USING DYNAMIC CHEMISTRY TO ACCESS RESPONSIVE ADHESIVES

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The dynamic bond can be defined as any class of bond that selectively undergoes reversible breaking and reformation, usually under equilibrium conditions. The incorporation of dynamic bonds (which can be either covalent or non-covalent) allows access to structurally dynamic polymers.[1] These polymers can exhibit macroscopic responses upon exposure to an environmental stimulus, on account of a rearrangement of the polymeric architecture. In such systems, the nature of the dynamic bond not only dictates which stimulus the material will be responsive to but also plays a role in the response itself. We have been studying semi-crystalline, structurally dynamic networks that contain disulfide bonds. These materials exhibit both shape memory (upon moderate heat exposure) and crack/scratch healing (upon high heat or UV light exposure) properties.[2] The shape memory function is a consequence of the melting transition (T_m ca. 60 °C) of the networks crystalline domains. The disulfide bonds within the network undergo dynamic exchange upon exposure to heat at ca. 150 °C or light that results in a significant drop in the material's viscosity and allows the healing of scratches. Such a reversible drop in viscosity may also allow these materials may act as stimuli-responsive reversible adhesives. The concept here is that when exposed to an appropriate stimulus, the dynamic bond will undergo continuous exchange/cleavage that results in a significant decrease in the material's viscosity, which promotes flow and facilitates wetting on a substrate. Removal of the stimulus results in bond reformation and the restoration of the materials original stiffness, thereby forming a rigid adhesive bond. Simply exposing the material to the same stimulus results in a drop in the viscosity again and thus debonding. We have been interested in the potential of such systems to access new stimuli-responsive adhesives.[3] Using this concept, we have shown that shape-memory and actuating adhesives can be obtained that exhibit two levels of reversible adhesion (Figure 1), depending on the stimulus used and have carried out initial studies to understand the polymer structure/adhesive relationships in this class of material.

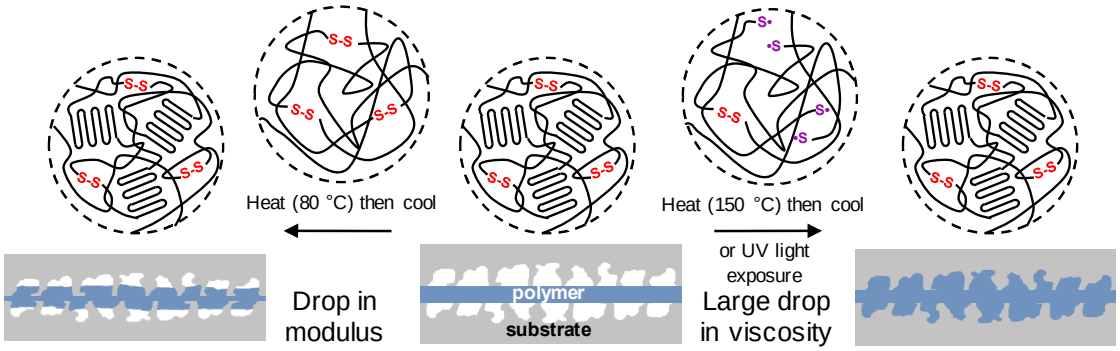

Figure 1. Schematic showing the proposed mechanism of adhesion of a structurally dynamic polymer

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2 Michal B. T.; Jaye, C. A.; Spencer, E. J.; Rowan S. J. Inherently Photohealable and Thermal Shape-Memory Polydisulfide Networks *ACS Macro Lett.* **2013**, *2*, 694-699.

3 Michal, B.T.; Spencer, E.J.; Rowan, S.J. Stimuli-responsive Reversible Two-Level Adhesion from a Structurally Dynamic Shape Memory Polymer *ACS Appl. Mater. Interfaces* **2016**, *8*, 11041-11049.