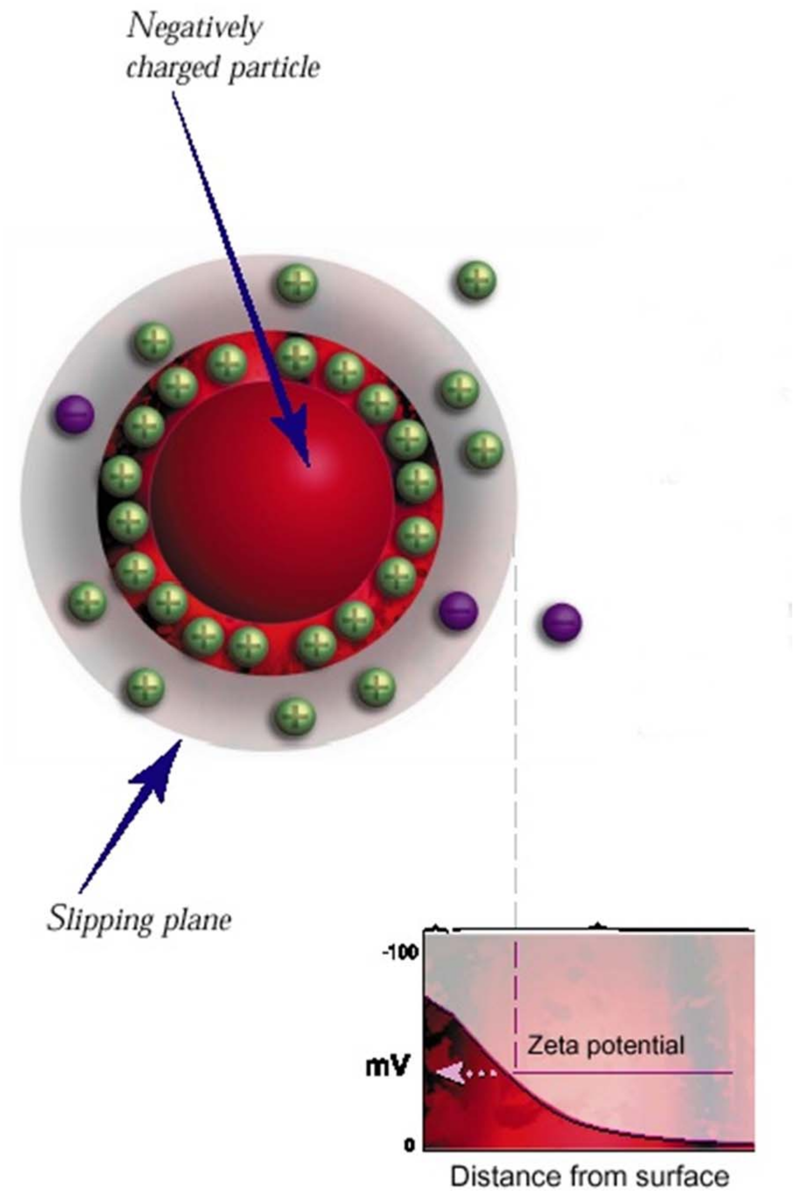
Nanosphere Process & Technology Laboratory

Polymer Colloid Science

Jung -Hyun Kim Ph. D.
Nanosphere Process & Technology Lab.
Department of Chemical Engineering, Yonsei University

National Research Laboratory Project
the financial support of the Korea Institute of S&T Evaluation
and Planning (KISTEP) made in the program year of 1999



Colloidal Aspects

♣ *What is a polymer colloids* ?

- Small polymer particles suspended in a continuous media (usually water)

- EXAMPLES
  - Latex paints
  - Natural plant fluids such as natural rubber latex
  - Water-based adhesives
  - Non-aqueous dispersions

- COLLOIDS
  - The world of forgotten dimensions
  - Larger than molecules but too small to be seen in an optical microscope

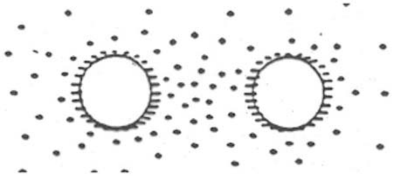
♣ *What does the term “stability/coagulation imply?*

- There is no change in the number of particles with time.
- A system is said to be colloidally unstable if collisions lead to the formation of aggregates; such a process is called coagulation or flocculation.

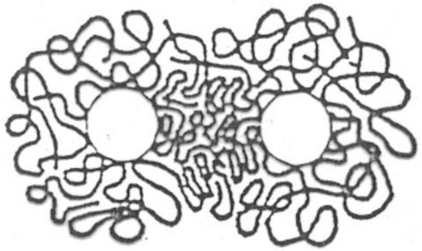
♣ *Two ways to prevent particles from forming aggregates with one another during their colliding*

1) Electrostatic stabilization by charged group on the particle surface
   - Origin of the charged group
     initiator fragment (COOH, OSO_3^-, NH_4, OH, etc)
     ionic surfactant (cationic or anionic)
     ionic co-monomer (AA, MAA, etc)

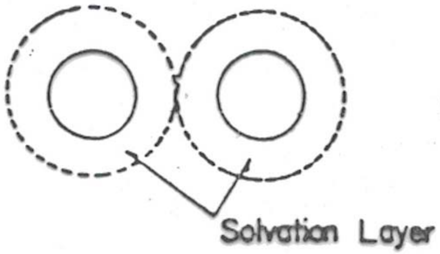
2) Steric stabilization by an adsorbed layer of some substance
3) Solvation stabilization



ELECTRIC DOUBLE LAYER



STERIC



SOLVATION

Stabilization Mechanism

■ Electrostatic stabilization

- Electrostatic stabilization

Balancing the charge on the particle surface by the charges on small ions of opposite sign in the solution phase (counter ions)

- Surface potential

$$\psi_r = \psi_s (a/r)\exp[(-x(r-a)]$$

$$x = (8\pi e^e n_A / 1000\varepsilon kT)I$$

$1/x$: Thickness of electrical double layer
ε : dielectric constant of the medium
I : Ionic strength

■ Steric stabilization

- Hairy particles with uncharged hairs extending into nonaqueous medium as noncharged polymer chain

■ Electrosteric stabilization

- Combination of electrostatic and steric stabilization by grafting to a polymer core particle polyelectrolyte chains

Forces Between Two Approaching Colloidal Particles

- London-van der Waals force or dispersion force
- Coulombic force associated with electrostatically charged particles
- Force arising from solvation, adsorbed layers, etc.

Electrostatic Stabilization

- **Electrical double layer**
  - Stern layer
  - Diffuse layer

- **Coulombic force**
  - Electrostatic repulsion force to be dependent on the overlap of diffuse double layer
  - Potential energy of electrostatic repulsion, VR to be obtained by integration of repulsion force with respect to distance

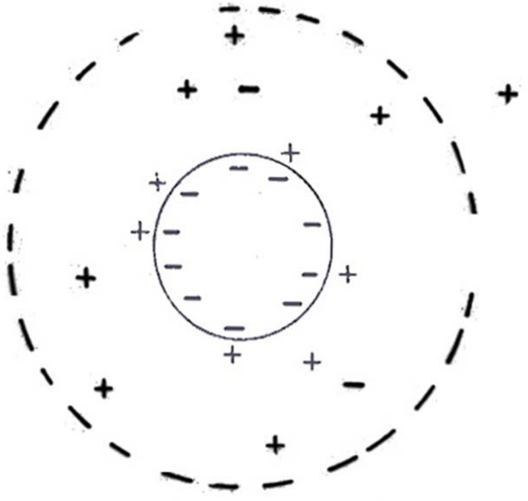


Figure. Schematic illustration of a negative charged spherical polymer latex particle with an electrical double layer.
---represents the range of influence of electrostatic forces.

- **London-van der Waals force**
  - Potential energy of attraction, VA to be obtained by integration of attraction force with respect to distance

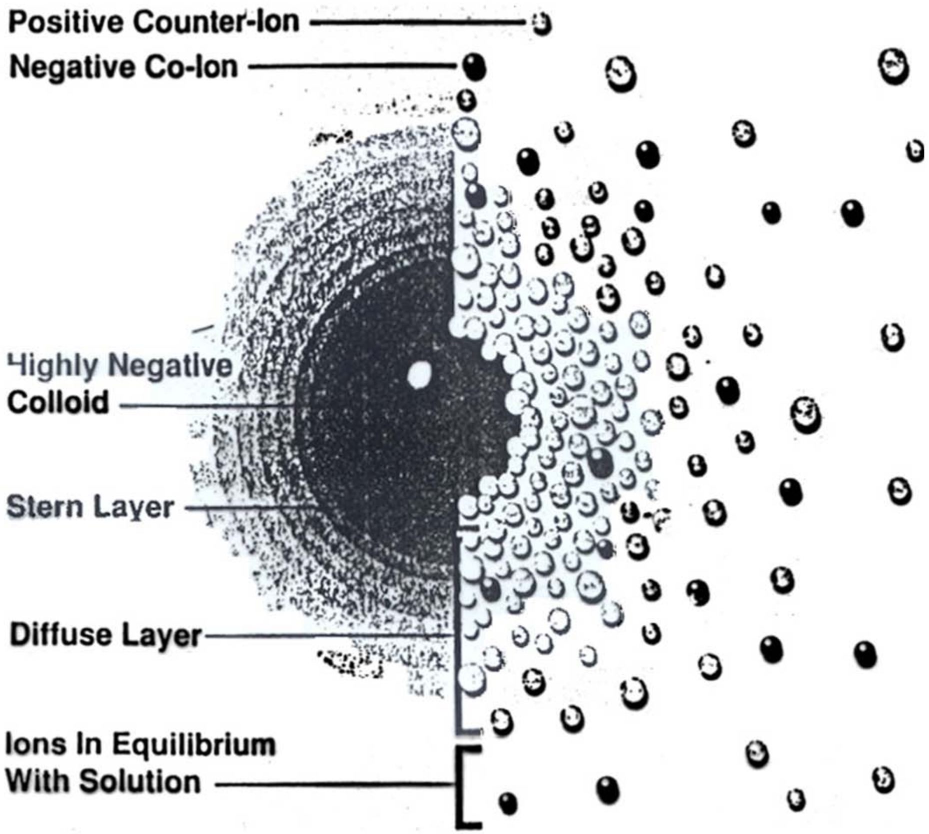


Figure 12. Simplified illustrations of the electrical double layer around a negatively charged colloidal emulsion droplet. The left view shows the change in charge density around the droplet. The right view shows the distribution of ions around the charged droplet. (Courtesy of L. A. Ravina, Zeta-Meter, Inc., Long Island City, NY.)

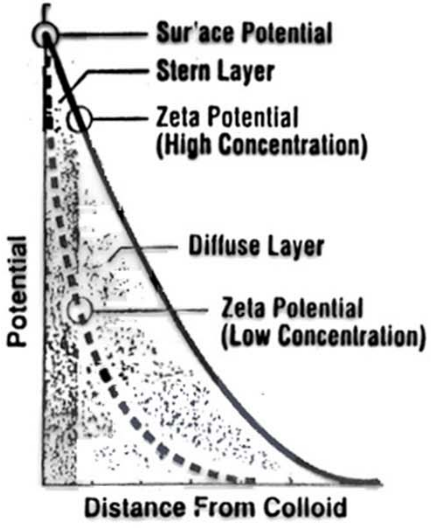


Figure 13. Simplified illustration of the surface and zeta potentials for a charged emulsion droplet dispersed in high and low electrolyte concentration aqueous solutions. (Courtesy of L. A. Ravina, Zeta-Meter, Inc., Long Island City, NY.)

Electrostatic Stabilization

■ DLVO theory

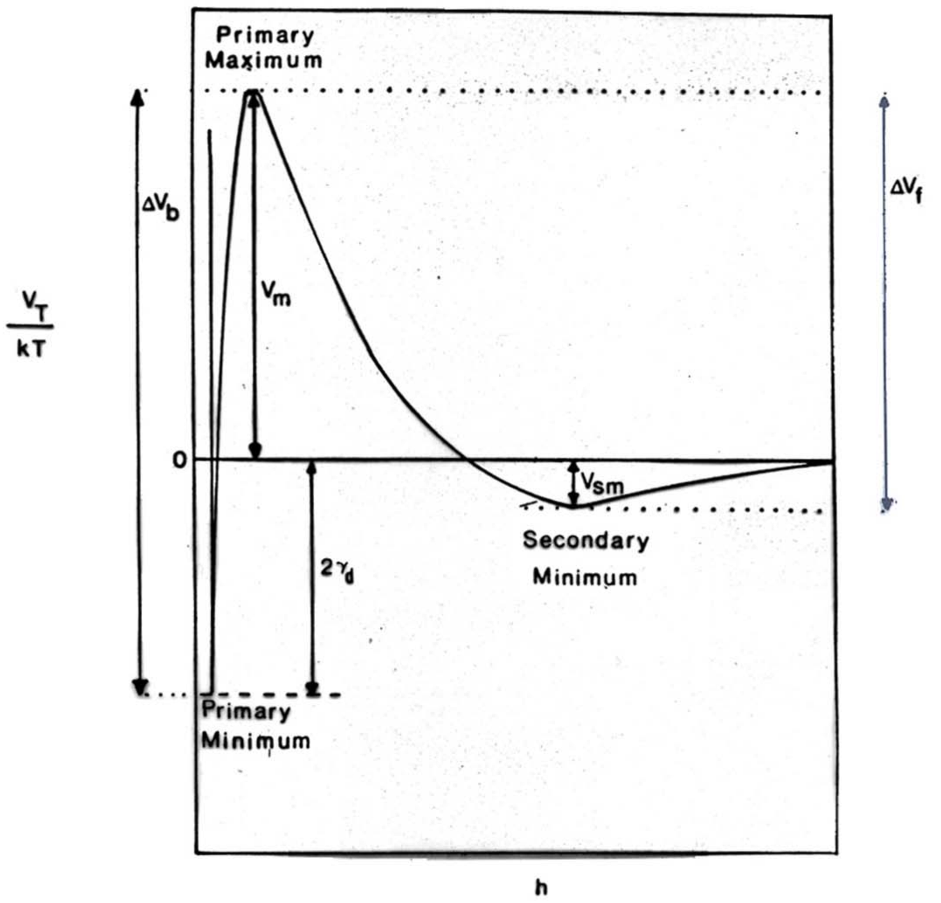
- Attraction decays as the inverse power of distance of separation.
- Repulsion decays as an exponential of distance.
- At both short and long distances of separation : ***Attraction > Repulsion***
- Critical coagulation concentration; a concentration at which the primary maximum becomes zero.

■ Advantages of electrostatic stabilization

- Providing stability in nonaqueous systems where electrical effects are week.
- Providing tolerance against high level of electrolyte
- Stabilizing much greater particle concentrations

■ Disadvantages of electrostatic stabilization

- Flocculation if coverage of particle is low



Schematic illustration of a potential energy against distance of surface separation curve to illustrate the main features used in discussing colloid stability. ΔV_f = energy barrier to coagulation; ΔV_b = energy barrier to peptization; γ_d = dispersion free energy of the polymer–water interface; V_m = height of the primary maximum; V_{SM} = depth of the secondary minimum.

■ DLVO theory

- Derjaguin and Landau(1941) and Verwey and Overbeek(1948)
- Total potential energy of interaction

$$V_T = V_R + V_A$$

- Potential energy of electrostatic repulsion

$$V_R = 3.469 \times 10^{19} \varepsilon (kT)^2 a \gamma^2 \exp(-\kappa h) / \nu^2$$

- Potential energy of the van der Waals attraction

$$V_A = -\frac{A}{12}\frac{1}{x^2+2x} + \frac{1}{x^2+2x+1} + 2\ln\left(\frac{x^2+2x}{x^2+2x+1}\right)$$

Steric Stabilization

- Polymer must be strongly adsorbe at particle surface but not so strong as to be collapsed.

- Polymer chains should extend as far as possible into solution
  - enhanced by solvent in which polymer is readily soluble.

- Most effective polymers are block copolymers; part strong acids and part weak acids.

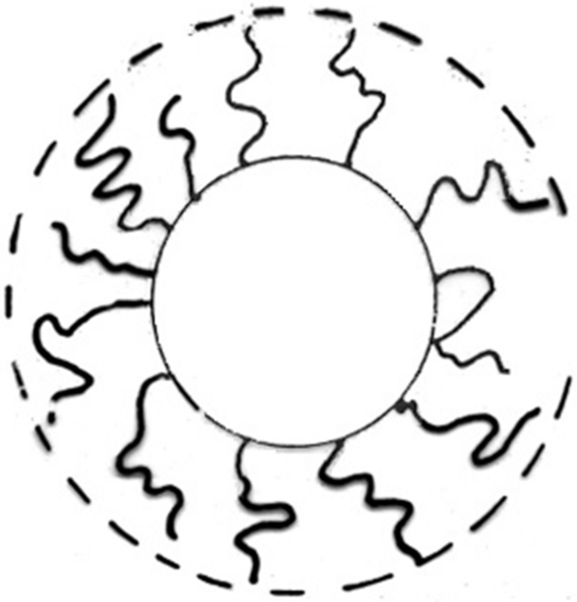


Figure. Schematic illustration of a noncharged polymer latex particle with adsorbed or grafted nonionic polymer chain.
---represents the range of influence of steric forces.

Comparison of the Properties of Electrically and Sterically Stabilized Dispersion

■ Electrostatic Stabilization

- Coagulates on addition of electrolyte
- Mainly effective in aqueous dispersion media
- Coagulation often irreversible
- Freezing often induces irreversible coagulation

■ Steric Stabilization

- Insensitive to electrolyte
- Equally effective in aqueous and non-aqueous dispersion media
- Equally effective at high and low volume concentration
- Reversible flocculation common
- Good freeze-thaw stability

Synthetic Methods of Polymer Colloids

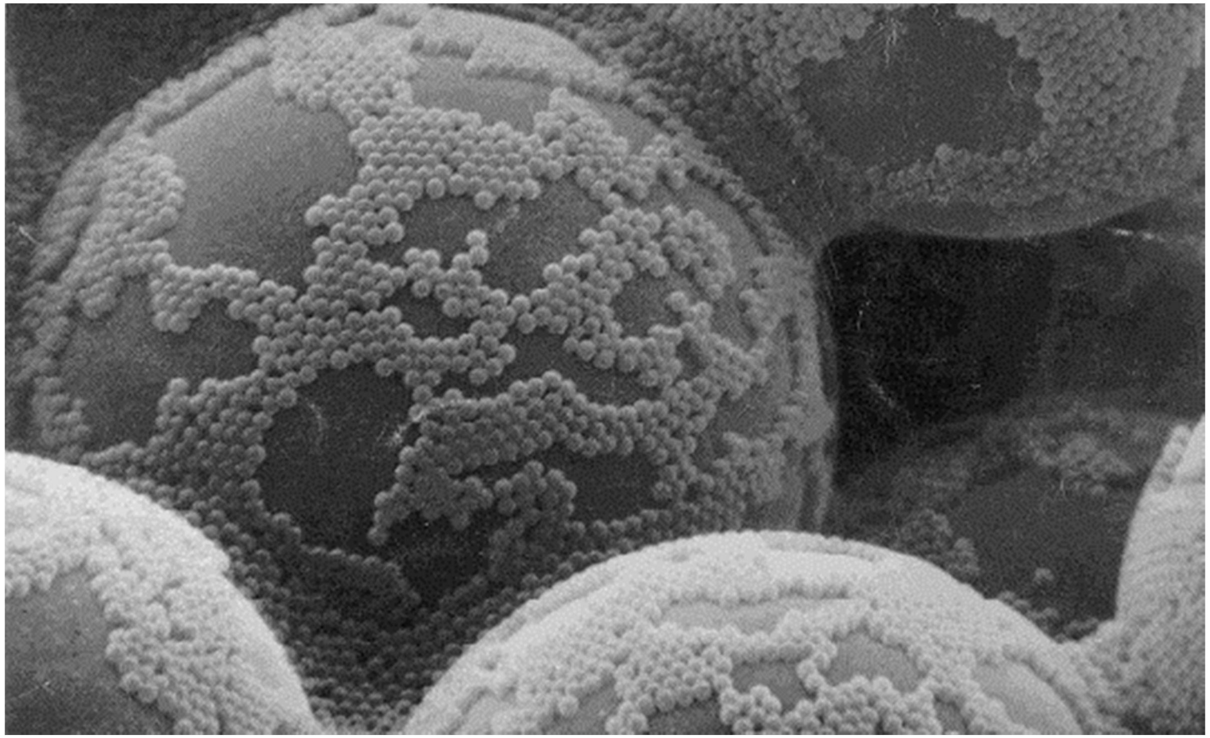


Table. The differential types of heterogeneous polymerization systems

Type	Typical Particle Radius	Droplet size	Initiator	Continuous Phase	Discrete phase (particles)
Emulsion	50 – 300 nm	≈ 1 – 10 μm	water or oil soluble	Water	Initially absent, monomer-swollen polymer particles form
Dispersion	≥ 1μm	-	oil soluble	Organic (poor solvent for formed polymer)	Initially absent, monomer-swollen polymer particles form
Suspension	≥ 1 μm	≈ 1 – 10 μm	oil soluble	Water	Monomer + formes polymer in pre-existing droplets
Inverse Emulsion	$10^2 – 10^3$ nm	≈ 1 – 10 μm	water or oil soluble	oil	Monomer, cosurfactant + formed polymer
Microemulsion	10 – 30 nm	≈ 10 nm	water soluble	Water	Monomer cosurfactant + Formed polymer
Miniemulsion	30 – 100 nm	≈ 30 nm	water soluble	Water	Monomer, cosurfactant + formed polymer

Dispersion polymerization

■ Constitution

- Initiator : water or oil soluble
- Continuous phase : water, alcohol, solvent
- Discrete phase : initially absent, monomer -swollen polymer particles form
- Steric stabilizer

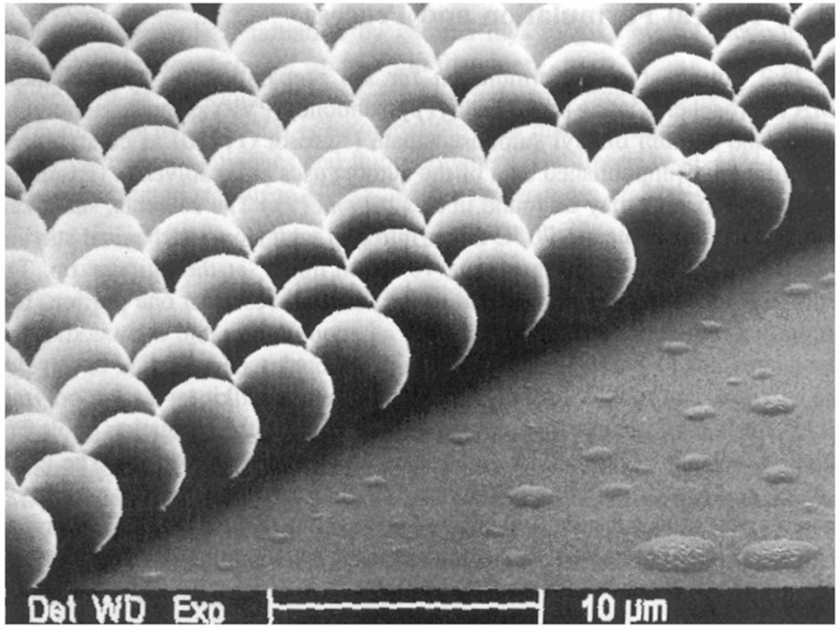


Figure 22.1 Scanning electron micrograph of polystyrene microspheres prepared by *dispersion polymerization.* (Photomicrograph courtesy of T. Groves/A. Rowley, Ilford Ltd)

■ Characteristics

- In the medium : monomer & initiator is soluble, polymer is precipitated
- Initiation : in the medium and inside the particles
- Occurrence of phase separation at an early stage : the formation of primary particles
- Particles are swollen by a mixture of the monomer and the medium
- Typical particle radius : more than 1 ㎛

Dispersion polymerization

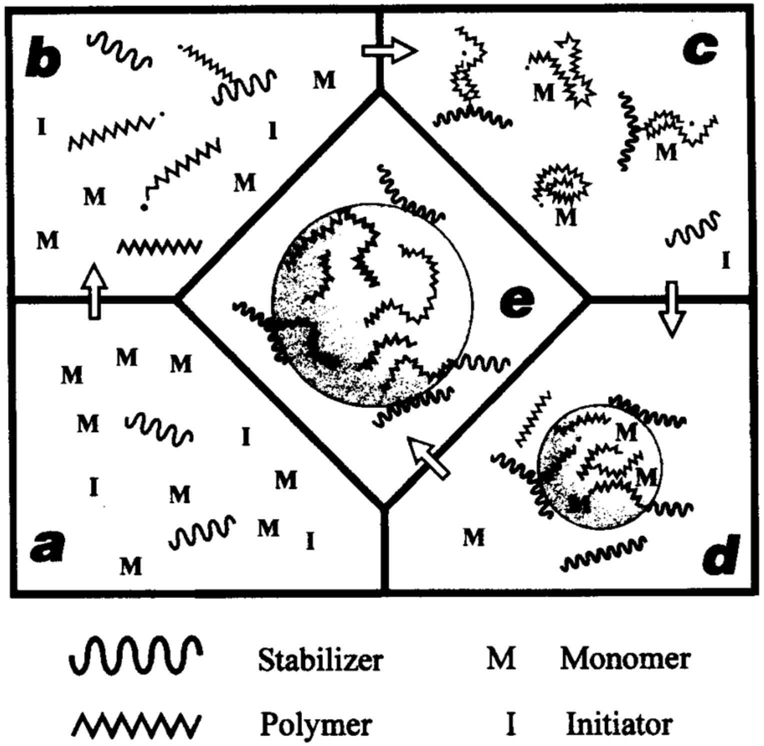


Figure Schematic of particle growth in dispersion polymerization. (a) Homogeneous solution of monomer, initiator and stabilizer. Initiator decomposes to give (b) oligomeric radicals which begin to precipitate once they reach the critical chain length, and grafting with the stabilizer begins. (c) Self-nucleation and aggregation of nascent polymer species. (d) Particle growth by monomer swelling and further polymerization within particles; stabilization via grafted and adsorbed stabilizer. (e) Continued growth may occur by accretion of dead polymer to give final particles

Suspension polymerization

■ O/W suspension polymerization

Discrete phase	monomer (oil-soluble) initiator (soluble in the monomer) chain transfer agent(oil-soluble)
Suspension medium	water

- Initiator & monomer : insoluble in the suspension medium
- The volume ratio of the monomer to water : 0.1-0.5
- Typical particle radius : > 1 ㎛
- Polymer particles obtained by suspension polymerization have a relatively broader size distribution

■ W/O suspension polymerization

- Inverse suspension polymerization
- The suspension medium : a water immiscible liquid (toluene, dichloroethane, etc)
- Monomer & initiator : soluble in water
- Diluent : water or highly polar organic liquid

Suspension polymerization

■ O/W suspension polymerization

– Constitution

Water : medium
Initiator : soluble in the monomer, insoluble in the medium
Monomer : insoluble in the medium
Stabilizer

- Controlling variables of particle size

Reactor and process type
Stirring rate
Monomer/water ratio
Nature and concentration of stabilizer
Rate of polymerization

- Diluted O/W suspension polymerization

Monomer is diluted with a water-immiscible liquid (diluent)

Suspension polymerization

■ Suspension process of poly(vinyl chloride)

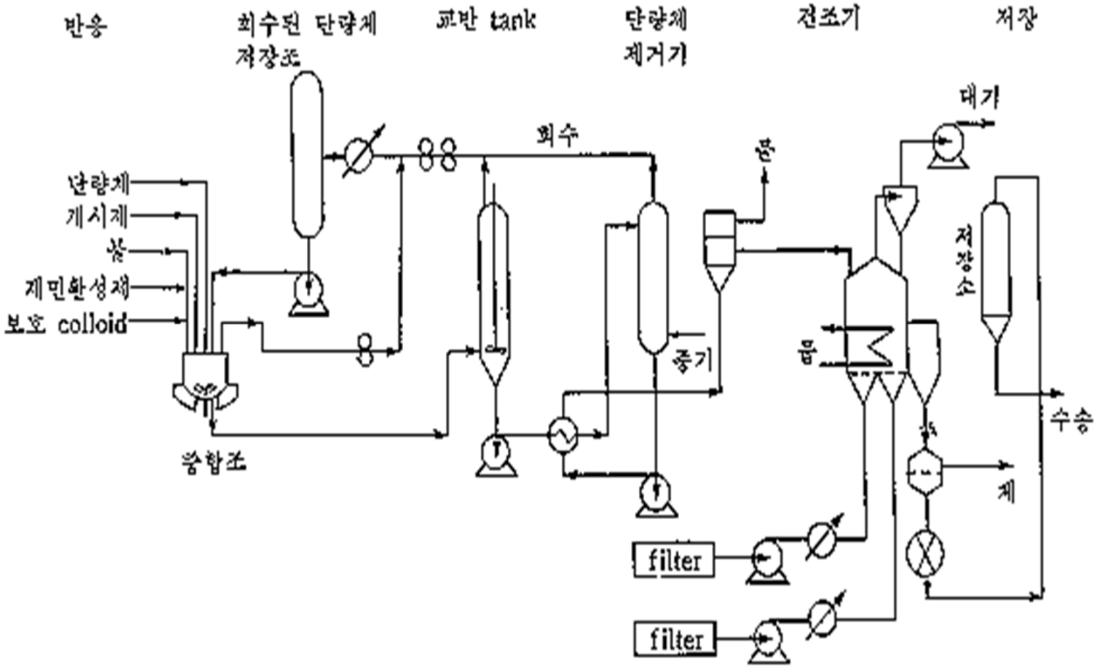


Fig. Schematic diagram of suspension polymerization of poly(vinyl chloride)

- **Components**

vinyl chloride	3500 (g)
water	5000 (g)
surfactant/stabilizer	0.7 (g)
poly(vinyl alcohol)	3.5 (g)
lauroyl peroxide	1.5 (g)

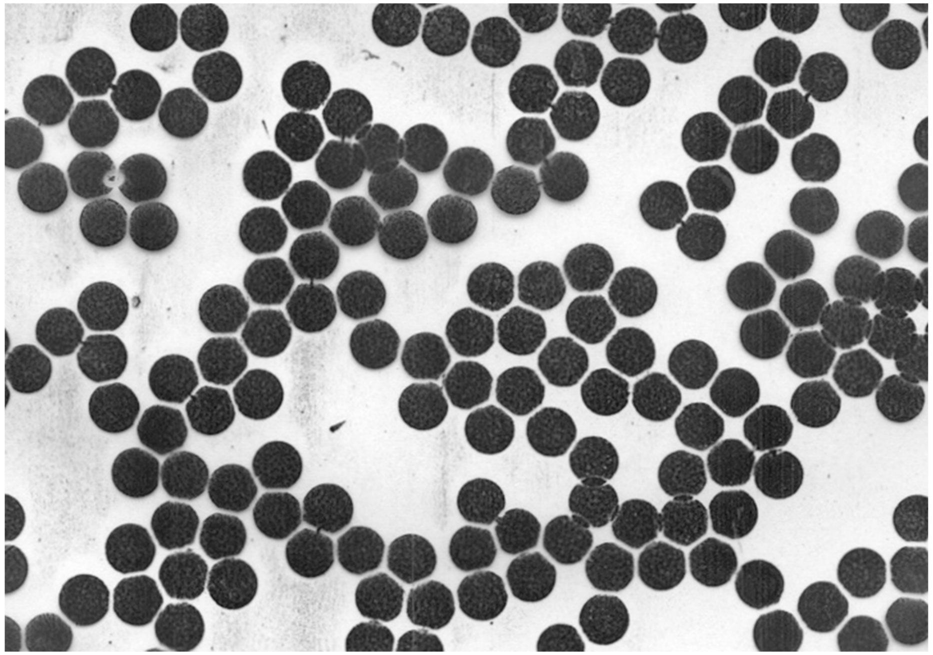
Emulsion polymerization

- **Production**

  Billions of metric tons/year

- **Advantage**

- High rate of polymerization
- High molecular weights
- Low viscosity
- Excellent heat transfer
- High conversions
- Continuous production possibility



Emulsion polymerization

- **Characteristics of emulsion polymerization**

A. Water-immiscible monomer emulsified in water using oil-in-water emulsifier and polymerized using a water-soluble or oil-soluble initiator

B. Product is a colloidal dispersion of submicroscopic polymer particles in water
: Average diameter usually 0.1-0.3 ㎛

C. Monomer emulsion droplet size : usually 1-10 ㎛

D. Proposed mechanism for initiation of polymerization

1. Monomer-swollen micelles
2. Adsorbed emulsifier layer
3. Aqueous phase
4. Monomer droplets

Emulsion polymerization

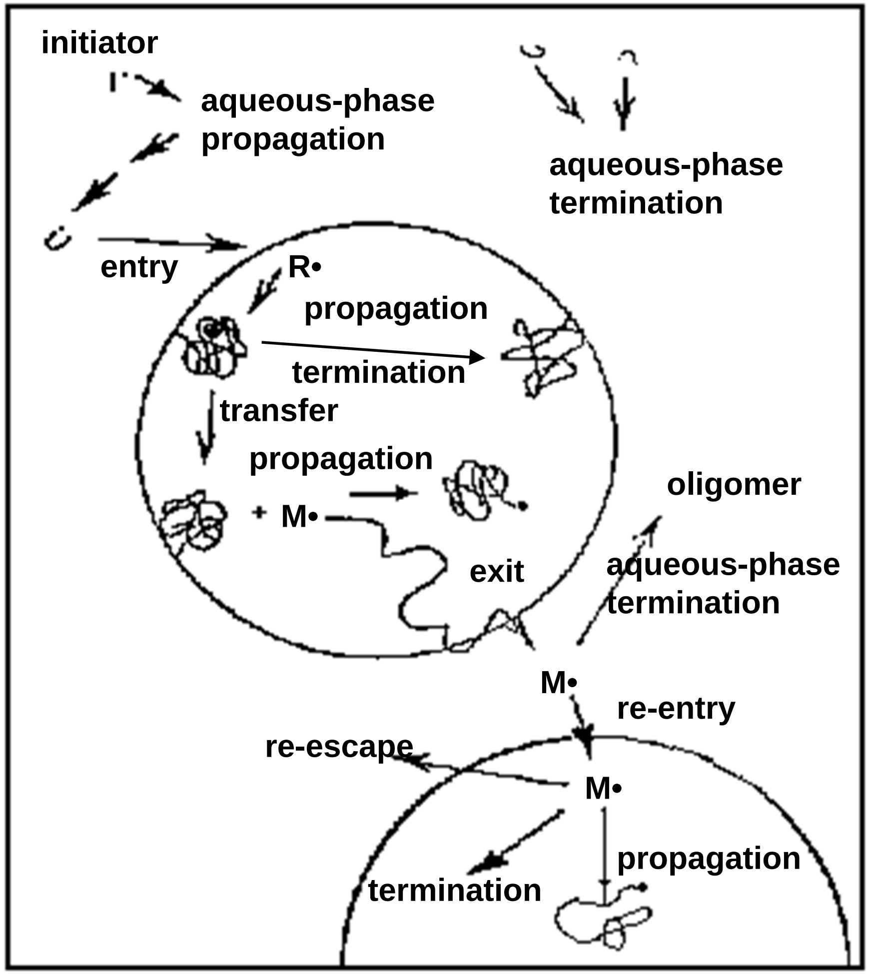


Fig. The various events that occur subsequent to initiator dissociation in an emulsion polymerization. Note particularly the aqueous-phase event : propagation and termination, both of radicals derived directly from initiator from initiator and of those arising from exit

▪ *Important considerations in emulsion polymerization*

1. Particle formations
- A. Emulsifier micelles
- B. Homogeneous nucleation
- C. Monomer droplets
- D. Flocculation of primary particles

2. Particle growth
- A. Internal polymerization
  - a. Small volume reactor
  - b. Gel-effect at high conversion
- B. Flocculation
  - a. Deposition of smaller particles
  - b. Flocculation among mature particles
- C. Shrinkage of particles at high conversions

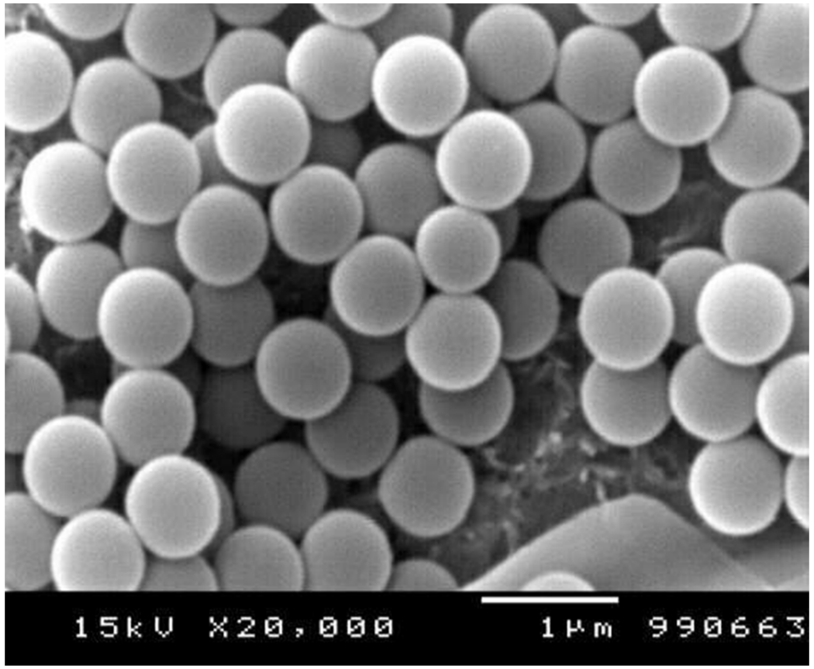
3. Particle stabilization
- A. Added emulsifier
- B. Effects of initiator end groups
- C. Functional monomers

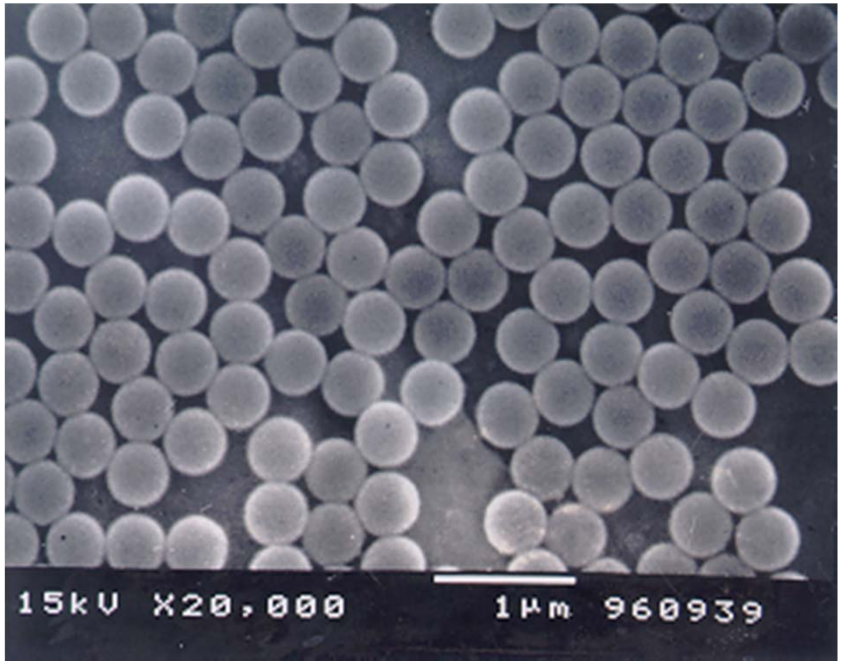
4. Particle morphology
- A. Uniform
- B. Core-shell
- C. Aggregate of smaller particles

5. Molecular properties
- A. Molecular composition
- B. Molecular weights
- C. Molecular architecture

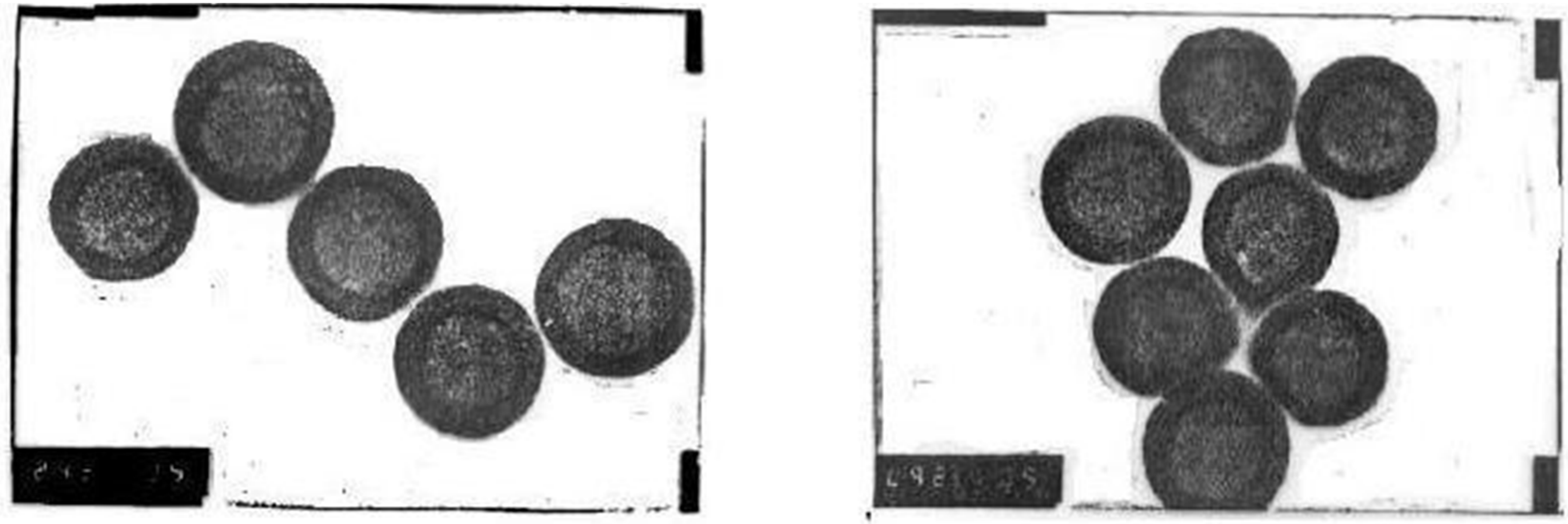
6. Transport and distribution of recipe ingredients
- A. Free radicals
- B. Emulsifier
- C. Monomer

○ Polymer Colloids





- **TEM micrograph of hollow particles**



Comparison between Conventional Emulsion Polymerization and Inverse Emulsion Polymerization

Conventional Emulsion Polymerization

- Water-immiscible monomer emulsified in water using oil-in-water emulsifier and polymerized using a water-soluble or oil-in-soluble initiator.
- Product is a colloidal dispersion of submicroscopic polymer particles in water : Average diameter usually 0.1~0.3 μm
- Monomer emulsion droplet size usually 1~10 μm.
- Proposed mechanism for initiation of polymerization
  1. Monomer-swollen micelles
  2. Adsorbed emulsifier layer
  3. Aqueous phase
  4. Monomer droplets

Inverse Emulsion Polymerization

- Water-soluble monomer, usually in aqueous solution, emulsified in continuous oil phase using water-in-oil emulsifier and polymerized using an oil-soluble or water-soluble initiator.
- A Product is a colloidal dispersion of submicroscopic polymer particles, often swollen with water-in-oil : Average diameter usually 0.05~0.31 μm

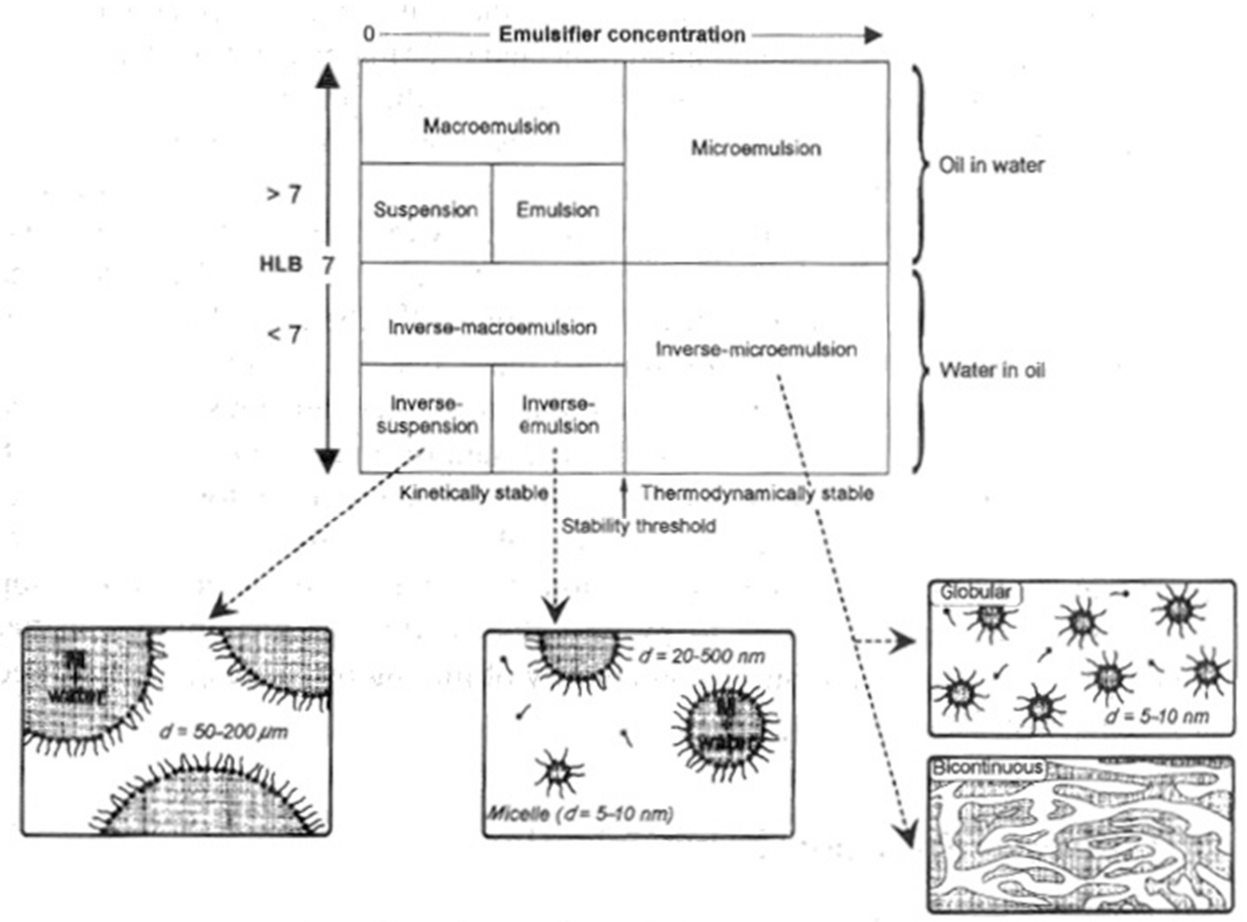
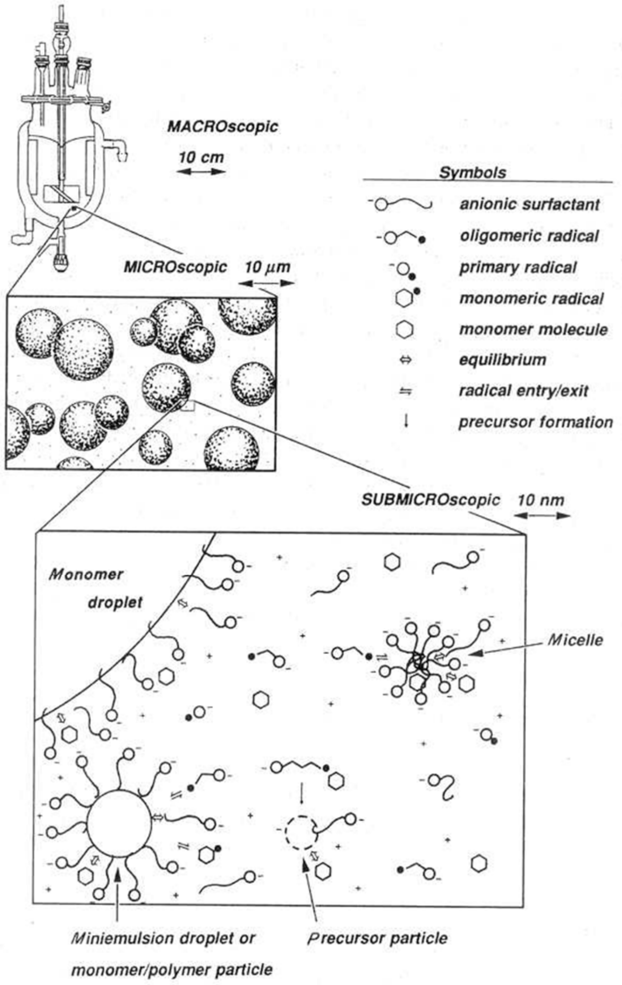


Figure Heterophase polymerization domains as a function of the HLB of the emulsifier and its concentration

▪ Miniemulsion polymerization

- Monomer droplet :
  - 100-500 nm
  - Similar to latex particle size
  - Significant loci for nucleation and polymerization

- Additive (fatty alcohol or alkane) :
  - To stabilize emulsion
  - To decrease the droplet size
  - To increase amount of adsorbed emulsifier
  - No relationship with kinetics

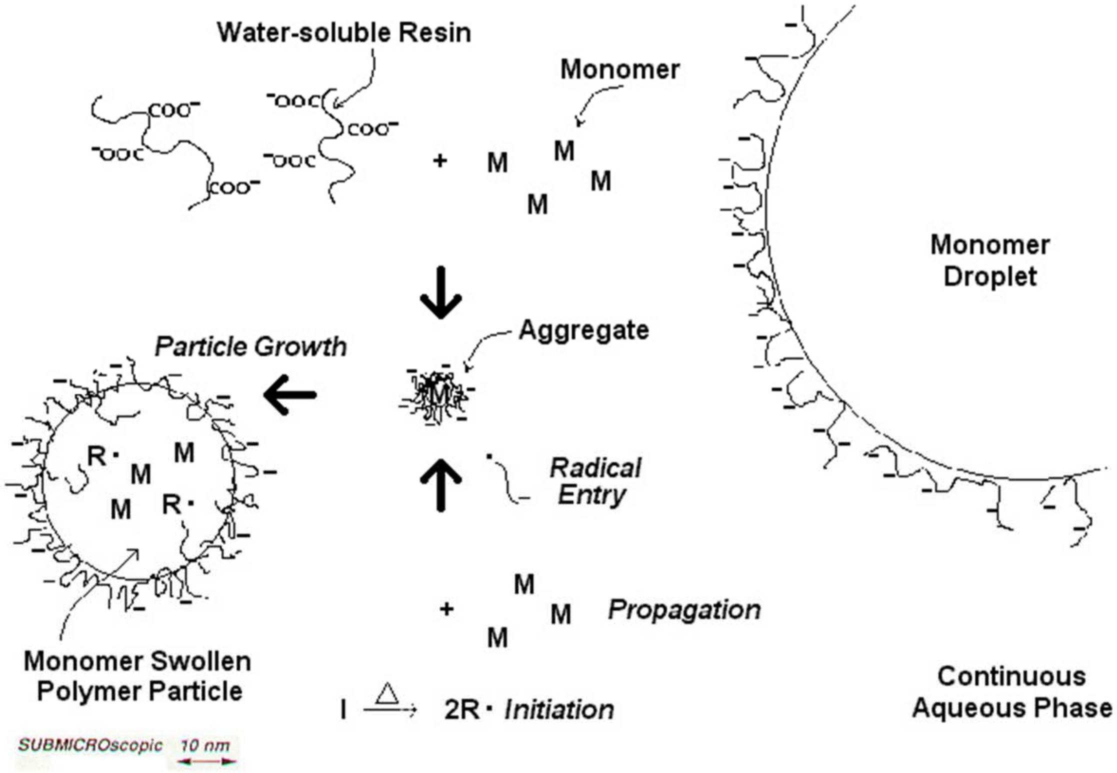


Schematic representation of the early stages of emulsion polymerization illustrating three scales of observation: macroscopic, microscopic and submicroscopic. (Reprinted with permission from E. D. Sudol, E. S. Daniels and M. S. El-Aasser, in Polymer Latexes: Preparation, Characterization, and Applications, E. S. Daniels, E. D. Sudol and M. S. El-Aasser, (eds), ACS Symp. Ser., Vol. 492, 1992, p 1 Copyright © 1992 American Chemical Society)

Application Fields of Colloids

Area	Example
Industrial	Paints, Adhesives, Floor polishes, Print inks, Carpet backing, Paper sizing, Water/sewage treatment, Secondary oil recovery, Rubberized concrete
Research	Size standard for electron microscopy High resolution chromatography column packing
Medical	Magnetic particles targeted drug delivery Immunodiagnostics Controlled released drugs
Chemical	Catalysts, Colloids & surface chemistry, Coagulation kinetics Model liquid crystals, Rheology, Dielectric spectroscopy Particle interaction *Dispersion forces *Electrostatics *Steric stabilization

PROGRESS & KINETICS OF EMULSION POLYMERIZATION



▪ *Three stage of emulsion polymerization*

- **Interval I** : Particle initiation stage
  - Continuous until micelles have disappeared

- **Interval II** : Particle growth stage
  - Constant number of particles plus monomer emulsion droplets
  - Particles grow until monomer droplet phase disappears and all monomer is in the particles

- **Interval III** : Particle growth stage
  - Particles grow until monomer is completely polymerized or initiator is exhausted

INTERVAL 1

INTERVAL 2

INTERVAL 3

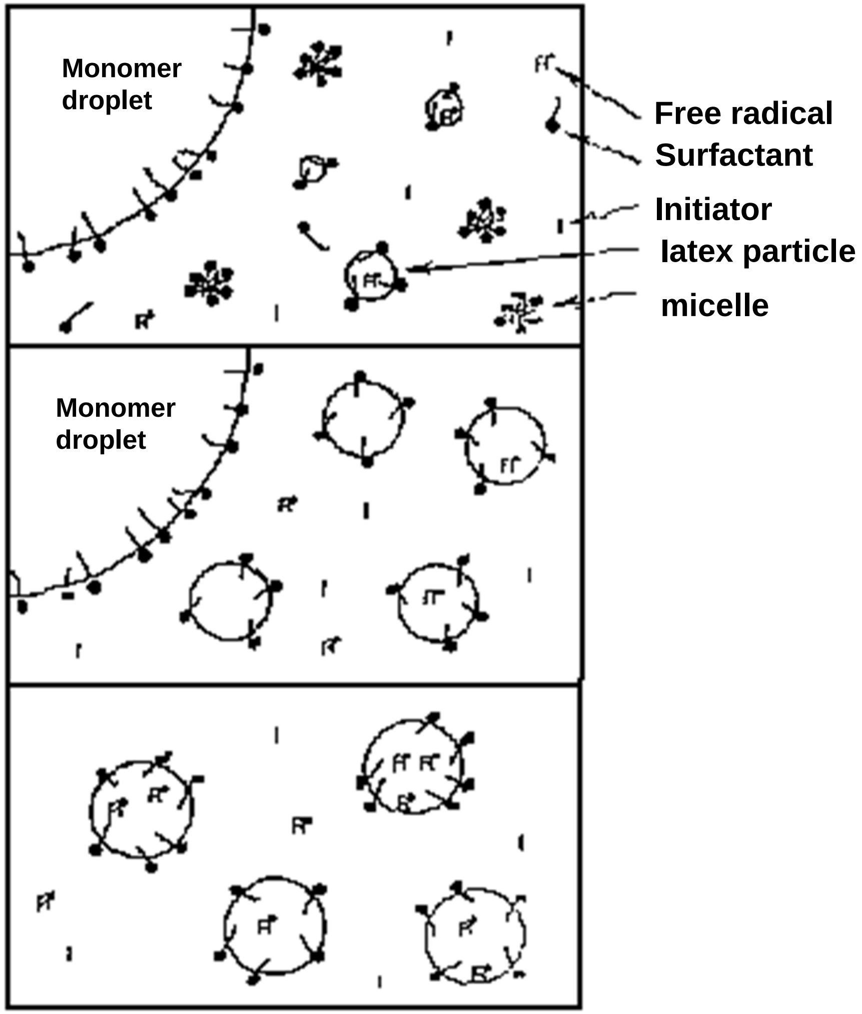


Fig. The three Intervals of emulsion polymerization

▪ *Kinetics of emulsion polymerization*

◆ **Polymerization rate**

☞ Steady state (initiation rate = termination rate)

$R_p = k_p [R \bullet] [M]$ $[R \bullet]$: unknown radical concentration

- Assumption : Rate of formation and destruction is equal

$R_i = k_i [I_2] = R_t = k_t [R \bullet]^2$

$$R_p = \left\{ \frac{k_p}{k_t^{1/2}} \right\} R_i^{1/2}$$

☞ Kinetic chain length v : 활성 사슬당 소요된 단량체의 수로 정의

$$v = R_p / R_i = R_p / R_i = \left\{ \frac{k_p}{R_i^{1/2} \cdot k_t^{1/2}} \right\} [M]$$

▪ *Kinetics of emulsion polymerization*

◆ Polymerization rate

☞ Disproportion termination $X_n = \upsilon$

☞ Combination termination $X_n = 2\upsilon$

☞ Case in transfer reaction

X_n : (rate of proportion) / (sum of the rates of all reactions leading to polymer molecules)

☞ Rate of emulsion polymerization

$$R_p = k_p[M]\left(\frac{\langle n\rangle N}{N'_A}\right)R_i^{1/2}$$

The rate of polymerization

$$R_p = k_p[M][P\bullet]$$

$[P\bullet]$: the product of the conc. Of active particles

$$[P\bullet] = \frac{10^3 N'\overline{n}}{N_A}$$

N' : the product of the conc. Of active particles

$\overline{n}$: the average # of radicals per micelle plus particle

$$R_p = \frac{10^3 N'\overline{n}k_p[M]}{N_A}$$

$$R_p = \frac{10^3 N\overline{n}k_p[M]}{N_A}$$

This eq. Applies to Interval II and III where only polymer particles exist (no micelles)

The value of $\overline{n}$ during Interval II and III is of critical importance in determining R_p.

Degree of Polymerization

The rate ***r_i*** at which primary radicals enter a polymer particle

$$r_i = \frac{R_i}{N}$$

The same as the rate of termination ***r_t*** of a polymer chain for Case 2 behavior

The degree of polymerization is the rate of growth of a polymer chain divided by the rate at which primary radicals enter the polymer particle.

$$\overline{X} = \frac{r_p}{r_i} = \frac{Nk_p[M]}{R_i}$$

The degree of polymerization in an emulsion polymerization is synonymous with the kinetic chain length.

The rate and degree of polymerization can be simultaneously increased by increasing the number of polymer particles at a constant initiation rate.

Number of Polymer Particles

The number of polymer particles is the prime determinant of the rate and degree of polymerization since it appears as the first power in both Eq 4-5 and 4-7

$$N = k\left(\frac{R_i}{\mu}\right)^{2/5}\left(a_s S\right)^{3/5}$$

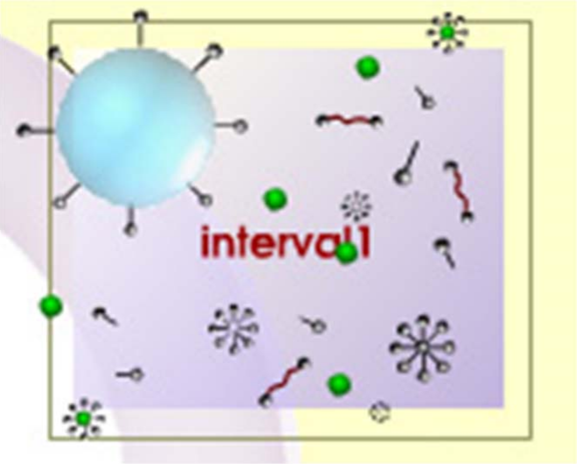
The number of particles that can be stabilized is dependent on the total surface area of surfactant present in the system $a_s S$

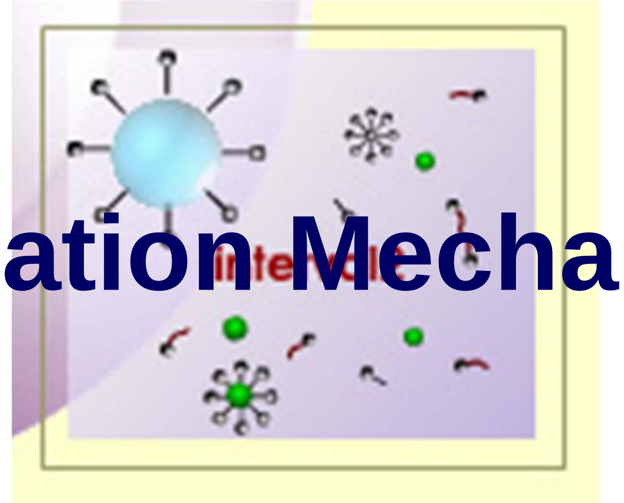
The practical viewpoint one can simultaneously increase R_p and $\overline{X}_n$ by increasing N.

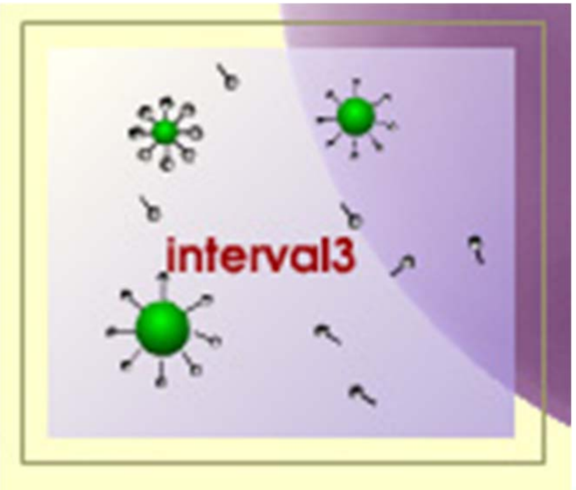
The predicted dependence of ***N*** and ***S*** and ***R$_i$*** for the formation of polymer particles by micellar and homogeneous nucleation followed by coagulative nucleation is given as follows

$$N \propto R_i^{2/5} S^{0.4-1.2}$$

Nucleation Mechanism







Nucleation Mechanism

- **Micellar Nucleation**

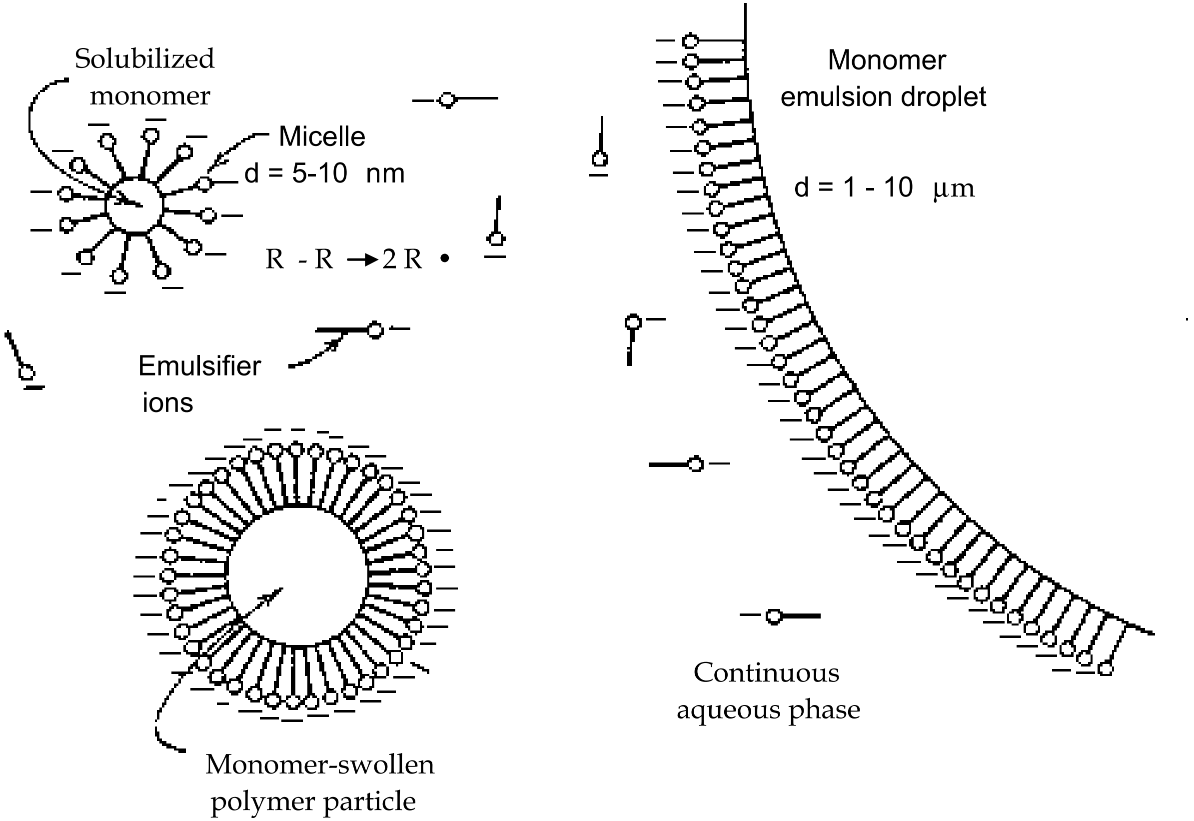
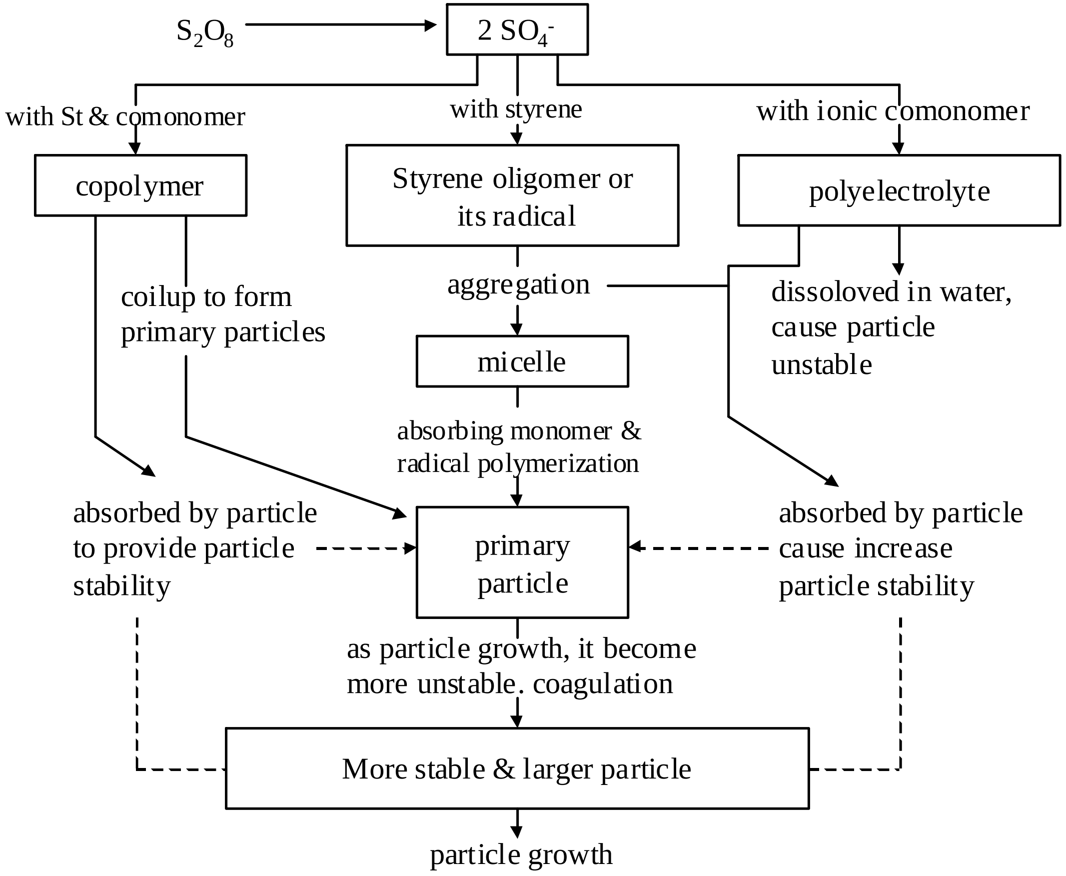


Fig. Emulsion polymerization during interval (2), the number of micelles, particles, and droplets are arbitrary; d is diameter

▪ *Micellar Nucleation*

- Example of micellar nucleation scheme



S_2O_8 → $2\ SO_4^-$

with St & comonomer

copolymer

coilup to form primary particles

absorbed by particle to provide particle stability

with styrene

Styrene oligomer or its radical

aggregation

micelle

absorbing monomer & radical polymerization

primary particle

as particle growth, it become more unstable. coagulation

More stable & larger particle

particle growth

with ionic comonomer

polyelectrolyte

dissoloved in water, cause particle unstable

absorbed by particle cause increase particle stability

▪ *Homogeneous Nucleation Mechanism*

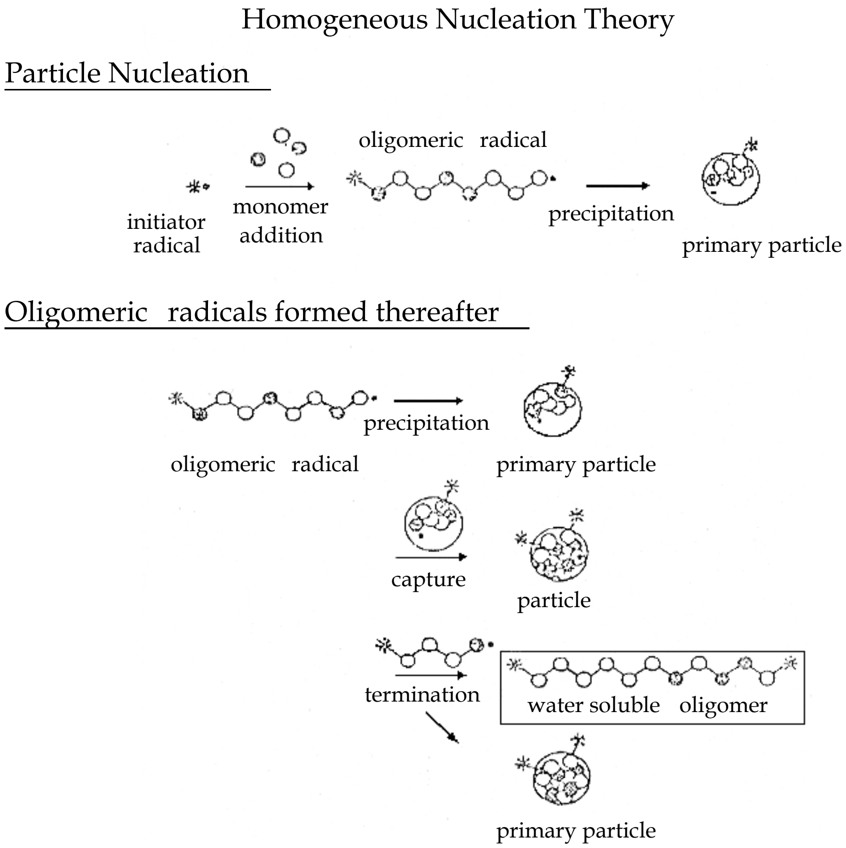


Fig. Schematic of the homogeneous nucleation theory

▪ *Homogeneous Nucleation Mechanism*

- ◆ **Appreciable water soluble monomer**
- ◆ **Free radicals generated in aqueous phase**
- ◆ **Formation of 'primary' particles**
- ◆ **Propagation**
- ◆ **Flocculation**

◎ **Emulsifier-free emulsion polymerization**

Stability : Electrostatic stabilization of initiator portion

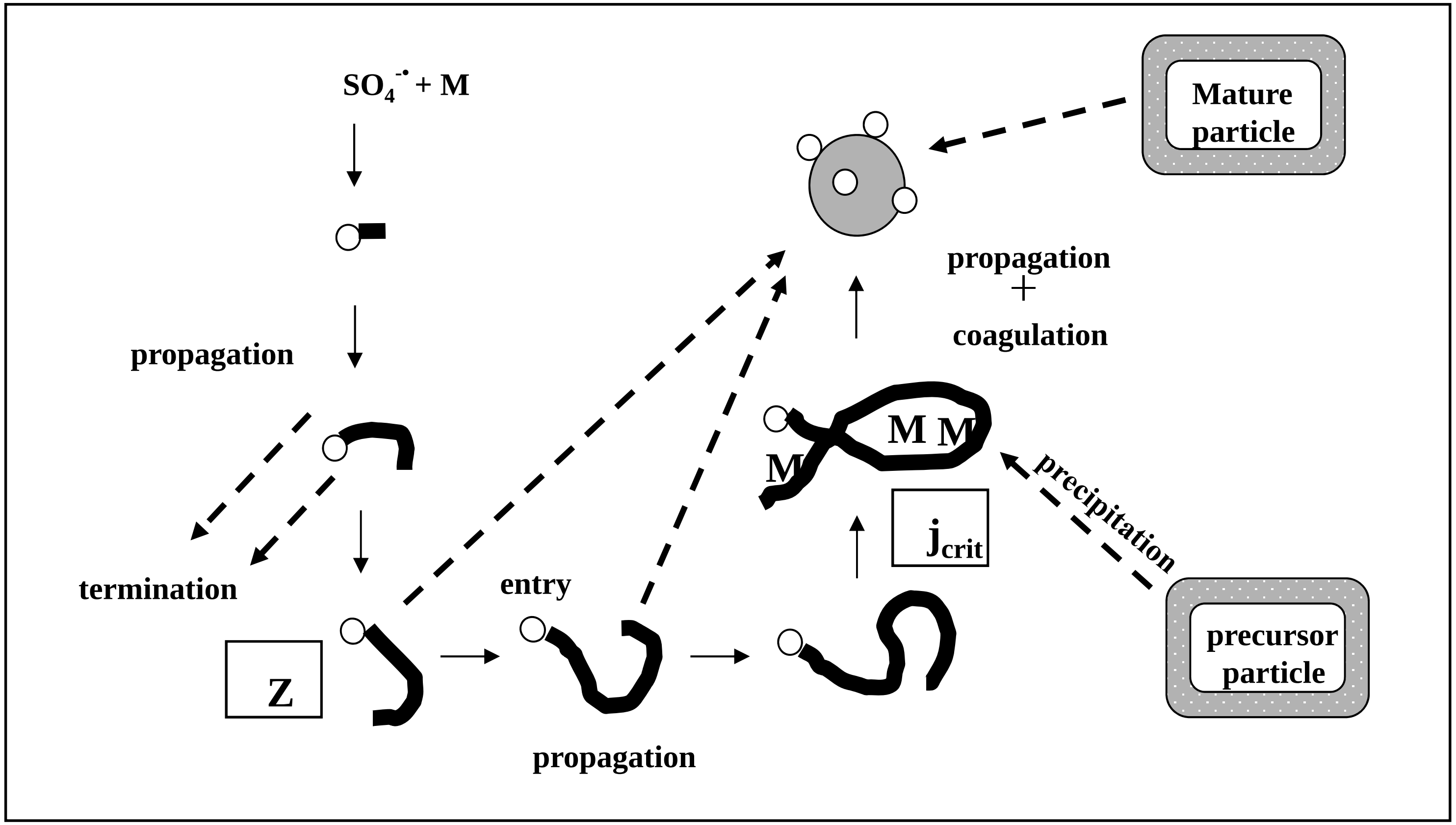
▪ *Coagulative Nucleation Mechanism*

◆ Two step nucleation (Napper & Gilbert)

- First step ; 'precursor' particle formulation

- Second step ; 'mature' particle formulation by aggregation of precursor particle

▪ *Coagulative Nucleation Mechanism*



$SO_4^{-\bullet} + M$

propagation

termination

Z

entry

propagation

M

M M

j_{crit}

propagation + coagulation

Mature particle

precipitation

precursor particle

Fig. More detailed illustration of the homogeneous coagulative (HUFT) nucleation description of particle formation, which dominates for surfactant concentrations below the cmc.

▪ *Nucleation in Monomer Droplet*

- **Monomer droplet** :

  1 - 10 ㎛ size

  Small number → Small surface area

  Capture size

- **Decrease size of monomer droplet**

  100 - 500 nm size

  Miniemulsion & Microemulsion polymerization

- **Final latex particle size** ;

  Initial droplet size

Nucleation in Monomer Droplet

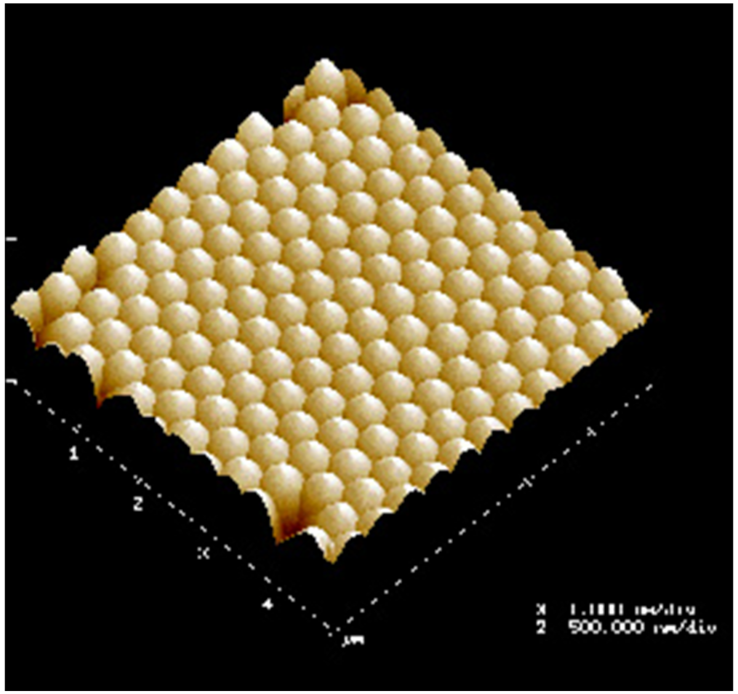
Role of additives in miniemulsion

- Formation & stabilization of small size droplet
  → adsorption of emulsifier
- Increase of monomer-swollen ratio
- Decrease equilibrium concentration of monomer in monomer droplet

Microemulsion polymerization

- Initial droplet size : 5 - 40 nm
- Increase of polymerization rate
- Interval I : Until microemulsion droplet disappeared
- Interval II : Until polymerization rate decreases
- High M.W. polymer formation

Other Considerations of Emulsion Polymerization



- **Variation common to most polymerization process** :
  - Monomer mixture
  - Programmed addition
  - Other ingredients : solvent, CTA, dissolved polymer etc.
  - Molecular weight characteristics
  - Grafting

- **Additional variations possible with emulsion polymerization** :
  - Particle size characteristics
  - Particle morphology
  - Composition variations
    - within individual particles
    - among particles of different size
  - Particle surface characteristics
  - Rheology : particle contributions, continuous phase contributions
    interfacial phenomena
  - Continuous phase characteristics

Development sequence for polymer latex systems

Selection of Monomer System	T_g, MFFT, Durability, Water Properties
Choice of surfactant	Type, Level, CMC, HLB
Catalyst System and Polymerization Conditions	Temperature Control, Molecular Weight

▪ Selection of monomer system

<removability, water resistance, stability>

- Inter-relation of all these properties
- Dependence of the structural features in the polymer
- Important factors
  : Removability, Resistance balance
    1. Reactive monomers
    2. Polarity
    3. Molecular weight
    4. Glass transition temperature

▪ *Selection of Surfactant*

◆ Surfactant for emulsion polymerization

☞ Most Important Factor in Successful Design

☞ Functions :

Activity as Primary Site for the Polymerization
Stabilization of the Polymer Emulsion

☞ Type

Anionics	Sulfates Sulfonates Sulphosuccinates Phosphates
Nonionics	Octyl, Nonyl Phenolethoxylates Alkyl Alcohol Ethoxylates Propylene Oxide-Ethylene Oxide Block Polymers
Cationics	Alkyl Amines and Ethoxylate Derivatives Quaternary Ammonium Halides

▪ *Selection of Surfactant*

◆ Protective Colloids

☞ Water soluble polymeric structures of varing compositions and molecular weight functioning as stabilizers

☞ Example
Hydroxyethyl Cellulose
Carboxylmethyl Cellulose
Polyvinyl Alcohol
Polyelectrolytes (e.g. Polyacrylic Acid)
Polyacrylamide

▪ *Selection of Surfactant*

◆ Major effects of surfactant

☞ Particle Size :
No. of particles - amount of Surfactant above CMC
Particle size - magnitude of CMC and amount of surfactant

☞ Polymerization rate :
Same relationship with CMC,
Surfactant concentration

☞ Stability :
Type and amount of surfactant

Monomer Water Solubility at 25 °C

Vinyl Acetate	2.3
Acrylonitrile	7.4
Styrene	0.03
Ethyl Acrylate	2.0
Butyl Acrylate	0.2
Methyl Methacrylate	1.5

▪ *Selection of Surfactant*

◆ Methods of selection

☞ Empirical Selection

☞ Promise approach :

HLB (hydrophile lipophile balance) concept

☞ HLB calculations :

① HLB (Nonionic) :

$$\frac{Weight\ \ Percentage\ \ Hydrophilic\ \ Portion}{5} = HLB$$

②HLB (Emulsifier Blends) :

$$\frac{W_A \times HLB_A + W_B \times HLB_B}{W_A + W_B} = HLB$$

▪ *Selection of Catalyst*

◆ Catalyst system

<Type, level, redox or heat activated>

☞ Catalyst : Free Radical Initiators

☞ Type

- Oil soluble (Benzoyl Peroxide) - large particle size
- Water soluble (Persulfates, Hydrogen Peroxide) - most popular type
- Redox (Hydroperoxides)

☞ Level of Catalyst

- Properties of final product
- Compromise between as adequate polymerization
- Rate and high M.W.

☞ Redox Systems

-Oxidation-reduction reactions

-Advantage - low Temp., High M.W., color and lower coagulum

◆ Polymerization condition

☞ Temperature :

- Control of temperature is still a major concern
- Minimize viscosity buildup - heat transfer problems
- Reflux cooling : control of the foaming

☞ Addition Methods :

- Batch : suitable for low solids emulsions usually with a single monomer
- Semi-Batch : increase solids but increase resident time
- Continuous : good control of T, polymer uniformity
- Pre-Emulsion : larger particle, more stable latex

☞ Agitation :

- Dispersion of monomer into droplets
- Aids in temperature control