



Mechanism of Emulsion Polymerization and its Kinetics

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BRIEF NOTE

Emulsion polymerization is one of the most important methods for the polymerization of a large number of monomers, like vinyl acetate, vinyl chloride, chloroprene, acrylamide, acrylates, and methacrylates. It is also used for the production of various copolymers, like acrylonitrile-butadiene-styrene (ABS).

Emulsion polymerization has many advantages than other polymerization methods; for example, it is more quick process than bulk or solution polymerization at same temperature, the conversion is essentially 100%, and the average molecular weight is normally (much) higher than at the same polymerization rate in bulk or solution polymerization [1]. And also, heat dissipation and viscosity control are much less complicated than in bulk polymerization.

In general, an emulsion polymerization system contains a dispersing medium, monomer, emulsifier, initiator and modifiers. Water is usually the continuous phase in which the different constituents are dispersed by the emulsifiers. The monomers are only slightly soluble in water. They form tiny droplets that are suspended and stabilized by the emulsifiers, that is the emulsifier molecules associate and form micelles that surround small amounts of monomer. The remaining monomer is dispersed in droplets.

Common emulsifiers are anionic and non-ionic surfactants whereas cationic surfactants, such as quaternary ammonium salts are used in rare time [2]. Particular anionic emulsifiers are sodium, potassium, or ammonium salts of fatty acids and C12-C16 alkyl sulfates. Particular non-ionic surfactants are polyethylene oxide, polyvinyl alcohol and hydroxyethyl cellulose. A combination of these two anionic and nonionic surfactants will frequently improve the stability of the dispersed droplets.

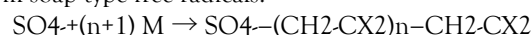
This process can be divided in three distinctive stages:

Stage I: In emulsion polymerization, the mixture contains of the continuous water phase with dispersed surfactant micelles and emulsified monomer droplets of 1-10 microns. Most monomer is localized in these droplets and some are dissolved in the micelles and a little amount in the water phase. The micelles are in

dynamic equilibrium with the dissolved emulsifier molecules. Nucleation stops when the surface area enhances large enough to absorb all of the emulsifier molecules [3]. The polymerization starts when initiator is added to it. A usual initiator is (water soluble) potassium persulfate. It decomposes in the water and forms negatively charged sulfate radicals.



These radicals will react with the in water dissolved monomers and form soap type free radicals.



They either mixed with the dissolved emulsifier molecules to micelles or they become into existing micelle droplets [4]. In the first stage of the polymerization, monomers continuously migrate from large monomer droplets through the water phase into the micelles and are added to the growing polymer chains. At the same time, new particles are formed by the initiators. Some polymerization takes place in the water phase due to the solubility of monomers and initiators, whereas the monomer droplets does not provide loci for polymerization because the negatively charged surfactant molecules surrounds these droplets and are virtually impossible to penetrate by the negatively charged initiator molecules.

Stage II: The number of polymer particles and the rate of polymerization increase as long as new radicals and polymer micelles are formed. In the end, all surfactant in the system will be absorbed or all initiator molecules are used by the polymer particles. At this moment, the rate of polymerization remains more or less constant. The particle number stabilizes at rather low value which is only small fraction, typically about 0.1% of number of micelles are initially present. The diffusion of free radicals into monomer droplets are generally not important to the reaction rate during the growth stage and rate of monomer diffusion is usually adequate to supply enough number of monomers to keep the reaction in the particles on going [5].

Stage III: As the size of the latex all particles increases the size of the monomer droplets, decreases, and eventually they disappear.

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At this stage, the reaction mixture consists solely of monomer swollen polymer particles, the so called latex particles, and dissolved monomers. Since monomer droplets are no longer present, both the monomer concentration and the reaction rate steadily decrease with time. With increasing polymer concentration, some cross-linking reactions and branching can also be expected. The reaction ends when either all monomers are used up or when a second radical diffuses into the polymer particles and causes immediate bimolecular termination by disproportionation or recombination of two radicals. If no termination occurs, the system reaches a conversion of essentially 100%. The final polymer particles are spherical in shape and have a diameter in the range of 50-300 nm which is between the initial micelle and monomer droplet size.

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