

THE INFLUENCE OF (MACRO)MONOMER FUNCTIONALITY ON REACTIVITY IN RADICAL (CO)POLYMERIZATION

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Short-chain polyester methacrylate macromonomers with alkyl, tertiary amine, carboxyl, and hydroxyl end-group functionalities have been synthesized by ring-opening polymerization and subsequent modification. The functionality controlled in the synthesis is imparted onto the comb-polymer structures formed via radical polymerization, with an even greater diversity of materials accessible through copolymerization. This presentation will provide an overview of the materials produced and their applications, which range from degradable cationic flocculants for treatment of oil sands tailings to nanoparticles with tunable biodegradability for drug delivery.

Specialized techniques have been applied to compare the radical (co)polymerization kinetics of the macromonomers to the analogous monomers. The propagation rate coefficients (k_p) determined by pulsed laser polymerization experiments for bulk polylactic acid ethyl ester methacrylate (PLA_NEMA) macromonomers with $N=1$ and 5 average number of polyester units are not significantly different, but are elevated by 60% compared to methyl methacrylate. The results indicate that the nature of substituents several units beyond the methacrylic group does not decisively impact bulk k_p measurements.

The effect of macromonomer length and end-group functionality on relative reactivity is studied by tracking monomer conversions and composition drift during batch radical copolymerization with styrene using an *in situ* NMR technique. Whereas the effects of end-group functionality and hydrogen bonding are pronounced for the analogous monomers, the polyester spacers significantly dilute these effects in macromonomer copolymerization. Instead, the chemical identity up to several units from the methacryloyl group is the most important indicator of macromonomer relative reactivity.