

Degradable polymers from thionolactone radical ring-opening copolymerization

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Polymers synthesized via traditional radical techniques have resulted in the creation of commonplace materials such as Styrofoam and Plexiglass. The unreactive carbon-carbon backbone of these polymers leads to their robust nature but also prohibits polymer degradation. To provide functionality into the backbone of these polymers, a new class of radical ring-opening (rRO) monomers containing a thionolactone has been developed. The radicophilic nature of the thiocarbonyl group and modular design of the thionolactone structure facilitates the tuning of monomer reactivity allowing for incorporation of thioesters into common monomer families (styrene, acrylates, and acrylamides). The resulting thioesters in the polymer backbone are stimuli responsive and can be utilized in post-polymerization modifications. One monomer, a seven-membered thionolactone, has been identified to incorporate evenly within acrylate copolymer. Therefore, only a small number of thioester responsive units is required for full polymer degradation. Further investigation into a second monomer derivative has resulted in the discovery of a six-membered thionolactone which is highly reactive with acrylamides. This reactivity has been leveraged to make precision degradable junctions in acrylamide block copolymers. Through further monomer design, a wide scope of thionolactone monomers can be synthesized to match the desired reactivity with various comonomers allowing for targeted comonomer incorporation and responsivity.

