

Particle Formation in Emulsion Polymerisation Reactions under Monomer-Starved Conditions

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The main body of the research regarding particle formation in emulsion polymerisation reactions concerns interval I. In interval I, the particles and, thus, the aqueous phase are saturated with monomer. For many industrial emulsion polymerisation reactors, such as semibatch and continuous stirred tank reactors and even batch reactors with a high emulsifier/monomer ratio, particle formation is not confined to interval I and partly or even wholly occurs in interval III. In interval III the monomer concentration in the aqueous phase and in the particles is lower than the saturation value and micelles are only partially swollen with monomer.

A systematic approach has been taken to investigate particle formation under monomer-starved conditions. A seeded polymerisation of styrene was carried out to assimilate interval III of a batch emulsion polymerisation. The number of secondary particles initially increased with decreasing monomer concentration in the polymer particles, but after reaching a maximum, decreased at a higher range of conversion and eventually reduced to zero. The reduction in the rate of particle formation in the later stage of interval III (at high conversions) could not be simply explained by existing theories which rely on the decrease in monomer concentration in the aqueous phase as a means to explain the decrease in the rate of radical capture. The decreased rate of radical entry into partially monomer-swollen micelles can be explained by the variations in structure of micelles with monomer concentration. Only a certain population of radical can enter partially monomer-swollen micelles, whereas a wider population of radicals can enter particles. Models were developed which could fit the experimental data.

An important characteristic of particle formation in semibatch and continuous emulsion polymerisation reactors is the reduced rate of growth of particles. The particle formation and the particle growth are competing in the course of an emulsion polymerisation reaction. In conventional batch emulsion polymerisation, the rate of particle growth is thermodynamically controlled at a constant level by monomer diffusion from monomer droplets to polymer particles. In semibatch and continuous processes the rate of particle growth can be controlled by the rate of monomer addition. Models, together with a comparison with experimental data, are presented for particle nucleation in semibatch emulsion polymerisation of styrene, methyl methacrylate (MMA), butyl acrylate and vinyl acetate (VA) under monomer-starved conditions. An appropriate correlation for prediction of number of polymer particles in terms of surfactant and initiator concentrations and monomer addition rate was also derived as $N_p = k (a_s S_0)^{1.0} \rho^{2/3} R_a^{-2/3}$ which applies to styrenic type monomers. The models can explicitly explain, for the first time, why the application of semibatch emulsion polymerisation will lead to the formation of a large number of polymer particles. The radical desorption from small polymer particles was found to be the main reason for the large number of polymer particles formed in VA and MMA semibatch emulsion polymerisation under monomer starved conditions.