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Proton-Coupled Mechanochemical Transduction: A Mechanogenerated Acid

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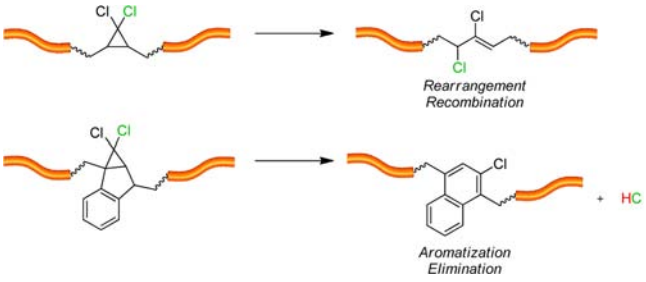
Supporting Information

ABSTRACT: A novel mechanophore with acid-releasing capability is designed to produce a simple catalyst for chemical change in materials under mechanical stress. The mechanophore, based on a *gem*-dichlorocyclopropanated indene, is synthesized and used as a cross-linker in poly(methyl acrylate). Force-dependent rearrangement is demonstrated for cross-linked mechanophore samples loaded in compression, while the control shows no significant response. The availability of the released acid is confirmed by exposing a piece of insoluble compressed polymer to a pH indicator solution. The development of this new mechanophore is the first step toward force-induced remodeling of stressed polymeric materials utilizing acid-catalyzed cross-linking reactions.

Mechanoresponsive materials, especially those with the ability to self-heal, are actively being pursued.[1] Healing of polymers has been demonstrated using light[2] or heat,[3] which provide the energy necessary to pass the barrier to create or re-form chemical bonds. Inspiring examples are the heat-induced re-formation of perfluorocyclobutanes which were selectively detached by mechanical stress[3e] and the photoinduced cross-linking of polymers by sulfur-based chain-transfer agents.[2b] Despite their success in achieving appreciable healing, the need for human intervention limits an intrinsic, autonomic response. Autonomic systems in which the mechanical force that causes the damage is the activating signal for the healing to commence are rare, and their development is divided between two main approaches: the use of encapsulated "healing chemicals"[4] and mechanochemical transduction.[5] The first approach requires that mechanical force ruptures capsules, releasing healing agents (liquids) that flow into the damage. The second approach envisages the reactive chemicals in the latent form of mechanophores, which can respond in a productive fashion to mechanical stimuli.[6,7] Damage is mitigated without additional material, for example by increasing cross-linking density. Mechanochemical production of a catalyst[7] that promotes cross-linking is conceivably a useful way to amplify mechanical input through turnover.

Craig et al. reported *gem*-dihalocyclopropane mechanophores that undergo rearrangement to 2,3-dihaloalkenes under mechanical stress; heating the same material causes acid by elimination.[8] Since acid plays a pivotal role in transduction through cross-linking reactions,[9] we suggest that a mechanophore that rearranges mechanically and spontaneously releases H^+ will be a powerful starting point for mechanochemically triggered productive chemistry. Reese et al. studied the *gem*-dihalocyclopropane systems and demonstrated how electronic and steric effects direct the electrocyclic ring-opening to either rearranged 2,3-dihaloalkenes or elimination products.[10] Some known examples are the eliminations of *gem*-dichlorocyclopropanated cyclopentadiene to chlorobenzene and of *gem*-dichlorocyclopropanated indene to 2-chloronaphthalene.[11] The stability provided by a double bond or aromatic system to the carbocation intermediate accelerates the reaction, while aromatization provides the driving force to elimination (Scheme 1).

Scheme 1. Rearrangement or Elimination of *gem*-Dichlorocyclopropanes[8]



By analogy, a *gem*-dichlorocyclopropane mechanophore based on a 1,3-substituted indene[12] was synthesized (Scheme 2). Ring-opening of caprolactone by indene in the presence of a strong base,[13] followed by $LiAlH_4$ reduction of the diacid, provides diol **1**. After protection with tetrahydropyranyl (THP) groups under acidic conditions, the *gem*-dichlorocyclopropane is formed by cycloaddition of dichlorocarbene to the double bond. The diol is deprotected under acidic conditions, and methacrylate groups are introduced to form cross-linking mechanophore **4**.[14]

Methyl acrylate was polymerized in the presence of 5 mol% of mechanophore **4** as a cross-linker using dimethylaniline (DMA) and benzoyl peroxide (BPO).[15] For control, the same

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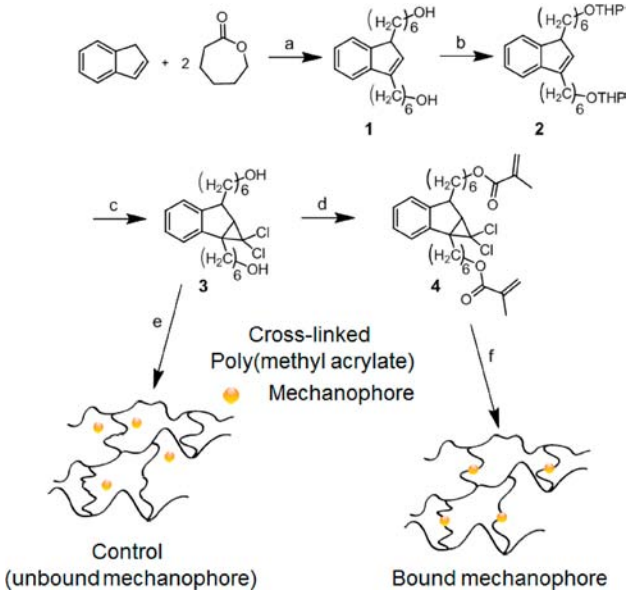
Scheme 2. Preparation of Mechanophore-Containing Polymers[a,7]



[a]Reaction conditions: (a) 1. KOH, 200 °C, 2 days; 2. $LiAlH_4$, Et_2O, 40 °C, 1 day, 40% yield in two steps; (b) DHP, PTSA, CH_2Cl_2, 3 h, 88% yield; (c) 1. $CHCl_3$, benzyltriethylammonium bromide, NaOH 50%, 35 °C, 2.5 h; 2. PTSA, CH_2Cl_2, MeOH, 3 h, 74% yield in two steps; (d) methacrylic anhydride, DMAP, THF, 30 min, 87% yield; (e) methyl acrylate, benzoyl peroxide, dimethylaniline, ethylene glycol dimethacrylate, 4–8 °C, 16 h, quant; (f) methyl acrylate, benzoyl peroxide, dimethylaniline, 4–8 °C, 16 h, quant.

polymerization was carried out using 5 mol% of ethyleneglycol dimethacrylate (EGDMA) as cross-linker and 5 mol% of **3** (**3** did not influence the radical polymerization). The quantity of active mechanophore in the polymers is determined via differential scanning calorimetry (DSC). DSC of the mechanophore-containing polymers exhibits an exotherm starting at ca. 70 °C, which is associated with the ring-opening reaction and subsequent aromatization (Figure 1). The thermal transformation was verified by heating **3** to 50 °C overnight, giving the expected naphthalene in good yield as the only product (see the Supporting Information).

The cross-linked poly(methyl acrylate) (PMA) was cut into ca. 50 mg samples[16] and compressed at 88, 176, 264, and 352 MPa (calculated according to initial area; see the Supporting Information for details) using an Aldrich KBr pellet press in a Carver press. Pressures were measured using a Gauge Carver manometer.[17] Mechanophore activation percentage is calculated by normalizing the integrated heat flow of the compressed sample to the value obtained from the non-compressed polymer. The lowest of these pressures activated almost 10% of the mechanophore, while the highest activated almost 20% of the mechanophore. A monotonic rise in activation against applied pressure indicates that the rearrangement is caused by mechanical force (Figure 2). The control material presents the same exotherm in the DSC, but only a 6% decrease in the exotherm is observed after compressing it under 352 MPa (see the Supporting Information). This experiment shows that covalent cross-linking is necessary for compression activation. Moreover, it also excludes the possibility that activation is caused by thermal or other means during the compression loading experiment.

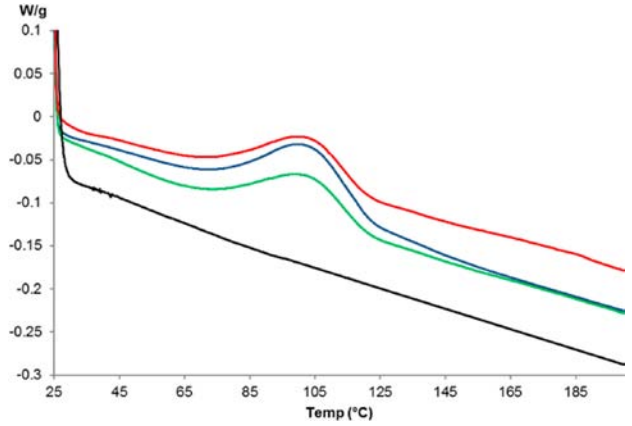


Figure 1. Exotherm in the DSC analyses of PMA containing 5 mol% of EGDMA and 5 mol% of **3** (red); 5 mol% of **4** (blue); 5 mol% of **4** after compression with 352 MPa load (green); and 5 mol% of EGDMA (black). Integration of the peak gives energy density, which is correlated to the quantity of **3** and **4** in the material. DSC conditions: 25–200 °C, 5 °C/min.

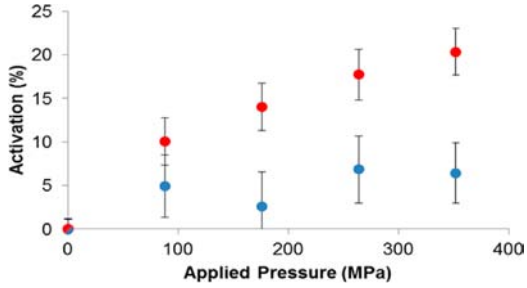


Figure 2. Plot of applied pressure and mechanophore activation based on calorimetric measurement of compressed samples of PMA containing 5 mol% of **3** (blue) or 5 mol% of **4** (red).

Confocal Raman spectroscopy was used to confirm the molecular change (Figure 3). After compression of PMA cross-linked with **4** to 352 MPa, new aromatic C=C stretch peaks appear at 1363, 1379, 1406, and 1572 cm^{-1}.[18] These peaks also appear in a sample of **3** which was shown to be pure substituted 2-chloronaphthalene by NMR and mass spectrometry (see the Supporting Information) after heating to 50 °C overnight.

To further confirm the release of acid, ca. 50 mg pieces of PMA containing 5 mol% of **3** or **4** were compressed under a load of 352 MPa. Assuming 20% mechanophore activation and full transfer of the protons to 2 mL of solvent, a pH of 3.3 is expected, which is well below the pK_a of methyl red in water (5.1). In acetonitrile, methyl red gives an orange color in the absence of added acid. The color becomes pink when acid is present. As observed in Figure 4, the pH indicator in acetonitrile clearly changes color to pink when exposed to a compressed sample of PMA cross-linked with **4**, while it maintains the neutral orange color when exposed to the control containing unbound **3** under otherwise identical conditions. No immediate color change is observed when the pH indicator solution is added to non-compressed PMA cross-linked by **4**, but the same instantaneous color change is seen when it is added to PMA containing **4** that was heated to 120 °C for 2 h in a closed flask. A pH electrode for organic solvents was used to confirm the acidity: a pH of 3.17 was measured for the compressed sample of PMA cross-linked by **4**, and 4.23 was the observed pH for compressed PMA containing **3**, compared to

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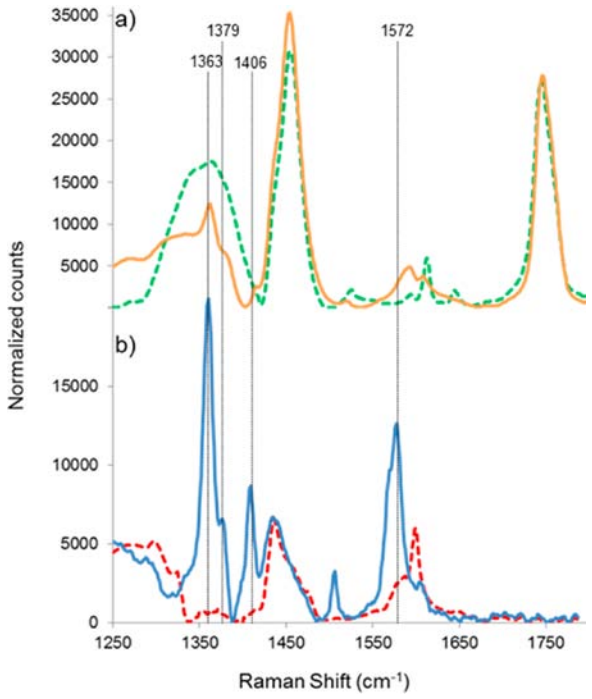

Figure 3. C═C stretch peaks in Raman spectra of (a) PMA with 5 mol% of **4** (dashed green) or compressed PMA with 5 mol% of **4** (orange), and (b) **3** (dashed red) or heated **3** (blue).

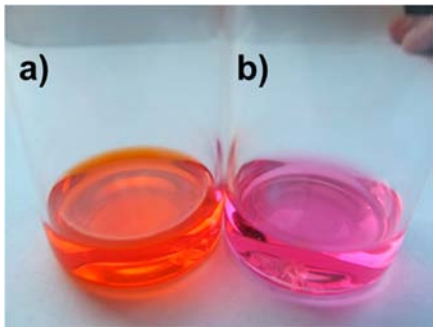

Figure 4. Methyl red in acetonitrile added to compressed polymers containing (a) unbound **3** and (b) covalently bound **4**.

5.50 in pure acetonitrile.[19] This outcome indicates that acid is mechanically generated for the covalently bound mechanophore, but not for the unbound mechanophore, where only a minor thermal activation can be measured.

In conclusion, a new mechanophore with the ability to release acid under mechanical stress has been designed and used as a cross-linker in PMA. Mechanophore activation correlates with compressive loading. Activation was confirmed through DSC analysis of the exothermic rearrangement of the mechanophore: the higher the pressure, the greater the activation. Significantly less activation was observed for unbound mechanophore versus the bound mechanophore under similar mechanical stimuli, confirming that covalent attachment provides efficient force transduction. A methyl red indicator corroborated the release of acid upon activation. This acid-releasing mechanophore extends the possibilities in autonomous self-healing materials. While several issues still need to be overcome before practical advances can be made (such as thermal stability, crucial in processing and lifetime, and a more streamlined synthesis), clever use of the acid catalyst to transform this discovery into adaptable materials by force-induced initiation of covalent cross-linkages is the topic of future studies.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, synthetic procedures, NMR spectra, and DSC analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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