

EFFECT OF REACTION CONDITIONS ON THE DISTRIBUTION OF HYDROXYL FUNCTIONAL GROUPS IN HEA-BMA COPOLYMER

Loretta A. Idowu, Department of Chemical Engineering - Queens's University at Kingston, Canada
16lai@queensu.ca

Jan E. S. Schier, Department of Chemical Engineering - Queens's University at Kingston, Canada
Amin Nasresfahani, Department of Chemical Engineering - Queens's University at Kingston, Canada
Robin A. Hutchinson, Department of Chemical Engineering - Queens's University at Kingston, Canada

Keywords: copolymer composition distribution; radical polymerization kinetics; semi-batch starved feed; hydroxyl-functional

Non-functional monomer feedstocks containing alkyl meth(acrylate) components such as butyl acrylate (BA) and butyl methacrylate (BMA) have been replaced or augmented with functional monomers such as 2-hydroxyethyl methacrylate (HEMA) and 2-hydroxyethyl acrylate (HEA) to produce reactive polymer chains of lowered molecular weight (MW) for application in solvent-borne automotive coatings. The polar and functional reactants affects the radical copolymerization kinetics and introduces solvent dependencies.^[1] A series of BMA/HEA experiments have been performed at 138 °C to determine the influence of these changing kinetic parameters under starved-feed semi-batch operating conditions. A comparison with BMA/BA copolymerization shows that the influence of hydrogen bonding is small, with the semi-batch system well controlled to HEA contents of up to 50 wt%. Thus, the experiments are well represented by a comprehensive generalized copolymerization model formulated in PREDICI® that considers relevant methacrylate and acrylate side-reactions and uses the chain growth parameters measured in previous kinetic investigations.^[2]

As well as controlling overall copolymer composition, understanding the distribution of the hydroxyl functional groups among the polymer chains is of importance, as non-functionalized lower-MW chains will not crosslink into the polymer network formed upon application of the coating. A series of BMA/HEA copolymers containing 6.25, 12.5 and 25 wt% HEA were synthesized with weight-average polymer MWs varied between 3000-10000 Da through manipulation of reaction temperature (138 and 160 °C) and initiator loading (2 to 4 mol% relative to monomer) during starved-feed semi-batch operation; at the higher temperature the influence of BMA depropagation becomes more apparent. The amount of non-functional material in the samples is experimentally determined by solvent extraction after forming a crosslinked film, and MWs and HEA contents of the extractable fractions are measured. These experimental results will be compared with predictions from the PREDICI® model as well as a kinetic Monte Carlo representation that calculates how the reactive groups are distributed as a function of polymer chain-length.

[1] J. E. S. Schier, R. A. Hutchinson, "The influence of hydrogen bonding on radical chain-growth parameters for butyl methacrylate/2-hydroxyethyl acrylate solution copolymerization", *Polym. Chem.* 2016, 7, 4567-4574.

[2] J. E. S. Schier, M. Zhang, M. C. Grady, R. A. Hutchinson, "Modeling of Semi-batch Solution Radical Copolymerization of Butyl Methacrylate and 2-Hydroxyethyl Acrylate", *Macromol. React. Eng.* 2018, submitted.