

Transient Materials: from the Molecular to the Monolithic

Adam M. Feinberg and Jeffrey S. Moore

The thermally-triggered depolymerization mechanism of the transient material cyclic poly(phthalaldehyde) (cPPA) was investigated, and a cohesive mechanistic model is presented. Supported by the observed effects of additives and impurities on the degradation behavior of cPPA, a convergent triggering mechanism is proposed, wherein both Lewis acid catalysis and single electron transfer (SET) oxidation of cPPA lead to a cationic polymer unzipping pathway. Applications of the novel SET triggering pathway are presented, including selective depolymerization via chemical and photochemical oxidation. Additionally, use of the proposed mechanistic model to tailor the transient behavior of cPPA, resulting in the fabrication of a monolithic transient material, is discussed.

Rhodium-catalyzed Asymmetric Hydroamination of Allyl Amines

Evan P. Vanable and Kami L. Hull

To date, the enantioselective hydroamination of unactivated olefins is poorly developed. Current reports rely on the use of significant excesses of one reagent, high temperatures, and often suffer from poor enantioselectivities. Given the prevalence of chiral amine-containing compounds in pharmaceuticals, the development of an asymmetric hydroamination reaction is a significant challenge facing synthetic chemists. A Rh-catalyzed, highly enantioselective, hydroamination of allyl amines to afford 1,2-diamines is presented. A wide array of functionalized cyclic and acyclic secondary amine nucleophiles can be utilized; and furthermore, nucleophiles and directing groups with deprotectable functionality are tolerated, allowing for highly diversifiable products. The conditions are quite mild; they utilize nearly 1:1 stoichiometry and only modest heating. This method is a step towards completely atom-economical enantioselective hydroamination of α -olefins – a highly desired goal in transition-metal catalysis.

