CHAPTER I

INTRODUCTION AND THEORY

1.1 Overview

Emulsion polymerization is the method of conducting the polymerization of a monomer in a dispersing medium (usually water) that leads to the formation of a polymer dispersion with particles of a colloidal degree of dispersity. The simplest recipe for an emulsion polymerization starts with water, surfactant (soap), a water-insoluble monomer (e.g. styrene), and water-soluble initiator (e.g. potassium persulfate). The system is agitated to form an emulsion. The polymerization reaction starts with the decomposition of the initiator by heating the system, then the free radical will react with the monomers. The end result of the polymerization process is a latex comprising polymer particles, each containing many polymer chains, with any desired morphology, composition, sequence distribution, surface group, molecular weight distribution, particle size distribution, particle concentration, degree of crystallinity, and film forming properties.. The polymer particles constitute a disperse (or discrete) phase in a continuous aqueous (or serum) phase. These latex particles are typically 200 nm in diameter. They are stabilized against coalescence by surfactant (Figure 1.1), and comprise a new phase that is formed early in the process. The latex can be used directly (e.g. as an adhesive or surface coating) or, for other applications, the polymer can be extracted [1].
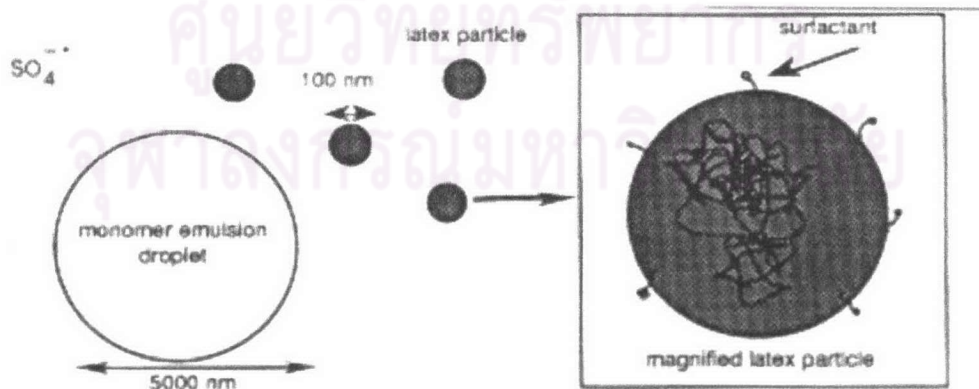

Figure 1.1 The basic component of an emulsion polymerization

Emulsion polymerization usually occurs in the monomer-swollen latex particle: the term emulsion polymerization is a misnomer.

Emulsion polymerization is economically important: for example, in Western countries alone, current product of all polymers is in excess of 10^8 tonnes per year, and approximately 30% of this polymer is made by free-radical means; emulsion methods are used for effecting 40 – 50% of these free-radical polymerization. Some of these products are commodity materials, e.g. artificial rubber and latex paints, while others are high value added, such as for diagnostic kits in biomedical applications [2].

1.2 Ingredients for emulsion polymerization

1.2.1 Monomers

The major polymerizable component of an emulsion polymerization is a monomer which has limited water solubility, and that swells its product polymer. The monomers used in emulsion polymerization usually are the vinyl type, $CH_2=CHX$. X maybe C_6H_5 (when the monomer is styrene), CN (acrylonitrile), O_2CCH_3 (vinyl acetate), Cl (vinyl chloride) or CO_2R (acrylates: for acrylic acid R is a hydrogen atom, while if R is a butyl group then the monomer is butyl acrylate). There are also di-substituted vinyls, $CH_2=CR_1R_2$: for methacrylate, R_1 is CH_3 and R_2 is CO_2R: e.g. methyl methacrylate (MMA) and butyl methacrylate [1].

1.2.2 Initiators

A source of free radicals is needed for water-borne emulsion polymerization, most initiators used in emulsion polymerization are water-soluble. A commonly used is potassium persulfate ($K_2S_2O_8$, properly potassium peroxodisulfate), or other persulfate salts such as ammonium persulfate. Persulfate produces sulfate radical as a result of bond scission; the activation energy for this process is quite high, so persulfate is usually employed at high temperatures above 50°C. A side-product of persulfate decomposition is HSO_4^-, produced by reaction of $S_2O_8^{2-}$ with water. Since HSO_4^- alters pH, which can drastically reduce initiator efficiency, buffer thus should be used with this initiator if controlled conditions are desired. Another class of water-soluble thermal initiators comprises water-soluble azo compounds such as 2,2'-azobis(2-amidinopropane)

dihydrochloride, commercially known as V-50 (Figure 1.2). This dissociates to give N_2 and two $(CH_3)_2CC(NH)NH_3^+$ radicals [3].
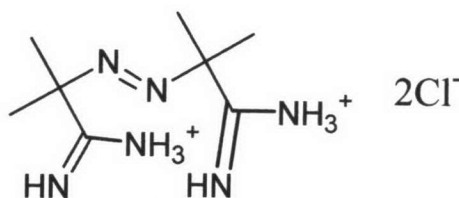

Figure 1.2 The initiator 2,2'-azobis(2-amidinopropane) dihydrochloride (V-50)

At the temperatures lower than 50 °C, a redox system such as sodium formaldehyde sulfoxylate and cumene hydroperoxide [4], or dimethylhydroperoxide, or persulfate and metabisulfite, is often used. It is cheaper to perform industrial emulsion polymerizations at low temperatures through the use of a redox initiator. In the case of synthetic rubbers, this also reduces the amount of branching of the chains, which in turn reduces the time required to incorporate carbon black into the rubber.

Another initiating system is free radicals OH$^\bullet$, H$^\bullet$ and e_{aq}^- generated via γ-radiolysis or in an electron beam. The rate of production of free radicals is almost temperature-independent with this technique [5].

Finally, it is possible to employ an organic-phase initiator such as AIBN (azobisisobutyronitrile, Figure 1.3) in an emulsion polymerization. Oil-soluble initiators can be employed under special circumstances in emulsion polymerizations: e.g. in the preparation of large-particle size-monodisperse polystyrene latex using AIBN and water-soluble inhibitor in seeded emulsion polymerizations. Oil-soluble initiators also find use in emulsion polymerization [6].
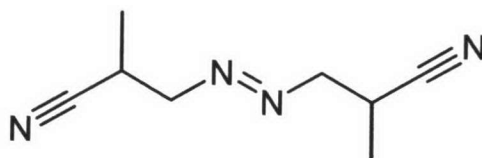

Figure 1.3 The organic phase initiator azobisisobutyronitrile (AIBN)

1.2.3 Surfactants

Surfactant (emulsifier or stabilizers) is used to stabilize the latex particles. There are three basic types of surfactants: (a) electrostatic stabilizers such as anionic or cationic soaps, which prevent coagulation by electrostatic repulsion from the charges located on the particle surfaces and their associated electric double layers (Figure 1.4), (b) polymeric (steric) stabilizers such as partially hydrolyzed poly(vinyl acetate), which stabilize the particles through the entropic repulsion caused by trying to pack two chains in the same space, and (c) electrosteric stabilizers, such as polyelectrolytes. Electrosteric stabilizer displays the characteristics of both of the surfactant types (a) and (b), as suggested in Figure 1.5 [7].

In industrial emulsion polymerizations, polymeric stabilizers (protective agents) are often used, e.g. to impart good freeze-thaw stability to paint.

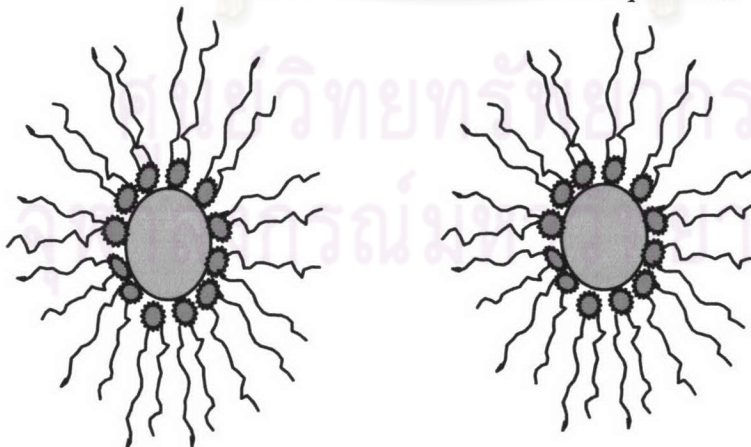**Figure 1.4** The action of anionic surfactant to stabilize the particles

Figure 1.5 The action of nonionic surfactant to stabilize the particles

1.2.4 Other ingredients

It is often common to add a modifier in commercial emulsion polymerization: chain transfer agent to control molecular weight, buffers to control pH and initiator efficiency. Electrolytes may also be added to induce particle size monodispersity. It is also common to add a chaser to reduce residual monomer at the end of the polymerization process. Typically a chaser may be a shot of redox initiator added later in the polymerization batch.

1.3 Advantages and disadvantages of emulsion polymerization

1.3.1 Advantages

The advantages of emulsion polymerization are (1) provide higher rate of polymerization, molecular weight and conversion of monomer into polymer than bulk polymerization, (2) the reaction temperature is easy to control, (3) the polymer product is easy to handle because it formed as a latex rather than as the solid or as the viscous liquid and (4) there is no solvent in the process which reduces environmental hazards.

1.3.2 Disadvantages

The emulsion polymerization also has some disadvantages, (1) the system contains many additives which may impair the quality of the final product, (2) it is very difficult to separate the polymer from the water (if necessary) and (3) its mechanism is extremely complex which is hard to understand and control.

1.4 The three intervals of emulsion polymerization

It is convenient to divide emulsion polymerizations into the three stages or intervals (Table 1.1).

Interval I is characterized by an increasing in the number of the particles and the rate of the reaction.

Interval II starts when particle nucleation ceases. All three possible phases are present: an aqueous phase, latex particles, and monomer droplets. Latex particles maintain constant monomer/polymer ratio. Monomer concentration within the latex particle (Cp),

concentration or number density of particles (Nc) and the reaction rate does not change during Interval II.

Interval III is the final stage of the reaction. As the polymerization progresses and the monomer is consumed, the monomer droplets eventually become exhausted and disappeared. Only latex particles and aqueous phase are present during this final period [8].

The various phases present in each of these three stages of polymerization are shown in Figure 1.6.

Table 1.1 Qualitative details of the three intervals of emulsion polymerization

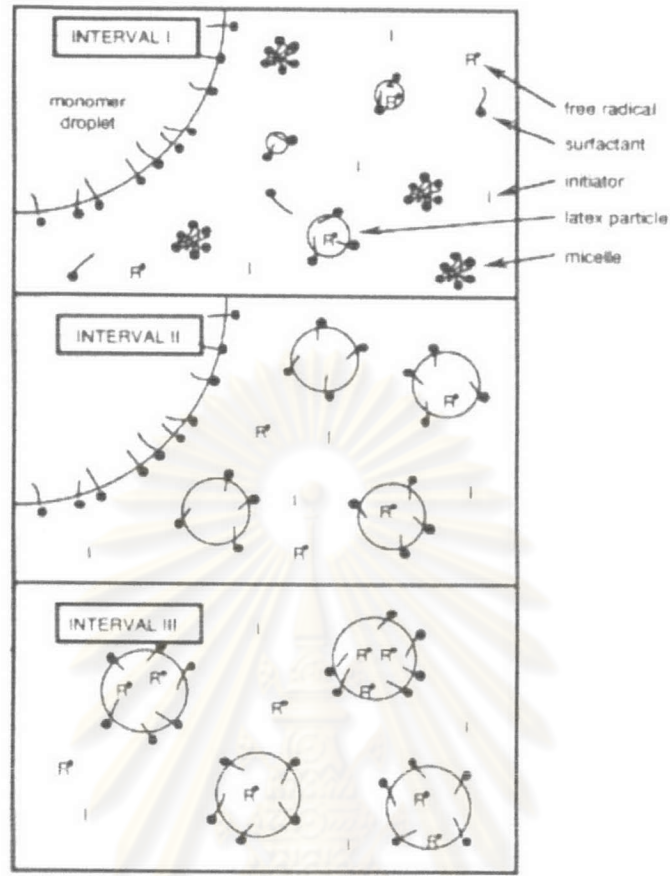| interval	typical % conversion range	micelles	monomer droplets	particle number	particle size	comments
I	0 – 10	present	present	increase	increase	nucleation period
II	10 – 40	absent	present	constant	increase	C_p constant
III	40 - 100	absent	absent	constant	roughly constant	C_p decrease

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Figure 1.6 The three intervals of an emulsion polymerization

1.5 Particle formation

1.5.1 Particle formation below the CMC (Critical Micelle Concentration) [9]

Below the CMC, no micelles formed from added surfactant, the nucleation mechanism below the CMC is in situ micellization. This mechanism involves the micelles formed by in situ surfactant, which can arise from the reactions of species derived aqueous-phase reactions of initiator. The homogeneous-nucleation mechanism is shown in Figure 1.7. A charged moiety from initiator decomposition propagates with monomer in the aqueous phase until it has a sufficiently high degree of polymerization (j_{crit}) which is about 5 for styrene to undergo a transition to a coiled-chain conformation which excludes water. It thereupon metamorphoses to a precursor particle upon becoming swollen with monomer. Colloidal stability is imparted by charged groups formed from initiator. Precursor particles

grow by propagation in the now monomer-rich interior, and also by coagulating with other precursor particles. Termination also takes place between aqueous-phase oligomeric radicals.
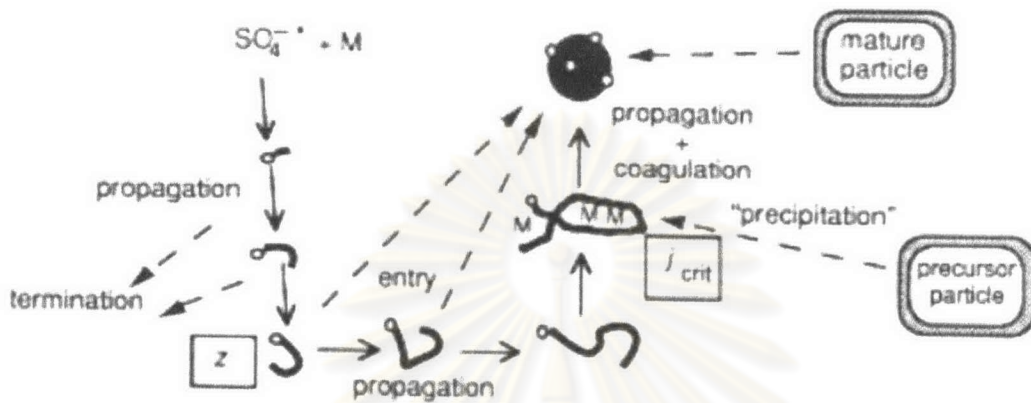

Figure 1.7 The detail of particle formation by homogeneous-nucleation

1.5.2 Particle formation above the CMC

Most commercial emulsion polymerizations use surfactant concentration at above the CMC. The mechanism at above the CMC is shown in Figure 1.8. Free radical initiator propagates until it reaches a critical degree of polymerization (z) to become surface-active. The z-mer may enter a micelle, or aggregate with surfactant molecules. Surfactant is adsorbed onto particles, the consumption of surfactant by the particles cause the amount of free surfactant being reduced . The z-mer may also propagate further to form j_{crit}-mer, although this is kinetically insignificant while there is sufficient free surfactant for the system to be above the CMC. Entry into, and exit from, these precursor particles also takes place; a desorbed radical might form a new particle (i.e., the particle number can be greater than the total number of radicals formed by initiator decomposition). Eventually the precursor particles grow sufficiently large in size and number to capture all newly formed aqueous-phase free radicals so that no new particle formation occurs. Nucleation ceases when the rate of capture of new free radicals (formed from initiator in the aqueous phase) by pre-existing particles and termination greatly exceeds the rate at which newly born aqueous-phase free radicals can themselves form new particles.
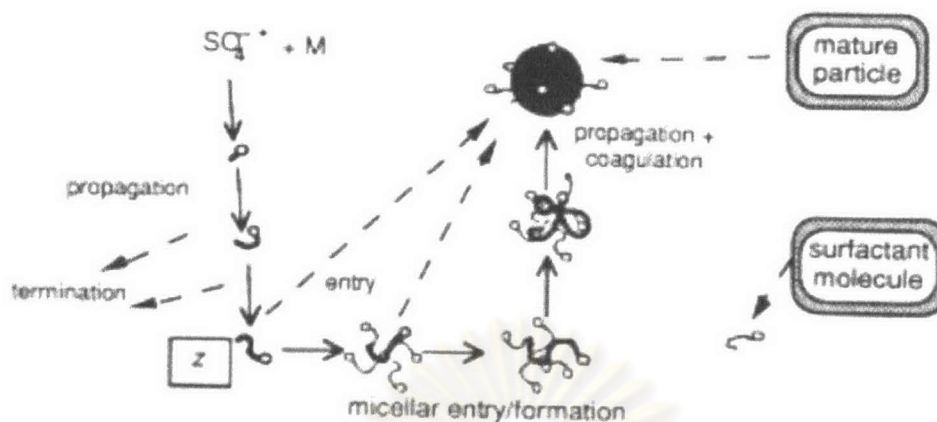
Figure 1.8 Illustration the main features of the extended micellar description of   particle formation

1.6   Effects of the choice of emulsifier in emulsion polymerization [10]

Emulsion polymerization without the use of an emulsifier may be achieved by uses an ionic end groups initiator such as potassium persulfate groups that can stabilize the polymer latex particles produced electrostatically. Type and concentration of the surfactant used affects the number of latex particles formed, which in turn determines the rate of polymerization and, depending also on the rate of initiation, the molecular weight of the polymer formed. Although the physical properties of the polymer are primarily dependent on its molecular weight and molecular weight distribution, the properties of the latex depend on its concentration, average particle size, particle size distribution, and the viscosity of the aqueous phase. The best emulsifiers for stabilizing the monomer emulsion are not necessarily those that for stabilize the polymer latex because the mechanical agitation during polymerization can provide the dispersion of the monomers, whereas the latex is likely to be required to remain in dispersion for a prolonged period without agitation. In latex application as adhesive or paint, the effect of the emulsifiers on film properties (e.g., water sensitivity) may be of the utmost importance. The effects of emulsifiers in emulsion polymerization systems may be enumerated as follows: (1) stabilization of the monomer in emulsion, (2) solubilization of monomer in micelles, (3) stabilization of polymer latex particles, (4) solubilization of polymer, (5) catalysis of the

initiation reaction and (6) action as transfer agents or retarder which leads to chemical binding of emulsifier residues in the polymer obtained.

1.6.1 Monomer emulsification [11]

The emulsification of the monomer is not usually primary importance in emulsion polymerization, if the size of emulsion droplets can be reduced by the special methods of emulsification. For nonionic surfactant, the important factor for selecting the surfactant used is Hydrophile-lipophile balance (HLB).

The HLB scale was introduced as an aid particularly to the use of nonionic surfactants in the formulations of cosmetics. HLB value (Table 1.2) is related to the solubility of the materials in water: for nonionic surfactants on poly(ethylene oxide) the HLB number may be found simply by dividing the percentage of ethylene oxide in the surfactant by five [12].

Table 1.2 The HLB scale and water solubility of surfactants

solubility in water	HLB number	application
	0	
not dispersible	2	
	4	emulsifier for water in oil emulsion
poorly dispersible	6	
unstable milky dispersion	8	wetting agents
stable milky dispersion	10	
translucent solution	12	
	14	detergents emulsifier for oil in
clear solution	16	water emulsion
	18	solubilizers

1.6.2 Emulsion polymerization with nonionic emulsifiers

The mechanism of emulsion polymerization with nonionic emulsifiers alone is different fundamentally from emulsion polymerization with ionic emulsifiers. The characteristics of emulsion polymerization with nonionic emulsifiers alone would appear to be similar to emulsifier-free emulsion polymerization in which the final latex particles are

formed by primary particles which coalesce until a stable size is reached. This would imply that even though micelles are present and presumably solubilize monomer, the locus of polymerization is exclusively in the aqueous phase. Adsorption of the nonionic emulsifiers would greatly increase the size which oligomeric radicals could attain without precipitating.

1.6.3 Emulsion polymerization with ionic emulsifiers

The Smith-Ewart theory can be used for the systems with ionic emulsifiers The theory may not be applicable when nonionic emulsifiers are used alone or when mixtures of ionic and nonionic emulsifiers are used. The parameter characteristic of the emulsifier in Smith-Ewart theory is a_s, the area occupied by an emulsifier in a saturated monolayer at the polymer-water interface. It is assumed that the area occupied by an emulsifier molecule on the latex particle surface and in the micelle is the same. Since the present of micelles containing solubilized monomer is postulated to be essential for the nucleation of latex particles, it follows that it should not be possible to nucleate additional latex particles once all emulsifier has been adsorbed on the existing particles. The reason that emulsifier should adsorb on the latex particle rather than aggregate in micelles in solution is not explained, although it is an experimental fact that the micelles do usually disappear from solution (as shown by an increase in the surface tension) at approximately the same time as new latex particles cease to form [13].

1.6.3.1 Effect of emulsifier on number of latex particles formed

The number of polymer latex particles formed N is determined by the area a_s which the emulsifier molecule occupies in a saturated monolayer at the polymer-water interface,

$$N \alpha (a_sS)^{3/5}$$

where S is the surfactant concentration.

The CMC decreases as alkyl chain length increases at the same total emulsifier concentration. Although the Harkins model postulates micellar nucleation of latex particles, the micelles are not actually considered in the Smith-Ewart theory: it is assumed that the total concentration of emulsifier is all adsorbed on the latex particles at the end of Interval I and that the equilibrium concentration in solution (which is likely to be of the order of the CMC) may be neglected. This is possible for many commonly used emulsifiers that have a

low CMC (e.g., potassium state) but it is not for the more weakly adsorbed emulsifiers (e.g., resin acid salts and even for sodium dodecyl sulfate) [14].

1.6.3.2 The effect of micelle size

Although the absolute values of the aggregation numbers may be incorrect as the different results from different techniques, there is no doubt that micelle size increases with alkyl chain length. Consequently, at constant micellar concentration the number of micelles must decrease as their size increases. Clearly the number of micelles initially present does not determine the number of latex particles formed. However, at a given micellar concentration, the total surface area of the micelles is constant because the increasing size of the micelles may be the factor determining the rate at which initiator radicals are captured by micelles and hence the number of latex particles formed.

Because of their greater size, the efficiency in capturing initiator or oligomer radicals by the latex particles is greater than that of the micelles. Consequently, when the area of the latex particles has increased sufficiently to ensure capturing of all initiator radicals, particle formation ceases because there is no chance of any remaining micelles capturing radicals. The small micelles of the lower members of homologous emulsifier series are less efficient in capturing initiator radicals than the larger micelles of the higher members of the series, which leads to a longer duration of Interval I meaning that the particle size distribution is much broader when the critical surface area of the latex particles is ultimately attained. The efficiency of radical captured by micelles differs for different emulsifiers and will be the factor determining the breadth of the particle size distribution in batch polymerization.

1.7 Methods of emulsion polymerization of acrylic monomers [15,16]

A. One-stage and semi-continuous methods

These methods were studied for butyl methacrylate polymerization and for the copolymerization of methyl acrylate (MA), methyl methacrylate (MMA), and butyl acrylate (BA) with acrylic (AA) and methacrylic acid (MAA). In so doing, the following three methods of polymerization were compared:

1. one-stage or batch, in which all reactants are introduced simultaneously into the reactor at the beginning of the process;

2. semicontinuous, in which the monomer is added portionwise to a solution of emulsifier and initiator as it is consumed;

3. semicontinuous, in which the monomer and emulsifier solution in a given ratio or an emulsion of the monomer is added gradually to an aqueous solution of the initiator.

It has been shown that the kinetics of polymerization, the polymer molecular weight, mechanism of particles formation, stability, and physicochemical properties of acrylate latexes differ depending on the method of introducing the reacting components, i.e., on their ratio in the reaction system at a given time.

The polymerization by the first method was rapidly and frequently was accompanied by the formation of coagulum. The polymerization rate in the second method was lower and coagulation was not observed during the process.

The viscosity-average molecular weight of the polymer by the first method was higher than the second method. It is characteristic of polymerization by the first method that the molecular weight remains constant, whereas a certain increase in molecular weight is observed toward the end of the polymerization by the second method.

The number of particles in both cases remains constant. During polymerization by the first method, particles of larger size are formed than during polymerization by the second method. In the conclusion, the first method polymerization occurs mainly in the volume of the particles while the second method occurs on their surface. This can be associated with the fact that during the second method the particles at all stages contain very small amounts of monomer, which, being absorbed by the particle surfaces, is polymerized without entering the interior of the particles due to hindered diffusion. In the first method, diffusion of the monomer into the interior is more feasible since the particles comprise a solution of polymer in the monomer from the very beginning stages of the process.

B. Continuous method

It has become economically worth to adopt a continuous method of emulsion polymerization. The complexity of creating a continuous process in this case is associated with the problem achieving a steady stage condition in the continuous sequence of

polymerization stage, not only respect to the kinetics of the process, but also with respect to the colloidal properties of the system. Therefore, in creating a continuous method, it is necessary to first investigate the relationships among these factors and the basic parameters of the system including the residence time (the length of time the system is in the reactor).

C. Industrial methods of preparing acrylic latexes

Two industrial methods are most frequently used for preparing acrylic latexes: the redox and reflux. In redox method, the initiator used is an oxidation-reduction system, and all of the reacting components are charged simultaneously. During polymerization, the components of the reaction mixture are charged into the reactor in the following sequence: water, surfactant, buffer (if necessary), monomer or monomer mixture, and chain-transfer agent (if used). Before adding the other components, the surfactant should be completely dissolved, which may be effected by cooling to room temperature before adding the monomers.

The redox components are added normally as aqueous solution at 15 − 45 °C, depending on the composition temperature. After the induction period, polymerization begins, as indicated by an increase in temperature. After 15 − 45 min, the temperature reaches the maximum, remains constant for a certain period, and then slowly decrease to the initial value. Sometimes additional initiator is added for complete conversion of the monomers. The one-stage redox process is normally used for preparing latices with solid contents of 25 − 30%.

The reflux method is used for water-soluble peroxide initiators with gradual addition of the reactive components during the process at a temperature normally close to the boiling point of the reaction mixture. In the reflux process, an emulsion of monomers is prepared in the presence of surfactants, other additives, and initiator in water (80% of the total amount of water). The remaining 20% of the water and equivalent volume of the prepared emulsion are charged to the reactor, the mixture is heated to the boiling point, and the emulsion added over 1–4 hours. The amount of heat given off is regulated by the feed rate.

1.8 Literature survey

In 1974, Lunadon *et al.* [17] presented the behavior of 4 nonionic surfactants of the nonyl phenol ethoxylate type with various number (n) of ethylene oxide units in emulsion copolymerization of vinyl acetate by synthesized at 60 °C according to a commercial recipe [18]. The results showed that the ratio of the polymerization rate (Rp) to initial monomer concentration ($[M]_0$) was constant from about 15% conversion up to about 80% and was proportional to $[S]^{0.35}$ and $[I]^{0.8}$, where [S] and [I] were the surfactants and initiator concentrations. They found that after nucleation was completed, the number of particles per volume (N/cm^3) was constant and proportional to $[S]^{3.0}$ and $[I]^{0.5}$. A qualitative kinetic model of the polymerization was proposed to partially occur in the aqueous phase and partially in the particles. The solubility of vinyl acetate and the solubilizing power of the surfactants for the monomer and the active and dead oligomers were the important factors for the reaction in aqueous phase.

In 1997, Chern *et al.*[19] used the mixed SDS/NP-40 (anionic/nonionic surfactant) in emulsion polymerization of styrene to examine the generality of Smith-Ewart theory which was originally proposed for the emulsion polymerization systems containing anionic surfactants. The results were consistent with Smith-Ewart theory only when the amount of NP-40 in the surfactant mixture was less than 30% by weight. However, the reaction system deviated from Smith-Ewart theory dramatically when the amount of NP-40 was greater than 50%. The stability of latex which used pure NP-40 as surfactant was not satisfactory because the steric stabilization effect was not strong enough to prohibit the attracting particles from flocculating with one another, while the mixed surfactant system can greatly improve its stability *via* the synergetic effects provided by both the electrostatic and steric stabilization mechanism. So the flocculation process was retarded. The best ratio of the mixed surfactant system SDS/NP-40 was 20/80 by weight because it resulted in the best reproducibility of the experiment and the greatest polymerization rate.

In 1997, Chern *et al.* [20] studied the critical micelle concentration of mixed SDS/NP-40 (anionic / nonionic surfactant) and its role in polymerization of styrene. the critical micelle concentration (CMC) of mixed SDS/NP-40 was determined for various ratios at 25 °C and 80 °C by measuring the surface tension of the mixture. The system of mixed micelles showed a quite non-ideal behavior, especially at lower temperature (25 °C).

Only small amount of the anionic surfactant SDS was added into the polymerization system can reduce the particle size of the latex and increase the concentration of latex particles in system.

In 1998, Heldmann *et al.* [21] investigated the influence of nonionic ethylene oxide surfactants on the properties of vinyl acetate/VeoVa 10 and vinyl acetate/ethylene emulsion and paint made thereof. The increasing of the nonionic emulsifier concentration and of the length of ethylene oxide chain decreased the particle sizes of the latex with increasing viscosities. The pigment binding capacity of the interior paint maximum at the emulsifier concentration of about 2–3% and at the degree of ethoxylation of 17–28 mol ethylene oxide (EO number). In semi-gloss and gloss paints, an increase of the emulsifier concentration improves the gloss of the paint films and reaches a constant value at around 4% of the surfactant with EO number of 17. The use of nonionic surfactant at concentration 2–3% and an EO number of 17–28 mol gave the maximum scrub resistance of the paint films. The blocking of the films showed a drastic increase at a concentration above 4% and the surfactant contains EO number greater than 17.

In 2002, Cannon *et al.* [22] studied the film forming process in MMA—ethyl hexyl acrylate latex copolymers stabilized with nonyl phenol ethoxylate (NP) by investigating a real time dielectric relaxation in the frequency range from 10^{-2} to 10^{5} Hz. Three systems were investigated by, conductimetric analysis, dielectric spectroscopy under ambient conditions and dielectric thermal analysis of film formation, for the indentical latex compositions with various the EO number in NP stabilizer. The dielectric relaxation measurements allow charges in the dipolar nature of the medium to be monitored as the process of film formation and coalescence occur. The identification of various stages in the film formation process was a result from the combining of dielectric data with other observation of the coalescence process. The conclusion was the formation of a macrocrystaline phase between the emulsion particles by the longer ethoxyl chain surfactant, inhibited the coalescence process. Moreover, the stabilizer could also play a role in determining the dynamics of the molecules in the latex and in the overall coalescence process.

1.9 Scope of research

The objective of this research is to study the effect of ethoxylate surfactants (both of conventional and green surfactants of anionic and nonionic types) on physical and chemical properties of methyl methacrylate-butyl acrylate copolymer emulsion by varying EO number of the surfactants from 4 to 40 and concentration of surfactant from 0.25% - 1.05% w/w ratio. The controlled parameters were reaction temperature at 80 °C, monomers ratio of MMA : BA : MAA being 63.0 : 35.5 : 1.5, feeding time of monomer pre-emulsion was 3 hours, and initiator concentration at 0.28% w/w.