Controlled/living branching polymerization enabled by polymerization-induced activation: mechanistic study assisted development of catalytic systems

Mengxue Cao[1], Yutong Liu[1], Xiaowei Zhang[1], Feng Li[1], and Mingjiang Zhong[1]

1. Yale University, New Haven, Connecticut, United States

Polymers with branched structures exhibit superior mechanical, photonic, and electrical properties. In our previous study, site-specifically anchored branched polymers with controlled degrees of branching and molecular weights were successfully prepared via copper-mediated atom transfer radical copolymerization of conventional vinyl-based monomers and *n*-butyl α-bromoacrylate (BBA). BBA serves in this controlled branching polymerization as an *inibramer* (*ini*tiator + *bra*nching point + mono*mer*) that, exclusively after being polymerized, can produce a double-initiating center to form a branching junction. Despite the preliminary success, challenges such as a limited monomer scope and relatively low conversion of the comonomers remained unaddressed due to the inevitable radical termination that slows down the polymerization rate more rapidly compared to linear polymerizations. Polymerization kinetics was systematically investigated by combining experiments and numerical simulation, quantitatively providing the optimal profile of radical concentration for a sustainable polymerization. Guided by the knowledge attained from the mechanistic study, polymerization conditions and setups that are able to accurately regulate the radical concentration throughout the entire polymerization process were developed accordingly for various monomers. In this development, activator regeneration atom transfer radical polymerization was applied, in which an external power such as light or electricity was employed to regulate the concentration of propagating radicals, to suppress termination reactions and achieve high monomer conversion. Monomers with different reactivities, such as acrylate, acrylamide, styrene, and acrylonitrile, were successfully copolymerized with the *inibramer* to synthesize branched polymers.