

A Comprehensive Kinetic Investigation of the Inverse Suspension Copolymerization of Acrylamide: Theoretical and Experimental Studies

P. Pladis², O. Kotrotsiou², Ch. Gkementzoglou² and C. Kiparissides^{1,2}

¹Τμήμα Χημικών Μηχανικών, Αριστοτέλειο Πανεπιστήμιο Θεσσαλονίκης

²Ινστιτούτο Χημικών Διεργασιών & Ενεργειακών Πόρων, ΕΚΕΤΑ

Due to their excellent properties, polyacrylamide products are suitable in several applications like water treatment, oilfield and mining as well as paper chemicals. High molecular-weight homopolymers of acrylamide are used as pushing fluids in tertiary oil recovery, as drag reduction agents and as drilling fluids. Copolymers with various cationic monomers such as diallyldimethylammonium chloride (DADMAC) and dimethylaminoethyl acrylate (DMAEA) are used for fines retention in paper making, as flocculants, and, in general, wherever aqueous solid liquid separations are required.

Since acrylamide is solid at normal reaction temperatures it is usually polymerized in aqueous solutions. However, the polymerization of acrylamide is characterized by a very high heat generation rate ($\Delta H_p = 19.5$ kcal/mol) and by the formation of a highly viscous reaction medium. Furthermore, the reaction should be performed in neutral solutions and at moderate temperatures (i.e., less than 70°C) to avoid intermolecular imidization. Thus, industrially, the polymerization of acrylamide is often carried out in heterophase processes like inverse-suspension or inverse-emulsion. The inverse suspension process involves the emulsification of a water-soluble monomer, in solution, in a continuous organic phase. A water-in-oil steric stabilizer is used and the polymerization is carried out with either a water- or an oil-soluble initiator, although the latter is more common. The resulting microsuspensions have lower viscosities, provide easier heat removal and can be used at higher monomer concentrations than the solution process.

In the present work, a comprehensive theoretical and experimental kinetic investigation of the inverse suspension copolymerization of acrylamide is presented. The experimental work, which included both the homopolymerization of acrylamide and the copolymerization with DMAEA at various compositions, was carried out in a 1L jacketed reactor. Paraffin oil was employed as the oil phase and Span 80 (Sorbitan monooleate) was used as surfactant (HLB = 4.3) to stabilize the water-in-oil suspension.

A comprehensive mathematical model was developed based on a detailed kinetic mechanism to simulate the dynamic evolution of the monomer conversion and molecular weight developments (i.e., M_n , M_w , PD). The proposed kinetic mechanism of the acrylamide copolymerization comprises a series of elementary reaction steps, including initiator decomposition, chain initiation, propagation, chain transfer to monomer, termination by disproportionation and reaction with terminal double bond. Basic kinetic parameters were estimated using solution polymerization experiments at low conversion. The resulting kinetic model has been evaluated against experimental data for copolymerization of acrylamide with DMAEA. A very good agreement has been found between model predictions and the experimental data (literature and current work).