517b Kinetic Modeling of Acrylate Polymerization at High Temperature

Xinrui Yu, Linda J. Broadbelt, and Robin A. Hutchinson

The automobile coating industry is undergoing reformation driven by environmental regulations that demand low content of volatile organic compounds. Traditional solvent-borne acrylic resins consisting of high molecular weight polymers that are produced at low temperatures (< 80 ºC) need high levels of organic solvent (70%) to be processed as coatings. Alternatively, novel resin compositions consist of acrylic oligomers with multiple crosslinkable functional groups that can undergo reactions on the metal surface. Polymerization at high temperatures (>120 ºC) is an economical approach to produce such pre-polymers. However, higher reaction temperatures can result in secondary reactions that affect oligomeric quality. Given the potential complexity of resin recipes and the diversity of the reactions that can occur during polymerization at high temperatures, it is desirable to have a method that can predict the characteristics of the final product. In particular, methods for predicting rate coefficients for copolymerization and side reactions such as intermolecular and intramolecular hydrogen transfer and scission would be valuable since these quantities are difficult to access experimentally.

In collaboration with Professor Robin Hutchinson's group at Queen's University in Canada, ab initio molecular orbital calculations and transition state theory were employed to predict kinetic parameters of reactions relevant to acrylate polymerization at high temperature. A methodology was developed that was able to handle the complexity of the large systems required to mimic polymeric systems accurately. A first principles Monte Carlo method was devised that allowed conformational space to be explored comprehensively. A methodology was also created to handle low frequency modes that are best treated as hindered rotations in calculating thermodynamic properties via statistical mechanics. The use of a heavy atom approximation for the high molecular weight portion remote from the reactive center was also implemented and evaluated. Application to methyl acrylate and methylmethacrylate polymerization will be discussed.