

Emulsion Polymerization

Reference:

Aspen Polymers: *Unit Operations and Reaction Models*,
Aspen Technology, Inc., 2013.

1. Introduction

Emulsion polymerization is an industrially important process for the production of polymers used as synthetic rubber, adhesives, paints, inks, coatings, etc. The polymerization is usually carried out using water as the dispersion medium. This makes emulsion polymerization less detrimental to the environment than other processes in which volatile organic liquids are used as a medium.

In addition, emulsion polymerization offers distinct processing advantages for the production of polymers. Unlike in bulk or solution polymerization, the viscosity of the reaction mixture does not increase as dramatically as polymerization progresses. For this reason, the emulsion polymerization process offers excellent heat transfer and good temperature throughout the course of polymer synthesis.

In emulsion polymerization, free-radical propagation reactions take place in particles isolated from each other by the intervening dispersion medium. This reduces termination rates, giving high polymerization rates, and simultaneously makes it possible to produce high molecular weight polymers. One can increase the rate of polymerization without reducing the molecular weight of the polymer.

Emulsion polymerization has more recently become important for the production of a wide variety of specialty polymers. This process is always chosen when the polymer product is used in latex form.

2. Reaction Kinetic Scheme

To appreciate the complexities of emulsion polymerization, a basic understanding of the fundamentals of particle formation and of the kinetics of the subsequent particle growth stage is required. A number of mechanisms have been proposed for particle formation. It is generally accepted that any one of the mechanisms could be

responsible for particle formation depending on the nature of the monomer and the amount of emulsifier used in the recipe.

The two common mechanisms for particle formation are:

- ✓ Micellar nucleation
- ✓ Homogeneous nucleation

With *micellar nucleation*, micelles, which are aggregates of emulsifier molecules, act as the site of nucleation.

With *homogeneous nucleation*, the radicals produced in the aqueous phase polymerize with dissolved monomer and precipitate out to form precursor particles. The precipitated precursor particles coagulate with each other until a stable particle is formed.

2.1. Micellar Nucleation

Micellar nucleation is considered to be the primary mechanism for particle formation (Harkins, 1945; Smith & Ewart, 1948) in those emulsion polymerization systems for which the monomer is very sparingly soluble in water, and where the concentration of emulsifier is above the *critical micelle concentration* (CMC). As the name implies, the micelles, which are formed when the emulsifier concentration is above the CMC, act as the site for particle nucleation.

The reaction mixture consists of water, monomer, emulsifier and a water-soluble initiator. The monomer is dispersed in the form of droplets in the water by agitation. The droplets formed are stabilized by the emulsifier molecules which are adsorbed on the droplet surface. In addition to the droplets, monomer is also found dissolved in the aqueous medium and solubilized inside the micelles.

Similarly, the emulsifier is found in three locations: in the micelles, dissolved in the aqueous medium, and adsorbed on the monomer droplets. Since a water soluble

initiator is used, the initiator molecules will be mainly found dissolved in the water medium.

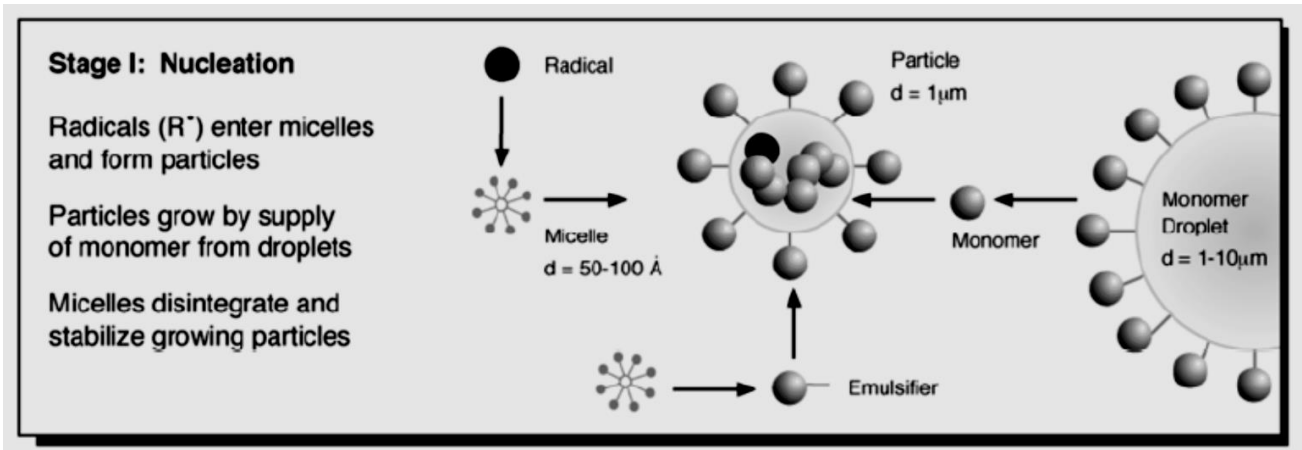
When a typical emulsion polymerization recipe is heated, the initiator dissociates in the aqueous medium and produces initiator radicals. Upon propagating with monomer in the water phase the initiator radicals form oligomeric radicals and enter the micelles, which are aggregates of emulsifier molecules inside which a small amount of monomer is entrapped. The capturing of a radical by micelle and reaction with the entrapped monomer signifies the formation of a particle from a micelle. As the propagation takes place in the newly created particle, a thermodynamic potential difference is created for the diffusion of the monomer from the monomer droplets into the growing particles.

As the particles grow, some of the micelles disintegrate and cover the growing particles to stabilize them. Therefore, the micelles are not only consumed in the formation of polymer particles, but also in the stabilization of growing polymeric particles. When no micelles remain in the reaction mixture, micellar nucleation ceases.

Stage I: Nucleation

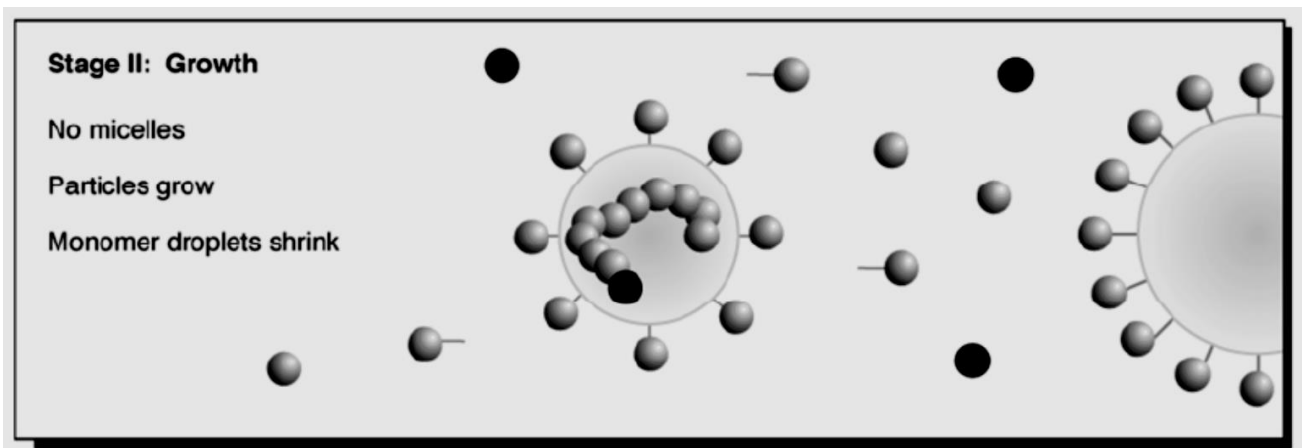
The time required for particle nucleation to be complete is also called the *nucleation time* or the *nucleation period*, and usually lasts 10-15 minutes in conventional polymerization systems. This is commonly referred to as the *seed stage*, or Stage I, in the emulsion polymerization industry. After the nucleation or seed stage, the number of particles in the reaction mixture remains constant if particles do not agglomerate.

The number of particles, usually in the range of 10^{16} to 10^{18} per liter of latex, is an important parameter in emulsion polymerization.



Stage II: Growth

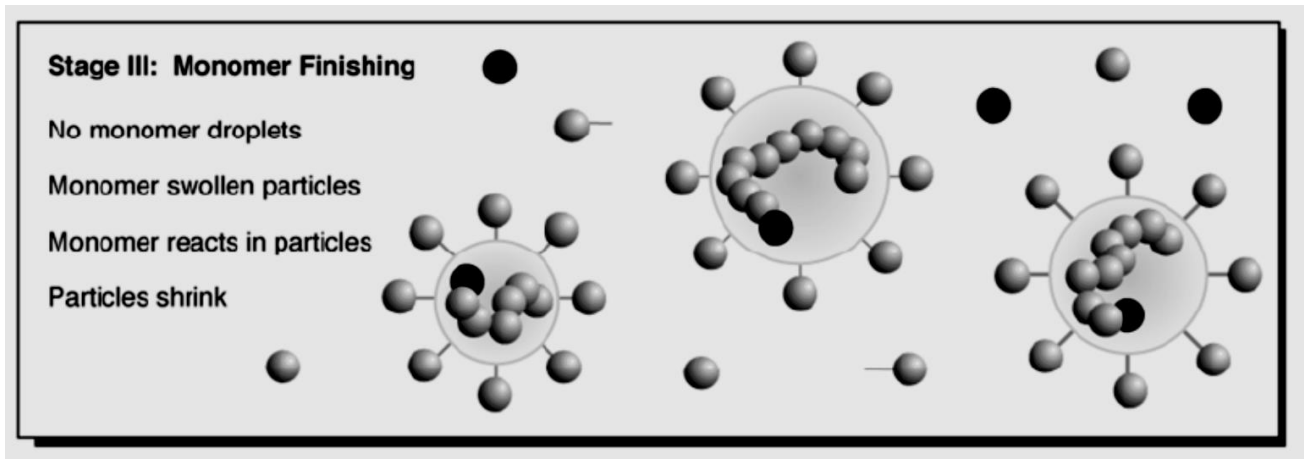
The stage following the seed stage is called the *growth stage* or Stage II of the emulsion polymerization. In Stage II, the polymer particles grow through a steady diffusion of monomer from the monomer droplets to the particles. Since the number of particles remains constant and the particles are saturated with monomer, this stage is marked by a constant rate of polymerization and could easily be observed on a conversion vs. time plot. Stage II is considered complete when the monomer droplets are totally depleted.



Stage III: Monomer Finishing

In Stage III, the monomer finishing stage, the reaction mixture consists of the monomer swollen polymer particles and the aqueous medium. Further polymerization of the monomer in the particles takes place. This results in a decrease of the particle

size due to higher density of the polymer compared to the monomer. During Stage III, the concentration of monomer dissolved in the aqueous phase falls rapidly, as does the concentration in the polymer particles. The final product obtained at the end of Stage III is called *latex*.



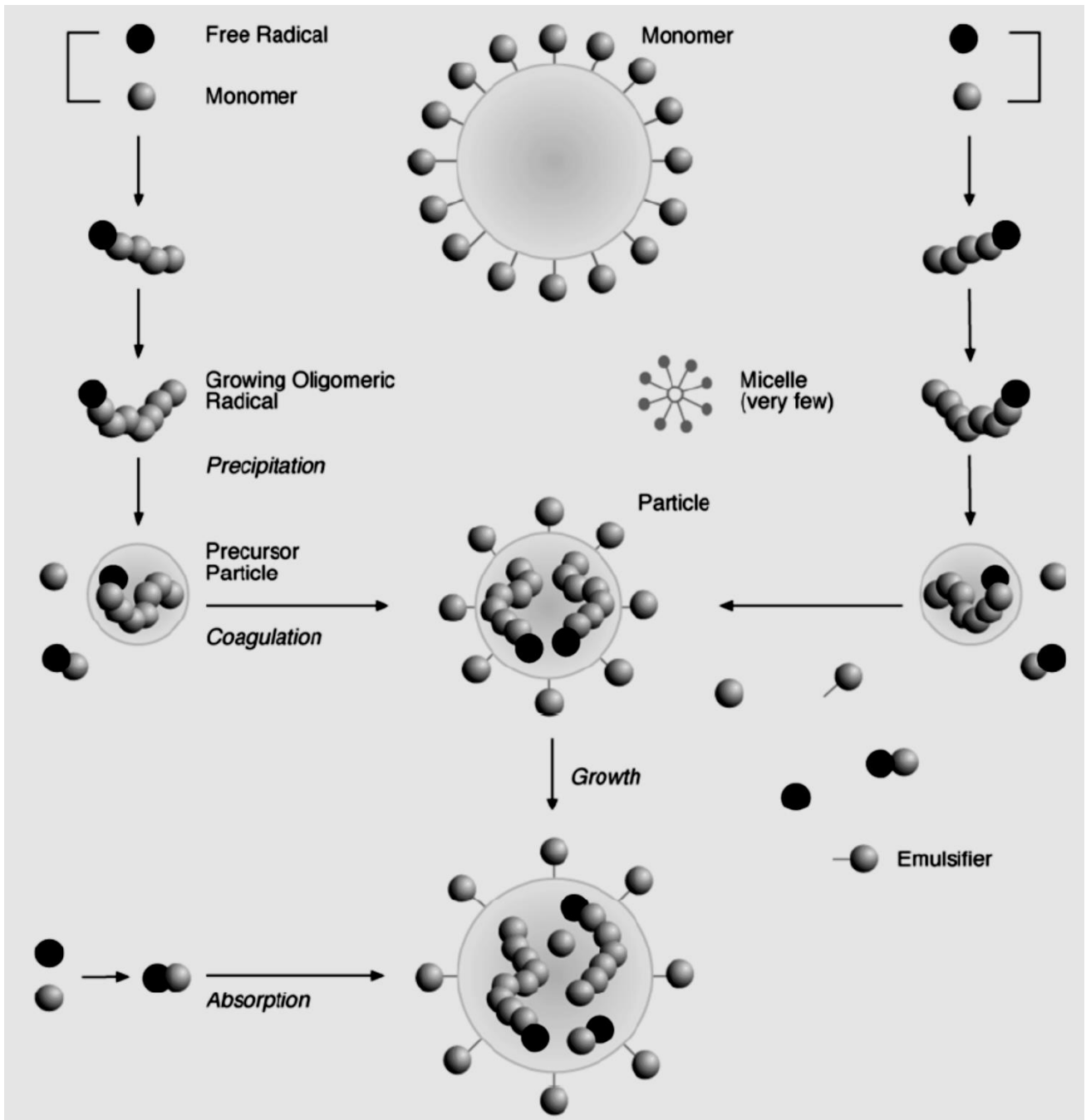
2.2. Homogeneous Nucleation

Homogeneous nucleation is the mechanism for particle formation when monomers are more water soluble and level of emulsifier is not high enough for the formation of micelles in the recipe.

When the reaction mixture is heated the initiator molecules dissolved in the water medium dissociate and produce the initiator radicals. These initiator radicals react with the dissolved monomer and quickly propagate into an oligomeric radical in the water phase.

As the size of the oligomeric radical increases it becomes insoluble in water and precipitates out of the water phase. This event signifies the formation of a primary polymer particle from the growing oligomeric radical in the water phase. However, these primary particles are not stable, and, hence, coagulate with each other until enough surface charge is developed to stabilize the particles. These surface charges are provided by the ionic end of the initiator molecules. In addition, the coagulated

particles are also stabilized by ionic and non-ionic emulsifier added to the emulsion recipe.



Once a stabilized particle is formed, it grows by getting a steady supply of monomer from monomer droplets by diffusion. As the particles grow and become large, the oligomeric radicals that are formed in the water phase are directly absorbed by the

particles. After sufficient number of particles are formed that are able to absorb all of the radicals in the water phase, no new particles are formed in the water phase and the number of particles becomes constant. Also in homogeneous nucleation the particle number reaches a constant value, as in micellar nucleation. The subsequent growth stage is similar to the growth stage in the micellar nucleation.

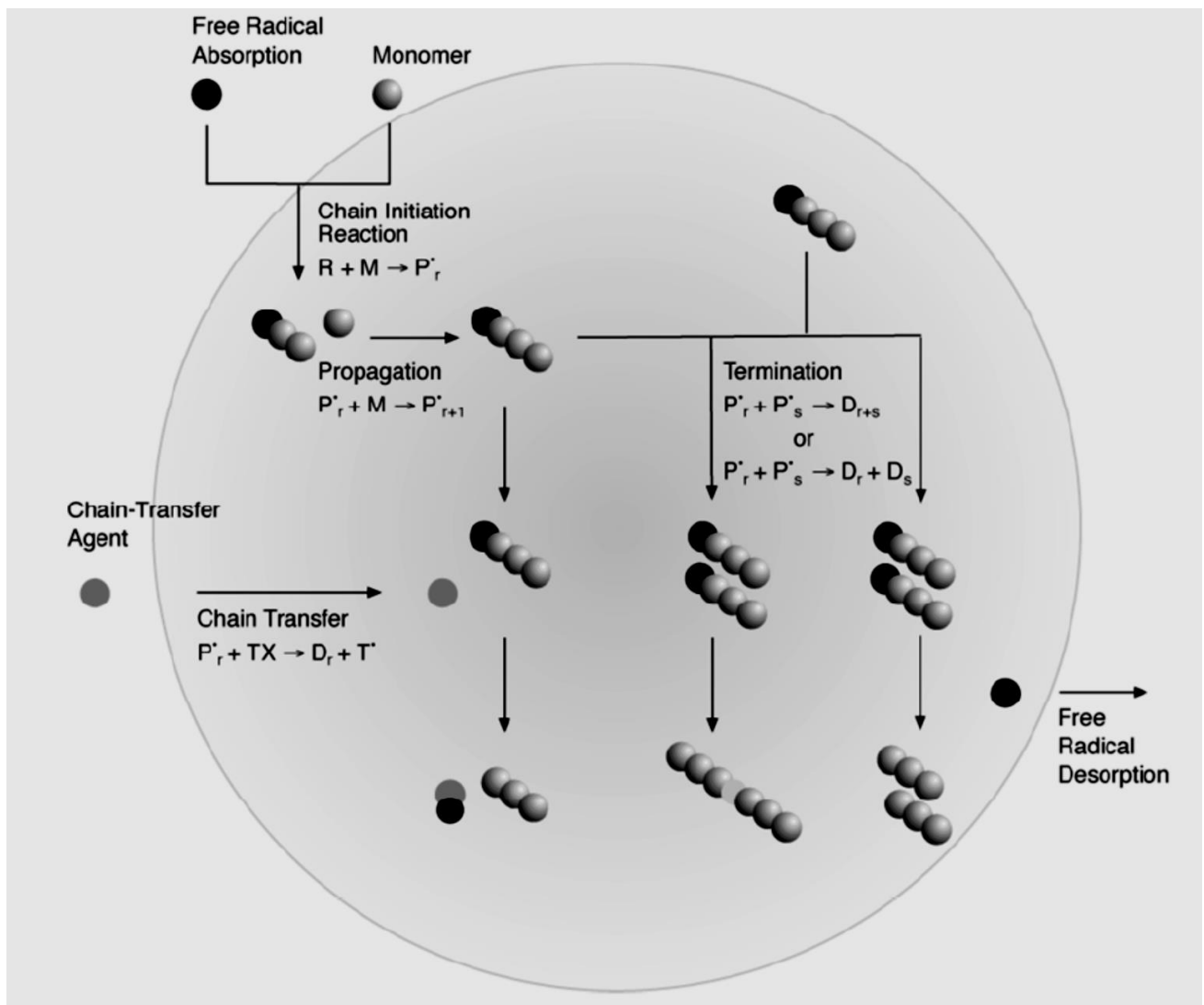
2.3. Particle Growth

Stage II, the growth stage, starts after the completion of the seed stage in the *in situ seed process*. In the *in situ seed process*, the micelles are used for the generation of the seeds. In the case of an *external seed process*, a well characterized seed is used as the starting material for emulsion production. If quality control tests indicate that the particle number and particle size distribution of the seed particles will not result in the desired end-product specifications, the batch is normally terminated. Therefore, in the growth stage it can be assumed that the desired number of particles, with the desired particle size distribution has already been formed.

It is generally agreed that the growth process is a well understood process and amenable to control. The growth reaction is responsible for developing molecular properties (molecular weights, composition, etc.) and morphology (core-shell, particle size distribution). Since the growth reaction lasts about 10-12 hours, there is great potential for optimizing the reaction time by increasing temperature or by keeping the particles saturated with monomer.

Once inside a particle, radicals induce the usual free-radical polymerization steps such as propagation, termination, chain transfer, etc. A growing radical can escape from a particle and return to the aqueous medium to participate in an aqueous phase termination reaction or enter into another particle. During Stage II, monomer continuously diffuses from the monomer droplets into the particle phase, providing a steady monomer supply for the growing polymer particle.

As the particles grow, the emulsifier molecules are continuously adsorbed onto or desorbed from the particles to maintain thermodynamic equilibrium. This dynamic exchange between various phases when added to the regular polymerization kinetics makes emulsion polymerization a more complex process than bulk or solution polymerization processes. The following figure illustrates the transport processes and reactions in a latex particle:



2.4. Kinetics of Emulsion Polymerization

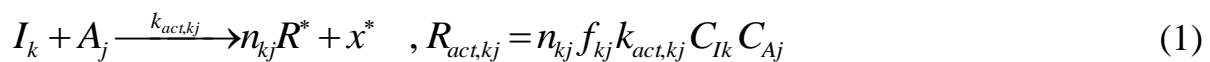
A general emulsion polymerization kinetics scheme involves simultaneous free-radical polymerization taking place in the dispersant phase, particle phase and the monomer droplet phase. However, in general the monomer droplet phase is regarded as an inert phase supplying monomer to the particle phase during reaction. In conventional emulsion polymerization, initiator decomposition takes place in the dispersant phase and the initiator radicals enter the polymer particle phase.

The polymer particle phase is considered to be the site for all the polymerization reactions. There is a dynamic exchange of radicals between the particle phase and the dispersion phase. The average number of radicals per particle is dependent on the steady state that is reached as a result of this exchange. The free-radical kinetics scheme used in the model is that used in the free-radical polymerization model.

Emulsion polymerization can handle activated initiation, redox initiation, absorption and desorption, and much of the kinetics described in the free-radical Reaction Kinetic Scheme, but not short chain branching or beta scission.

Activated Initiation

The mechanism for activated initiation is given as:



Where:

I_k = Initiator molecule

A_j = Activator molecules which promote the dissociation of the initiator molecules

R^* = Primary radical produced in the initiation reaction

x^* = Waste products that do not participate in the polymerization reactions

$R_{act,kj}$ = The radical generation rate for activated initiation

$k_{act,kj}$ = Rate constant for activated initiation

C_{Ik} = Concentration of initiator in the aqueous phase

C_{Aj} = Concentration of activator in the aqueous phase

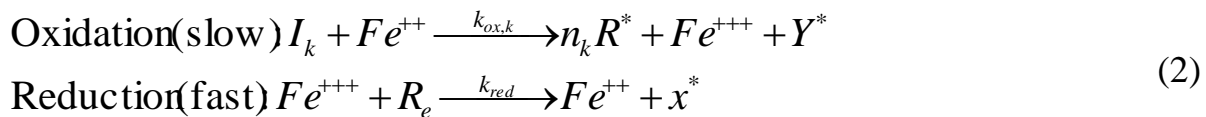
n_{kj} = Number of radicals produced per initiator molecules

f_{kj} = Initiator efficiency factor

In emulsion polymerization water soluble persulfate initiators are normally employed as initiators. In addition, water soluble sodium bisulfite is used as an activator in many emulsion polymerization reactions for accomplishing activated initiation of persulfates.

Redox Initiation

The mechanism for redox initiation is given as:



Similar to activated initiation, redox initiation is used in emulsion polymerization reactions to promote decomposition of initiators at a much lower temperature. For example, redox initiation is employed in cold rubber production. It is also used in emulsion polymerization reactions where high radical flux is needed.

I_k (the initiator, oxidant, or sometimes catalyst) decomposes in the presence of the reduced (ferrous) ions, Fe^{++} , to form one free radical, R^* , and the oxidized (ferric) ion, Fe^{+++} . The reductant, R_e , reacts with the ferric Fe^{+++} ion reducing it to ferrous Fe^{++} . x^* and Y^* are inactive byproducts of the reactions.

The activator system (or redox couple), a Ferrous salt (e.g. ferrous sulfate heptahydrate) plus a reductant (e.g. SFS, Sodium Formaldehyde Sulphoxylate), activates the initiator and regenerates the ferrous ion as previously shown.

Multiple initiators are common: for example, KPS (Potassium persulfate) and tBHP (tert -butyl hydroperoxide). KPS is used initially. At high conversion, the monomer concentration in the polymer phase is low and the $S_2O_4^-$ radicals cannot diffuse into the polymer phase because they are hydrophilic. tBHP, on the other hand, partitions into both the aqueous and the polymer phases and is, therefore, used for finishing in redox systems.

In the case of two initiators, two oxidation reactions and one reduction reaction should be specified.

As the ferrous and ferric ions get regenerated in the redox reaction, it is assumed that the total iron concentration remains constant in the reaction. Assuming stationary state hypothesis for the ferric and ferrous ion concentration in the redox initiation mechanism, one can derive an equation for the rate of generation of the radicals by the redox initiation as follows:

$$R_{ox,k} = \frac{k_{red} C_{Fe} C_{Re} \sum_k n_k f_k k_{ox,k} C_{Ik}}{\sum_k k_{ox,k} C_{Ik} + k_{red} C_{Re}} \quad (3)$$

C_{Fe} = Total concentration of the iron in the aqueous phase

$k_{ox,k}$ = Rate constant for oxidation step of initiator k

k_{red} = Rate constant for reduction step

C_{Ik} = Concentration of initiator k in the aqueous phase

C_{Re} = Concentration of reductant in the aqueous phase

n_k = Number of radicals produced per initiator molecule, k (default =1)

f_k = Efficiency factor for initiator k (default =1)

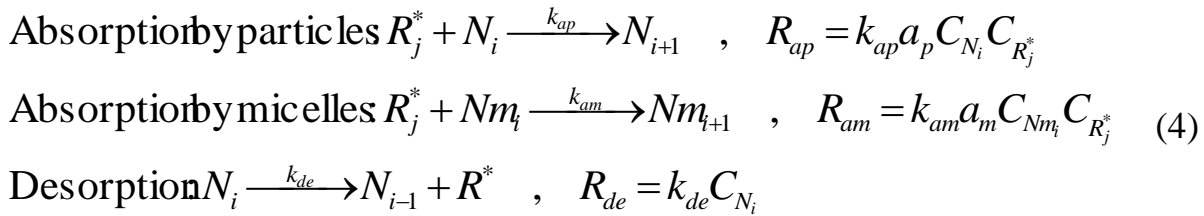
In thermal decomposition, typically each initiator molecule produces two radicals. The cage effect is when the radicals annihilate each other before they are able to diffuse

out of the cage into the aqueous phase. This effect is captured by the radical efficiency term for thermal decomposition.

In redox initiation, only one radical is generated from the initiator. Consequently, there is no cage effect because there is only one radical in the cage. Therefore, in redox initiation, there is typically no need for the two parameters: n_k and f_k . However, these parameters are provided and defaulted to a value of 1 to provide additional handles for the user to fit their model to plant data.

Absorption and Desorption

In addition, there is an exchange of radicals between the aqueous phase and the polymer phase. Radicals generated in the aqueous phase are absorbed by the micelles during micellar nucleation and by the particle during nucleation and subsequent growth. Radicals in the polymer phase can desorb from the particle and enter the aqueous phase. The kinetics of absorption and desorption are described as follows:



Where:

a_m = Area of a single micelle

a_p = Area of a single particle

Nm_i = Number of micelles with i radicals per cubic meter of aqueous phase

N_i = Number of particles with i radicals per cubic meter of aqueous phase

2.5. Model Assumptions

The emulsion polymerization process is extremely complex and involves phenomena for which a complete theoretical understanding has not been reached. Important assumptions are made in the emulsion polymerization model:

- ✓ The reaction mixture is perfectly mixed
- ✓ Particles are formed by the micellar or the homogeneous mechanism
- ✓ No agglomeration or breakage of particles occurs
- ✓ No secondary nucleation occurs
- ✓ All particles have the same average number of radicals and hence the same volumetric growth rate
- ✓ The particle size distribution is unimodal, with moments of PSD sufficient to describe the PSD
- ✓ There are no mass transfer limitations on the polymerization reactions
- ✓ Molecular weight is controlled by chain transfer reactions

2.6. Thermodynamics of Monomer Partitioning

Modeling of the kinetics involved in emulsion polymerization is complicated by the fact that the reaction mixture is multiphase. It is important to account for partitioning of the components among various phases. Up to four coexisting phases may be present in the reaction mixture (Vapor, aqueous, monomer and polymer phases). After the consumption of the monomer droplets, only three phases will remain in the system.

A short-cut partition coefficient methodology was used to handle the four phases. One benefit of using this approach is that NRTL parameters are not required for the polymer or its segments. The method assumes the polymer solubility is zero in the monomer, aqueous, and vapor phases and performs a rigorous 3-phase flash calculation to yield:

- ✓ Vapor phase - if present, contains water and monomers

- ✓ Aqueous phase - contains water, initiators, emulsifiers, activators and some dissolved monomer
- ✓ Monomer phase - contains monomer and some dissolved water

The user provides a partition coefficient for each component that may be present in the polymer phase. Following the rigorous 3-phase flash, an iterative algorithm calculates the amount of each component to transfer from the monomer phase, if present, and the aqueous phase to the polymer phase in order to satisfy the partition coefficient constraints. As monomer is transferred to the polymer phase, water is transferred from the monomer phase to the aqueous phase so that its concentration in the monomer phase is the saturation concentration calculated by the rigorous flash.

The user-supplied partition coefficients are provided as either:

- ✓ Monomer (L1) basis: $x_{pi} = k_{i,1} x_{i,1}$
- ✓ Aqueous (L2) basis: $x_{pi} = k_{i,2} x_{i,2}$

In either case, the partition coefficients are on a mass basis.

In addition, there are *two rigorous phase equilibrium approaches* to handle the thermodynamics of monomer partitioning. *The first rigorous approach* assumes the presence of two liquid phases. The distribution of water, monomers, and polymers is determined by fugacity relationships, and the fugacities of various species are computed by the physical property option set chosen for the system. *The second approach* performs rigorous four phase (vapor-liquid-liquid-polymer) flash calculations based on a newly available flash algorithm.

2.7. Polymer Particle Size Distribution

Polymer particle size and size distribution, among other factors, determine the rheological properties of the latex. Although actual particle size distribution is important, it is often measured in terms of certain averages such as number average

and weight average diameters. Further, rigorous tracking of the particle size distribution by discrete methods is computationally expensive.

In conventional emulsion polymerization where unimodal distributions are normally encountered, the moments of the particle size distribution give sufficient information about the nature of the particle size distribution. The particle size distribution can be described in terms of different independent variables such as diameter or volume of the particle. Since volumetric growth rate of the particle in emulsion polymerization remains almost constant (in Stage II of the process), the population balance equation is formulated in terms of the volume of the particles.