142d Mechanistic Modeling of Nitroxide-Mediated Controlled Radical Polymerization of Gradient Copolymers

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In recent years there has been high demand for polymeric and copolymeric materials with well-defined microstructures for use in highly specialized applications. One type of material that has garnered interest due to its applicability in compatibilization is gradient copolymers. Nitroxide-mediated controlled radical polymerization (NM CRP) has emerged as an attractive synthesis route for the production of these materials due to its compatibility with a wide range of monomers. These polymerizations are characterized by the presence of a stable nitroxide radical that undergoes reversible recombination with propagating radical chains, allowing control over chain length and architecture while maintaining a narrow polydispersity.

The use of NM-CRP to synthesize gradient copolymers of styrenic monomers (styrene and 4-acetoxystyrene) has been examined using a combined experimental and modeling approach. To conduct polymerizations at lower temperatures in order to reduce the effect of thermal polymerization, -methyl-styryl-di-tert-butyl nitroxide (A-T), wasαan alkoxyamine, utilized as a unimolecular initiator. When heated, A-T dissociates into an alkyl radical that initiates polymerization as well as a nitroxide radical which reversibly "caps" radical chains. In our early work, styrene/4 acetoxystyrene gradient copolymers were successfully synthesized using A-T under semi-batch conditions. Despite successful synthesis and characterization, ambiguity remained regarding the true mechanism of 4-acetoxystyrene polymerization. When thermally polymerized, molecular weights of poly(4 acetoxystyrene) exhibited drastically different qualitative trends when compared to polystyrene. Specifically, molecular weight values increased over time before reaching an asymptotic value, indicative of long chain branching reactions. Drawing upon previous modeling work used to analyze the NM CRP of polystyrene, mechanistic models were constructed to describe both the thermal and nitroxide-mediated polymerization of 4 acetoxystyrene and its copolymerization with styrene. Using the method of moments, detailed mechanistic models were developed which tracked product evolution and molecular weight averages based on end-chain structures. Kinetic parameters were specified using a combination of experimental values measured by our collaborators, Professor Robin Hutchinson and his group at Queen's University, and structure/reactivity relationships. The role of branching in directing the thermal polymerization of 4-acetoxystyrene and its effect on gradient copolymer synthesis will be discussed.