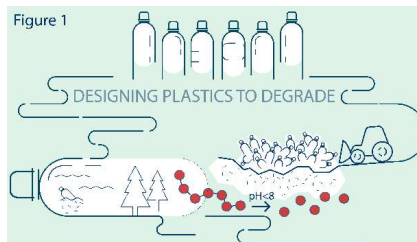
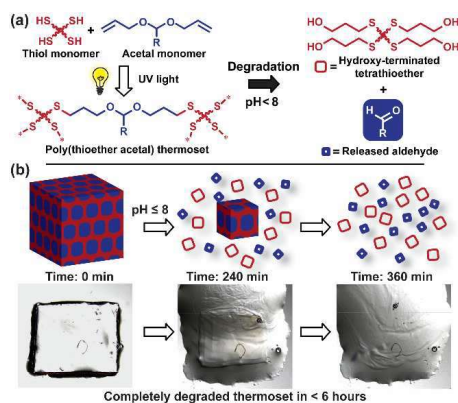


**Problem Statement:** As a modern society, we have generated 6.3 billion metric tons of plastic waste since 1950 – an astonishing 79% of this waste has accumulated in landfills or the natural environment. Despite an increase in plastic recycling programs, 75% of plastic products produced in 2015 was discarded in landfills – much of it from single-use applications.<sup>1, 2</sup>



Plastics are divided into two general categories, thermoplastics and thermosets. Thermoplastics, represented by the six primary recycling codes (e.g., 1-polyethylene terephthalate, 2-high density polyethylene, etc.) are amendable to recycling, yet sit in landfills for hundreds of years if discarded. Presently, aliphatic polyesters, such as polylactic acid (recycling code 7-other), represent one of the few thermoplastics that is both recyclable and potentially biodegradable or industrially compostable. Thermosets are more challenging with regard to recycling and environmental degradability – these materials cannot be reheated, remolded, or recycled using current approaches to thermoset chemistry. Beyond new recycling concepts, addressing the thermoset challenge requires the development of thermosets using chemistries that enable degradation under industrial or landfill processing conditions (Fig. 1).<sup>3</sup> Thermosets designed to degrade not only afford a viable route to eliminate thermosets from the environment, but also guide efforts for the development of degradable materials for specific applications, including adhesives, composites, controlled release packaging, and sacrificial coatings. Therefore, the goal of my research is to develop synthetic strategies that enable the design of degradable thermosets with tunable degradation profiles.

**Previous Research.** My research in the Patton Lab started by focusing on simple routes to thermosets using thiol-ene photopolymerization. These robust, highly efficient reactions proceed rapidly at room temperature, in the presence of oxygen and water, using inexpensive and non-toxic catalysts, create no byproducts and are highly tolerant to a wide range of functional groups.<sup>4</sup> These reasons alone exemplify the attractive nature of this chemistry for facile thermoset production. In the search for routes to degradable thiol-ene thermosets, we explored an underutilized functional group known as an acetal. Acetals exhibit outstanding stability under basic conditions while readily undergoing hydrolysis under neutral and mildly acidic conditions ( $\text{pH} < 8$ ) yielding aldehydes and alcohols as degradation byproducts. These characteristics are highly attractive for the design of thermoplastics capable of tunable degradation under mild environmental conditions. My initial work focused on the design and photopolymerization of an acetal-containing monomer derived from p-anisaldehyde – a naturally occurring benzaldehyde found in star anise seed. My role was to synthesize the acetal monomer from p-anisaldehyde, polymerize the monomer into a crosslinked thermoset, and then evaluate the degradation kinetics via a combination of optical microscopy and <sup>1</sup>H NMR spectroscopy. Thiol-ene photopolymerization of the acetal monomer with a multifunctional thiol monomer, as illustrated in Fig. 2a, yielded a crosslinked, fully degradable poly(thioether acetal) thermoset that exhibited pH dependent degradation (e.g., slow degradation at pH 7, rapid degradation at pH 1). Poly(thioether acetals) fully degrade into small molecule aldehyde and alcohol byproducts (Fig. 2b), which enables



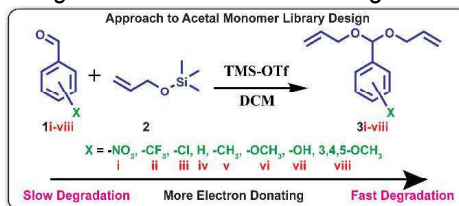
**Fig. 2** (a) Synthesis of degradable poly(thioether acetal) thermosets via thiol-ene photopolymerization. (b) Rapid degradation of poly(thioether acetal) thermosets under acidic aqueous conditions.

design of degradable thermosets with tunable degradation profiles. Achieving greater tunability of the degradation of poly(thioether acetal) thermosets starts with monomer design. In our previous work, we employed p-anisaldehyde as the benzaldehyde precursor for acetal monomer synthesis, which carries an electron donating methoxy substituent at the para-position of the aromatic ring. According to the well-established hydrolysis mechanism for acetals, the electronic character of substituents on the aromatic ring should substantially influence the stability of the acetal.<sup>6</sup> Electron withdrawing substituents, in the para-position of the benzaldehyde, stabilize the acetal resulting in a slow hydrolysis of the acetal, while electron donating substituents in the para-position increase the rate of acetal hydrolysis. With this information gleaned from literature, we seek the answer to the following key question: *What is the relationship between acetal monomer substituent effects and degradation behavior in poly(thioether acetal) thermosets?* We **hypothesize** that strong electron donating substituents, such as dimethylamine, will yield poly(thioether acetals) that degrade within minutes under acidic conditions, while strong electron withdrawing substituents, such as trifluoromethyl, will substantially extend the degradation profile such that materials degrade over several weeks under similar conditions. To test this hypothesis, we are pursuing the following **specific aim**: To synthesize a library of benzaldehyde-derived acetal monomers carrying various electron withdrawing and electron donating substituents to establish degradation profiles for the resultant poly(thioether acetal) thermosets.

My initial synthetic efforts have focused on the preparation of a difunctional acetal library using substituted benzaldehydes ranging from nitrobenzaldehyde (electron withdrawing) to trimethoxybenzaldehyde (electron donating). As shown in **Fig. 2**, monomers were

potential recovery and reuse of the p-anisaldehyde as a starting material. As it turns out, p-anisaldehyde also exhibits potent antimicrobial properties. In collaboration with Dr. Dmitri Mavrodi in the USM Department of Biological Sciences, we found that sustained release of p-anisaldehyde from degradable poly(thioether acetals) exhibited potent antimicrobial activity towards a range of fungal and bacterial pathogens. My contributions to this project resulted in a coauthored peer-reviewed publication in a prominent biomaterials science journal (*Acta Biomaterialia* **2018**, 67, 196-205).<sup>5</sup>

**Current Research.** Building on my previous experience, my current research efforts continue to focus on the initial goal of developing synthetic strategies that enable the

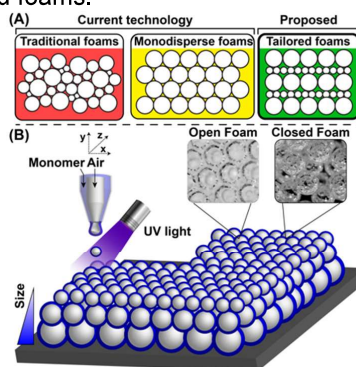


**Fig. 3** Synthesis of dialkene acetal monomers with various aromatic substituents to tailor degradation rates.

synthesized using a modified Noyori reaction of allyloxytrimethylsilane (**3**) with a benzaldehyde (**1**) in the presence of trimethylsilyl triflate.<sup>7</sup> With the library of monomers in hand, thiol-ene films are being prepared by photopolymerization of **3i-viii** with a stoichiometric amount of commercially available pentaerythritol tetrakis(3-mercaptopropanoate) (PETMP) as a polyfunctional thiol crosslinker. Knowledge gleaned from successful completion of this aim will provide a detailed set of design parameters for construction of degradable poly(thioether acetal) thermosets with tailor-made properties. This knowledge will also guide efforts for the development of these degradable materials for specific applications, including degradable single-use packaging, microcapsules as controlled release platforms and degradable 3-D printed foams.

**Future Possibilities.** Additive manufacturing (AM) builds 3D designed objects via a layer-by-layer approach. Although foams have been made via AM, these methods utilize non-degradable materials with multi-step processes and lack the capability to control foam pore size and connectivity on-the-fly. Recently, in collaboration with members of the Patton Lab and a small team at Harvard University, I was introduced to a 3D printing technique called Additive Manufacturing by In-Air Microfluidics (AMBIAM) and was involved firsthand in the construction of this platform at USM. AMBIAM works by injecting pressurized gas through the core of a core-shell nozzle with a co-flowing outer shell fluid to produce monodisperse gas-filled bubbles at various sizes. At the nozzle tip, a stream of bubbles is formed where bubble size and connectivity are controlled by gas pressure and liquid flow rate, as shown in Figure 2A. The ability to change the bubble size on-the-fly opens the door for the fabrication of tailored foams with complex hierarchical geometries, gradient porosities, and tuned cell structures within a single pre-designed 3D shape. The aforementioned advantages of thiol-ene photopolymerization, make it a synergistic choice for AMBIAM, as the fidelity of print resolution relies on the rapid curing of bubbles prior to impact on substrate. 3D foams with controlled hierarchical architecture offer great potential in transforming applications in acoustic dampening, energy storage/transfer materials, and packaging. I am excited to combine AMBIAM with my degradable poly(thioether acetals) chemistry to create fully degradable foam materials, offering a route to highly functional materials that rapidly degrade under landfill conditions once discarded.

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**Fig. 4** (a) Current and proposed foaming technologies. (b) AMBIAM process with thiol-ene photopolymerization yielding open and closed foams.