Faculty of Engineering and Applied Science
Chemical Engineering Seminar Series

The Synthesis of Acrylate-Based Macromonomers and Structured Copolymers by High-Temperature Semi-Batch Radical Polymerization

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Thursday, April 10, 2025, 2:30pm
Dupuis Hall, Room 217

A high-temperature starved-feed semi-batch operating policy is shown to be an effective means to produce poly(acrylates) with high macromonomer content, taking advantage of side reactions inherent to acrylate radical polymerization. This operating strategy has been used to polymerize *n*-butyl acrylate (BA) over a range of monomer (polymer content in solution) and initiator concentrations, reaching a maximum macromonomer content when monomer and initiator levels are reduced.[1] When the acrylate monomer is switched to isobornyl acrylate (iBoA), significantly higher macromonomer contents (>75%) are obtained while maintaining high monomer levels.[2] This is because steric hindrance favors fragmentation (i.e., terminal double bond (TDB) formation) over addition (i.e., short-chain or long-chain branch formation), thus increasing the p(iBoA) TDB content and decreasing polymer dispersity.[2] This increase is of commercial interest, as the reactive terminal double bond (TDB) units of macromonomers can be used to produce branched or multi-block copolymers for particle stabilization in coatings and adhesives without a mediating agent.

This presentation will describe the operating conditions required to synthesize iBoA-based macromonomers and their subsequent use to produce blocky or comb copolymers in a single-pot process controlled by sequential feeding. Methodologies are introduced to verify macromonomer incorporation including two-dimensional liquid chromatography and the addition of 2-hydroxyethyl acrylate as a crosslinking monomer to quantify the fraction of copolymer product formed by sequential feeding.

1. N. Heidarzadeh, R. A. Hutchinson, *Polym. Chem.* **2020**, *11*, 2137.

2. E. G. Bygott, R. A. Hutchinson, *Macromol. Chem. Phys.* **2024**, *225*, 2300321.