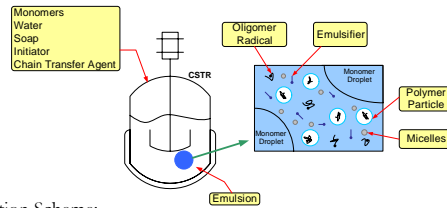


Modeling and Optimization of Emulsion Copolymerization

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Emulsion polymerization process is :

- An important process for manufacturing water based polymers. It is a free radical polymerization carried out under heterogeneous conditions and it is common process for latex production
- Very interesting industrial applications (SBR rubber, latex paints & adhesives, PVC "paste" polymers, coatings):
 - ✓ Low dispersion viscosity compared to bulk polymerization:
 - ✓ Good heat transfer and easy control of the process
 - ✓ High polymerization rate and high molecular weights
 - ✓ Direct application of latex
 - ✓ High separation costs , waste water problems, emulsifier as impurity of product
- Main components in emulsion copolymerization :
 1. Monomers, slightly soluble in water
 2. The dispersion medium (water)
 3. Water soluble Initiator(persulfates) and Emulsifier (sodium dodecyl sulfate)
- Some systems are: styrene/butadiene, styrene/acrylonitrile, Ethylene/vinyl acetate, methyl methacrylate/st., acrylonitrile/butadiene, Butyl acrylate/MMA/VAc



Reaction Scheme:

| Mechanism | Kinetics |
|---|--|
| Initiation: Thermal | $S_2O_8^{2-} \xrightarrow{k_d} 2SO_4^{\cdot-}$ |
| Redox | $SO_4^{\cdot-} + M_i \xrightarrow{k_{si}} R_{i,j}^{\cdot}$ |
| | $S_2O_8^{2-} + Fe^{2+} \xrightarrow{k_i} SO_4^{\cdot-} + Fe^{3+} + SO_4^{2-}$ $Fe^{2+} + RA \xrightarrow{k_2} Fe^{3+} + RA^{\cdot}$ $SO_4^{\cdot-} + M_i \xrightarrow{k_{si}} R_{i,j}^{\cdot}$ |
| Propagation | $R_{n,i}^{\cdot} + M_j \xrightarrow{k_{pij}} R_{n+1,j}^{\cdot}$ |
| Chain Transfer To Monomers | $R_{n,i}^{\cdot} + M_j \xrightarrow{k_{pmj}} P_{n,i} + R_{m,j}^{\cdot}$ |
| Chain Transfer To Polymer | $R_{n,i}^{\cdot} + P_{m,j} \xrightarrow{k_{pjm}} P_{n,i} + R_{m,j}^{\cdot}$ |
| Chain Transfer To CTA | $R_{n,i}^{\cdot} + T \xrightarrow{k_{stw}} P_{n,i} + T^{\cdot}$ |
| Termination: Combination | $R_{n,i}^{\cdot} + R_{m,j}^{\cdot} \xrightarrow{k_{tm}} P_{n+m}$ |
| Disproportionation | $R_{n,i}^{\cdot} + R_{m,j}^{\cdot} \xrightarrow{k_{td}} P_n + P_m$ |
| Chain Transfer to Inhibitor | $R_{n,i}^{\cdot} + MSI \xrightarrow{k_{msi}} P_{n,i} + MSI^{\cdot}$ |
| Internal and Terminal double bond reactions | $R_{n,i}^{\cdot} + P_m \xrightarrow{k_{ipm}} R_{m+n,i}^{\cdot}$ |
| | $R_{n,i}^{\cdot} + P_m \xrightarrow{k_{tpm}} R_{m+n,i}^{\cdot}$ |

Mass transfer events:

| Mechanism | Kinetics |
|------------------------|--|
| Micellar Nucleation | $R_i^{\cdot} + micelle \xrightarrow{k_m} Particle$ |
| Homogeneous Nucleation | $R_{i,j}^{\cdot} + M \xrightarrow{k_h} new\ Particle$ |
| Absorption of Radicals | $R_{j(aq)}^{\cdot} \xrightarrow{k_{aw}} R_{j(par.)}^{\cdot}$ |
| Desorption of Radicals | $R_{j(par.)}^{\cdot} \xrightarrow{k_{sw}} R_{j(aq)}^{\cdot}$ |

Development of Emulsion Polymerization Simulation Model :

- The goal is to develop a practical tool to predict polymer production rate and product quality. The procedure is:
 - ✓ Apply material and energy balances to determine polymerization rate, monomer conversion, temperature in the reactor
 - ✓ Apply particle population balances to determine polymer properties such as, polymer composition, the number and weight average molecular weights, the number and average size of the polymer latex particles, and branches frequency
 - ✓ The final model consists of a set of ode's describing the evolution of $x(t)$, $I(t)$, $S_p(t)$, $V_p(t)$ (material balances); of $N_p(t)$, $D_p(t)$, $A_p(t)$, $V_p(t)$ (Particle size balance); and of $\lambda_0, \lambda_1, \lambda_2$ and $B_N(t)$ and μ_0, μ_1, μ_2 molecular weight part
- The model should include the elements:
 - ✓ Molar balances for initiator, monomers and emulsifier
 - ✓ Molar balances for live radicals ,including application of population balance to determine the total moments of Live Radicals
 - ✓ Molar balances for Dead polymer, including application of population balance to determine the total moments of dead polymer
 - ✓ Population balance to describe the evolution of the PSD of the latex and the MWD of the polymer based on an age distribution analysis
 - ✓ Molar balances for SCB and LCB (Branching points)
 - ✓ An energy balance for the reaction mixture
 - ✓ In the case of copolymers , **pseudo-rate constants** are defined to account for the contribution of each monomer to the overall rate of reaction:

$$\phi_A = \frac{k_{pBA} f_A}{k_{pBA} f_A + k_{pAB} f_B}, \quad \phi_B = 1 - \phi_A; \quad f_A = \frac{[M_A]_p}{[M_A]_p + [M_B]_p}, \quad f_B = 1 - f_A$$

$$k_p = \phi_A (k_{pAA} f_A + k_{pAB} f_B) + \phi_B (k_{pBA} f_A + k_{pBB} f_B)$$

$$k_{fm} = \phi_A (k_{fAA} f_A + k_{fAB} f_B) + \phi_B (k_{fBA} f_A + k_{fBB} f_B)$$

$$k_{fca} = \phi_A k_{fcaA} + \phi_B k_{fcaB}$$

$$k_{fp} = \phi_A (k_{fpaA} \bar{F}_A + k_{fpaB} \bar{F}_B) + \phi_B (k_{fpbA} \bar{F}_A + k_{fpbB} \bar{F}_B)$$

$$k_p^* = \phi_A (k_{pAA}^* \bar{F}_A + k_{pAB}^* \bar{F}_B) + \phi_B (k_{pBA}^* \bar{F}_A + k_{pBB}^* \bar{F}_B)$$

➤ Population Balance Approach :

- ✓ In emulsion polymerization systems, accounting for the change in number of droplets or particles of a given size range is required. This is an example of population balances.
- ✓ A population balance is defined as a balance on a specified set of countable or identifiable entities that accounts for the net accumulation of such entities.
- ✓ The birth time of the polymer particles, τ is set to phase coordinate. $n(t, \tau)$ shows the class of particles in the reactor at time t , which were born in time τ . The number density of particles in the phase space, $n(t, \tau) d\tau$ is the class of particles in the reactor at time t which were born between times τ and $\tau + d\tau$.
- ✓ Any physical property, $p(t, \tau)$ of polymer particles (e.g. average diameter or area of a particle) is calculated by summing up the $p(t, \tau)$ over all classes of particles in the reactor.

$$P(t) = \int p(t, \tau) n(t, \tau) d\tau$$

- ✓ Differentiating the above equation with respect to time and using Leibnitz,s rule one can obtain the evolution of $P(t)$ with time.

➤ Polymer Reaction Equations:

✓ Reactants Molar Balances:

$$\frac{d[M(t)]}{dt} = \frac{[M(t)]_F}{\theta} - \frac{[M(t)]}{\theta} - R_p(t)$$

$$\frac{d[I(t)]_w}{dt} = \frac{[I(t)]_F}{\theta} - \frac{[I(t)]_w}{\theta} - K_d[I(t)]_w \quad (\text{Thermal Decomposition})$$

$$\frac{d[S(t)]}{dt} = \frac{[S(t)]_F}{\theta} - \frac{[S(t)]}{\theta}$$

✓ Moments of Distribution (Steady state hypothesis)

$$\frac{dV_p \mu_0}{dt} = \left(\tau + \beta / 2 - \frac{C_k \mu_1}{[M]_p} - \frac{K \mu_0}{[M]_p} \right) k_p [M]_p Y_0 V_p$$

$$\frac{dV_p \mu_1}{dt} = \left(1 + C_{fm} + \frac{C_{fca}[CTA]_p}{[M]_p} - \frac{C_{fmsi}[MSI]_p}{[M]_p} \right) k_p [M]_p Y_0 V_p$$

$$\frac{dV_p \mu_2}{dt} = \left(factor + 2 \left(1 + \frac{K \mu_1 + C_k \mu_2}{[M]_p} \right) \frac{bracket}{denom} + \beta \left(\frac{bracket}{denom} \right)^2 \right) k_p [M]_p Y_0 V_p$$

$$where: \quad \tau = \frac{k_d Y_0}{k_p [M]_p} + C_{fm} + \frac{C_{fca}[CTA]_p}{[M]_p} + \frac{C_{fmsi}[MSI]_p}{[M]_p}, \quad \beta = \frac{k_t Y_0}{k_p [M]_p}$$

$$factor = 1 + C_{fm} + \frac{C_{fca}[CTA]_p}{[M]_p} + \frac{C_{fmsi}[MSI]_p}{[M]_p} \quad denom = \tau + \beta + \frac{C_{fp} \mu_1}{[M]_p}$$

$$bracket = 1 + C_{fm} + \frac{(C_{fp} + C_k) \mu_2}{[M]_p} + \frac{K \mu_1}{[M]_p} + \frac{C_{fca}[CTA]_p}{[M]_p} + \frac{C_{fmsi}[MSI]_p}{[M]_p}$$

$$\frac{dV_p \mu_0 B_{N3}}{dt} = k_p Y_0 V_p (C_{fp} \mu_1 + K \mu_0), \quad \frac{dV_p \mu_0 B_{N3}}{dt} = k_p Y_0 V_p C_k \mu_1$$

$$C_{fm} = k_{fm} / k_p, \quad C_{fca} = k_{fca} / k_p, \quad C_{fmsi} = k_{fmsi} / k_p, \quad C_{fp} = k_{fp} / k_p, \quad C_k = k_t^* / k_p, \quad K = k_p^* / k_p$$

$$\mu_i(t) = \sum_{i=1}^{\infty} r^i [P_i(t)] \quad Y_0 = \frac{\bar{n} N_p}{V_p N_A} \quad \bar{M}_w = \mu_2 / \mu_1 M_{weff} \quad \bar{M}_n = \mu_1 / \mu_0 M_{weff}$$

Optimization of Emulsion polymerization:

- The objectives in Emulsion polymerization usually are to optimize production rates and to control product quality variables, such as polymer size distribution (PSD), particle morphology, copolymer composition, molecular weights, long chain branching (LCB), crosslinking frequency and gel content

➤ Classification of control variables

- ✓ Initiator variables: number and type of Initiator, flow rate and concentration
- ✓ CTA variables: number and type of CTA, flow rate and concentration
- ✓ Emulsifier variables :number and type of Emulsifier, flow rate and concentration
- ✓ Reaction Temperature

➤ Mathematical formulation of optimization problem

- ✓ The objective function is formulated based on maximum production rate (monomer conversion) to obtain a polymer with desired molecular properties (M_{nd} , PD_d).

$$J = w_1 (y_{nd} - y_m)^2 + w_2 \left(\frac{M_{nd}}{M_{nd}} - 1 \right)^2 + w_3 \left(\frac{PD_d}{PD_d} - 1 \right)^2$$

- ✓ Numerical methods to optimize:

- Nelder-Mead Simplex Method: Local optimization
- Successive Quadratic programming: Local optimization
- Simulated Annealing (SA): Global Optimization

SA analogy with annealing process of metals :

- ✓ When molten metal is cooled, individual atoms rearrange themselves into a regular array corresponding to a minimum energy to form a crystalline structure.
- ✓ At a given temperature, there is a probability of energy leap from E_1 to higher level E_2 , the probability is expressed by Boltzman formula: $p = \exp\left(-\frac{E_2 - E_1}{kT}\right)$

- ✓ In optimization, the objective function is analogized to the energy of the system.

- ✓ Artificial temperature $\beta = -\frac{1}{kT}$ is used, which is related to Boltzman Probability distribution.

- ✓ SA is a heuristic method characterized by random walk , objective is analogized with energy of system : $\Delta f = f_2 - f_1$

- ✓ Directions that increase the value of the objective are sometimes permitted to escape local optimum

| Step accepted $X = X_{new}$ | $f_2 < f_1$ | $f_2 > f_1$ |
|--------------------------------|---|---|
| | $p' = \text{random number}$ | |
| $p = 1$ | $\exp(\beta \Delta f) > p'$ | $\exp(\beta \Delta f) < p'$ |
| | new state probabilistically accepted . $X = X_{new}$ | New state probabilistically rejected $X = X_{old}$ |