

The Development and Mechanistic Study of Dual H-Bonding Organic Catalysts for the ROP of Cyclic Esters

Organic catalysis for the Ring Opening Polymerization (ROP) of cyclic monomers is a rapidly emerging field of study that gained interest in 2005 with the advent of dual H-bonding catalysts. Synthesizing catalysts that produce fast reaction rates with superior reaction control over molecular weight (M_n) and molecular weight distributions (M_w/M_n) are of great interest for materials applications. The incorporation of multi-armed H-bond donating (thio)urea species resulted in a drastic increase in reaction rate. The incorporation of an oxygen (urea) in substitution of a sulfur (thiourea) saw an increase for all H-bond donors tested. These reactions, while becoming extremely fast, remained well controlled ($M_w/M_n < 1.1$). The trisurea species is the fastest H-bonding organic catalyst for the polymerization of cyclic esters to our knowledge.

These H-bonding (thio)urea catalysts were subjected to the polymerization of caprolactone at elevated temperatures (22-110°C). **1-O** and **2-O** produced linear Eyring plots throughout the temperature range evaluated (22-110°C). All other catalysts deviated from linearity at 80°C. Evidence of catalyst decomposition at elevated temperatures (>80°C) is suggested to be the reason of deviation from a linear Eyring plot. A switch to polar solvent alleviated catalyst decomposition for some H-bond donors producing linear Eyring trends, while other remained curved. A mechanistic reasoning will be presented.

Polymer properties are directly related to the microstructure of the polymer backbone. The introduction of chiral architectures into the (thio)urea H-bonding catalyst scaffold made kinetic resolution of racemic lactide possible. The chiral H-bonding donors resulted in an increase in the isotacticity of the polymer (P_m). Multi armed chiral H-bond donors saw an increase in reaction rates versus chiral mono H bonding species. A decrease in reaction temperature produced enhanced the P_m values.