave a ρ value of -3.69 (Extended Data Fig. 2), consistent with values reported for traditional acetal hydrolysis via oxocarbenium ion formation.[20] This evidence for a significant positive charge build up on the acetal carbon supports the mechanism shown in Figure 1d.

Synthesis and degradation of polyurethane elastomers. Following the successful verification of the proposed cleavage mechanism, we sought to demonstrate an analogous acetal degradation in a crosslinked polyurethane.

Thus, elastomeric polyurethane film **10a** was prepared from tetrol **5** and toluene 2,4-diisocyanate terminated poly(propylene glycol) (PPG-TDI, M_n ~2,300) by mixing **5** and PPG-TDI in a 1:2 ratio (Fig. 2c,d). Different ratios of **5** with PPG-TDI were tested with a 1:2 ratio providing the lowest amount of **5** while maintaining the desired CATCH cleavage degradation. An analogous elastomeric film (**11**), physically indistinguishable from that shown in Fig. 2d, was prepared from tetrol **9** (Fig. 2c). Polyurethane film **11** serves as a control because **9** lacks the acetal group and therefore the ability to degrade by CATCH cleavage. Beyond the two films having identical physical appearances, their thermal and viscoelastic properties as measured by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) are similar (Fig. 2e). More importantly, thermal gravimetric analysis (TGA) of both films showed similar onset degradation temperatures (≳200 °C), indicating their comparable thermal stability (Extended Data Fig. 3). The TGA results provide evidence that thermal degradation is not impaired by the degradable bonds of the acetal moiety. Additionally, these data are consistent with industrially relevant polyurethane elastomers, which begin to decompose at or below 250 °C.[21] Film **10a** with a 2:1 PPG-TDI to tetrol ratio was further characterized by FT-IR, which showed a clear alcohol stretch at ca. 3400 cm^{-1} but no detectable residual isocyanate peaks. In contrast, film **10b** with a 5:1 PPG-TDI to tetrol ratio showed a residual isocyanate band at ca. 2270 cm^{-1} but a negligible alcohol absorption, consistent with nearly full reaction of all four alcohol groups. Based on the characterization and degradation data, the polyurethane elastomer prepared with a 2:1 PPG-TDI to tetrol ratio (**10a**) was used for further studies because each acetal unit was likely to have at least one residual unreacted alcohol group to participate in CATCH cleavage.

To test the potential degradation of the bulk polyurethane elastomeric materials, 40 x 10 x 1 mm films **10a** and **11** containing rhodamine B were immersed in a range of organic solvents containing methanesulfonic acid (MSA) as well as 1 M aqueous HCl (see Fig. 3 and Supplementary Figs. 1 and 2). Films of **10a** immersed in THF containing 1 M MSA completely dissolved within 20 min at room temperature (Supplementary Movie 1) but showed no visible change with immersion in 1 M HCl (aq) or 1 M MSA (aq) for at least 2 d. This striking difference supports the notion of rapid degradation of **10a** in low moisture environments *via* the CATCH cleavage mechanism and further highlights the stability of hydrophobic acetal-containing polyurethanes in strongly acidic aqueous environments (see Fig. 3d for logic gate table). In contrast, the acetal-free film **11** experienced swelling and some dye loss but otherwise remained fully intact upon immersion in THF with 1 M MSA.

Furthermore, the effect of acid concentration on degradation rate was investigated with both elastomer degradation studies and small molecule kinetic experiments. Lower concentrations of MSA resulted in slower degradation rates of elastomer **10a** (Extended Data Fig. 4a), with room temperature degradation being achieved in 1 h in 0.01 M MSA. Similar data was acquired in ^{1}H NMR kinetic experiments on small molecule model **6** (Extended Data Fig. 4b), wherein 1 mM MSA completely degraded **6** within 11 minutes. The lowest acid concentration tested (0.025 mM, 0.5 mol%) was sufficient to catalyze the complete degradation of **6** over 20 h. Both the elastomer and the small molecule model degraded at room temperature in the presence of a catalytic amount of acid, with higher acid concentrations allowing for more efficient degradation in both cases.

We performed tensile DMA studies to test the thermomechanical response of **10a** and **11** to gain more insight into their relative stability in aqueous acid. Films **10a** and **11** were soaked in 1 M HCl for 24 h and compared to their pristine counterparts. DMA studies on **11** indicated direct overlap of the tan δ and E' curves for the pristine and soaked films (Fig. 3e). Although **10a** has a slight shift in E' and tan δ after soaking in 1 M HCl, the rubbery plateau for the soaked films indicates that the bulk material remained crosslinked, providing evidence that bulk polymer degradation is limited under aqueous acidic conditions (Fig. 3f). Additional studies must be performed to determine the cause of these shifts in tan δ and storage modulus, but from a practical point of view, such durability in aqueous acid suggests that polyurethane materials derived from tetrol **5** perform well under real-world conditions. To further quantify the degradation and relative stability of these crosslinked polyurethane materials, we performed *in situ* storage modulus measurements while the films were immersed in a 1 M MSA in THF solution. We observed a rapid decrease of E' of **10a** after addition of 1 M MSA in THF at 100 s, indicating rapid degradation of the film, whereas the E' of **11** remained unchanged, providing further evidence that films without acetal groups were stable in MSA/THF solutions (Fig. 3g).

The DMA results indicate degradation for acetal-containing polyurethane **10a**, whereas **11** maintains its integrity. Indirect support for the importance of the hydroxyl groups in the breakdown of polyurethane **10a** comes from studies of **10b** prepared with a 5:1 PPG-TDI to tetrol ratio. Analogous to **11**, these elastomeric films minimally changed with the MSA/THF treatment, at least in part because nearly all the hydroxyl groups were converted to urethane linkages and thus not able to participate in CATCH cleavage. More direct support for the Fig. 1c mechanism was provided by NMR. The HSQC spectrum of the degradation mixture of **10a** showed a correlation between large and small ^{1}H resonances at δ 4.8 ppm and ^{13}C signals at 104 ppm, consistent with the acetal protons and carbons of 1,3-dioxolane (major) and 1,3-dioxane (minor) units of **12** (Fig. 4a and Extended Data Fig. 5). Importantly, this signal disappeared upon hydrolysis with aqueous HCl to give **13**. The extent and nature of the CATCH cleavage-based degradation was examined by MALDI-TOF MS and GPC on **12**. To better grasp how the degraded material compared to the starting material, we reacted PPG-TDI with two equivalents of hexylamine to give **14** (Fig. 4b) as a control. MALDI-TOF MS data indicated that the *m*/*z* values for the main mass series in Extended Data Fig. 6a are consistent with structure **13** where n ~35-45 PPG units, the same mass series present in **14** (Extended Data Fig. 6b). One higher mass series is observed for **13** that corresponds to two PPG-TDI segments tethered together by a glycerol unit. The origin of this degradation product can be traced to the reaction of two PPG-TDI units with a single 1,2-diol unit of **5** during the polymerization. This higher mass series is derived from the cross-linking that occurs during curing and is not seen in hexylamine-capped PPG-TDI control **14**. The GPC provided $Đ = 2.31$ and $M_n = 7.7$ kDa for **13** and $Đ = 1.93$ and $M_n = 2.85$ kDa for **14** (Extended Data Fig. 6c). The GPC data further support complete degradation with generation of the original PPG-TDI length and a smaller amount of higher molecular weight material derived from cross-linking. We predict that this product distribution should not affect the upcycling into new materials.

Repurposing elastomers into strong adhesives and coatings. In addition to their utility as elastomers, polyurethanes are frequently applied as coatings, adhesives, and sealants. Indeed, they are strong and desirable adhesives with an ability to adhere to various substrates, be water-repellant, and as thermosets, they have a wide range of operating temperatures.[22,23] Whereas facile degradation of crosslinked polyurethane materials into reprocessable components is an important first step towards a sustainable polyurethane lifecycle, the utility of the post-degradation materials for reuse or recycling is equally crucial.

To demonstrate the reusability of the degraded materials generated from **10a** *via* CATCH cleavage, we chose to re-formulate the post-degradation polyol urethane prepolymer, **13**, as an adhesive. Polyol **13** was polymerized with 15 wt% of industrially relevant poly[(phenylisocyanate)-co-formaldehyde] (M_n ~340), PAPI 2027 (**15**, Fig. 4c). Adhesives fabricated with PAPI 2027 exhibited strong adhesion to both aluminum and glass substrates. The adhesives withstood a 20 lb weight for 24 h and 3 h for glass and aluminum, respectively (Fig. 4c). The significantly stronger adhesion to glass likely arises from the hydrogen bonding between the polyurethane adhesive and the hydroxylated silicate surface.[24] Additionally, lap shear tests were carried out on the PAPI-based adhesive for both substrates. Our repurposed polyurethane adhesive exhibited a magnitude of shear strength on the aluminum substrate that was comparable to cyanoacrylate glue (super glue) (Fig. 4d). For the glass substrate, adhesion of super glue was measured to have a shear strength of 0.8 ± 0.3 MPa, but no measurement was obtainable with the available instrument for the repurposed polyurethane adhesive because the glass substrates fractured before any failure in the adhesive could be observed (Fig. 4e). That is, the adhesion was sufficiently strong that the glass substrate would break during the lap shear test. Thus, we were able to degrade and repurpose our polyurethane material into a practical product that demonstrates competitive performance and potential commercial value.

In addition to forming adhesives, polyol prepolymer **13** can also be repurposed for use in functional coatings.[22,25] Polyurethane coatings are ubiquitous, and their properties can vary depending on the desired application but are often hard, chemically resistant, and provide appealing high-gloss finishes. As a proof of concept, we focused on demonstrating the utility and versatility of the polyol prepolymer **13** to formulate a photochromic coating as a light responsive coating, loosely analogous to smart window coatings. Thus, we blended a neat mixture of **13**, 2,4,6-trioxotriazine-1,3,5(2H,4H,6H)tris(hexamethylene)isocyanate (**16**), and the well-studied spiropyran dye[26] **17** to generate a UV-responsive coating material. This mixture was applied onto a glass slide using a paintbrush and cured overnight (Fig. 5). The photochromic activity of the repurposed polyurethane coating was tested by incorporating a Z-shaped mask on top of the coating and irradiating the substrate with 365 nm light for 3 min, which generated a purple Z on the coated section of the glass slide corresponding to formation of the merocyanine dye **18**. The Z entirely disappeared in 30 min when exposed to white light. The process was repeated for four cycles (Fig. 5, Supplementary Movie 2).

Generality and sustainability of CATCH cleavage. From a sustainability perspective, the use of methanesulfonic acid in the elastomer degradation is advantageous, partially due to the relatively small amount necessary for efficient degradation of polyurethanes. Additionally, methanesulfonic acid is readily biodegradable and significantly less toxic than more commonly used mineral acids like hydrochloric acid.[27] The environmental impact of this approach can be further limited by isolating the solvent *via* vacuum distillation and successfully reusing it for additional degradation cycles (Supplementary Fig. 3). We have demonstrated that simple polyol monomer **5** forms thermally and aqueous stable polyurethane elastomeric films that can be degraded into new polyols that can be reused to make different polyurethane materials. From a sustainability standpoint, one disadvantage of **5** is that its preparation utilizes the toxic osmium tetroxide for dihydroxylation. To test the generality of the CATCH cleavage mechanism and provide a greener alternative to **5**, we prepared a new tetrol acetal from trimethylolethane as a starting material. The new acetal-containing polyol monomer **21** was conveniently prepared in three steps (Extended Data Fig. 7). Despite the alcohol groups all being primary and the CATCH cleavage mechanism exclusively forming six membered 1,3-dioxane rings, model polyurethane elastomeric films still degraded within 20 min under anhydrous acidic conditions, and the TGA exhibited a similar onset degradation temperature (251 °C) to **10a**.

To further explore the generalizability of this approach, we prepared additional polymeric materials using **5** as well as analogous monomers that could degrade via the proposed CATCH cleavage mechanism (Fig. 6). First, we prepared rigid polyurethane resins (**26**) from **5** and toluene 2,4-diisocyanate. Replacing PPG-TDI with a small molecule diisocyanate produced a hard resin with a higher crosslinking density and reduced swelling ability. Nonetheless, this material underwent degradation albeit slower, likely by surface erosion (Supplementary Fig. 4). To apply this methodology to other polymerizations, we copolymerized tetrol **5** and activated diester **22** to prepare a crosslinked polyester resin (**27**) that rapidly degraded in 1 M MSA in DCM at room temperature (Supplementary Fig. 5). Additionally, we synthesized diazide **24** and triyne **25**, which were copolymerized in the presence of copper (I) to form a rubbery crosslinked polytriazole material (**28**) that similarly degraded within minutes at room temperature in 1 M MSA in DCM (Supplementary Fig. 6).

Conclusions

Because bulk polyurethane waste is made up of highly durable thermosets, it is usually incinerated or simply discarded in the environment. With the demand for polyurethane growing unabated, the safe and economically viable management of polyurethane waste will remain a key challenge facing modern society. We developed an approach to this challenge by designing an acetal-containing polyol that is compatible with the current industrially relevant isocyanate-polyol polyurethane chemistry. The water resistant, crosslinked hydroxyacetal polyurethane demonstrated rapid acid-catalyzed degradation in various organic solvents at room temperature, whereas the acetal-free control polyurethane and the hydroxyl-free acetal polyurethane analogs were largely unaffected by the same treatment. Additionally, the recovered polyol from the degraded waste product was successfully repurposed in two practical applications: a polyurethane adhesive with comparable performance to super glue and a photochromic coating. Again, both processes employed commercially available, industrial polyisocyanates as co-reagents. The generality of the hydroxyacetal approach and compatibility with existing polyurethane technologies suggests its application to other polyurethane systems that include isocyanate-free polyurethane chemistries,[28,29] and thereby opening a practical pathway to a new generation of sustainable polyurethanes. More broadly, the CATCH cleavage strategy has shown promise in other polymer chain functionalities, allowing for facile breakdown of a variety of polymeric materials. It is encouraging that this degradation mechanism is not limited to polyurethanes and has potential to be implemented into other classes of polymers, thus increasing the long-term environmental benefits of this approach.

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Author Contributions

E.G.M, H-C.W, and S.C.Z conceived the idea. E.G.M., M.L.P., H-C.W. designed and synthesized the tetrol monomers and small molecule models. D.D., A.J., and A.R. assisted with the chemical synthesis. E.G.M fabricated the polyurethane materials, degradation characterization, and mechanical testing of elastomers, adhesives, and coatings. D.G.I. performed DMA and DSC studies of polyurethane elastomers and D.G.I. and N.R.S. analyzed data. M.L.P. designed and synthesized the monomers for the polytriazoles, fabricated the polytriazoles and polyesters, and characterized their degradation products. E.G.M, M.L.P., H-C.W., and S.C.Z. prepared the manuscript.

Competing Interests

The University of Illinois has filed a patent application on degradable polymers and monomers based on the hydroxyacetal chemistry described herein (US Application No. 17/217,512; inventors E.G.M., H.W., and S.C.Z.). The remaining authors declare no competing interests.

Figure Legends

Figure 1. Polyurethanes and Proposed CATCH Cleavage. a) Polyaddition polymerization of a polyisocyanate and an acetal or ketal-containing polyol monomer to give a polyurethane. Typical polyisocyanates produce hydrophobic polyurethanes that resist hydrolysis. **b)** Organic solvent can make the bulk polyurethane more permeable and deliver acid for sufficient acetal degradation. **c)** Generalized CATCH cleavage mechanism, wherein transient chain break (green) is trapped by pendant group (blue) in ring closing reaction. **d)** Acid-catalyzed formation of transient oxocarbenium ion **2b** that can be trapped by pendant alcohol group, giving cyclic acetal **3** (purple). Cleavage of acetal groups gives new polyol **4** corresponding to glycerol addition to polyisocyanate.

Figure 2. Preparation of acetal-containing polyurethane films. a) Preparation of tetrol monomer **5**. **b**) Model urethane acetal **6** undergoes CATCH cleavage. **c**) Preparation of polyurethane elastomeric films **10a** and **11** using PPG-TDI (M_n ~2,300) and polyol **5** or **9** with rhodamine B dye for visualization. Terminal oxygen atoms signify mixture of polymer main-chain or alcohol groups and also some cross-links. **d**) Typical 1 mm thick 40 x 5 mm elastomeric films **10a** prepared from 1:2 ratio of **5** to PPG-TDI with casting on a PTFE mold and curing at 95 °C

for 12 h. **e**) T_g values for films **10a** and **11** measured by DSC and DMA and storage moduli (E') at 25 °C. Values are averages of three independent runs, and errors are standard deviations.

Figure 3. Gated degradation of polyurethane elastomers. a) Dissolution of polyurethane film **10a** in 1 M methanesulfonic acid (MSA) in THF followed by removal of solvent. Degradation in anhydrous conditions supports intramolecular CATCH mechanism. **b)** Polyurethane **10a** in 1 M HCl (aq) and **c)** in 1 M MSA (aq) followed by removal of solvent. Lack of observable degradation demonstrates the material's stability in aqueous environments in the presence of organic and inorganic acids. **d)** Logic AND gate table, summarizing degradation results of **10a** in various conditions. Green check mark indicates complete degradation; red X indicates no observable degradation or dissolution. Both organic solvent and acid are necessary for degradation to occur. **e)** Representative thermomechanical response of **11** films and **f) 10a** films before and after soaking in 1 M HCl aqueous solution for 24 h, showing no change or minimal change in E' and tan δ from tensile DMA, indicating stability in aqueous acidic environments. Retention of the rubbery plateau indicates that the polymer remained crosslinked after this treatment. **g)** Storage modulus of **10a** films (blue) and control **11** films (red) immersed in 1M MSA in THF versus time from tensile DMA. Rapid decrease in E' of **10a** and not **11** demonstrates the requirement of an acetal for degradation to occur.

Figure 4. Repurposing of polyurethane elastomers to strong adhesives. **a**) Scheme showing possible degradation products from film **10a**. **b**) Preparation of urea **14** as a size standard for MALDI-TOF MS and GPC. **c**) Fabrication of PAPI-based polyurethane adhesive for steel and glass substrate. Scale bar, 1 cm. A 20 lb kettlebell supported by adhesive on glass substrate and steel substrate. Scale bar, 5 cm. **d**) Lap shear of repurposed adhesive on steel substrate and comparison with cyanoacrylate. Average of three independent runs with error bars representing standard error of the mean. **e**) Lap shear results using repurposed adhesive on glass showing shattered glass with lap-joint intact. Scale bar, 1 cm.

Figure 5. Repurposing of polyurethane elastomers to photochromic coating. Fabrication of photochromic polyurethane coating on a glass slide with coated (top) and untreated (bottom) halves. Photochromic ability of coating was demonstrated *via* 3 min irradiation with 365 nm longwave hand-held UV light through Z-shaped photo-masks. A purple "Z" was produced only on the coated half, signifying the conversion of **17** to **18** under UV irradiation. Subsequent exposure to white light (ambient fluorescent laboratory lights) for 30 min caused the coating to revert back to its original color. Scale bar, 1 cm.

Figure 6. Synthesis of additional CATCH-degradable polymers. Detailed synthetic procedures are included in the Supplementary Information. **a)** Polyurethane resin synthesis from **5** and 2,4-TDI. (i: THF; 95 °C, o/n) Scale bars, 1 cm. **b)** Polyester synthesis from **5** and activated ester **22**. (ii: DBU, THF, $CHCl_3$; rt for 4 h then 95 °C o/n). **c)** Polytriazole synthesis from diazide **24** and trialkyne **25**. (iii: H_2O, ^{t}BuOH, $CuSO_4{\bullet}5H_2O$, sodium ascorbate; rt, 18 h) Scale bar, 1 cm.

Methods

Materials

Unless otherwise noted, all solvents were ACS reagent grade and purchased from Acros Organics, Fisher Scientific, or Sigma-Aldrich and used without further purification. Solvents used for polymerization, such as dichloromethane (CH_2Cl_2) and tetrahydrofuran (THF), were purchased from Fisher Scientific and used directly from an MBRAUN solvent purification system. Chloroform ($CHCl_3$) used for polymerizations was purchased from Fisher Scientific, dried over calcium chloride, and distilled over 4 Å molecular sieves. Butyraldehyde, butyl isocyanate, allyl alcohol, polyethylene glycol 400 (PEG-400), 1',3'-dihydro-1'3'3'-trimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2'-2(2*H*)-indole], potassium osmate (VI) dihydrate, 50 wt% *N*-methylmorpholine *N*-oxide (NMO) in H_2O, trichloroacetic acid, *p*-toluenesulfonic acid monohydrate, sodium sulfite, 2-allyloxyethane, allyl bromide, *tert*-butanol, poly(propylene glycol), tolylene 2,4-diisocyanate terminated (average M_n ~2,300 (narrow MW distribution), isocyanate ~3.6 wt%), poly[(phenyl isocyanate)-*co*-formaldehyde] (average M_n ~340), 1,4-diazabicyclo[2.2.2]octane (DABCO), 60% sodium hydride (NaH) in mineral oil, toluene 2,4-diisocyanate, trimethylolethane, 2,6-lutidine, sodium ascorbate, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and benzaldehyde were purchased from Sigma-Aldrich and used as received. Isophthaloyl chloride and copper (II) sulfate pentahydrate were both purchased from Sigma-Aldrich and recrystallized before use (in *n*-hexane and water, respectively). (2,4,6-Trioxotriazine-1,3,5(2H, 4H, 6H)-triyl) tris(hexamethylene) isocyanate (Carbosynth Limited), sodium azide (Chem-Impex International), allyl bromide (Alfa-Aesar), 3-chloroperbenzoic acid (75%, *m*CPBA) pentafluorophenol, 4-(trifluoromethyl)-benzaldehyde (Oakwood Chemical), and 4-nitrobenzaldehyde (AK Scientific) were used as received. Sodium sulfate, magnesium sulfate, diethyl ether, sodium bicarbonate, and ethylenediaminetetraacetic acid (EDTA) disodium salt were purchased from Fisher Scientific and used as received. The purity and authenticity of commercial reagents were determined by NMR. After each isocyanate was used for the first time, its container was sealed with Parafilm and stored in desiccator for future use. Silica gel chromatography was performed using 230-400 mesh (40-63 μm) silica gel. All deuterated solvents were purchased from Cambridge Isotope Laboratory. CD_3CN used for small molecule degradation experiments was dried by passing the solvent through a 3 inch x 0.5 inch basic alumina plug and stored in a flame dried 25 mL RBF containing 20 wt% flame dried 4 Å molecular sieves for 24 h before use.

Instrumentation

Gel permeation chromatography (GPC) was performed on a Tosoh EcoSEC 8320 GPC system with 14.5 mM LiBr in DMF as the mobile phase. Samples were prepared by dissolving 2 mg of polymer in 1 mL of mobile phase and filtering the solution with a 0.2 μm Nylon syringe filter before injection into the GPC. A refractive index (RI) detector with polymethyl methacrylate (PMMA) standard was utilized to determine molecular weight (M_n and M_w) and dispersity ($Đ$).

Thermogravimetric analysis (TGA) was performed on Q50 Thermogravimetric Analyzer equipped with vertical beam balance (sample capacity: 1000 mg) and a purge gas system. Samples were prepared by cutting small pieces of polyurethane films (5-10 mg). Samples were heated at a rate of 5 °C/min from 25 °C to 600 °C under a nitrogen atmosphere.

Differential scanning calorimetry (DSC) was performed on a TA Instruments Discovery/DSC 250 with a RCS90 refrigeration system. 5-10 mg of each sample was placed in a Tzero pan and sealed with a Tzero lid. The samples were cooled to -85 °C then heated at a rate of 10 °C/min to 90 °C, cooled to -85 °C at the same rate, and the temperature was then increased at a rate of 10 °C/min until reaching 90 °C. The glass transition temperature (T_g) of the sample was determined by the maximum value of the derivative of heat flow with respect to temperature. Data were obtained for a minimum of three specimens per material.

Tensile dynamic mechanical analysis (DMA) was performed on a TA Instruments RSA III equipped with thin film grips and a liquid nitrogen cooling system. Samples were cured into rectangle geometries of 40 mm x 10 mm x 1 mm. The gauge length was maintained at 10 mm, and dynamic loading was performed at 1 Hz and 0.1% strain amplitude while increasing temperature linearly at 5 °C/min from -60 °C to 25 °C. The glass transition temperature of the samples was determined by the temperature where the peak of Tan δ occurred. Data were obtained for a minimum of three specimens per material.

^{1}H and ^{13}C NMR spectra were recorded on a 400 or 500 MHz Varian Unity Inova spectrometer and MestReNova software was utilized to process NMR spectra and the chemical shifts were recorded in parts per million (ppm). All ^{1}H and ^{13}C spectra are reported with residual solvent peaks as reference. The integration is provided along with coupling constants (J) that are reported in Hertz (Hz). Electrospray ionization mass spectra (ESI-MS) were obtained by using ESI on Waters Micromass Q-TOF spectrometer, FD on a Waters 70-VSE spectrometer. Attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR) measurements were performed in a Thermo Nicolet Nexus 670 at room temperature. The IR spectra was obtained by averaging 16 scans over 4000-600 cm^{-1} range.

For small molecule degradation studies, 6 mL glass vials were submerged in 1 M acetic acid overnight, then rinsed thoroughly with distilled water and acetone. The vials were dried in the oven for 6 h before use. In a 6 mL vial, a 0.5 mM solution of small molecule model **3** in CD_3CN was prepared, along with 0.3 mol equivalents of hexamethylbenzene as an internal standard. 0.6 mL of this solution was transferred to an NMR tube, along with 0.5 mol% TsOH. The reaction was monitored by ^1H NMR until complete degradation of **6** was observed. Percent of **6** remaining was calculated from the integration of the **6** acetal peak relative to the integration of the hexamethylbenzene peak.

Matrix- assisted laser desorption/ionization-time of flight (MALDI-TOF) mass spectrometry were performed on a Bruker Daltonics Ultraflex TOF mass spectrometer in reflection mode with 2,5- dihydroxybenzoic acid or 2-(4-hydroxyphenylazo)benzoic acid as the matrix.

Lap shear tests were performed on a Parker 081-6079 load frame with a Transducer Techniques 300 lb MDB series load cell at an extension rate of 1 mm/s. Strain within the samples was measured using a virtual extensometer. Samples were prepared according to ASTM D1002 standards. Briefly, 10 mg of adhesive mixture was evenly applied on 12.7 mm x 25.4 mm (L x W) overlap and lap shear tests were reported as an average and standard deviation of three measurements. All equipment was controlled *via* LabView and a custom program.

Supplementary Information

Supplementary figures as well as detailed experimental procedures, NMR spectra, additional characterization data, model studies, kinetic data, material characterization, and fabrication and degradation studies of polyurethane materials can be found in the Supplementary Information.

Data Availability

The data supporting the findings in this study are available within the Source Data and Supplementary Information.

Fig. 1

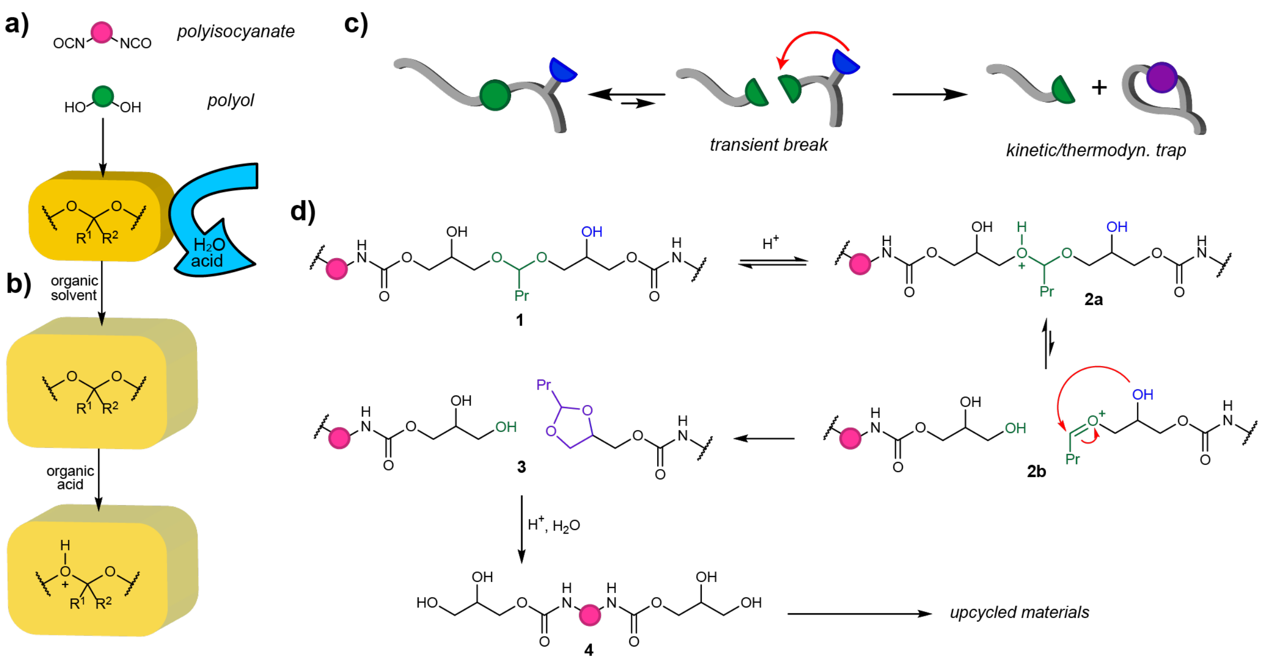
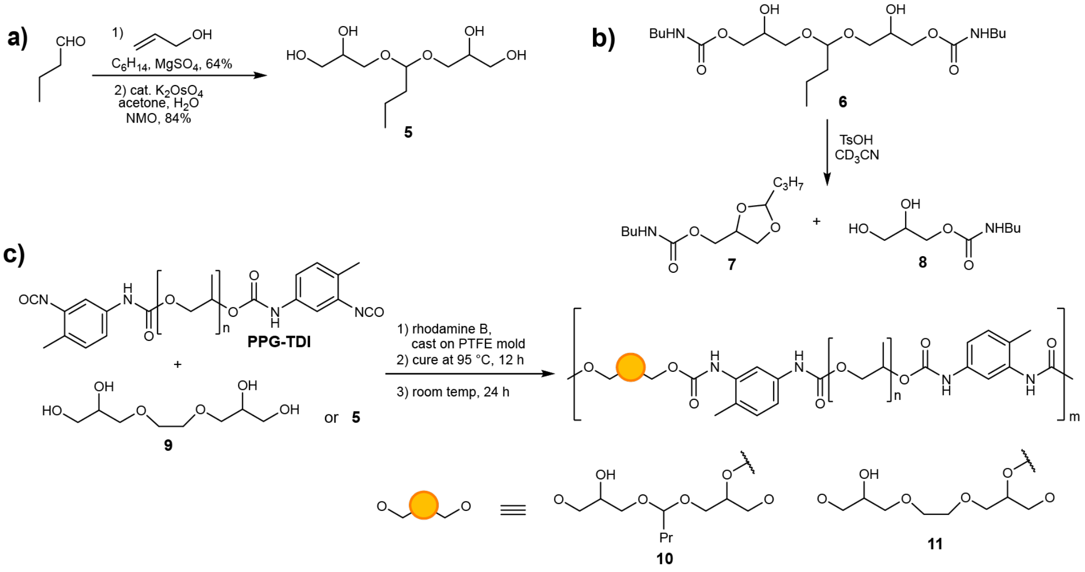


Fig. 2

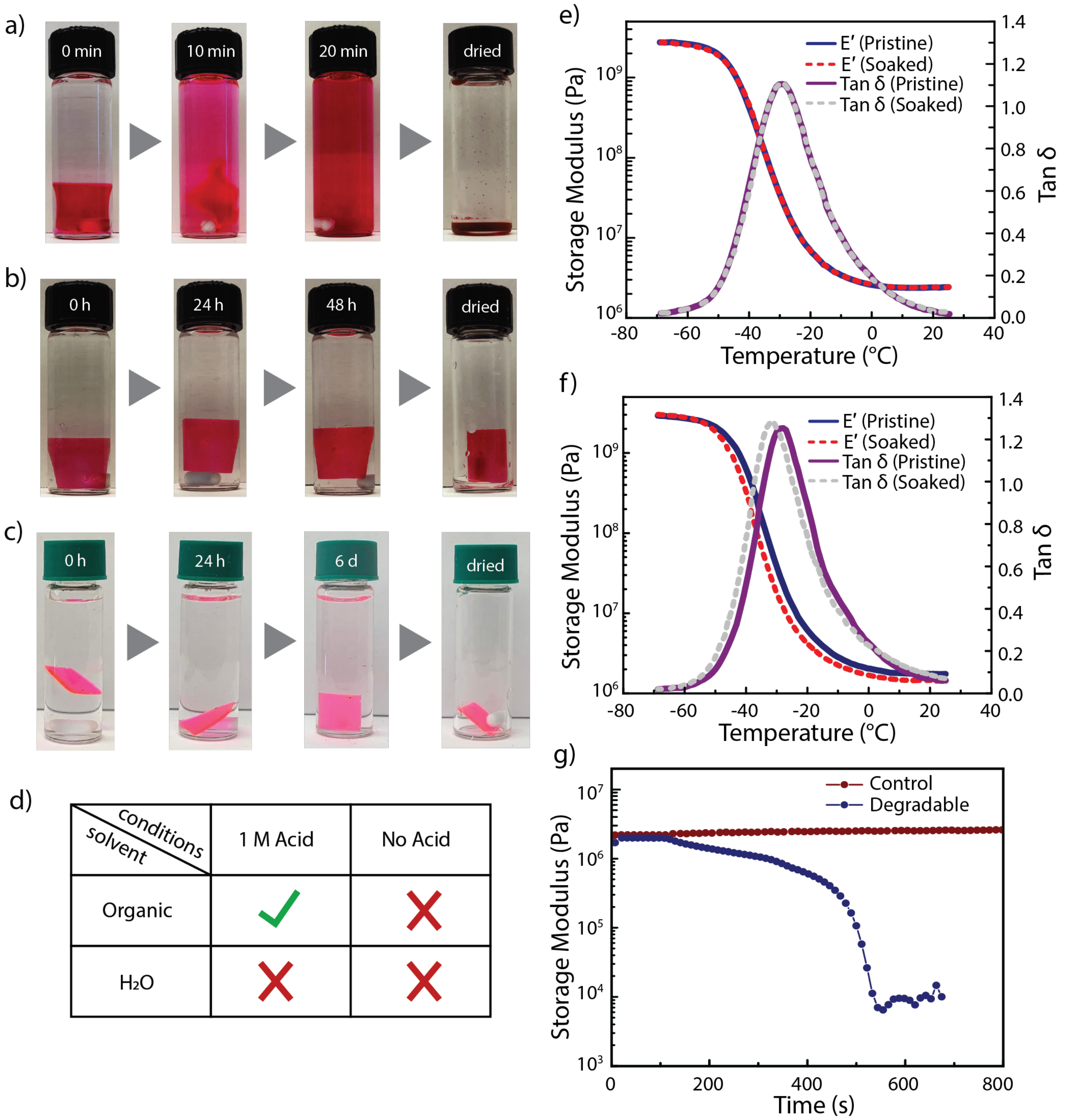


d)

e)

	T_g (°C)	
sample	DSC	DMA
10	-45.9 ± 0.1	-40.0 ± 0.2
11	-49.4 ± 0.4	-41.7 ± 1.3

Fig. 3



solvent \ conditions	1 M Acid	No Acid
Organic	✓	✗
H_2O	✗	✗

Fig. 4

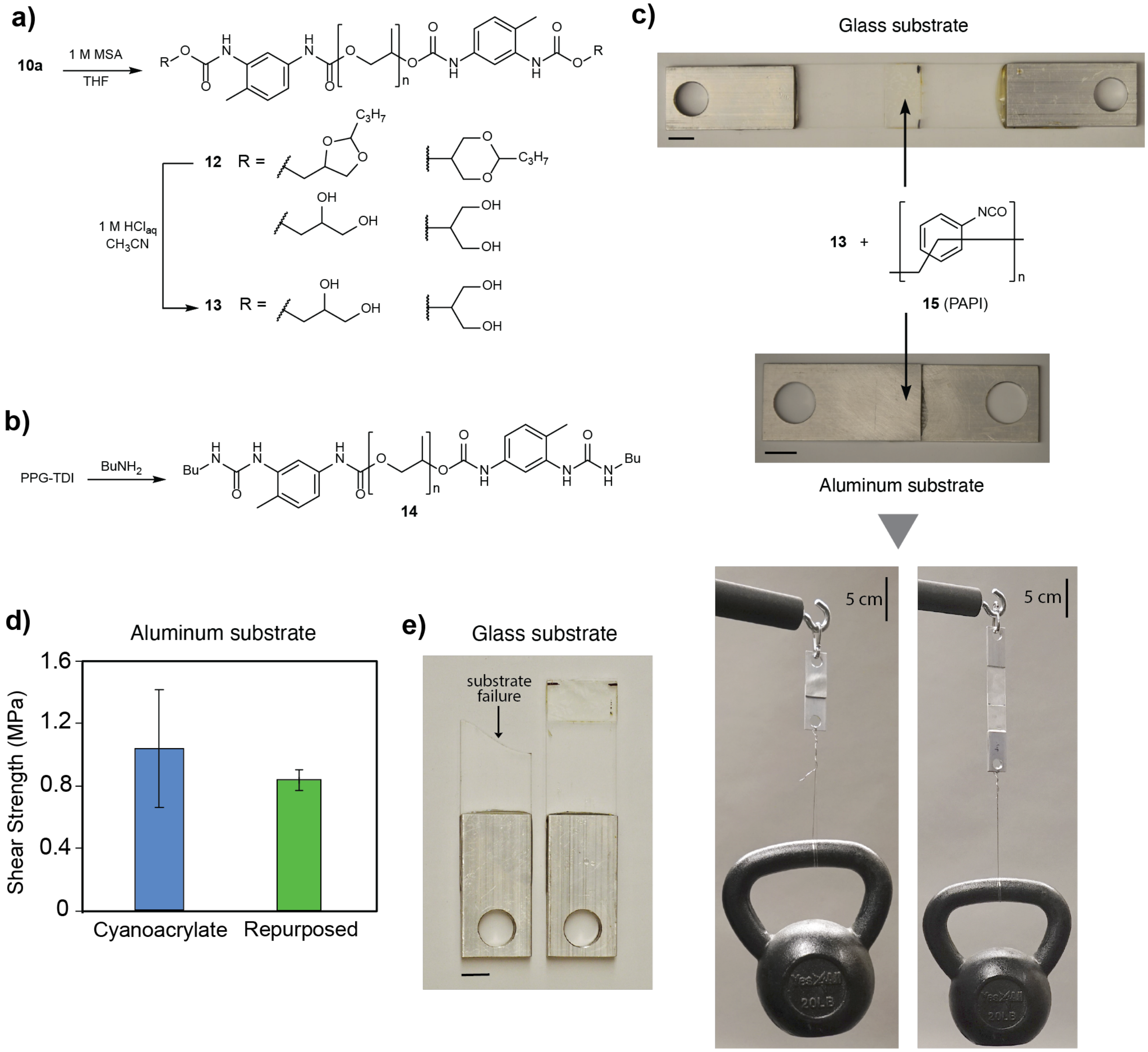
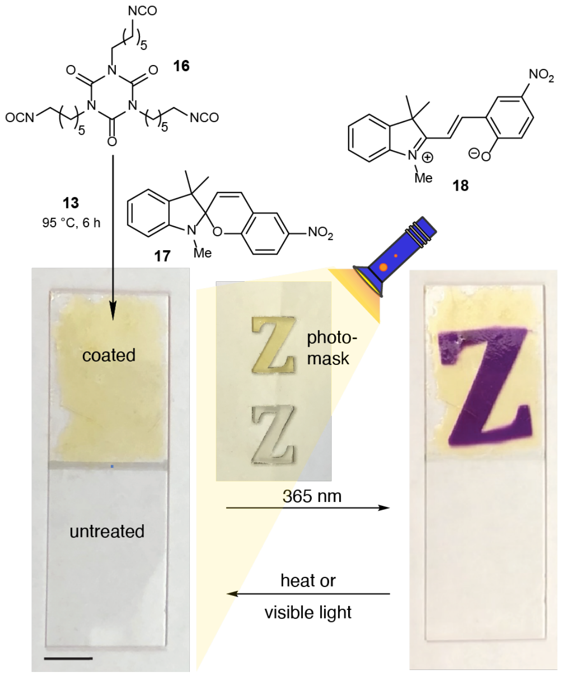
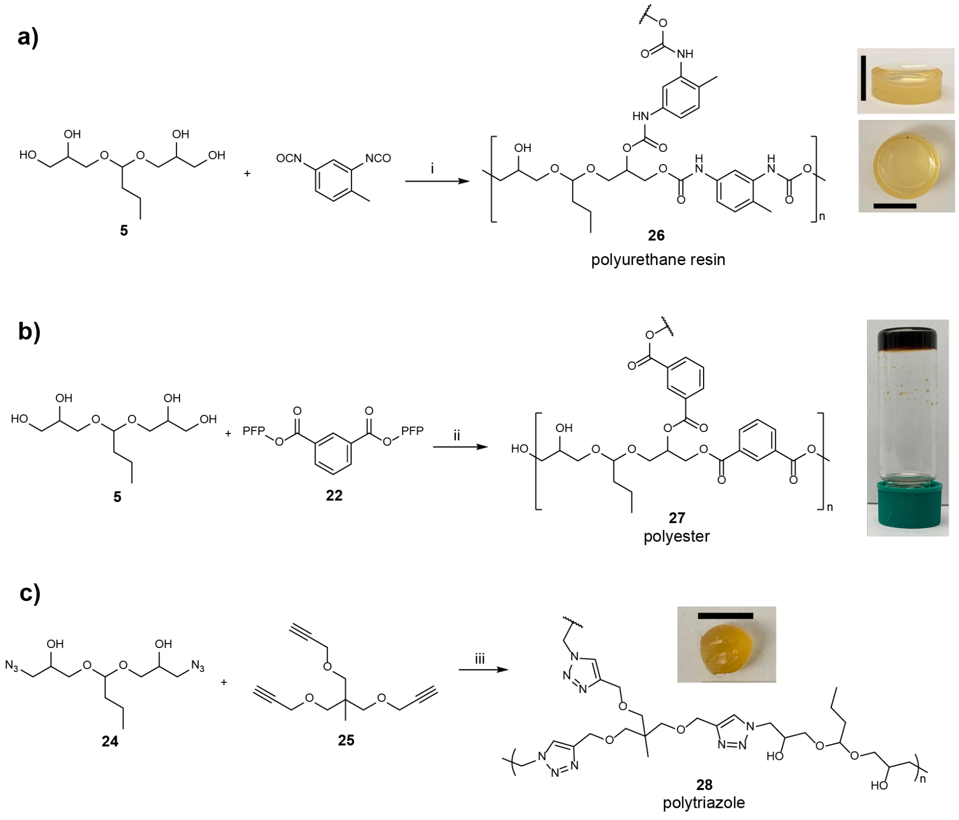

a)
10a
1 M MSA
THF
R
O
H
N
n
12
R =
C_3H_7
OH
1 M HCl_{aq}
CH_3CN
13
R =
b)
PPG-TDI
$BuNH_2$
Bu
14
c)
Glass substrate
13 +
NCO
15 (PAPI)
Aluminum substrate
5 cm
5 cm
20LB
d)
Aluminum substrate
Shear Strength (MPa)
1.6
1.2
0.8
0.4
0
Cyanoacrylate
Repurposed
e)
Glass substrate
substrate failure

Fig. 5



NCO
5
O
N
O
16
OCN
N
N
NCO
5
5
O
NO2
18
N⊕
Me
⊖O
13
95 °C, 6 h
N
O
NO2
17
Me
coated
photo-
mask
untreated
365 nm
heat or
visible light

Fig. 6



a)
O
NH
HN
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i
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O
N
H
N
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26
polyurethane resin
b)
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O
OH
OH
HO
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OH
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PFP
O
O
O
PFP
O
ii
OH
HO
O
O
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O
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polyester
c)
OH
OH
N3
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24
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28
polytriazole