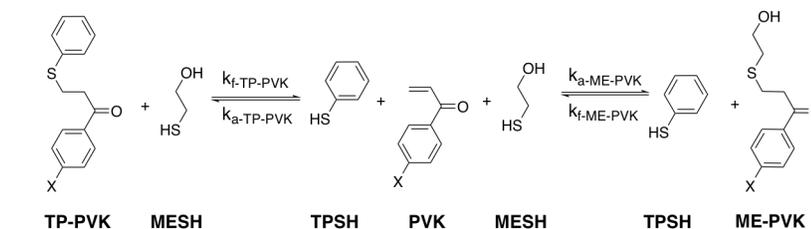


## Thiol-Michael Adducts for Dynamic Materials: Polymers; Single Networks; and Interpenetrating Networks

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The goal of this project is to explore *thiol-Michael* chemistry as a dynamic bond in polymer materials. The thiol-Michael reaction is a click-like reaction with high yield and efficiency under ambient conditions, although it can be subject to dynamic exchange upon external stimulus. Both thermal and pH stimulus have been explored in this project to date as methods of activating dynamic exchange.



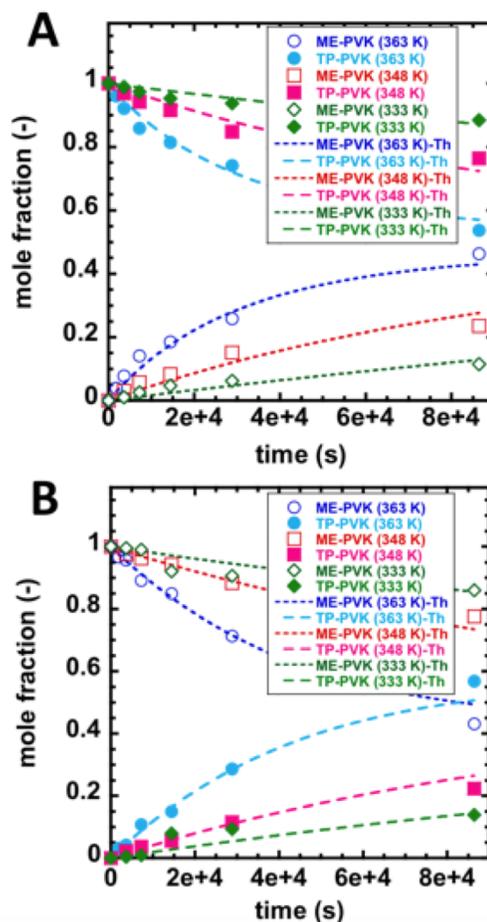
**Scheme 1:** Model for the exchange of thiol-Michael adducts

The aims of the original proposal are **1.** Determine the influence of the structure of the thiol-Michael adduct on its dynamic behavior as a function of temperature and pH. **2.** Incorporate dynamic thiol-Michael adducts into single networks, and characterize the dynamic and mechanical properties. **3.** Tune the dynamic nature by incorporating two different Michael acceptors, including using an interpenetrating network. Significant progress has been made on aims **1** and **2**, with preliminary work progressing on aim **3**. As shown in Scheme 1, a model system of thiol-Michael adducts was developed to probe aim 1 of the proposal. A kinetic model follow the proposed reaction pathway in Scheme 1 was also developed. Figure 1 shows the evolution of thiol-Michael adducts, both from experiment and also fit with the kinetic model as a function of temperature. The data clearly show temperature dependence with equilibration observed in 24h at 363 K, and slow exchange observed at 333K with 348K being between these two extremes. This work is progress towards aim 1 of characterizing the dynamic covalent chemistry of thiol-Michael adducts. This type of small molecule study is important as it guides the types of conditions that give efficient dynamic covalent exchange.

In addition to small molecule reactions which provide insights into the fundamental nature of this dynamic bond, polymer materials crosslinked with thiol-Michael adducts have been explored. As indicated in Scheme 2, the maleimide based Michael acceptor has been used as a pH and temperature responsive linker in polymer materials. To assess dynamic properties in polymer materials, self-healing experiments were performed as indicated in Scheme 2.

As indicated in Figure 2, efficient self-healing is observed both with thermal stimulus, as well as high pH stimulus. Figure 2 left clearly shows the longer times under thermal stimulus lead to greater recovery of mechanical properties, or self-healing. Similarly, Figure 2 right indicates that high pH (pH>8) stimulus is needed to activate dynamic covalent exchange and self-heal the material. Current ongoing work is towards aim 3, as well as understanding the pH driven small molecule exchange.

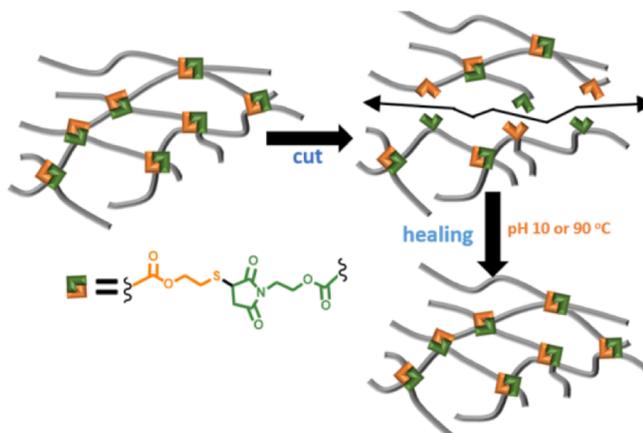
Currently ongoing work on this project utilizes reversible addition-fragmentation chain transfer (RAFT) polymerization to control the polymer microstructure in dynamic thiol-



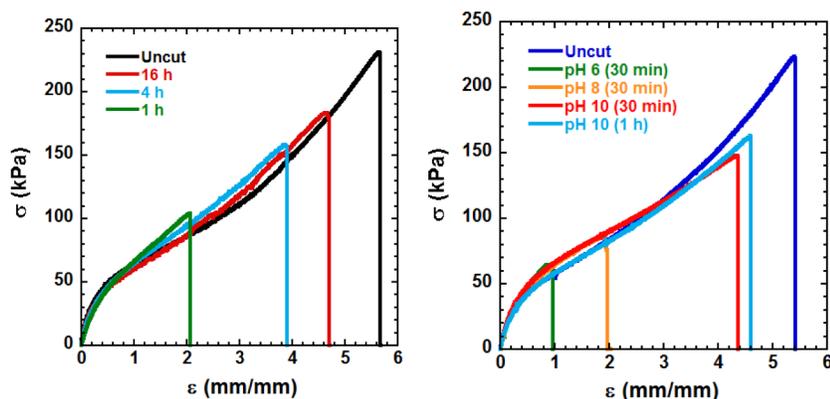
**Figure 1:** Experimental and simulated (Th) kinetics of dynamic covalent exchange experiments at temperatures 363, 348 and 333 K. A) Initialized from TP-PVK, B) Initialized from ME-PVK.

Michael crosslinked materials. RAFT enables control of the polymer microstructure, which is superior to that of the previously used conventional radical polymerization. Substantial progress has been made in studying polymer materials synthesized by RAFT and crosslinked with thiol-Maleimide adducts. This work has been very recently accepted for publication in the journal *Polymer Chemistry*. Additional work is developing interpenetrated network materials crosslinked with the thiol-Michael adducts.

**Impact.** Prior to receiving this award and its associated research, the Konkolewicz group focused on using existing chemistry to develop new materials with a particular focus on kinetics of polymerization reactions on thermoplastic or soluble polymers. The research support from the PRF has enabled the Konkolewicz group to develop new and simple dynamic covalent chemistry based on thiol-Michael chemistry and to gain skills in the field of polymer networks. This development of new dynamic covalent chemistry and associated experience with network materials is a new and potentially impactful area of research for the group. Students in the Konkolewicz group have diversified their skills, with experience in materials characterization, while also expanding their skills in reaction kinetics and physical organic chemistry. As a result of support from the PRF, graduate and undergraduate students are continuing to expand their skills in materials characterization especially with dynamic mechanical and rheological experiments. Development of dynamic thiol-Michael chemistry and materials characterization skills gained through this project enabled the Konkolewicz group to provide evidence of experience with materials characterization and dynamic chemistry which formed the basis of a successful National Science Foundation CAREER award to PI Konkolewicz.



**Scheme 2:** Dynamic polymer material crosslinked with thiol-Maleimide adducts.



**Figure 2:** Self-healing of thiol-Maleimide crosslinked materials Left: under thermal stimulus (363 K) as a function of time. Right: under different pH stimuli.