

PRODUCTION OF LOW MW REACTIVE POLYMERS BY CONVENTIONAL AND CONTROLLED RADICAL (CO)POLYMERIZATION

Robin A. Hutchinson

Department of Chemical Engineering, Queen's, University, Kingston, Ontario K7L 3N6, Canada
robin.hutchinson@queensu.ca

ABSTRACT

Many low-MW reactive commercial dispersants, surfactants and coatings resins are synthesized by free radical polymerization (FRP) using a functional comonomer such as glycidyl methacrylate, (meth)acrylic acid or 2-hydroxyethyl (meth)acrylate. While FRP offers great versatility, the sequencing of units along each chain is stochastically controlled. The distribution of functional comonomer units among polymer produced by starved-feed semibatch radical copolymerization has been modeled using three simulation approaches: a deterministic model formulated to separately track the homopolymer chains produced without the desired functionality, a kinetic Monte-Carlo (MC) model, and a novel hybrid deterministic/MC approach developed using new capabilities within the software package PREDICI[®]. Even under perfect control of overall copolymer composition, simulations indicate that almost half of the polymer chains produced (number-average length of 20, with a single functional group per chain on average) contains no functionality. Vinyl-terminated macromonomer prepared by cobalt chain transfer polymerization provides a means to control the placement of functionality while maintaining the advantages of FRP operation.

Controlled radical polymerization (CRP) has emerged as a promising route to overcome these limitations through the synthesis of low MW macromolecules with well-defined molecular weight, low polydispersities, and well controlled microstructure. The advantages of combining CRP with continuous reactors to increase the range of specialty products made for applications in coatings, inks, overprint varnishes and adhesives will be presented. A new alkoxyamine based on a highly thermally stable nitroxide has been used for the controlled homopolymerization of styrene and butyl acrylate at temperatures up to 200 °C. High monomer conversions are reached in a few minutes with a linear increase in polymer chain-length with conversion, a final dispersity index of ~1.2, and successful chain-extension of the resulting material with various monomers, including acrylic acid.