555f Model for Polymer Microstructure Monitoring and Control in Solution Polymerization of Alkyl Acrylates

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Industrial demand for reliable polymerization process models that can quantitatively predict polymer quality indices, has motivated the use of analytical technology (e.g. spectroscopic, calorimetric, chromatographic methods), in the model development. Inclusion of analytical technology in the model development allows for (a) the observation of the dynamics of polymer chain microstructure and (b) the development of new ways of expressing polymer quality indices. While the incorporation of analytical technology in model-based process monitoring and control strategies is a long-standing interest, the implementation has been limited to quality indices such as monomer conversion, molecular weight, copolymer composition and particle size distribution (Kammona et al., 1999). The use of NMR spectroscopic techniques for monitoring polymer microstructure evolution in polymerization processes is still limited to laboratory-scale experiments (Lutz and Matyjaszewski, 2005). A limiting step in the use of spectroscopic techniques in process monitoring is the identification or the assignments of signature peaks for the observation of polymer microstructure dynamics (polymer characterization). The development of practical hardware sensors, however, remains to be the main obstacle in the implementation of advanced analytical techniques in conventional polymerization processes. In the absence of the hardware sensors, one can often rely on soft sensors.

This Drexel-DuPont joint study concerns the development of process models which can describe the dynamics of conventional and spectroscopic measurements in high-temperature solution polymerization reactors. The specific polymerization system to be considered is the solution polymerization of n-butyl acrylate in xylene. Recent FT-MS and NMR spectroscopy studies of high-temperature (above 100C) solution polymerization of n-butyl acrylate showed the significance of branching and terminal double bond (TDB) formation through intra-molecular chain transfer (backbiting)-propagation and backbiting-scission mechanisms (Quan et al., 2002; Peck and Hutchinson, 2004, Quan et al., 2005). It was also observed that alkyl acrylates undergo substantial spontaneous polymerization at temperatures above 140 C (Grady et al., 2003). The exact mechanism by which the spontaneous polymerization is initiated is still not understood. Nevertheless, as branching, scission and the extent of the spontaneous initiation directly affect the resulting molecular weight distribution profile, a fundamental understanding of how the process variables (e.g., temperature and initial monomer content) affect the polymer properties is of interest.

Peak assignments by Ahmad (1998) and Quan et al. (2002, 2005) on 1H- and 13C-NMR for TDB and branch points are used as off-line sensors of polymer microstructure dynamics, while monomer conversion and molecular weight distribution profiles are obtained through off-line gravimetric and chromatographic measurements. The method of moments is used to develop a mechanistic model, and the measurements are used in off-line model parameter estimation. The model is then used to develop soft sensors for monomer conversion, molecular weight distribution, number of TDB and number of branch points and to calculate optimal control strategies. Performance of the soft sensors is compared against experimental data obtained in pilot-scale batch solution polymerization of n-butyl acrylate.

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