Synthesis of High Molecular Weight (~1 Million Daltons) Living Polymer via Dispersed Phase ATRP

Ryan W. Simms, Michael F. Cunningham*

Dept of Chemical Engineering, Queen's University, Kingston, Ontario, Canada K7L 3N6

The reverse atom transfer radical polymerization of butyl methacrylate in miniemulsion, initiated with the redox pair hydrogen peroxide/ascorbic acid and mediated with copper(II) bromide tris[2-di(2-ethylhexyl acrylate)aminoethyl]amine produced high-molecular weight poly(butyl methacrylate) (M_n ~1 million daltons, PDI = 1.25). The use of the redox pair to initiate the polymerization also facilitated a relatively fast rate of polymerization. The polymerization of methyl methacrylate produced well-defined high-molecular weight polymers with a controlled degree of polymerization and narrow molecular weight distribution. Compartmentalization was found to reduce the overall polymerization rate and improve the control over the polymerization. Both the particle's size and the number of polymer chains contained in the particle are important parameters to control when formulating an ATRP system that exhibits compartmentalization effects. It was determined that a particle size of less than 200 nm is sufficiently small to affect ATRP provided that each particle contains less than ~ 4000 polymer chains. The difference between a conventional free radical polymerization and ATRP are highlighted by the opposing impact that compartmentalization has on the kinetic of the polymerizations.