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Self-Immolative Polymers Containing Rapidly Cyclizing Spacers: Toward Rapid Depolymerization Rates
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Category

Synthesis of Materials and Unnatural Products

Key words

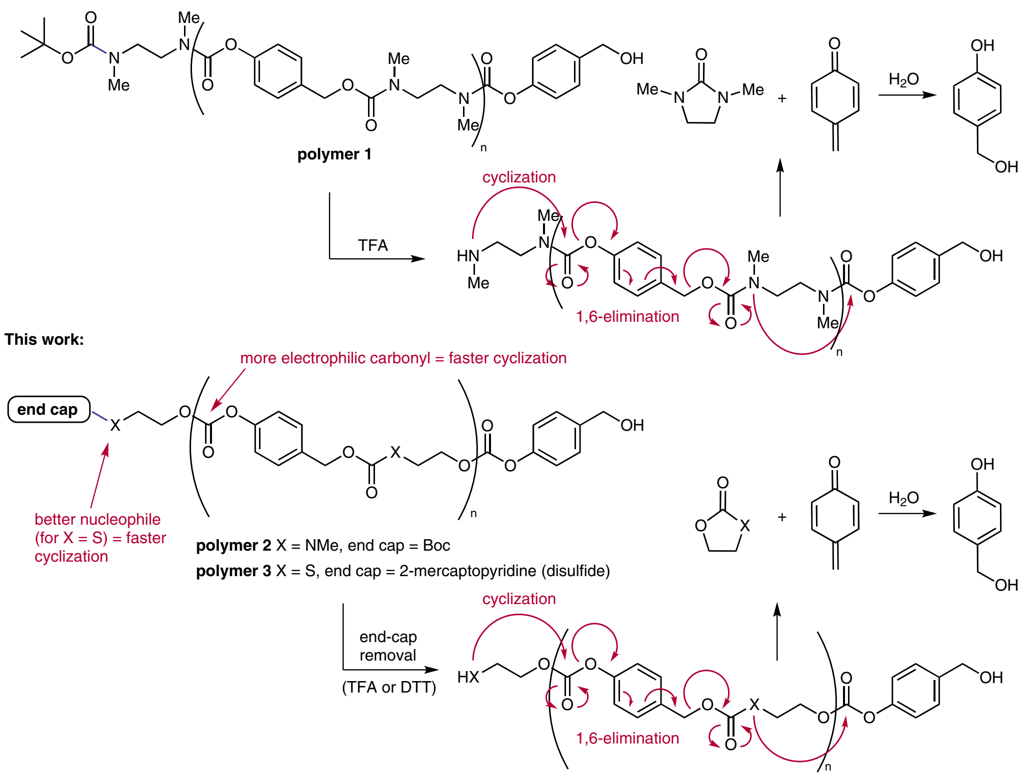
degradable polymers

controlled depolymerization

cyclization kinetics

Depolymerization Kinetics of Self-Immolative Polymers

Previous work (*J. Am. Chem. Soc.* **2009**, *131*, 18327):



overall depolymerization rates: polymer 3 (7.8×10^{-2} min^{-1}) > **polymer 2** (2.6×10^{-2} min^{-1}) > **polymer 1** (6.8×10^{-2} h^{-1})

Significance: Self-immolative polymers are materials that degrade into small molecules by an intramolecular cascade reaction upon removal of an end-capping group. Due to their backbones primed for degradation, self-immolative polymers require strategic design and synthesis. Here, Gillies and co-workers have synthesized two new self-immolative polymers with different degradation rates by altering the nucleophilicity and electrophilicity of the functional groups participating in the intramolecular cascade reaction.

Comment: Previously reported self-immolative polymer **1** depolymerizes through a cyclization–1,6-elimination pathway with the cyclization being the rate-determining step. By increasing the electrophilicity of the carbonyl by changing it from a carbamate to a carbonate, as seen in polymer **2**, the rate of depolymerization was increased 500-fold. A further increase in depolymerization was achieved when the nucleophile was changed from an amine to a thiol (polymer **3**). Polymer **3** is of particular interest due to its redox-sensitive depolymerization, which could be used for cytosolic drug delivery.

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