MATHEMATICAL MODELING OF STYRENE/DIVINYLBENZENE COPOLYMERIZATION COMPRISING DIFFUSIONAL EFFECTS AND CYCLIZATION KINETICS

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A previously developed kinetic model, based on population balance equations in terms of generating functions was improved considering diffusional effects on termination reactions through a free-volume model and the consumption of pendent double bonds by intramolecular propagation. The rate of these cyclizations was estimated through mass balances of “paths” represented by fragments along the polymer chains with reactivity depending on the length of the cycle. Predictions were obtained for our own experimental data obtained from styrene-divinylbenzene free-radical copolymerizations carried out under solution and suspension conditions. Good agreement was obtained between model and experiments concerning simultaneously conversion, gel fraction and average molecular weights of soluble polymer, both before and after gelation, with the following parameters: free-volume parameter for termination reactions $\beta_t = 0.465$, volumetric expansion coefficient $\alpha = 1x10^{-3}$ K^{-1} for monomers and $4.8x10^{-4}$ K^{-1} for the copolymer, proportionality factor for reaction-diffusion termination constant $C^0_{RD} = 135$ L/mol, activation energy of cyclization 32.5 kJ/mol, rate constant of cyclization for the smallest cycle (3 units) $2.0x10^{-3}$ s^{-1} at 60 ºC and intermolecular propagation over pendent double bonds 53 % of styrene homo-propagation; other rate constants are literature values. This study shows that despite their complex chemistry, these systems can be successfully modeled, with obvious benefits for process and product engineering.

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