REACTIVITY RATIO ESTIMATION FOR CO- AND TERPOLYMERIZATION OF N-BUTYL ACRYLATE, METHYL METHACRYLATE AND 2-ETHYLHEXYL ACRYLATE

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N-butyl acrylate (BA), 2-ethylhexyl acrylate (EHA) and methyl methacrylate (MMA) are commonly used as monomers in coatings, adhesives and many other applications. Our current interest is in BA/MMA/EHA terpolymer formulations for the production of pressure sensitive adhesives. For the purposes of controlling polymer adhesive performance, kinetic parameters such as the reactivity ratios, are required. Reactivity ratios for BA/MMA are available in the literature\(^1\), while that for BA/EHA and MMA/EHA are not. The bulk copolymerization reactivity ratios for BA/EHA and MMA/EHA were determined at 60 °C using statistically designed free-radical polymerizations at low-conversion (<10%). The estimates were then validated using high-conversion copolymerizations. These reactivity ratio estimates were used, along with the literature values for the BA/MMA system, for the prediction of BA/MMA/EHA composition in a series of high conversion bulk terpolymerizations.

The reactivity ratio estimates for BA/EHA were \(r_{BA} = 0.994\) and \(r_{EHA} = 1.621\), for MMA/EHA were \(r_{MMA} = 1.496\) and \(r_{EHA} = 0.315\), and for BA/MMA\(^1\) were \(r_{BA} = 0.343\) and \(r_{MMA} = 2.022\). These copolymer reactivity ratios were shown to predict the terpolymer composition of high conversion BA/MMA/EHA experiments at molar feed ratios of 80/10/10, 10/80/10 and 10/10/80 (see Figure 1). Number-average and weight-average molecular weights for selected high conversion samples were also measured. Modeling of conversion, composition and molecular weight using these reactivity ratios is planned.


![Figure 1 – Terpolymer composition versus conversion for bulk BA/MMA/EHA (10/10/80 molar ratio) at 60 °C with 0.08 wt.% [AIBN]](image-url)