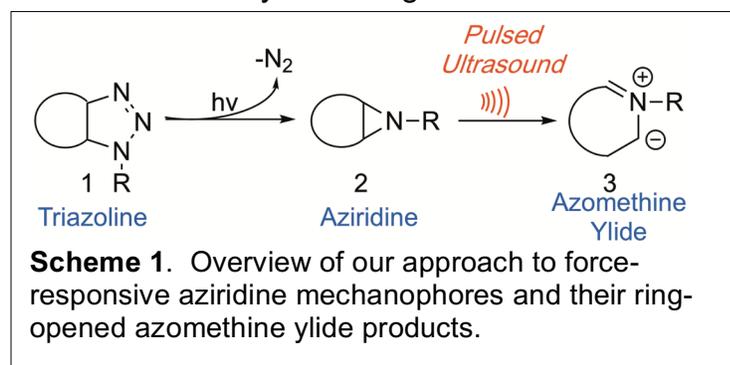


1. PRF #: 56464
2. Title: Unlocking the Rich Mechanochemistry of Aziridines Using Triazoline Synthons
3. PI: Peter M. Iovine, University of San Diego
4. Co-PI: None

*Overview.* The aim of this research program is to uncover the mechanochemical potential of aziridines and train the next generation of scientists. Year 2 was challenging scientifically. We encountered some significant road blocks that required a change of strategy. We have made the appropriate adjustments and, as year 2 folds over into year 3, we are now on track to produce the target polymers.

Aziridines are reactive three-member ring structures that, when embedded in a polymer main chain or side chain, function as cross-linking points. Accessing polyaziridines, however, is challenging and few examples exist. Our approach does not involve the direct synthesis of polyaziridines but rather an indirect route via the thermal or photochemical decomposition of polytriazolines. We intend to use triazolines as aziridine synthons. This approach circumvents the majority of synthetic challenges associated with synthesizing aziridines from other organic precursors and allows for a



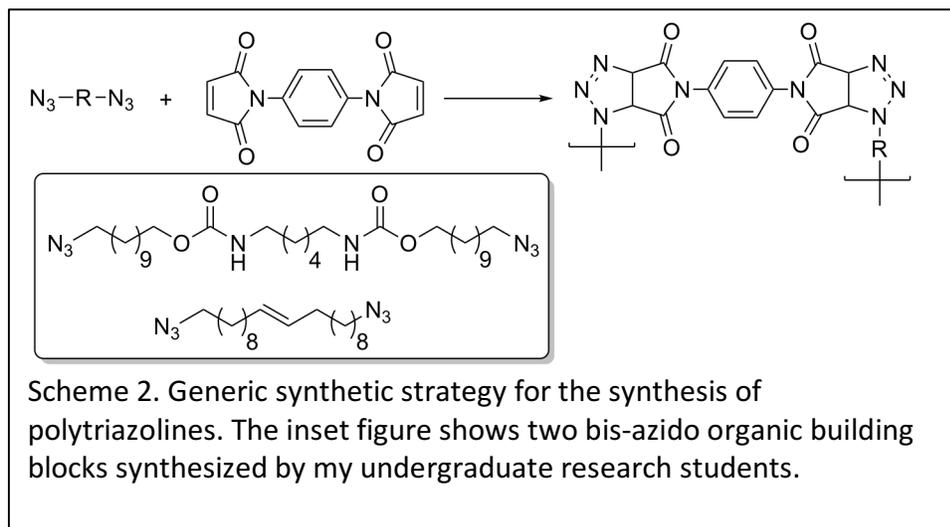
more comprehensive investigation of high density aziridine-containing polymers. Once the polyaziridines are in hand, we intend to probe how the application of mechanical force impacts the conversion of these strained three member rings into reactive intermediates (Scheme 1). We intend to mechanochemically generate azomethine ylides (structure 3,

Scheme 1) from aziridine precursors (structure 2, Scheme 1) and explore productive chemistries associated with these reactive intermediates including cross-linking (strengthening) as well as heterocycle formation (increase in structural complexity).

*Year 2 Progress.* Our overall synthetic strategy to produce polytriazolines is shown in Scheme 2. In practice, commercially available N,N'-(1,4-phenylene)dimalimide was used exclusively as the dipolarophile while bis-azido dipolar building blocks were synthesized in house. My undergraduate research students synthesized the two long chain aliphatic bis-azido compounds shown in Scheme 2. These compounds were safe to handle (Nitrogen/Carbon  $\geq$  3), soluble in common organic solvents, and active in cycloaddition reactions with maleimide. Polymerizations of these building blocks gave oligomeric triazolines with disappointingly low molecular weight and poor solubility.

Our original plan was to synthesize polymers with triazolines embedded in the main chain. The triazolines would then be converted thermally or photochemically to aziridines. After synthesizing our oligomeric triazolines we investigated the conversion of the main chain triazolines to aziridines. Unfortunately, thermal denitrogenation required very high temperatures and photochemical treatment did not work. One important

conclusion from this work was that aliphatic triazolines, derived from aliphatic azides, do not denitrogenate as easily as aromatic triazolines. In regard to the photochemical denitrogenation of aliphatic triazolines, the triazolines lack of long wavelength absorption



prohibited the selective conversion of this species to aziridines under mild conditions.

We have moved away from aliphatic triazolines; our focus now is exclusively on aromatic triazolines. We

now understand that aromatic triazolines can be converted to aziridines photochemically whereas aliphatic triazolines cannot. Students have recently synthesized a series of aromatic triazolines. We are in the process working out polymerization conditions. Solubility remains a challenge. We hypothesize that the poor solubility in our initial designs were a result of the stacking interactions of the phenyl maleimide building blocks. So, more recently, we have focused on norbornene type dipolarophiles instead of maleimides. Although the spectroscopic characterization of norbornene-derived triazolines is more complex versus maleimides, the solubility is superior.

In summary, we have made two significant changes to our synthetic plans. First, we are using aromatic azides as precursors to triazolines instead of aliphatic azides. Second, we are focused on norbornene dipolarophiles instead of maleimides.

*Undergraduate Training.* Two undergraduate students participated in this research during year 2. The first student, Andrew Saiz, joined my lab in the fall 2016 semester. The second student, Jacob Hughes, joined the lab in the spring 2018 semester. Both students conducted research during the summer 2018 season and were paid stipends through this ACS PRF grant. Andrew Saiz spent a good portion of the summer working in Professor Stephen Craig's lab at Duke University. Professor Craig is a collaborator on this project. Andrew learned new techniques and developed expertise in instrumentation related to mechanochemical analysis.

*Goals for Year 3 (September 2018-August 2019).* Year 3 will focus on polymerizing aromatic triazoline monomers. Polyesters are our initial target but we are also interested in embedding the aromatic triazoline units into a polyurethane backbone. Undergraduate mentoring remains our top priority with an emphasis on graduate school applications, writing, oral presentations, and job searching.