Abstract: Polymers are all around us – from our daily use to biopolymers and therapeutics. Inspired by recent advances in chemistry, molecular pharmaceutics and biotechnology, on-demand and triggerable “smart” systems offers opportunities from precisely synthesis of polymers to delivering drugs in dose-, spatial- and temporal-controlled manners. This seminar will mainly discuss our ongoing efforts in controlling synthesis of degradable polyesters by external stimuli such as light and electricity. I will focus on the chemical synthesis of stereoregular, high-molecular-weight polyesters with various pendant functional groups. Our synthetic strategies allow for the preparation of various syndiotactic and stereoblock copolymers from racemic monomers. The mechanistic exploration of such triggerable polymerizations inspired us to develop a scalable synthetic method to prepare stereosequence-controlled copolymers with improved toughness and shape memory properties.