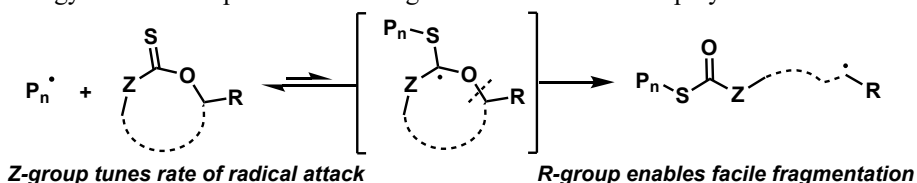


### 1. Impact of Research

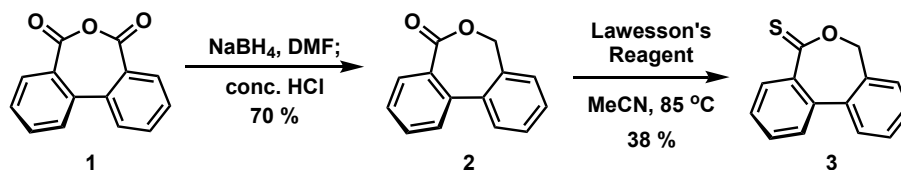
The central goal of this project is to identify cyclic thiocarbonyl molecules that are capable of efficient copolymerization with common petroleum-derived monomers (styrene, acrylates, acrylamides). Given the privileged nature of thiocarbonyl moieties as radical acceptors, it was proposed that this reactivity could be leveraged to generate a new platform for radical ring-opening polymerization (rROP) in which thioester functionality is introduced into the polymer backbone (Figure 1). If successfully used as a comonomer with petroleum-derived monomer families, these additives could serve as hydrolytically labile points on a polymer chain to produce value-added responsive and degradable materials. Our studies over the past year have focused on identifying molecules that feature a Z-group capable of stabilizing the radical intermediate in the ring-opening process, along with installing R-type functionality that lead to low energy radicals compatible with living reversible deactivation polymerization methods.



**Figure 1.** General overview of the radical ring-opening concept for cyclic thiocarbonyl monomers.

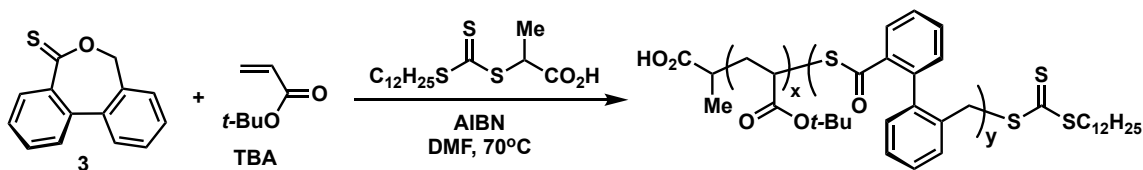
#### Initial Monomer Design and Synthesis.

Significant progress has been made in the understanding of structural elements needed to efficiently copolymerize thiocarbonyl-containing cyclic molecules with acrylate monomers, culminating in the identification of seven-membered thionolactone **3** (Figure 2). This new thionolactone monomer can be readily prepared in two operations starting from diphenic anhydride (**1**) using a known reduction/lactonation protocol, followed by thionation of the lactone product (**2**) with Lawesson's reagent. Key design elements of this structure include the presence of an aromatic substituent adjacent to the thiocarbonyl to increase stability of the intermediate radical adduct and the formation of a benzylic radical leaving group that is generated upon fragmentation.



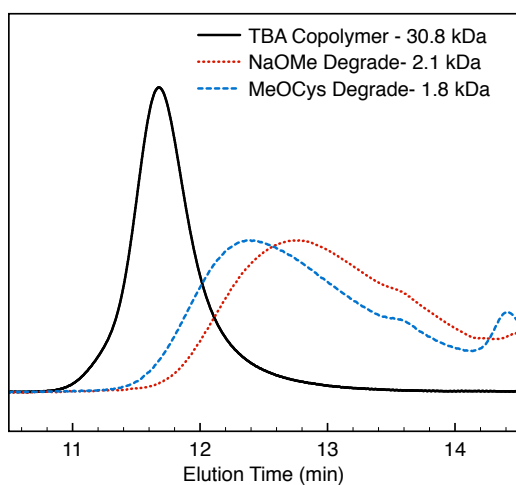
**Figure 2.** Synthesis of thionolactone **3** identified for copolymerization of acrylate monomer families.

The central hypothesis of the proposal was validated through copolymerization experiments with *tert*-butyl acrylate (TBA) using standard conditions for reversible addition-fragmentation chain-transfer (RAFT) polymerization (Figure 3). Proton NMR spectroscopy confirmed the incorporation of the **3** in the polymer chain through the observation of broad aromatic peaks characteristic of the biaryl protons unique to this monomer. The molecular weights of the polymers produced using 5 mol% of **3** were found to be controlled by the monomer-to-initiator ratio, with low dispersities obtained for molecular weights up to 32.6 kDa that indicates a controlled, living polymerization. It was found that higher feed ratios of **3** led to slower initial rates of polymerization, possibly due to the higher concentration of thiocarbonyl groups capable of reversible addition at early stages. Kinetic studies performed on the copolymerizations found that **3** reacts slightly faster than TBA in the polymerization to give slightly gradient polymer compositions. This result is significant, as all prior monomers for rROP have displayed very poor copolymerization with acrylate monomer families. Further confirmation of the living nature of the copolymerization was demonstrated by successful chain-extension of an isolated TBA copolymer with *n*-butyl acrylate to give low dispersity diblock polymers. The developed conditions proved to be general for several other acrylate monomers (methyl acrylate, benzyl acrylate, trifluoroethyl acrylate) and all resulted in materials with low dispersities and controlled molecular weights.



Target Degree of Polymerization	Thionolactone Feed	Total Conversion	$M_n$	$\bar{D}$
25	5 %	>98 %	4.4 kDa	1.1
50	5 %	>98 %	7.6 kDa	1.1
100	5 %	98 %	13.4 kDa	1.1
250	5 %	98 %	32.6 kDa	1.3
100	10 %	96 %	16.8 kDa	1.1
100	35 %	86 %	14.5 kDa	1.2
100	50 %	62 %	12.2 kDa	1.1

**Figure 3.** RAFT-mediated copolymerization of **3** and *tert*-butyl acrylate (TBA).



**Figure 4.** Size-exclusion chromatogram showing the degradation of a TBA copolymer prepared with 5 mol% thionolactone **3**.

Copolymerization with styrene led to low overall consumption **3** at high styrene conversions, and methyl methacrylate fully homopolymerized with no observable reaction with **3**. With knowledge gained from the project to date, efforts are currently underway to modify this parent monomer to tune the reactivity in copolymerization and also explore entirely new monomer designs that will enable copolymerization with styrene and methacrylate families in order to further expand this platform to other widely used petroleum-based materials.

## 2. Impact on PI and Student Careers

Over the course of the past year, this project has been led by a graduate student in the PI's laboratory, Ronald Smith, who was fully funded by the grant during his second year of the Ph.D. program. In addition to substantial training in small molecule and macromolecular synthesis, the success of this project has led to a publication this year (*J. Am. Chem. Soc.* **2019**, *141*, 1451) with Mr. Smith's as the first author and his oral presentation at the Spring ACS meeting in Orlando, Florida. During the course of the funding period, Mr. Smith passed his candidacy exams for the Ph.D. program, and he also trained an undergraduate researcher, Mr. Owen McAteer, to assist with block polymer synthesis and additional polymer characterization. The travel funding provided in the budget has led to the presentation of these results by the PI at the Southeastern Regional ACS meeting in 2018 and the ACS National meeting in Spring 2019. In addition, funding from the PRF has assisted in the selection of the PI as a 2019 PMSE Young Investigator, and preliminary results from this work have prompted new directions for this research in order to explore future funding through the Department of Defense.

After demonstrating this new monomer class was capable of controlled radical ring-opening polymerization, degradation studies of the products were pursued. Since the overall process results in thioester functionality in the backbone of the polymer, it was predicted that this would lead to significant breakdown of the polymer chain. Figure 4 shows size-exclusion chromatograms of the degradation of a TBA copolymer containing 5 mol% of thioester units arising from thionolactone **3**. In addition to strongly nucleophilic reagents, such as sodium methoxide (NaOMe), it was also found that copolymer degradation could be initiated with cysteine methyl ester (MeOCys). In both cases, the high molecular weight starting polymer (30.8 kDa) was dramatically reduced in size to fragments with number-average molecular weights around 2 kDa. This is consistent with the feed ratio of the monomer and the slightly gradient nature of the copolymerization.

While thionolactone **3** proved to be an advance in the radical ring-opening copolymerization of acrylates, other monomer families were found to be less successful.