THE ART OF FALLING APART:
USING ADDRESSABLE BONDS TO CREATE RESPONSIVE MATERIALS

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The ability to respond to a variety of cues is crucial to the development of smart materials. In recent years, incorporating chemical moieties that can be shifted between two or more characteristic states (i.e. chemical switches) into polymer materials has emerged as a powerful approach to fabricate stimuli-responsive materials. There now exist numerous switches that selectively degrade in response to specific environmental stimuli. This technology enables polymers that maintain their physical properties during a product's life cycle and fail when it is no longer in service. We have been studying polymeric materials containing both one- and two-way switches. One-way switches undergo irreversible changes in response to external stimuli. For example, we have developed poly(vinyl alcohol)-based adhesives functionalized with difunctional azo crosslinkers.[1] The adhesives exhibit excellent long-term stability under ambient conditions, yet rapidly decrosslink when exposed to UV light (320-390 nm). In doing so, the adhesive undergoes cohesive failure and allows for debonding "on demand". By contrast, two-way switches can be repeatedly cycled between on and off states. The reversibility of these switches can be achieved through either covalent interactions (i.e. dynamic covalent bonds) or non-covalent interactions (i.e. hydrogen bonding, metal-ligand coordination, ionic interactions, etc.) that reform after breaking. Using this concept, we have shown that ultrasound-induced dissociation can be used as an alternative method of inducing failure in some metallosupramolecular polymer networks.[2] We are currently expanding this toolbox to respond to a variety of other stimuli such as electrical field and heat. Specifically, we are looking at permanent dipole such as charge-transfer complexes and permanent dipoles as a mean to impart stimuli-responsiveness.

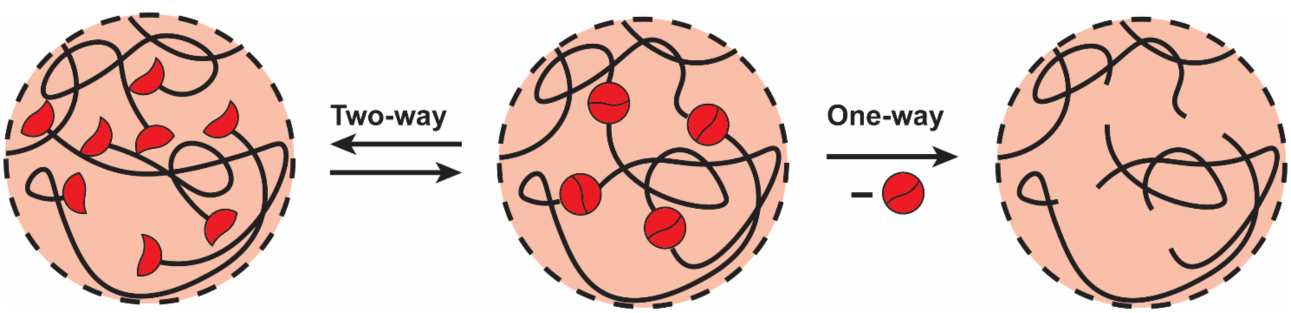

Figure 1. One-way switches induce irreversible changes to polymer architecture whereas two-way switches reform after breaking.

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(2) Balkenende, D. W. R.; Coulibaly, S.; Balog, S.; Simon, Y. C.; Fiore, G. L.; Weder, C. Mechanochemistry with Metallosupramolecular Polymers. *J. Am. Chem. Soc.* **2014**, *136* (29), 10493–10498.