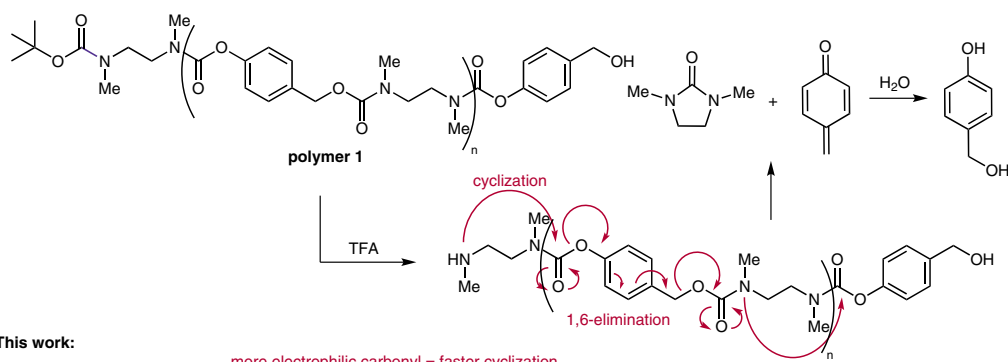
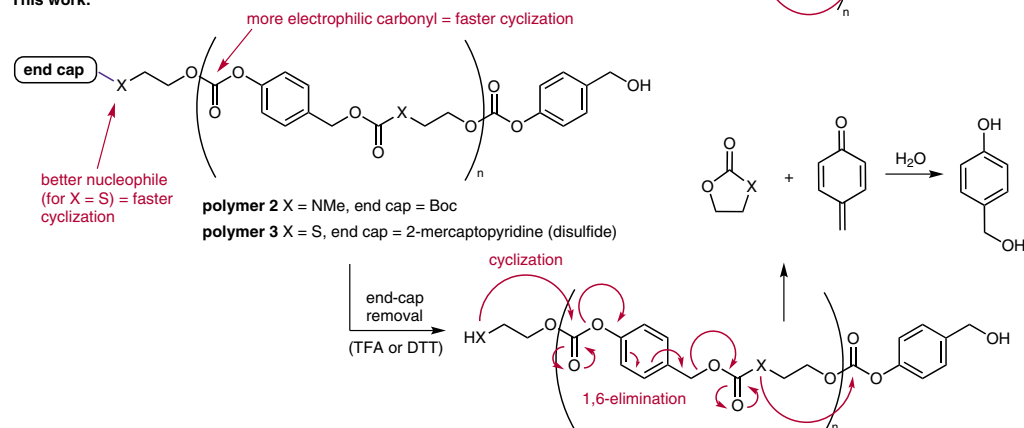


# Depolymerization Kinetics of Self-Immolative Polymers

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



This work:



overall depolymerization rates: polymer 3 ( $7.8 \times 10^{-2} \text{ min}^{-1}$ ) > polymer 2 ( $2.6 \times 10^{-2} \text{ min}^{-1}$ ) > polymer 1 ( $6.8 \times 10^{-2} \text{ h}^{-1}$ )

**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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