Abstract
We live in a material world. The ubiquity of synthetic polymers is not only proof of their utility, but also evidence of their transformative capacity. The convergence of organic and polymer chemistry holds the key to making materials smarter, more functional, and more sustainable. Herein I will describe efforts that leverage chemoselective transformations to introduce new reactivity and function to macromolecules. My graduate work sought to exploit the versatile reactivity of ketenes in polymer chemistry. New materials synthesized take advantage of Meldrum’s acid as both a synthetic building block and a thermolytic precursor to dialkyl ketenes. In many cases, ketenes are directly detected by their characteristic infrared absorption, among other methods, and are stable in ambient conditions. The inherent property of ketenes to provide crosslinking via dimerization, to act as a reactive chemical handle via addition, or both, provides a simple methodology for the downstream engineering of synthetic polymers. Subsequently, recognizing the significant potential of continuous flow chemistry in polymer synthesis, I created a semi-automated system for the synthesis of sequence-defined, unimolecular macromolecules. The Flow-IEG system performs three reactions and an in-line purification in 10 minutes, effectively doubling the molecular weight of an oligomeric species in an uninterrupted reaction sequence with unprecedented speed and efficiency. Subsequent iterations through the Flow-IEG system enable an exponential increase in molecular weight, providing rapid access to unimolecular polymers. Introduction of monomers with alternate structures and/or branching units to the Flow-IEG system provides control over both polymer sequence and architecture.