CHAPTER 2

MECHANISM AND KINETIC

2.1 Mechanism of emulsion polymerization

Harkins(1947) was the first to propose the mechanism of emulsion polymerization. He adduced the following essential postulates for the nucleation of polymer particles and progression of polymerization reaction.

1 Micelles are the principle loci for nucleation of polymer particles. Free radicals produced in the aqueous phase are captured by the micelles. The monomer in micelles are polymerized. The polymerization reaction is in progress as monomers present, then micelle are transformed into polymer particles.

2 The principle locus of polymer formation is the monomer-swollen polymer particle.

3 The monomer droplets serve as reservoirs, monomer molecules are feed to the growing polymer particles by diffusion of the aqueous phase monomer which equilibrium with the monomer in monomer droplets. Since the total surface area of the monomer droplets is much smaller than that of the micelles and the polymer particles, only a very small fraction of the free radicals enter the monomer droplets, therefore little or no polymers are formed in monomer droplets.

According to Harkins's postulations, emulsion polymerization may be considered as a three stage processes, according to Hamielec and Friis(1975), Gardon(1977), Odian(1981) and Pirrma(1982).

Stage I.

Polymer particles are generated in this stage. The mechanism
for particle nucleation is described in two simultaneous processes.

1 Micellar nucleation,primary radicals or oligomeric radicals
from aqueous phase are entered into micelles and polymer particles
nuclei are generated. This process is the predominate mechanism for a
highly water insoluble monomer with low water solubility and high
emulsifier concentration.

2 Homogeneous nucleation, oligomeric radicals in water phase
become insoluble and precipitate on themselves. The precipitating
species become stabilized by adsorbed emulsifier and upon subsequent
adsorption of monomers. This is predominant process for water soluble
monomer with high water solubility and low emulsifier concentration.

Micelles are used for both nucleation of polymer particles and
disintegrate to deliver the emulsifier molecules for stabilization of
growing particles. Very small fraction of micelles are used for
particle nucleation. most of them desorp to deliver the emulsifiers
necessary for the particle stabilization. The major species present in
this period are micelles of 0.005 - 0.01 μ in diameter. newly formed
and growing monomer-swollen polymer particles of 0.03 - 0.3 μ in
diameter and monomer droplets of 1 - 5 μ in diameter.

During stage I the overall rate of polymerization increase
with time as the number of polymer particles increase. At the end of
this stage all micelles are consumed. thus the generation of polymer
particles ceases. In typical emulsion polymerization the final number
of polymer particles per litre emulsion is of the order 10^{16} - 10^{18}
and average particle diameter is 0.1 - 0.3 μ at complete conversion.

This stage is the shortest of the three stages. its duration
is in the range 2 - 15 % conversion. This stage is short for high
initiation rate and high water soluble monomer.

All micelles are disappeared at the end of this stage.

Stage II

In this stage polymer particles grow steadily because free radical polymerization takes place inside the monomer-swollen polymer particles. The monomer concentration in particle remains constant in this period because monomers from monomer droplets rapidly diffuse into the polymer particle, thus particles are saturated with monomers as long as the separated momomer droplets are presentd. Rate of polymerization remain constant or increase in this period. If the growth of the particles does not effect the average number of free radicals per particle, rate of polymerization remain constant because there is no change in monomer concentration and average number of free radicals per particle. If the growth rate of polymer particles give an increase in monomer concentration and/or average number of free radicals per particle, the rate of polymerization increase. The average number of free radicals per particle is controlled by the rate of radical adsorption into, desorption from and termination inside the particle. Thus the volumetric growth rate of polymer particles is controlled by average number of free radical per particle and monomer concentration in the monomer-swollen polymer particles.

At the end of this stage the monomer droplets vanish, thus at this time monomers are present in two loci, in monomer-swollen polymer particles and in aqueous phase. The conversion that correspond to the first disappearance of monomer droplets is known as the critical conversion, X_c. This quantity is changed for the different polymer-monomer system.

Stage III

The monomer-starved period, in this stage the emulsion consist of two phases, the water phase and the polymer phase. Since no more monomer supplied to the polymer particles the concentration of monomer in the particles decrease steadily. The polymerization reaction continuously occurs inside the polymer particles because of residual monomers. Rate of polymerization may increase, constant or decrease,

depending on the extent of gel effect. The polymer particles shrinks during stage III because its density is usually higher than that of the corresponding monomer.

Stage IV

This stage is the product of extensive work of Harkins's kinetics study. In classical batch emulsion polymerization, the polymerization reaction ends with stage III. The reaction is terminated by the absence of monomer inside the particles or the deactivation of free radicals by inhibitors.

In the later experimental works, accroding to Pramojaney(1982), it is observed that new particles are generated during stage III. The re-appearance of micelles, which are essential for the production of new polymer particles, is caused by the desorption of emulsifiers from the diminished and crowded surface of the shrinking polymer particles. Stage IV is characterized by the presence of micelles in the absence of monomer droplets, thus no new particles are generated.

The point of transition from one stage to another depends on the nature of monomer, type and concentration of emulsifier. In typical batch emulsion polymerization the particle nucleation is completed within the first 5 - 10 % conversion. The conversion at which the monomer droplet disappears depend on the solubility of the monomer in its polymer.

Schematic presentation of experimental variation of conversion rate with time in stage I,II,III (Fig. 2) shows that polymerization rate increases steadily in stage I because of high particle nucleation rate and/or high proportion of particles containing propagating radicals (curve AC). The maximum rate of polymerization is observed for many monomer when the initiation rates are sufficiently high (curve AB). Polymerization proceeds in the polymer particles as the monomer concentration in particles is at the equilibrium level by diffusion of monomer from solution. In stage II the polymerization rate is constant(curve D) or slightly increase with time(curve E) due

to gel or Trommsdroff effect. For high solubility monomer, the transition from stage II to stage III occurs at low conversion. The number of polymer particles in stage III is the same as stage II but monomer concentration in polymer particle decrease with time, then polymerization continue at a steady decreasing rate (curve G,H). Curve H shows that gel effect occurs in this stage but rate of polymerization decrease as monomer concentration in particles decrease.
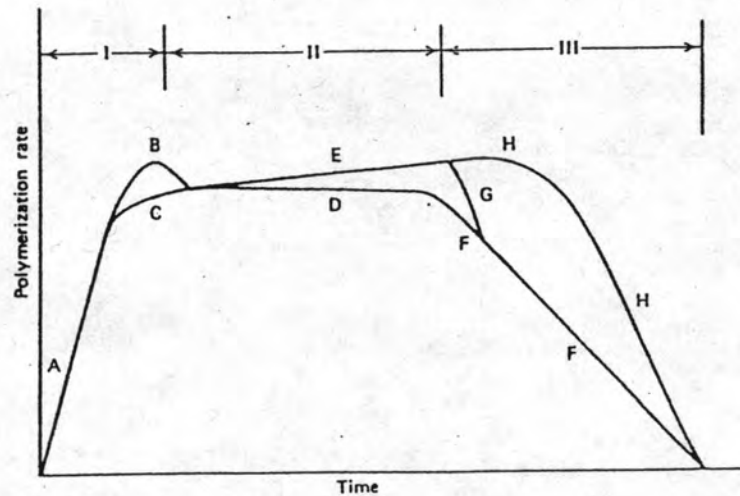

Fig. 2.1 Different rate behaviors observed in batch emulsion polymerization (Gardon, 1977; Odian, 1982).

Table 2.1 The Schematic distinction of the four stages in batch emulsion polymerization.

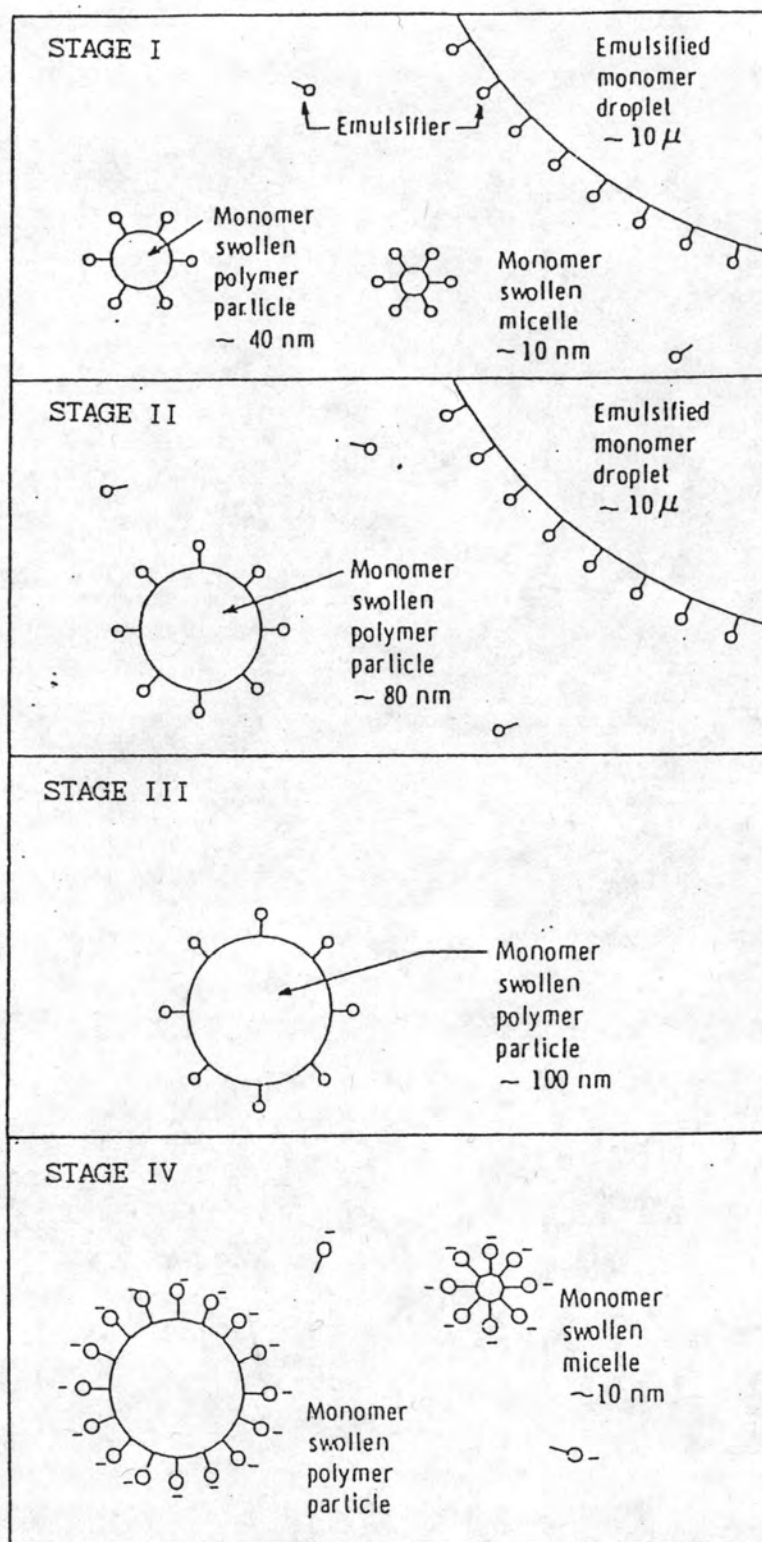| components	Stage I	Stage II	Stage III	Stage IV
monomer droplets	appear	appear	disappear	disappear
micelle	appear	disappear	disappear	appear
particle number	increase	constant	constant	constant

Fig. 2.2 The schematic illustration of phase separations in batch
emulsion polymerization during stage I, II, III, IV.
(Hamielec and Friis, 1975; Pramojaney, 1982)

─────── hydrophobic end   o   hydrophilic end

2.2 Kinetic of emulsion polymerization

Based on the mechanism proposed by Harkins in 1947, the first kinetics theory of emulsion polymerization was presented by Smith and Ewart in 1948.

The basic assumptions of the Smith and Ewart theory are

1 All free radicals are initiated in the dispersion medium and enter into the polymer particles.

2 Particle nucleation occures in micelle.

3 Particles are produced until all micelles are disappeared.

4 No particles coalescence occurs in the system.

5 Polymer particles are the main locus for polymerization.

6 The rate of radical absorption is proportional to the total surface area of polymer particles and the rate of radical generation.

7 The monomer concentration in polymer particle remains constant if monomer droplets are present.

8 The volumetric growth rate of a polymer particles is constant until the monomer droplets disappear.

2.2.1 Average number of free radical in polymer particle.

In order to calculate the average number of free radicals per particle, q, it is necessary to establish rate expression for the various reactions that control the kinetic. Newly formed primary radicals may either be terminated by another radical or diffuse into polymer particles. If a radical enters a polymer particle, it starts reaction in the particle and grows continuously until it is terminated.

For a system having N_p suspended polymer particles, each of which has a volume v and an interfacial area a. There are three rates that control average number of free radicals per particle.

1 Rate of entrance of free radical into a single locus.

$$\frac{dq}{dt} = \frac{R_a}{N_p} \qquad (2.1)$$

2 Rate of radical transfer out of the locus.

$$\frac{dq}{dt} = -k_o a \left| \frac{n}{v} \right| \tag{2.2}$$

3 Rate of mutual termination of free radical in polymer particle.

$$\frac{dq}{dt} = -2k_{tp} \left[\frac{n(n-1)}{v} \right] \tag{2.3}$$

Factor 2 arises from the fact that two radicals are destroyed for each event. At a steady state, rate of formation of N_n polymer particles is equal to the rate of disappearance of those loci.

rate of formation of N_n = rate of disappearance of N_n

$$N_{n-1}\frac{R_a}{N_p} + N_{n+1}k_o a \frac{(n+1)}{v} + N_{n+2}k_{tp}\frac{(n+2)(n+1)}{v} = N_n\frac{R_a}{N_p} + k_o a \frac{n}{v} + k_{tp}\frac{n(n-1)}{v} \tag{2.4}$$

A discussion on kinetic of an emulsion polymerization is given into three cases.

CASE I q < 0.5

Free radicals have a high probability of transfer out of particle. then at any time only a small number of particles will have a free radical. thus average number of free radicala per particle is much smaller than unity.

In this case, reactions are divided into two groups depending on the termination mode.

1 Termination reaction is dominant in dispersion medium. The reaction rate is independent on the size of the polymer particles but only on their total volume.

Rate of termination of free radical in dispersion medium.

$$\frac{dq}{dt} = -2k_{tw}(c_w)^2 \tag{2.5}$$

Rate of polymerization.

$$R_p = k_p[M_p]V_p m \left| \frac{R_I}{2k_{tw}} \right|^{1/2} \qquad (2.6)$$

Average number of free radicals per particle.

$$q = \frac{V_p m}{N_p} \left| \frac{R_I}{2k_{tw}} \right|^{1/2} \qquad (2.7)$$

τ_p: average lifetime of free radical in polymer particles.

$$\tau_p = \frac{[\text{number of free radicals in polymer particles}]}{[\text{termination rate of free radicals}]}$$

$$= \frac{V_p m}{(2k_t R_I)^{1/2}} \qquad (2.8)$$

2 Termination reaction is dominant in polymer particle. Suppose that polymer particles are so small that instantaneous mutual termination occurs when a free radical enters a particle already contain a radical.

Rate of disappearance of free radical.

$$\frac{dq}{dt} = \frac{-2(4\pi D^2)V_p c_w^2}{k_o} \qquad (2.9)$$

Rate of polymerization.

$$R_p = k_p[M_p] \left| \frac{R_I V_p}{2k_o a} \right|^{1/2} \qquad (2.10)$$

Average number of free radicals per particle.

$$q = \frac{1}{N_p} \left| \frac{R_I V_p}{2k_o a} \right|^{1/2} \qquad (2.11)$$

Average polymerizing lifetime of free radical.

$$\tau_p = \left| \frac{2V_p}{R_I k_o a} \right|^{1/2} \qquad (2.12)$$

To determine which case of termination is dominant, we must make our concern on termination rate of free radical. Termination in water phase is dominant if

$$k_{tw} \gg \frac{4\pi D^2 V_p}{k_o} \qquad (2.13)$$

CASE II   q = 0.5

Assumptions for this case :

1 No free radicals in polymer particles transfer to the water phase.

2 Mutual termination is occured instantaneously when a free radical enters a polymer particle alredy contain a free radical.

3 Average time of termination is small compared with the average time for a radical enters polymer particle.

According to above assumptions, approximately one-half of the particles contain single free radical and the others contain none.

Rate of polymerization inside polymer particles.

$$R_p = \frac{k_p [M_p] N_p}{2} \tag{2.14}$$

Average number of free radicals per particle.

$$q = 0.5 \tag{2.15}$$

Mean polymerizing lifetime.

$$\zeta_p = \frac{N_p}{2R_i} \tag{2.16}$$

CASE III q >> 0.5

Assuming that all polymer particles contain the same number of free radical. This is a good approximation if q is large enough.

Rate of polymerization.

$$R_p = k_p [M_p] \left[\frac{V_p R_a}{2k_{t_p}} \right]^{1/2} \tag{2.17}$$

Average number of free radicals per particle.

$$q = \frac{1}{N_p} \left[\frac{V_p R_a}{2k_{t_p}} \right]^{1/2} \tag{2.18}$$

Mean polymerizing lifetime.

$$\zeta_p = \left[\frac{V_p}{2k_{t_p} R_a} \right]^{1/2} \tag{2.19}$$

2.2.2 Number of polymer particles.

Number of polymer particles is the key parameter in emulsion polymerization, it not only affect the polymerization rate and polymer quality development but also the properties of the final latex such as stability, viscosity, film forming properties.

The processes considered are based on assumption that polymer nucleies are generated by micelle. Consider the early stages of an emulsion polymerization, the emulsifiers present either as micelles or adsorbed molecules on the surface of the polymer particles.

On the basis of the micellar initiation hypothesis we will consider two idealize situatinos. Firstly, it is assumed that all free radicals in aqueous phase are captured by micelles. No radicals enter polymer particles as long as micelles present. secondly, it is supposed that free radicals enter both micelles and latex particles to avoid complication arising from strict application of diffusion laws. It is assumed that the interfacial area of polymer particles and micelles have the same effectiveness. If radicals are captured by simple diffusion process, rate of diffusion into a particle or micelle will be proportional to its radius and the radical flux through each unit area of interface should be inversely proportional to the radius.

Both idealize considerations lead to the expression of N_p as a function of initiation rate and emulsifier concentration as

$$N_p = k \left| \frac{R_I}{u_p} \right|^{2/5} (a_s [S])^{3/5} \qquad (2.20)$$

Where $0.37 < k < 0.53$.