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Chapter 1

Emulsion Polymerization Mechanism

Abdelaziz Nasr Moawed Bakr El-hoshoudy

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http://dx.doi.org/10.5772/intechopen.72143

Abstract

Emulsion polymerization is a polymerization process with different applications on the industrial and academic scale. It involves application of emulsifier to emulsify hydrophobic polymers through aqueous phase by amphipathic emulsifier, then generation of free radicals with either a water or oil soluble initiators. It characterized by reduction of bimolecular termination of free radicals due to segregation of free radicals among the discrete monomer-swollen polymer particles. The latex particles size ranged from 10 nm to 1000 nm in a diameter and are generally spherical. A typical of particle consist of 1–10,000 macromolecules, where macromolecule contains about 100–10^6 monomer units.

Keywords: emulsion polymerization, emulsified monomers, particle nucleation and polymerization mechanism

1. Introduction

Emulsion polymerization is a unique process involves emulsification of hydrophobic monomers by oil-in water emulsifier, then reaction initiation with either a water soluble initiator (e.g. potassium persulfate ($K_2S_2O_8$) or an oil-soluble initiator (e.g. 2,2-azobisisobutyronitrile (AIBN)) [1, 2] in the presence of stabilizer which may be ionic, nonionic or protective colloid to disperse hydrophobic monomer through aqueous solution [3, 4]. Typical polymerization monomers involve vinyl monomers of the structure (CH_2=CH-). These emulsion polymers find a wide range of applications such as synthetic rubbers, thermoplastics, coatings, adhesives, binders, rheological modifiers, plastic pigments [1]. Emulsion polymerization is a rather complex process because nucleation, growth and stabilization of polymer particles are controlled by the free radical polymerization mechanisms in combination with various colloidal phenomena [1]. Aside from other polymerization techniques, emulsion polymerization affords increasing molecular weight of the formed latexes through decreasing polymerization rate by either decreasing initiator concentration or lowering reaction temperature [5, 6].

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Systems of emulsion polymerization involve (1) conventional emulsion polymerization, in which a hydrophobic monomer emulsified in water and polymerization initiated with a water-soluble initiator [5]. (2) Inverse emulsion polymerization [7], where organic solvents of very low polarity as paraffin or xylene used as a polymerization media to emulsify hydrophilic monomers [5], then initiation proceed with the aid of hydrophobic initiator [5]. These two polymerization types known as oil-in-water (o/w) and water-in-oil (w/o) emulsions [5]. (3) Mini emulsion polymerization involves systems with monomer droplets in water with much smaller droplets than in emulsion polymerization and characterized by monomer droplet =50–1000 nm, surfactant concentration < critical micelle concentration (CMC), water insoluble co stabilizer as hexadecane to prevent Ostwald ripening, polymer particle size equal monomer droplet size = 50–1000 nm, and both water soluble and oil soluble initiator used [4, 8]. (4) Microemulsion polymerization with very much smaller monomer droplets, about 10–100 nm, and characterized by surfactant concentration > CMC, polymer particles = 10–50 nm, water-soluble initiator are commonly used [9, 10]. Miniemulsion, microemulsion and conventional emulsion polymerizations show quite different particle nucleation and growth mechanisms and kinetics [1]. Many articles discuss different types of emulsion polymerization found in literature [1, 11–16].

2. Components of heterogeneous emulsion polymerization

The main components of emulsion polymerization media involve monomer(s), dispersing medium, emulsifier, and water-soluble initiator [5, 17–19]. The dispersion medium is water in which hydrophobic monomers is emulsified by surface-active agents (surfactant). When surfactant concentration exceeds critical micelle concentration (CMC) it aggregate in the form of spherical micelles, so surface tension at the surface decrease, as a result hydrophobic monomers enter in to the vicinity of micelle and reaction continue until all monomer droplets are exhausted and micelle containing monomers increase in size. Typical micelles have dimensions of 2–10 nm, with each micelle containing 50–150 surfactant molecules [5]. Water-soluble initiators enter into the micelle where free radical propagation start. In general, monomer droplets are not effective in competing with micelles in capturing free radicals generated in the aqueous phase due to their relatively small surface area [1], so the micelle act as a meeting site of water-soluble initiators and hydrophobic vinyl monomers. As polymerization continue inside micelle, the micelle grow by monomer addition from monomer droplets outside and latex are formed. Schematic representation of emulsion polymerization shown in **Figure 1**. Emulsion polymerization carried out through three main intervals as shown in **Figure 2**.

There is a separate monomer phase in intervals I. The particle number increases with time in interval I and particle nucleation occurs in interval I. At the end of this stage most of surfactants are exhausted (i.e. micelles are exhausted) [5]. About one of every 102–103 micelles can be successfully converted into latex particles [1]. Particle nucleation process is greatly affected by surfactant concentration, which in turn affect particle size and particle size distribution of latex [1]. The lower the surfactant concentration, the lower the nucleation period the narrow the particle size distribution. At interval II (Particle growth stage), the polymerization continue and polymer particles increase in size until monomer droplets exhausted. Monomer droplets act as reservoirs to supply the growing particles with monomer and surfactant species. At interval

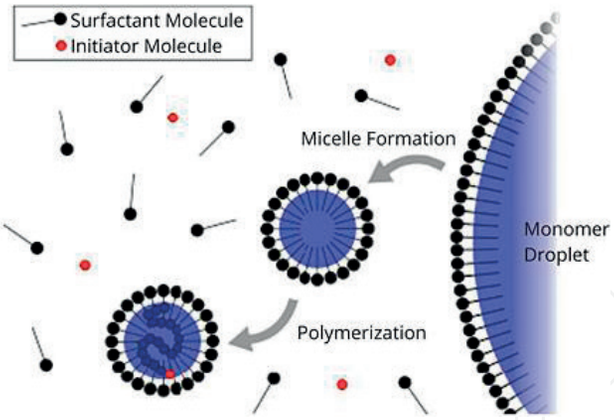


Figure 1. Schematic representation of emulsion polymerization.

III, the polymer size increase as latex particles become monomer-starved and the concentration of monomer in the reaction loci continues to decrease toward the end of polymerization [1].

2.1. Initiators

Initiator act to generate free radicals by thermal decomposition, or redox reactions. The initiators may be; (1) water-soluble initiators like 2,2-Azobis(2-amidinopropane) dihydrochloride, $K_2S_2O_8$, APS (Ammonium persulfate) and (H_2O_2) hydrogen peroxide. (2) Partially water-soluble peroxides like t-butyl hydroperoxide and succinic acid peroxide and azo compounds such as 4,4-azobis(4-cyanopentanoic acid) [14]. (3) Redox systems such as persulfate with ferrous ion, cumyl hydroperoxide or hydrogen peroxide with ferrous, sulfite, or bisulfite ion [5, 20]. Other initiators such as surface active initiators which "inisurfs," for example; bis[2-(4′-sulfophenyl)alkyl]-2,2′-azodiisobutyrate ammonium salts

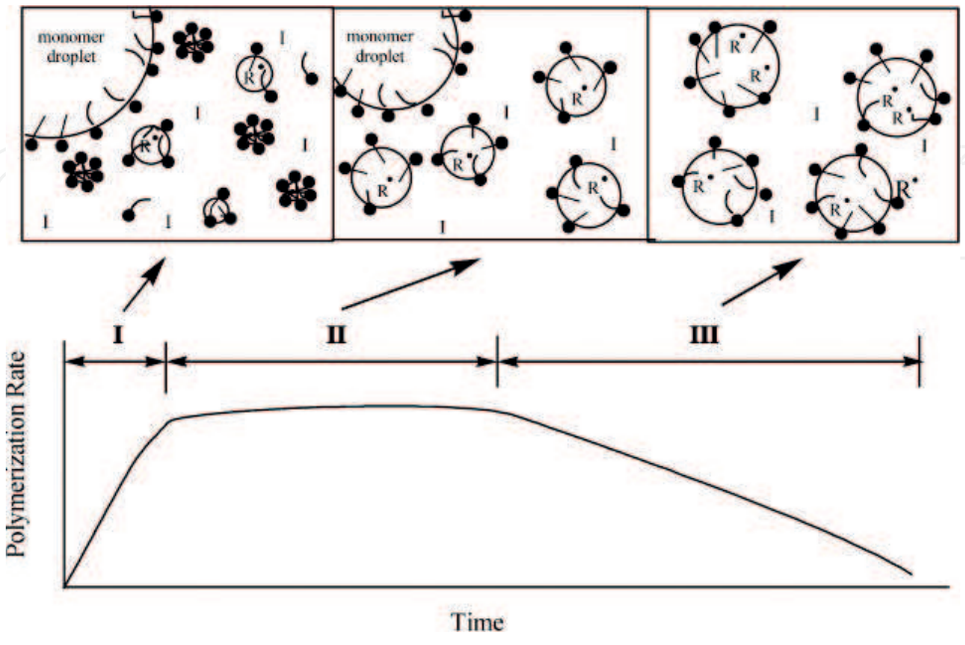


Figure 2. Emulsion polymerization intervals.

and 2,2′-azobis(N-2′-methylpropanoyl-2-amino-alkyl-1-sulfonate). These initiators initiates emulsion polymerization without the need of stabilizers.

2.2. Surfactants

Act to decrease interfacial tension between monomer and aqueous phase, stabilize the latex and generate micelles in which monomers emulsified and nucleation reaction proceed. Surfactants increase particle number and decrease particle size, these surfactants may be (1) Anionic surfactants such as fatty acid soaps (sodium or potassium stearate, laurate, palmitate), sulfates, and sulfonates (sodium lauryl sulfate and sodium dodecylbenzene sulfonate); (2) Nonionic surfactants such as poly (ethylene oxide), poly (vinyl alcohol) and hydroxyethyl cellulose; (3) Cationic surfactants such as dodecylammonium chloride and cetyltrimethylammonium bromide [5, 21]. For ionic surfactants, micelles formed only at temperatures above the Krafft point. For a nonionic surfactant, micelles formed only at temperatures below the cloud point. Emulsion polymerization carried out below the cloud temperature and above the Krafft temperature [5]. Polymerizable surfactants (surfactants with active double bond) such as sodium dodecyl allyl sulfosuccinate [13, 22–24] also used to produce latexes with chemically bound surface-active groups [5, 25–30, 31]. Polymerized surfactants (surfactants with active double bond) consist of amphipathic structure comprising hydrophobic tail and hydrophilic head group [32], in addition to polymerized vinyl groups [33] in their molecular structure, which acquire them unique physicochemical properties other than traditional surfactants moieties [34] such as;

A. They have surface activity like ordinary surfactants and polymerized vinyl group like vinyl monomers, so they have the ability to undergo polymerization reactions.

B. Due to their amphoteric structure and polymerization ability, they serve to synthesize inorganic/organic nanocomposite, and applied to emulsion polymerizations as polymerized emulsifiers, to stabilize the formed latexes, to prepare novel water-soluble hydrophobically associating polymers with strong thickening properties [35] so, they greatly applied in the field of enhanced oil recovery [36].

C. Allow developing hybrid Nano sized reaction and templating media. Moreover surfmer serve as hydrophilic monomer to copolymerize with acrylamide derivatives (AM) forming hydrophobically associating polyacrylamide (HAPAM), which acquire wide application in improved oil recovery coats and paintings and drilling fluids [37].

Freedman et al., [38] reported about the first synthesis of vinyl monomers which serve as emulsifying agents [39]. Active vinyl groups comprise vinyl, allyls, acrylates, methacrylates, styryl and acrylamide [40]. Polymerized groups may be “H-type” where, i.e. located in the hydrophilic head group, or “T-type” where, i.e. located in the hydrophobic tail have a profound effect on surfactant self-assembly and properties [41]. All kinds of polymerizable traditional surfactants, including cationic [41], anionic [42] and nonionic [43] have been synthesized to study the influence of the molecular structure on the properties and application. Anionic polymerizable surfactants seem to be the most promising for utilizing in coatings, adhesives and enhanced oil recovery.

2.3. Dispersion medium

Water is the frequently used dispersion medium in emulsion polymerization as it is cheap and environmentally friendly. It represents the medium of transfer of monomer from droplets to particles and as a solvent for emulsifier, initiator, and other ingredients.

2.4. Monomer

Emulsion polymerization require free radical polymerizable monomers. Generally, vinyl monomers are used in this type of polymerization such as acrylamide, acrylic acid, butadiene, styrene, acrylonitrile, acrylate ester and methacrylate ester monomers, vinyl acetate, and vinyl chloride [1] and many other vinyl derivatives [25]. Depending on monomer solubility in aqueous phase, there is three categories of typical emulsion polymerization monomers which comprise (1) monomers of high solubility such as acrylonitrile, (2) monomers of medium solubility as methyl methacrylate and monomers insoluble in aqueous phase such as butadiene and styrene [44].

2.5. Other constituents

Other components involve emulsion polymerization medium that is generally deionized water. Antifreeze additives which involve inorganic electrolytes, ethylene glycol, glycerol, methanol, and monoalkyl ethers of ethylene glycol to allow polymerization at temperatures below 0°C. Sequestering agents which used to solubilize the initiator system or to deactivate traces of hardness elements (Ca^{+2}, Mg^{+2} ions) such as ethylene diamine tetra acetic acid or its alkali metal salts. Buffers used to stabilize the latex toward pH changes such as phosphate or citrate salts [5, 20]. Chain transfer agents like mercaptans.

3. Surfactant free emulsion polymerization

Used for manufacture of adhesives and water resistant polymers. By absence of surfactant, intensive coagulation of the particles greatly reduces the number of particles per unit volume of water so, particle nucleation and growth reduced [1]. Several literature had been reported about surfactant free emulsion polymerization, in this section a brief hint about these publications will be considered. Tauer et al. [45] studied the surfactant-free emulsion polymerization of styrene initiated by KPS. Wang and Pan [46] studied the surfactant-free emulsion polymerization of styrene with the water soluble co-monomer as 4-vinylpyridine. Ni et al. [47] studied mechanism of particle nucleation through adding 8% ethyl acetate at low speed agitation (100–200 rpm) through polymerization of 4-vinyl pyridine and styrene. Ou et al. [48] investigated the effect of the hydrophilic co monomer (vinyl acetate or methyl methacrylate) on particle nucleation in the surfactant-free emulsion polymerization of styrene. Yan et al. [49] investigated the surfactant-free emulsion copolymerization of styrene, methyl methacrylate and acrylic acid initiated by ammonium persulfate. Other literature reported by Mahdavian and Abdollahi, Zhang et al., Shaffei et al., and Sahoo and Mohapatra [50–53].

3.1. Emulsion polymerization mechanism

Emulsion polymerization is a free radical polymerization protocol occurs in three distinct steps; initiation, propagation, and termination.

3.1.1. Initiation

In which the initiator decomposed to free radicals either by (1) hemolytic fission (hemolysis) through thermal decomposition or radiation and by (2) chemical reaction through redox reactions. Rate of initiator dissociation (R_d) is the rate determining step and given by Eqs. (1)–(3);

$$I \xrightarrow{K_d} 2R\bullet \tag{1}$$

$$R_d = 2fK_d[I] \tag{2}$$

$$R\bullet + M \xrightarrow{K_i} RM\bullet \tag{3}$$

Rate of initiation (R_i) is given by Eq. (4);

$$R_i = 2fK_i[I] \tag{4}$$

K_d rate constant for initiator dissociation

f Initiator efficiency

$[I]$ Initiator concentration

K_i rate constant for initiation

3.1.2. Propagation

Involve continuous addition of monomer particles to active centers ($RM^{\bullet}$) to form polymer chains.

Rate of polymerization (R_p) given by Eq. (5);

$$R_p = -\frac{d[M]}{dt} = k_i[R\bullet][M] + k_p[M\bullet][M] \tag{5}$$

Where [$R^{\bullet}$] is the free radicals concentration, [M] is the monomer concentration and [$M^{\bullet}$] is the total concentration of active monomers. Since consumed monomers in initiation stage is very small as compared to propagation, so the term "$k_i[R\bullet][M]$" can be neglected and rate of polymerization is determined by rate of propagation; Eq. (6).

$$R_p = k_p[M\bullet][M] \tag{6}$$

3.1.3. Termination

Termination leads to loss of two growing polymer chains [3]. It occurs by either recombination or disproportionation. Recombination involves reaction of one polymer chain with another growing one and reactive sites are blocked according to the following equation.

$$P_n\bullet + P_m\bullet \xrightarrow{K_t} P_n + m \tag{7}$$

Disproportionation where one chain abstract a hydrogen proton from another leaving it with unsaturated end group according to the following equation. This termination mechanism result in two polymer chain fractions one is saturated and the other is unsaturated [31].

$$P_n\bullet + P_m\bullet \xrightarrow{K_t} P_n + P_m \tag{8}$$

Termination may occur by chain transfer reactions, which involves removal of atom and formation of new radical which may initiate the reaction forming other segments or cannot initiate the reaction so, the propagation progress ceased [31]. Other literature reported about termination occur by addition of retarders or inhibitors like phenols and catechol's to terminate active sites [31, 54].

3.2. Kinetics of emulsion polymerization

Since rate of polymerization expressed by Eq. (9);

$$R_p = k_p[M\bullet][M] \tag{9}$$

Where $[M\bullet]$ expressed by Eq. 10;

$$[M\bullet] = \frac{N^{'}n}{NA} \tag{10}$$

N concentration of micelles plus particles

n the average number of radicals per micelle plus particle

N_A is the Avogadro number

$$R_p = \frac{N^{'}nkp[M]}{NA} \tag{11}$$

The value of "n" determine rate of polymerization and depend on radical diffusion out of the polymer particles (desorption), the particle size, modes of termination, and the rates of initiation and termination relative to each other and to the other reaction parameters [5]. Depending on "n" value there are three cases that can be summarized as;

3.2.1. Case 1: n = 0.5

Means that at any given moment half of the polymer particles contain one radical and are growing while the other half are dormant, and known as zero–one systems to indicate that a polymer particle contains either zero or one radical at any given moment [5].

3.2.2. Case 2: n < 0.5

In which radical desorption from particles and termination in the aqueous phase are low especially for small particle sizes and low initiation rates.

3.2.3. Case 3: n > 0.5

In which particle size is large or the termination rate constant is low while termination in the aqueous phase and the initiation rate is fast, as some polymer particles contain two or more radicals.

- Degree of polymerization (X_n) is defined as the rate of growth of a polymer chain divided by the rate at which primary radicals enter the polymer particle and given by the following Eq. (12);

$$X_n = \frac{r_p}{r_i} = \frac{NKp[M]}{R_i} \tag{12}$$

This equation neglect any termination by chain transfer, if chain transfer occur the degree of polymerization given by Eq. (13).

$$X_n = \frac{r_p}{r_i \sum r_t} \tag{13}$$

where, $\sum r_t$ is the sum of termination reactions by chain transfer.

- Number of polymer particles is dependent on the total surface area of surfactant present in the system and given by Eq. (14);

$$N = K\left(\frac{Ri}{\mu}\right)^{2/5}(a_s S)^{3/5} \tag{14}$$

a_s is the interfacial surface area occupied by a surfactant molecule

S is the total concentration of surfactant in the system (micelles, solution, monomer droplets)

μ is the rate of volume increase of polymer particle

The number of polymer particles can be increased by increasing the emulsifier concentration while maintaining a constant rate of radical generation.

4. Conclusion

Emulsion polymerization has wide application on academic and industrial applications. This chapter discuss importance of heterogeneous emulsion polymerization and its constituents; moreover, a comprehensive analysis of the kinetics of emulsion polymerization has been presented. Other emulsion polymerization characteristics like inverse emulsion, mini emulsion and micro emulsion discussed briefly.

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