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Rapid, On-Command Debonding of Stimuli-Responsive Cross-Linked Adhesives by Continuous, Sequential Quinone Methide Elimination Reactions

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Abstract: *Adhesives that selectively debond from a surface by stimuli-induced head-to-tail continuous depolymerization of poly(benzyl ether) macro-cross-linkers within a poly(norbornene) matrix are described. Continuous head-to-tail depolymerization provides faster rates of response than can be achieved using a small-molecule cross-linker, as well as responses to lower stimulus concentrations. Shear-stress values for glass held together by the adhesive reach 0.51 ± 0.10 MPa, whereas signal-induced depolymerization via quinone methide intermediates reduces the shear stress values to 0.05 ± 0.02 MPa. Changing the length of the macro-cross-linkers alters the time required for debonding, and thus enables the programmed sequential release of specific layers in a glass composite material.*

Removing adhesives from a surface is a difficult, labor-intensive process typically requiring mechanical force and ultimately limiting our ability to recycle multicomponent materials. Likewise, finding a balance between strong binding and easy removal is a significant challenge when developing biomedical adhesives.[1] Thus, new adhesives are needed for overcoming these limitations, in particular, strong adhesives that can be removed easily, on demand, and without damaging the underlying surface. The challenge in creating such adhesives is designing a polymer that is capable of displaying the dual and opposing properties of strong adhesion and stimuli-induced weakening of the adhesive to enable debonding under mild conditions.[2]

Herein, we describe one solution to this problem where the reaction of an adhesive with a specifically applied stimulus, in this case fluoride, leads to disproportionately large changes in the structure of the adhesive relative to the intensity of the applied signal (Figure 1). This large change enables the adhesive to debond rapidly (ideally within only seconds to minutes after exposure to the applied stimulus), even when the adhesive is exposed to trace quantities of the stimulus.

Our design is based on using cross-linking to form an adhesive (polymer **1** in Figure 1) and de-cross-linking to debond the adhesive (polymer **2**). In this design, less than 1 mol% of a stimuli-responsive monomer (in the form of a macromonomer) is needed to cross-link an abundant, readily accessible monomer to create a strong, stimuli-responsive adhesive. Stimuli-induced depolymerization[3,4] of the macro-cross-linker (a poly(benzyl ether)) leads to disproportionately large changes in the structure, which enable the selective, sensitive, and rapid switching of a strong adhesive into a debonded material. Depolymerization provides these features because it breaks many cross-links simultaneously and thus gives rise to amplified changes in the structure and properties of the adhesive.

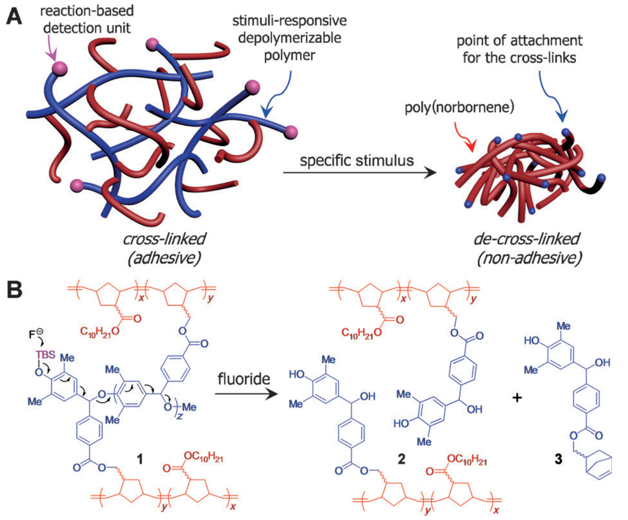

Figure 1. A) Schematic representation of the macro-cross-linked adhesive and its stimuli-induced de-cross-linking by depolymerization. B) A specific polymer and the stimulus (fluoride) used in this work. The *tert*-butyldimethylsilyl group (TBS) functions as a reaction-based detection unit.

We demonstrate these features using polymer **1**, which requires two monomers for its preparation (Scheme 1): poly(benzyl ether) **6** and an appropriate norbornene monomer **4**. In initial studies, we used a poly(benzyl ether) variant that had a number average molecular weight (M_n) of 21 kDa and a *tert*-butyldimethylsilyl (TBS) ether end cap as the fluoride-responsive detection unit. This polymer served as a macro-cross-linker for poly(norbornene) **5** (Scheme 1) to generate polymer **1**, which is an adhesive when the molar feed ratio of monomers **6** and **4** is 1:526, and when monomer **4** was polymerized first for 20 min to form **5**,[5] followed by addition of cross-linker **6** for an additional 12 h of polymerization. In contrast, simultaneous copolymerization of **6** and **4** from the outset of the reaction resulted in a cross-linked polymer that

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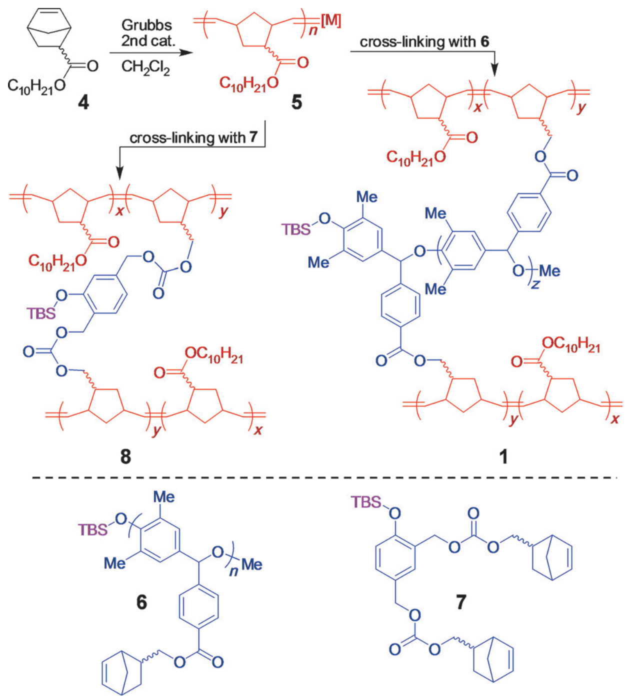

Scheme 1. Synthesis of cross-linked polymer **1** and control polymer **8**.

was not tacky to touch (i.e., negligible adhesion properties), as did ROMP polymerization of just **4** or **6**.

The substantially different solubility of polymer **1** compared to those of either **4** or **6** provided initial evidence for the successful cross-linking reaction. In fact, the limited solubility of cross-linked polymer **1** thwarted attempts to characterize the polymer by NMR spectroscopy and gel-permeation chromatography (GPC).[6] The results from differential scanning calorimetry (DSC) experiments (Supporting Information, Figure S1), however, were consistent with a cross-linked polymer. For example, prior to cross-linking, polymer **6** had a glass transition temperature (T_g) of 123 °C. After cross-linking with **5** to form **1**, no glass transition was observed, as would be expected for a cross-linked polymer.

We also prepared a control cross-linked polymer (**8**, Scheme 1) that featured small-molecule cross-linker **7**, which is responsive to fluoride (Figure S2; like the macro-cross-linker), but in which only a single cross-link is broken per reaction with fluoride instead of amplifying the number of cross-links that are broken.

With both polymers in hand, we tested whether macro-cross-linker **6** was capable of switching the properties of polymer **1** by fluoride-induced depolymerization. Exposure of **1** (20 mg mL^{-1}) in THF to fluoride (0.5 M TBAF) at 23 °C for two days (to ensure complete reaction between fluoride and the detection units) resulted in release of the hydrated derivative of the quinone methide monomer (see **3** in Figure 1 as well as Figure S3). This product was expected as every repeating unit in macro-cross-linker **6** contains a norbornene ester, but not all will have participated in the ROMP-mediated cross-linking reactions. Therefore, upon depolymerization of **6**, the unreacted norbornene groups will be released into solution.

The other product from the de-cross-linking reaction, residual polymer **2**, was analyzed by ^{1}H NMR spectroscopy and confirmed to be a poly(norbornene) derivative arising from **4**. The ^{1}H NMR spectrum further revealed that the polymer did not contain measurable quantities of macro-cross-linker **6** (Figure S3).

Remaining poly(norbornene) **2** is readily soluble in organic solvents, and we thus used GPC to estimate the length of the polymer, which could not be accomplished for polymer **1**. This GPC analysis revealed a 44 kDa (M_n) polymer, confirming that the ROMP reaction had been successful, and that approximately 11 % of the repeating units in polymer **1** (before exposure to fluoride) originated from the poly(benzyl ether) macro-cross-linker **6**.[7]

We used shear stress measurements to quantify the strength of adhesive **1**. The procedure for these measurements was based on the ASTM D1002 lap shear test guideline, which involves pulling two substrates that are glued together in opposite directions parallel to the bonding plane. To perform this experiment, we soaked polymer **1** for 1 min in THF (which swells the polymer), then placed the polymer between two glass microscope slides. This glass/polymer composite was held together using a binder clip and dried under reduce pressure (125 mmHg) for one day, after which the lap shear tests were performed.[8]

The results of these tests reveal that dry **1** (made using 21 kDa **6** with a molar feed ratio of **6**/**4** = 1:333) is highly effective at gluing together the glass slides (i.e., 0.51 ± 0.10 MPa of shear stress was required to break the adhesive bond between slides; Figure S5). This shear stress value is comparable to the strength of commercial Krazy Glue (poly(ethylcyano acrylate)), which provides a shear stress value of 0.63 ± 0.12 MPa when gluing together similar glass slides. Unlike Krazy Glue, however, exposure of the glass slides containing **1** to 0.1 M TBAF in THF for 20 min and then drying the slides resulted in adhesion that required only 0.05 ± 0.02 MPa of shear stress to separate the glass slides. This value of 0.05 MPa is identical to the shear stress value for pure poly(norbornene) **9** that we prepared from monomer **4** (0.04 ± 0.01 MPa for polymer **9**). As poly(benzyl ether) cross-linker **6** has no adhesive properties by itself, these combined results support the hypothesis that **1** only functions as an adhesive when cross-linked.[9]

We surmised that adhesive **1** would be responsive to lower concentrations of an applied stimulus than polymer **8** (which is cross-linked with small molecule **7** rather than polymer **6**), and likewise would provide faster responses when exposed to the stimulus. We reasoned that a single reaction of fluoride with **8** would break a single cross-link, whereas the reaction of one molecule of fluoride with **1** should, in principle, break many cross-links as a result of the ensuing depolymerization reaction. To test this hypothesis, we prepared batches of **1** and **8** that differed in the feed ratios of norbornene monomer **4** relative to cross-linkers **6** and **7**, and then used the various cross-linked polymers to bond glass slides. Lap shear tests of these polymers (Figure 2 A) revealed the feed ratios that provided the strongest adhesives for **1** and **8**. For example, for polymer **1**, the highest shear value (0.51 ± 0.10 MPa) was obtained using 21 kDa (M_n) **6** in a molar feed ratio of **6**/**4** =

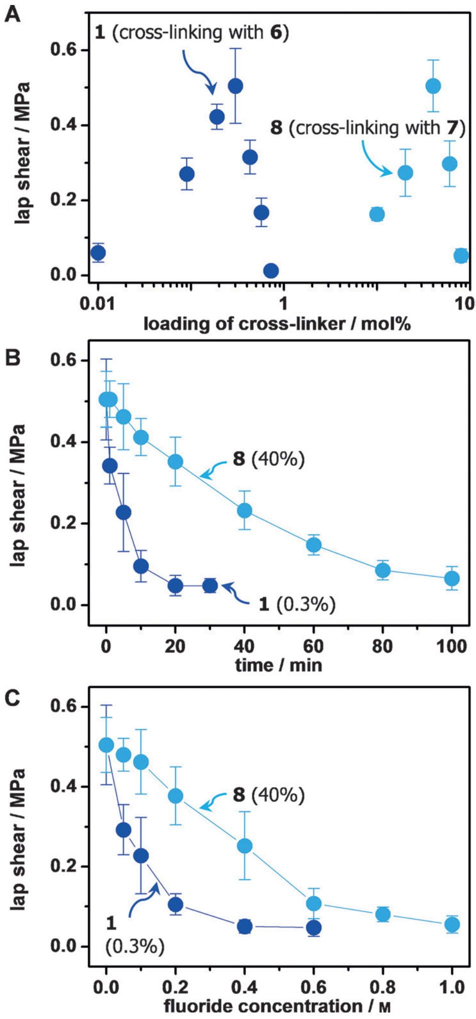

Figure 2. A) Lap-shear stress values as a function of the molar ratio of **6** to **4** (for polymer **1**) and **7** to **4** (for polymer **8**). B) Time-dependent change in the lap-shear stress values for **1** (containing 0.3 mol% of 21 kDa **6**) and **8** (40% incorporation of **7**) after exposure to 0.1 M TBAF in THF. C) Changes in the lap-shear stress values for the same polymers as in (B) after 5 min of exposure to different initial concentrations of fluoride in THF. The data points for all graphs are the average of four independent measurements, and the error bars reflect the standard deviations of these averages. The data points are colored blue to correlate the data with the structures in Scheme 1. The lines in (B) and (C) are provided as guides to facilitate visualization of the data.

1:333, whereas the highest shear value for **8** (0.51 ± 0.07 MPa) required 40% incorporation of **7** into polymer **8**.

As polymer **1** (containing 0.3 mol% of 21 kDa **6**) and polymer **8** (40 mol% of **7**) have equivalent shear strengths, we used these polymers to compare the responses of the two cross-linkers to fluoride. For example, polymer **1** (containing 0.3 mol% of **6**) completely debonded from the glass slides five times faster than polymer **8** (40 mol% of **7**) when both adhesives were exposed to 0.1 M TBAF in THF at 23 °C (Figure 2B). This increase in rate for cross-linker depolymerization is particularly impressive given that polymer **1** requires 133 times fewer moles of cross-linker than polymer **8**.

Depolymerizable macro-cross-linker **6** also increases the sensitivity of the adhesive to the applied stimulus (Figure 2C). In this context, polymer **1** debonded completely in 5 min when exposed to fluoride concentrations that are 2.5 times lower than those required for debonding polymer **8** (same exposure time). Taken together, these results indicate that depolymerizable cross-linkers are substantially more effective than small-molecule cross-linkers in providing rapid and sensitive debonding in response to stimuli.

To further illustrate the rapid debonding of **1**, we glued two polypropylene (PP) squares (surface area 1 cm × 1 cm) to a glass slide using **1** (21 kDa **6** with a feed ratio of **6**/**4** = 1:333; Figure 3). As illustrated in Figure 3, we used tweezers to suspend the glass slide vertically. The addition of several drops of a 1:9 THF/water solution at the PP–glass interface of the top edge of the PP square on the left had no observable effect on the bonding between the PP and glass, even after 30 min of exposure to the solution. In contrast, addition of several drops of the same solvent mixture, but containing 0.1 M TBAF as well, to the PP–glass interface of the PP square on the right (marked by the letter F) caused the square to abruptly and nearly instantaneously slip down the glass slide. This contrasting behavior reveals the ability of **1** to serve as a selective stimuli-responsive adhesive. Movie S1 depicts the dynamics of this response.

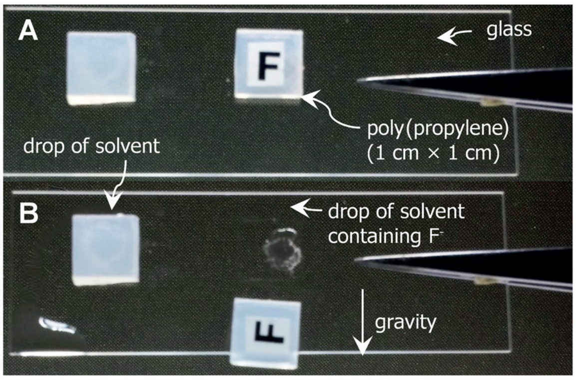

Figure 3. Selective fluoride-induced debonding of polypropylene (PP) from glass. A) Photograph of two polypropylene squares (surface area 1 cm × 1 cm) attached to a glass microscope slide using **1**. B) Several drops of 1:9 THF/water solution had no effect on the adhesion between PP and glass (left PP square), whereas when several drops of the same solvent, but now also containing 0.1 M TBAF, were added to the right square, it immediately dislodged the PP from the glass (see also Movie S1).

Furthermore, we prepared three variants of **6** (all having molar feed ratios of **6**/**4** = 1:526) using three lengths of **6** (short, medium, and long, corresponding to $M_n = 4$, 21, and 145 kDa, respectively) to evaluate the relationship between exposure time to the applied stimulus (fluoride in this case) and the extent of debonding (Figure 4). Prior to exposure to fluoride, all three variants of **1** provided equal shear stress values for the bonding of glass slides (0.43 ± 0.02, 0.42 ± 0.03, and 0.44 ± 0.02 MPa for the polymers containing different lengths of **6** listed in the same order as above). Upon exposure

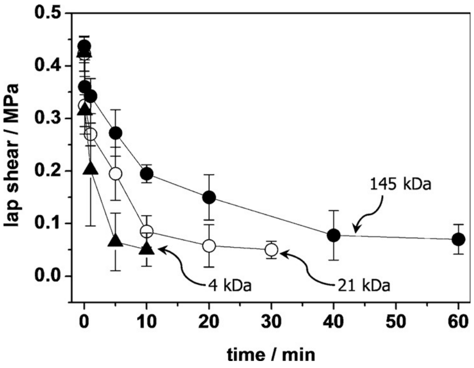

Figure 4. Time-dependent changes in the shear stress of three variants of cross-linked adhesive **1** (all with molar feed ratios of **6**/**4** = 1:526) made from cross-linkers **6** with three different molecular weights: ●: 145 kDa **6**; ○: 21 kDa; ▲: 4 kDa. The data are the average of four independent measurements, and the error bars represent the standard deviations. The lines are provided as guides to clarify the trends in the data.

to a 0.1 M TBAF solution in THF, however, the shortest cross-linker (M_n 4 kDa) debonded first (within 10 min; Figure 4), the 21 kDa cross-linker debonded within 20 min, and the 145 kDa cross-linker debonded in approximately 40 min. Clearly, the length of cross-linker **6** in **1** provides a means for tuning how quickly an adhesive is capable of debonding.

Given the ability of **1** to rapidly debond when exposed to fluoride, we reasoned that differential rates of debonding based on the length of cross-linker **6** in **1** could be used not only as a surface separation technique, but also as a method for purifying materials as they are debonded from a larger composite. This concept is illustrated in Figure 5 and Video S2. The demonstration involved gluing together four 1.5 cm × 1.5 cm × 2.6 mm squares of colored glass (each of a different color) using three variants of **1** (all having molar feed ratios of **6**/**4** = 1:526, where cross-linker **6** varied in length from 4 kD to 21 kD to 145 kDa). Polymer **1** with the 4 kDa cross-linker was used to glue together the green and light blue pieces of glass; the 21 kDa cross-linker bonded the light blue glass to the red glass; and the 145 kDa cross-linker secured the red glass to the dark blue piece (Figure 5 A).

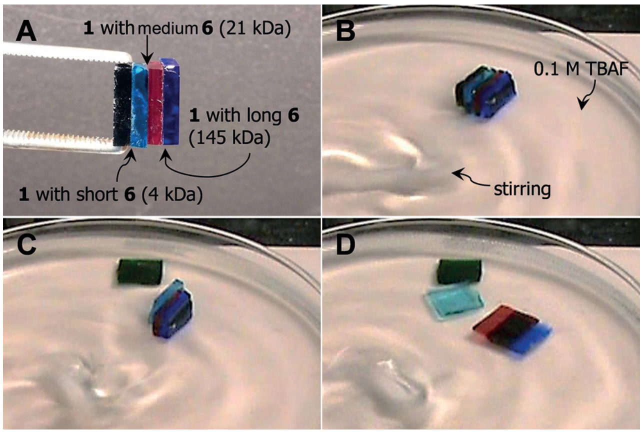

Figure 5. Polymer **1** enables the programmed separation and purification of components of a composite. A) Photograph of a four-layered stack of colored glass (from left to right: green, light blue, red, and dark blue; each piece of glass has the same dimensions: 1.5 cm × 1.5 cm × 2.6 mm). B–D) Photographs of the immersed glass stack in the stirred solution (0.1 M TBAF in 1:9 THF/water) taken after 1 min (B), 15 min (C), and 1 h (D). Movie S2 shows the dynamics of the sequential separation.

The four-layer composite was immersed in a stirred 1:9 THF/water solution containing 0.1 M TBAF (Figure 5 B). Within 15 min, the green glass separated from the composite, which is expected given that **1** containing the 4 kDa cross-linker was used as the adhesive (Figure 5 C). After one hour of exposure to fluoride, the light blue glass detached from the composite (Figure 5 D), which again was expected as this adhesive contained the 21 kDa cross-linker. When the light blue glass separated from the stack, the remaining stack tipped over and the red and dark blue squares of glass began to detach. These two pieces of glass, which are held together by **1** containing the 145 kDa cross-linker, did not separate completely until after three hours of exposure (Movie S2).[10]

In conclusion, this work demonstrates that depolymerizable poly(benzyl ether) macro-cross-linkers are capable of selective, rapid, and sensitive non-reversible switching from bonding into debonding adhesives. If this concept can be expanded to other depolymerizable macro-cross-linkers and other stimuli (by changing the detection unit), then a general strategy may emerge for transforming simple, non-adhesive polymers (e.g., poly(norbornene)) into tunable stimuli-responsive adhesives. Compared with recent demonstrations of stimuli-responsive adhesives[2] (including those that debond by de-cross-linking induced by specific stimuli),[2g–k] this new approach offers the potential for generality in terms of the stimulus to which the adhesive responds (while maintaining specificity), as well as rapid macroscopic responses provided by the amplification reaction (i.e., depolymerization).

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[5] After de-cross-linking of **1**, we characterized polymer **5** by GPC and NMR spectroscopy.

[6] The limited solubility of **1** also thwarted characterization of the three-dimensional structure of **1**. For example, it is unclear whether **1** is similar to a star polymer (see the references below) or a simple cross-linked network. Future efforts will focus on various strategies for polymerizing **4** and **6**, including polymerizing **4** from **6** and/or changing the feed ratios of the two monomers with the two goals of 1) achieving full characterization of **1** and 2) improving adhesion; see: a) X. Hu, J. Hu, J. Tian, Z. Ge, G. Zhang, K. Luo, S. Liu, *J. Am. Chem. Soc.* **2013**, *135*, 17617–17629; b) X. Hu, G. Liu, Y. Li, X. Wang, S. Liu, *J. Am. Chem. Soc.* **2015**, *137*, 362–368.

[7] The 11% value is based on the molar loading of the poly(benzyl ether) during the polymerization reaction (0.19 mol%; molar feed ratio of **6**/**4** = 1:526), the length of the poly(benzyl ether) (21 kDa), and the length of the poly(norbornene) (44 kDa).

[8] The contact area of the adhesives between slides was measured using Vernier calipers.

[9] As fluoride is the model stimulus and glass is the model substrate, it might be possible that the observed change in adhesion could be the consequence of fluoride–silicon interactions with the glass substrate, rather than depolymerization of the cross-linker in **1**. Therefore, we pretreated glass slides with 0.1 M TBAF in THF for 30 min, rinsed the glass three times with THF followed by three times with distilled water, and then dried the glass under reduced pressure for one day. The shear stress value for **1** (made using 21 kDa **6**; feed ratio of **6**/**4** = 1:526) on this treated substrate is 0.44 ± 0.02 MPa, whereas the shear stress value for untreated glass is 0.42 ± 0.03 MPa. Therefore, we conclude that fluoride–silicon interactions between the stimulus and the glass substrate do not affect the strength of adhesion.

[10] Three hours is longer than anticipated based on the relative results in Figure 4, but this result likely is caused by the reduced shear forces placed on the glass duplex that, once tipped, was oriented parallel rather than perpendicular to the surface of the solution. Overall, however, this demonstration clearly illustrates that **1** can be used not only for stimuli-induced debonding, but also for programmed, sequential separation and purification of materials from a larger composite.

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