Sidechain-alkyne to backbone-allene editing of polyurethanes in solution and solid-state

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Skeletal editing of polymer backbones can enable precision polymer synthesis, unlock new modes of polymer deconstruction, and shift material properties between isomeric backbones. Currently, only a handful of chemical functionalities have been edited into polymer backbones through solution-based chemistry. Herein, we describe transition metal catalysis of a [3,3]-oxo rearrangement that can transform polyurethanes with propargylic carbamates to a new class of polyurethane materials containing backbone allenylic carbamate functionality. Through small molecule studies, we discovered that AgNTf2 efficiently catalyzed this rearrangement in propargylic esters, and this transformation generalizes to analogous carbamates. We observed this rearrangement proceeds through a non-dissociative mechanism and exhibits equilibrium first-order kinetics. We then developed a scalable synthesis of poly(propargylic urethane)s and demonstrated that the rearrangement proceeds efficiently both in solution and, critically, in plasticized films. While subtle thermal property (i.e., Tg, Td,5%) differences emerge between the rearranged product poly(allenylic urethane)s and starting poly(propargylic urethane)s, the rearrangement enables hydrolytic deconstruction and crosslinking of the resulting allene-containing polyurethane.