Notes

Coagulative Nucleation in Surfactant-Free Emulsion Polymerization

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In a recent communication to the Editor, Zhang, Gao, and Wu[1] report the preparation of narrowly distributed, surfactant-free polystyrene nanoparticles with diameters of 35−117 nm using microwave radiation as a heating method. The authors observe an increase in particle size with increasing initial monomer concentration at fixed initiator concentration. An increase in particle size is also observed with increasing initiator concentration at fixed initial monomer concentration. The authors use a microemulsion mechanism, in which monomer droplets are the main locus of polymerization, to explain these observations. The experimental conditions,[2] however, are closer to those of a conventional emulsion polymerization[3] and the observations can be readily explained within the more appropriate framework of homogeneous coagulative nucleation theory, as described below. The likelihood of radical entry and subsequent propagation in monomer droplets depends on the total surface area of the droplets relative to the surface area of homogeneously nucleated particles, or, before many particles are present, on the relative rates of radical-droplet encounter and homogeneous nucleation. Surfactant-free emulsions have limited stability, and the droplet size of a stirred emulsion is typically large enough to rule out significant radical entry.[4] Finer emulsions in which droplet entry is dominant—"miniemulsions" or "microemulsions"—require the use of a surfactant or an anionic emulsifier−fatty alcohol combination[5] for stabilization.

In a conventional styrene emulsion polymerization with persulfate initiator, charged radicals are generated in the aqueous phase and react with water-solubilized monomer molecules to form oligomeric radicals. As propagation continues, the radicals become insoluble and precipitate to form precursor particles. These precursor particles are colloidally unstable and coagulate to produce stable particles. Polymerization continues in these stable particles, which are kept swollen with monomer. The coagulation process removes small particles from the system and results in particle size distributions with positive skewness, as observed for the dispersions produced by Zhang et al.

In a surfactant-free system, stabilization is purely electrostatic and depends on two parameters: the surface charge density of the particles and the ionic strength of the aqueous medium. The initiator acts as a source of surface charge and ionic strength and thus has both stabilizing and destabilizing effects. Small precursor particles are unstable to coagulation because of their low surface charge density and high surface-to-volume ratio.

Coagulation of precursors occurs rapidly until the resulting aggregates attain the minimum surface charge density and radius R for electrostatic stability. The functional variation of the minimum stable radius R with initiator concentration I can be deduced by considering the following simple model for coagulation. The critical coagulation concentration $C(R,I)$ is the concentration of ions in the aqueous medium required to induce rapid coagulation, so if C increases above the initiator concentration then rapid coagulation will cease. Assume coagulation occurs via the aggregation of identical spherical precursors, each having identical surface charge, and that the charge from the precursors spreads evenly over the surface of the resulting spherical particle. A particle made up of N_p precursors therefore has radius

$$R \propto N_p^{1/3} \tag{i}$$

and surface charge density

$$\sigma \propto N_p/R^2 \propto R \tag{ii}$$

The Debye layer thickness κ^{-1} depends on the initiator/ion concentration I via

$$\kappa \propto I^{1/2} \tag{iii}$$

An approximation for the (weak) surface potential $\psi(R)$ of the particle is,[6] using (ii) and (iii),

$$\psi(R) \propto \sigma/\kappa \propto R/I^{1/2} \tag{iv}$$

For such weak potentials the critical coagulation concentration varies as[6]

$$C \propto \psi^4(R) \tag{v}$$

and setting the initiator concentration to be the critical coagulation concentration gives the minimum stable particle radius:

$$R \propto I^{3/4} \tag{vi}$$

The minimum size for stability against coagulation therefore increases with the initiator concentration. Equivalently, initiator destabilizes, and more identical precursor particles are required to produce one stable particle. Increasing the initiator concentration while keeping the initial monomer concentration constant will result in fewer (but larger) stable particles at the conclusion of the particle nucleation stage. A lower particle number means a correspondingly larger final particle size, in agreement with the experimental observations of Whang et al.

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If the initiator concentration is kept constant, then the number of stable particles produced during the coagulation process is constant. Under these conditions, a higher monomer concentration allows for a longer particle-growth period and leads to larger final particle size.

In conclusion, a mechanism of homogeneous nucleation followed by coagulation of unstable precursors is sufficient to explain increases in particle size with initiator and monomer concentrations in a surfactant-free system. It must be noted that the simple argument given here ignores coagulation between differently sized particles[7] and assumes low surface potentials. The latter assumption is, however, reasonable for very small precursor particles.[3]

References and Notes

(1) Zhang, W.; Gao, J.; Chi Wu, C. *Macromolecules* **1997**, *30*, 6388−6390.

(2) A reaction flask containing 250 mL of a styrene/water mixture (5.44×10^{-4}−3.04×10^{-2} g/mL monomer) was stirred at 300 rpm for 10 min at 70 °C before addition of initiator.

(3) Goodwin, J. W.; Ottewill, R. H.; Pelton, R.; Vianello, G.; Yates, D. E. *Br. Polym. J.* **1978**, *10*, 173−180.

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(7) Feeney, P. J.; Napper, D. H.; Gilbert, R. G. *Macromolecules* **1987**, *20*, 2922−2930.

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