

## ***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**