281d Reaction Network Identification in High-Temperature Polymerization of N-Butyl Acrylate: a Simultaneous Parameter Estimation Approach

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Increasingly higher average reaction temperature used in many industrial-scale polymerization reactors has motivated improvement in existing ‘low-temperature' polymerization reactor models. The inability of the existing mechanistic models in predicting the dynamics of high-temperature polymerization processes is due to the significant contribution of secondary reactions at the higher temperatures (Quan et al., 2002; Peck and Hutchinson, 2004). At lower temperatures, these secondary reactions contribute little to the overall rate of polymerization and are usually ignored. For example, 1D-NMR and FT-MS studies in high-temperature polymerization of ethyl acrylate point to the creation of a slower intermediate radical which can undergo scission to form terminal double bonds (TDB) or propagate further to create chain-branching (Quan et al., 2002, 2005; Peck and Hutchinson, 2004).

Polymer characterization results only provide snapshots of chain characteristics. Thus, more than one polymerization reaction mechanism can often explain the formation of a certain micro-structure. For example, the formation of TDB in n-butyl acrylate can be explained through intra-molecular chain transfer followed by beta-scission, and can also be explained by the occurrence of chain transfer to monomer. The hypothesis of the backbiting-scission mechanism points to the creation of an intermediate, near-chain-end, tertiary radical which can (i) upon further propagation create short chain branches, or, (ii) undergo beta-scission to create a dead chain with TDB and a live chain. Hence, the branch formation is in direct competition with TDB formation. Another possible explanation is that propagating radicals can abstract hydrogen from monomers, and create secondary radicals with their double bond intact (Busch and Muller, 2004), which, upon further propagation forms TDB. The latter mechanism is plausible due to the large concentration of monomer present compared to the concentration of tertiary radicals. This example illustrates how a formation of a micro-structure can lead to the postulation of multiple reaction pathways. Furthermore, for mechanistic models to be useful for quantitative predictions, a set of reliable kinetic parameter estimates is required to quantitatively describe the dynamics of species and polymer-quality indices of interest. Parameter estimation through experimental techniques that can isolate the occurrence of dominant reactions [e.g., pulsed laser initiated polymerization (Asua et al., 2005)] usually provides reliable estimates for dominant reactions such as propagation and termination. Other parameters of interest are then obtained through fitting model predictions to combinations of gravimetric (species conversion profile), chromatographic (molecular weight distribution profile) and spectroscopic measurements (microstructure profile). Alternatively, all or almost all parameters can be simultaneously estimated by fitting a set of measurements. By employing the latter approach, the reaction network is considered as a whole, and the extent at which each reaction proceeds compared to the others (reactivity ratios) can always be readily quantified. The approach, however, is often hindered by (i) the high degree of nonlinearity inherent in the parameter estimation problems, (ii) the large scale of the optimization problem, and (iii) the obtainment of a set of parameters that do not reflect the significance of the dominant reaction mechanisms.

Automated or computer-aided approaches have been developed/used to identify dominant reactions in complex systems such as hydrocarbon pyrolysis (Susnow et al., 1997) and polymer degradation (Poutsma, 2003). The use of these approaches needs a mature knowledge of underlying mechanistic pathways and a sufficient number of reliable rate constant estimates (Savage, 2000). The mechanistic complexities in high-temperature polymerization systems are considerably much less than that observed in free radical chain degradation and pyrolysis. However, there is little knowledge and agreement on possible reaction networks for high temperature polymerization systems. Furthermore, reliable estimates of rate constants in the polymerization systems are limited to a few specific reactions. For high temperature polymerization systems, a more comprehensive treatment that can simultaneously evaluate alternative postulated reaction networks and the corresponding rate constants is needed.

Motivated by the above, this study concerns the development of an iterative and data-driven approach to identifying plausible reaction networks in polymerization systems. The approach includes: (i) postulation of reaction networks followed by the development of polymerization kinetic models, (ii) formulation of simultaneous parameter estimation problems, and (iii) systematic evaluation of the networks and parameter estimates. Postulation of reaction networks are based on polymer characterization studies and typical reactions observed in chain homo-polymerization systems, where polymerization kinetic models are developed based on the method of moments. In the simultaneous parameter estimation step, measurements of molecular weight distribution, monomer conversion, number of TDBs and number of chain branches (1D-NMR) are used as basis for parameter estimation. Measurements are assumed to be reliable (free from severe uncertainties). Finally, plausible reaction networks are those that simultaneously (a) fit all the measurements and (b) yield parameter estimates that are physically meaningful and are in agreement with reliable estimates (if any) reported in the literature (e.g., estimate of the propagation rate constant obtained through pulsed laser initiated polymerization). The application of the approach is shown through the development of a polymerization kinetic model for high-temperature polymerization of n-butyl acrylate in xylene.

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