

## THE USE OF HIGH-TEMPERATURE SEMI-BATCH RADICAL POLYMERIZATION TO SYNTHESIZE ACRYLATE BASED MACROMONOMERS AND STRUCTURED COPOLYMER DISPERSANTS

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A high temperature starved-feed semi-batch operating policy has been demonstrated to be an effective means to produce poly(acrylates) with high macromonomer content, taking advantage of intrinsic side reactions inherent to acrylate radical polymerization. This operating strategy has been used to polymerize butyl acrylate (BA) over a range of monomer and initiator levels, reaching a maximum macromonomer content when monomer (polymer content in solution) and initiator concentrations are reduced.<sup>1</sup> When the acrylate monomer is switched to isobornyl acrylate (iBoA), the macromonomer content is 50% higher than that for poly(BA) under identical operating conditions. This significant increase is of commercial interest, as the reactive terminal double bond (TDB) units of macromonomers can be used to produce functionalized branched structures and multi-block copolymers for particle stabilization in coatings, dispersants, and adhesives. It is hypothesized that steric hindrance of the bulky isobornyl group explains this difference, favoring fragmentation (i.e., TDB formation) over addition (i.e., short-chain or long-chain branching) reactions, thus increasing the TDB content and decreasing polymer dispersity. The resultant macromonomer solution has been shown to serve as an excellent addition-fragmentation agent for polymerization of a second monomer in a single pot process controlled through sequential feeding.

This presentation will describe the operating conditions required to synthesize iBoA based macromonomers, as well as their subsequent use to produce acrylate based blocky or comb copolymers without the need for a mediating agent. Furthermore, characterization methods to accurately estimate macromonomer chain incorporation and determine polymer structure are addressed. The development of a sequential monomer feeding strategy to efficiently synthesize block and comb copolymers by radical polymerization without the use of a mediating agent will eliminate the processing steps required to remove additives, reducing manufacturing costs and the environmental impact of using large amounts of solvent.

1. N. Heidarzadeh and R. A. Hutchinson, *Polym. Chem.*, 2020, 11, 2137–2146.