Emulsion Polymerization

◆ Description of Process

* Utility: Started during World War II for SBR. Now predominant process for VAc, CR, SBR, Acrylates,…etc.

Advantages:
1) Thermal and viscosity problems are less significant: colloidal state.
2) Latex can be used directly as adhesives, coatings, finishes,…etc.
3) Special kinetics: Unique process that can increase MW without lowering polymerization rate.

◆ Qualitative Picture

* Components and Their Locations.
* Composition of a SBR Recipe for Emulsion Polymerization of Styrene-Butadiene.

Normal radical polymerization:
\[ v = k_p [M]^2/2k_Rp \]
\[ = k_p [M]/2(fk_d k[I])^{1/2} \]

Typical Formulation (GR-S)

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrene</td>
<td>25 (wt%)</td>
</tr>
<tr>
<td>Butadiene</td>
<td>75</td>
</tr>
<tr>
<td>Water</td>
<td>180</td>
</tr>
<tr>
<td>Emulsifier (Dresinate 731)</td>
<td>5</td>
</tr>
<tr>
<td>N-Dodecyl mercaptan</td>
<td>0.5</td>
</tr>
<tr>
<td>NaOH</td>
<td>0.061</td>
</tr>
<tr>
<td>Cumene hydroperoxide</td>
<td>0.17</td>
</tr>
<tr>
<td>FeSO₄</td>
<td>0.017</td>
</tr>
<tr>
<td>Na₃P₂O₇·10 H₂O</td>
<td>1.5</td>
</tr>
<tr>
<td>Fructose</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Fructose

\[ \text{CH₃} \quad \text{CH₃} \quad \text{OOH} \quad \text{Fe}^{2⁺} \quad \text{CH₃} \quad \text{CH₃} \quad \text{C} \quad \text{O} \quad \text{O} \quad \text{CH₃} \quad \text{CH₃} \quad \text{+ OH}⁻ \quad \text{+ Fe}^{3⁺} \]
Critical Micelle Concentration (CMC): 0.001~0.1 mole/L (0.1~3 wt%) 
Transformation of a solution to the colloidal state as the surfactant conc. exceeds the CMC.

Minimized free energy, marked change in surface tension, conductivity, ion activity, viscosity,...etc.

Water solubility of monomers (determine the amount in micelle):

<table>
<thead>
<tr>
<th>Monomer</th>
<th>g/L</th>
<th>$\phi_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrene</td>
<td>0.07</td>
<td>0.6</td>
</tr>
<tr>
<td>Butadiene</td>
<td>0.8</td>
<td>0.5</td>
</tr>
<tr>
<td>Vinyl chloride</td>
<td>7</td>
<td>0.3</td>
</tr>
<tr>
<td>Methyl methacrylate (MMA)</td>
<td>16</td>
<td>0.71</td>
</tr>
<tr>
<td>Vinyl acetate (VAc)</td>
<td>25</td>
<td>0.85</td>
</tr>
</tbody>
</table>

$\phi_m$: volume fraction of monomer in particle

The amount of micellar monomer is 2-, 5-, and 40-fold larger than that in water for MMA, butadiene, and styrene, respectively. The largest portion of the monomer is dispersed as monomer droplet (>95%).
**Site of Polymerization**
Mainly in micelles due to their large number & surface area (> 2 orders) as compared to monomer droplets (> 95%).

**Particle nucleation:** depend on water solubility & surfactant concentration.
MMA (water solubility: 16 g/L) and Styrene (0.07 g/L): 99% by micellar nucleation when surfactant conc. is well above CMC.
Solubility in water is not important when surfactant conc. is well above CMC.

* Micellar particle nucleation (Heterogeneous particle nucleation)
  SM: well above CMC
  Entry of radicals from aqueous phase to the micelles.

* Homogeneous particle nucleation (VAc): below CMC
  Solution-polymerized radicals is insoluble & precipitate as particle.

* Coagulative nucleation: particle growth: coagulation of precursor particles (<CMC).

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* Progress of Polymerization: 3 intervals: based on N and monomer droplet.

Interval I: (Induction period; particle nucleation): $R_p$ and particle number $N$ increases with time: 2~15% conv. depending on water-solubility and $R_i$.

Intervals II: (Zero-order region) No particle generation, monomer conc. in polymer particle is constant. Ends when monomer droplets disappear. 15~80% depending on water-solubility and volume fraction of monomer ($\phi_m$) in particle.

Interval III: (First-order region) Monomer droplet disappear.

Transition from II to III: occurs at 70~80% conv. for monomer with low water solubility and low $\phi_m$ (VCI). But occurs at lower conv. for monomer with high water solubility and high $\phi_m$ (VAc: 15%, MMA: 25%, SM & BD: 40~50%).

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Quantitative Description

a) Rate of Polymerization

Interval I: $\sim 10^{21}$ micelles/l, $R_i = 10^{16}$ radicals/l-sec $\rightarrow$ 10$^6$ sec (27.8 hr)
Interval II: $\sim 10^{17}$ particles/l $\rightarrow$ 10 sec

$r_p = k_p[M]$ in each propagating particle.

$R_p = k_p[M][P.]$

where $[P.] = N'n/N_A$
$N'$: (No. of micelle + particle)/L
$n$: average no. of radical/ (micelle + particle)
$N_A$: Avogadro number

$* N'$ decreases and $n$ increases with time during interval I.

$R_p = N'nk_p[M]/N_A$

$= Nnk_p[M]/N_A$  $N$: $N'$ for steady-state (D)
n is important during Intervals II and III and depending on:
* desorption of radicals (radical diffusion out)
* Particle size
* Mode of termination
* Rate of initiation & termination

Case 1: \( n < 0.5 \) (VAc, VCl: ~0.1)
Radical desorption from particle and termination in the aqueous phase are not negligible.
* Small particle size
* High chain transfer to monomer
* Low initiation rate

Case 2: \( n = 0.5 \) (SM)
No desorption of radicals
* Particle size is too small to accommodate more than one radical.
* Termination rate constant is large.
* High initiation rate. \( (n= 0.5 \rightarrow 0.2 \text{ when } [I] \text{ decreases from } 10^{-2} \text{ to } 10^{-5} \text{ M}) \)

Case 3: \( n > 0.5 \)
Some particles contain \( \geq 2 \) radicals
* Particle size is large & high conversion
* Termination rate is low
EX. 0.7 \( \mu m \): \( n = 0.5 \rightarrow 0.6 \text{ at } 90\% \text{ conv.} \\
1.4 \( \mu m \): \( n = 0.5 \rightarrow 1.0 \text{ at } 80\% \text{ conv.} \& > 2.0 \text{ at } 90\% \\

Which factor determine \( N \)?
* Initiation rate: \( R_i \)
* Concentration of emulsifier: \( S \)

\[
N = k (R_i/\phi)^{2/5} (a_s S)^{3/5}
\]
\( \phi \): rate of volume increase of polymer particle
\( a_s \): interfacial surface area occupied by a emulsifier molecule
\( S \): total concentration of emulsifier
\( k: 0.37\sim0.53 \)
\( R_i \): initiation rate
\[ R_p = 10^3 N k_p [M] / N_A \]
\[ N = k (R/\phi)^{3/5} (a_s S)^{3/5} \]

\[ R_p \propto R_i^{2/5}, \quad R_p \propto S^{3/5} \]

**b) Degree of Polymerization**

The rate primary radicals enter a polymer particle: \( r_i = R_i/N \)

\[ X_n = r_p/r_i = N k_p [M]/R_i = \nu \]

\[ X_n \propto R_i^{-3/5}, \quad X_n \propto S^{3/5} \]

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**Fig. 4-3** Plot of percent conversion vs time for emulsion polymerizations of styrene with different concentrations of potassium laurate at 60°C. The moles of emulsifier per polymerization charge (containing 180 g H₂O, 100 g styrene, 0.5 g K₂CO₃) are 0.0035 (plot 1), 0.007 (plot 2), and 0.014 (plot 3). After Williams and Bobalek [1966] (by permission of Wiley-Interscience, New York).
\[ R_p \propto R_i^{2/5} \]

**Fig. 4-4** Plot of percent conversion versus time for emulsion polymerization of vinyl chloride at 50°C for monomer/water ratio of 26:74 and 0.883% surfactant. The initiator concentrations are 0.0012% (plot 1), 0.0057% (plot 2), and 0.023% (plot 3). After Vidotto et al. [1970] (by permission of Huthig and Wepf Verlag, Basel).

\[ X_n \propto S^{3/5} \]

**Fig. 4-5** Plot of viscosity-average molecular weight versus percent conversion for emulsion polymerizations of styrene with different concentrations of potassium laurate at 60°C. The moles of emulsifier per polymerization charge (containing 180 g H₂O, 100 g styrene, 0.5 g K₂S₂O₅) are 0.0035 (plot 1), 0.007 (plot 2), and 0.0014 (plot 3). After Williams and Bobulek [1966] (by permission of Wiley-Interscience, New York).
Other characteristics of Emulsion Polymerization
a) Initiators; b) Surfactants; c) Other Components
d) Propagation and Termination Rate Constants
e) Energetics (kraft point and cloud point)
f) Molecular Weight and Particle Size Distribution
g) Surfactant-free Emulsion Polymerization
h) Core-Shell Model; i) Inverse Emulsion Polymerization

Kraft point (ionic surfactant): also known as Kraft temperature; critical micelle temperature, the minimum temperature at which surfactant form micelles: The Kraft temperature is a point of phase change below which the surfactant remains in crystalline form, even in aqueous solution.

cloud point (non-ionic surfactant): the cloud point of a fluid is the temperature at which dissolved solids are no longer completely soluble, precipitating as a second phase giving the fluid a cloudy appearance.