

Basics of Creating Latex Particles with Controlled Size and Chemistry

Session 1

- Course introduction and overview
- Course objectives and expectations of participants
- Basic chemical mechanisms and modes of reaction for emulsion polymers
 1. Free radical polymerization reactions
 2. Polymer chain characteristics, radius of gyration, entanglements
 3. Chain structure – linear, branched, grafted, crosslinked
 4. Reaction rates in free radical polymerization
 - Homopolymerization – free radical and monomer concentrations, influence of temperature and viscosity
 - Copolymerization – reactivity ratios, cross-termination, copolymer composition control, chain transfer to polymer reactions
 5. Molecular weight control
 - Chain growth and stopping events, number average chain length
 - Molecular weight distributions, most probable distribution, dependence on monomer and radical concentrations, chain transfer agent
 6. Modes of reaction
 - Batch reactions – time dependencies, reaction rates
 - Semi-batch reactions – monomer feeding profiles, control of monomer concentrations, copolymer composition control, temperature variations, residual monomers

Session 2

- **Creating polymer particles in emulsion polymerization**
 1. Chemical and physical mechanisms involved in batch reactions
 2. Physical chemistry of surfactant micelles
 3. Initiation of radicals in water phase, z-mer concept, radical entry
 4. 3-time intervals of reaction, distinctive boundaries between intervals
 5. Homogeneous nucleation of particles (without micelles)
 6. Particle size control
 - *Ab initio*
 - Growth from seed
 - Control of particle size distribution
- **Details for rates of reaction during emulsion polymerization**
 1. Smith-Ewart approach – quantitative – difference equations
 - Cases for $\bar{n} = 1/2$ --- instantaneous termination in latex particles
 - Cases for $\bar{n} < 1/2$ --- radical exit
 - Cases for $\bar{n} > 1/2$ --- diffusion controlled termination, pseudo bulk
 2. Batch reaction rates vs. time of reaction (conversion), Intervals I, II and III
 3. Semi-batch processing alternatives
 - Why use semi-batch?
 - Effect on [M] and on polymer viscosity in particles
 - a) How far can radicals penetrate into particles?
 - b) How do polymer particles grow? Accretion? Monomer swelling?
 - c) Effect of polymer T_g and [M] on reaction rates; diffusion controlled termination, chain transfer to polymer in acrylates
 - d) Residual monomer

4. Initiator systems

- Thermal dissociation
 - a) Water phase initiation, oil phase initiation
 - b) Initiator end groups, especially for water phase initiation
 - c) Dead end polymerization, feeding initiator during process
- Redox systems
 - a) Commonly used oxidant/reductant pairs
 - b) Reactivity of oxygen vs. carbon centered radicals
 - c) Initiator efficiencies (oil phase, water phase)
- Methods of addition – distinguish between addition during polymerization process and during the finishing operation (to remove residual monomer)

Session 3

- **Details for latex particle size control**
 1. *Ab initio* processes in batch process
 - Micellar mechanism
 - CMC values; temperature and ionic strength effects
 - Interval I in Harkins mechanism of particle formation
 - a) Time and conversion duration of this interval
 - b) Possible size difference between youngest and oldest particles
 - Intervals II and III in Harkins mechanism
 - a) Particle growth during interval II; monomer concentration in particles
 - b) Interval III (no growth); finishing the polymerization
 - Colloidal stability during Intervals I and II
 - a) Controlling surfactant coverage
 - b) Consequences of too much surfactant (secondary nucleation)

- c) Consequences of too little surfactant during growth interval – coagulation

2. Seeded latex particle growth

- Size of seed vs. final, desired size, stage ratio
- Residual surfactant and initiator in seed latex – possible need for extra
- Monomer feed alternatives
 - a) Batch process; [M] in particles at start of seeded reaction
 - b) Semi-batch; *starved* and flooded conditions
 - c) Power feeds for some copolymer systems
 - d) Reaction rates during semi-batch operations
- **Details for molecular weight control**
 1. Kinetic chain length, $\langle X_N \rangle$; special considerations for emulsion polymerization
 - Radical entry rate
 - Chain termination in particles; long-short termination
 - Chain transfer to monomer effects (only in batch reactions)
 - Chain transfer to external agents
 - a) Solubility in water issues
 - b) Transport to latex particles
 - c) Chain transfer constants

Session 4

- **Details for molecular weight control, continued**
 2. Molecular weight distributions (MWD)
 - Linear chains; changing conditions of [M] and radical entry rates
 - Branching reactions; chain transfer to polymer, addition of divinyl monomers
 - Crosslinking reactions; natural/inherent as in acrylates and dienes; with added divinyl monomers
- **Details for copolymer composition control**
 1. Batch reactions
 2. Semi-batch reactions
- **Introduction to colloidal stability**
 1. Electrostatic stability mechanism; temperature and ionic strength issues
 2. Steric stability; entropy considerations, non-ionic stabilizers
- **Review of important lessons learned and conclusion of workshop**