CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Free Radical Chain Polymerization and Copolymerization

The most important used chain polymerization is free radical chain polymerization and there are three fundamental steps that determine the course of the reaction: the radical production (initiation), the growth of these radicals by a sequential addition of monomer molecules (propagation) and the cease of the growing chains (termination), either by a bimolecular termination or chain transfer (24-27). These reactions will be discussed in detail in the following sections.

2.1.1 Initiation

Initiation of polymerization is usually carried out using an initiator, denoted by I. Radical formation can take place via several pathways: for example, homolytic scission of a single bond and single electron transfer to or from an ion or a molecule (*e.g.* a redox couple).

The homolytic scission usually occurs by absorption of heat or radiation (usually ultra-violet) to produce two free radicals ($R^{\bullet}$),

$$I \xrightarrow{k_d} 2R^{\bullet} \qquad (2\text{-}1)$$

where k_d is the rate constant of initiator decomposition and this step is the rate determining. Two examples of initiators used in the polymerizations are potassium persulfate (in emulsion polymerization) and 2,2'-azobisisobutyronitrile (in bulk, solution and emulsion polymerizations). The persulfate anion dissociates in the aqueous phase at 50°C to yield two sulfato radicals, $SO_4^{-\bullet}{}_{(aq)}$, by oxygen-oxygen bond scission ($k_d = 1 \times 10^{-6}\ s^{-1}$ at 50°C (28)). Similarly the 2,2'-azobisisobutyronitrile undergoes thermolysis at 50°C to produce two cyano radicals ($k_d = 2.16 \times 10^{-6}\ s^{-1}$ at 50°C (29)). The structures of these initiators are shown in Figures 2-1 and 2-2, respectively.

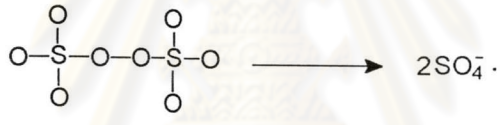

Figure 2-1 Structure of the persulfate anion.

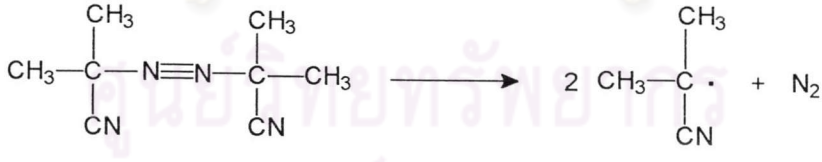

Figure 2-2 Structure of 2,2'-azobisisobutyronitrile.

The primary radicals derived from the initiator can add to the first monomer molecule to produce the chain initiating species $M_1^{\bullet}$, with a rate constant k_i.

$$R^{\bullet} + M \xrightarrow{k_i} M_1^{\bullet} \qquad (2\text{-}2)$$

where M represents a monomer molecule and k_i is the rate constant for the initiation step.

Since initiator decomposition is the rate-determining step, the rate of initiation can then be expressed by:

$$R_i = 2 f k_d [I] \qquad (2\text{-}3)$$

where f is the initiator efficiency and [I] is the initiator concentration. The initiator efficiency is a fraction of initiator radicals initiating a polymerization. Normally the initiator efficiency is in the range of 0.2 – 0.7 due to recombination of the primary radicals.

2.1.2 Propagation

In propagation, growth of the polymer chain is achieved by sequential addition of monomer unit to the monomer radical. The generic equation for propagation is:

$$M_n^{\bullet} + M \xrightarrow{k_p} M_{n+1}^{\bullet} \qquad (2\text{-}4)$$

where k_p is the propagation rate constant and $M_n^{\bullet}$ signifies any free radical containing n monomer units, whether the free-radical is initiator-derived one (an $RM_n^{\bullet}$ species), or obtained as a result of chain transfer to monomer ($M_n^{\bullet}$) or originates from chain transfer to an added chain-transfer agent ($AM_n^{\bullet}$). The rate of polymerization can then be written as:

$$R_p = k_p[M][M^{\bullet}] \qquad (2\text{-}5)$$

where [M] is the monomer concentration and [M•] is the total free-radical concentration in the system. Experimental and theoretical evidence exists that the propagation rate constant is chain length dependent (30-34). The chain length dependence of k_p is important only for short chains and becomes unimportant for over a few monomeric units (35). The value of rate constant for propagation of chain of the first degree of polymerization, k_p^1, may be 4 – 10 times higher that the long chain value of k_p.

2.1.3 Termination

Bimolecular termination is an important mechanism for the loss radical activity in free-radical polymerization and a formation of dead polymer chains. There are two pathways by which termination can occur, via combination and disproportionation.

Termination by combination is usually a simple head-to-head coupling of the radicals involved, resulting in the formation of a dead polymer chain equal to sum of the length of two combining radicals, and denoted as M_{n+m}

$$M_n^{\bullet} + M_m^{\bullet} \xrightarrow{k_{tc}} M_{n+m} \qquad (2\text{-}6)$$

In this equation k_{tc} is the rate constant for termination by combination and this process is considered to be diffusion controlled (36, 37). Termination by combination is the predominant mode of termination in polymerization of styrene (38).

In contrast to termination by combination, termination by disproportionation takes place by atom transfer (mostly β-hydrogen atom to the radical end) from one polymeric radical to another, thus resulting in the formation of two polymer molecules–one saturated and one unsaturated, which have chain lengths the same as those of their corresponding radicals before termination as shown in eq. 2-7.

$$M_n^{\bullet} + M_m^{\bullet} \xrightarrow{k_{td}} M_n + M_m \qquad (2\text{-}7)$$

where k_{td} is the rate constant for termination by disproportionation. The predominant mode of termination in a system depends on the propagating radical. Termination of styrene polymerization predominantly occurs by combination, whereas termination of polymerization with methyl methacrylate mainly involves disproportionation (39).

The relative amounts of termination either by combination or disproportionation affect the molecular weight distribution of a polymer but not the kinetics of the reaction and therefore termination is often described using a single termination rate constant, k_t:

$$M_n^{\bullet} + M_m^{\bullet} \xrightarrow{k_t} \text{dead polymer} \qquad (2\text{-}8)$$

where the particular mode of termination is not specified and

$$k_t = k_{tc} + k_{td} \qquad (2\text{-}9)$$

The term dead polymer signifies the cessation of growth for the propagating radical. The propagation reaction would proceed indefinitely until all the monomers in a reaction system were exhausted if it were not for the strong tendency toward termination. Typical termination rate constants are in the range of 10^6–10^8 dm^3 mol^{-1} s^{-1} or orders of magnitude greater than the propagation rate constants. The much greater value of k_t (whether k_{tc} or k_{td}) compared to k_p does not prevent propagation because the radical species are present in very low concentrations and because the polymerization rate is dependent on only the one-half power of k_t.

Dead polymer chains are formed in the termination step. The rate of radical loss in termination is given as:

$$-\frac{d[M^{\bullet}]}{dt} = 2\,k_t\,[M^{\bullet}]^2 \qquad (2\text{-}10)$$

In this equation, the factor of two is used as recommended by IUPAC (40) and the k_t is assumed to be independent of degree of polymerization of the species involved. However, more sophisticated kinetic treatments take account of the fact that termination is diffusion-controlled (41), and it is likely that the termination rate coefficient will be a function of chain length (41-52).

2.1.4 Chain Transfer

In free radical chain polymerization, another mode of terminating a growing polymer chain is by chain transfer. Chain transfer can occur to monomer, initiator, polymer (this would result in dead of one polymer chain, and the generation of a new chain), solvent or added chain transfer agent. Usually, chain transfer occurs via atom abstraction reactions. The chain transfer mechanism may be represented by eq. 2-11.

$$M_n^{\bullet} + AX \xrightarrow{k_{tr}} M_n\text{–}X + A^{\bullet} \qquad (2\text{-}11)$$

The rate of chain transfer to a species AX is given by:

$$-\frac{d[M_n^{\bullet}]}{dt} = k_{tr}\,[AX]\,[M_n^{\bullet}] \qquad (2\text{-}12)$$

where k_{tr} is the rate constant for chain transfer to chain transfer agent (AX) and [AX] is the concentration of chain transfer agent.

2.2 Emulsion Polymerization

Emulsion polymerization is a heterogeneous polymerization process that involves the polymerization of water insoluble monomers via free radical chain polymerization, to produce a colloidal dispersion of submicron-sized polymer particles, which is also known as a latex. Emulsion polymerization has several advantages over bulk and solution polymerizations such as: (i) higher molecular weight of polymers is often formed compared to bulk or solution polymerization, which is due to the compartmentalization effects. (ii) the heat generated during the exothermic reaction is easier to control in the aqueous phase; (iii) since water is used as a continuous phase in the polymerization it is more environmentally friendly.

The initial model for emulsion polymerization was published by Harkins (53), which was then further developed by Smith and Ewart (54). In their model emulsion polymerization is simply divided into three distinct intervals. Interval I is the initial stage where particle formation takes place (nucleation). In interval II, the particle number remains constant and polymerization takes place in the presence of monomer droplets; the monomer in the particles is replenished from the monomer droplets. Interval III begins with the disappearance of swollen monomer droplets, after which the monomer concentration within the particle begins to decrease.

These three intervals are represented schematically (25) in Figure 2-3.

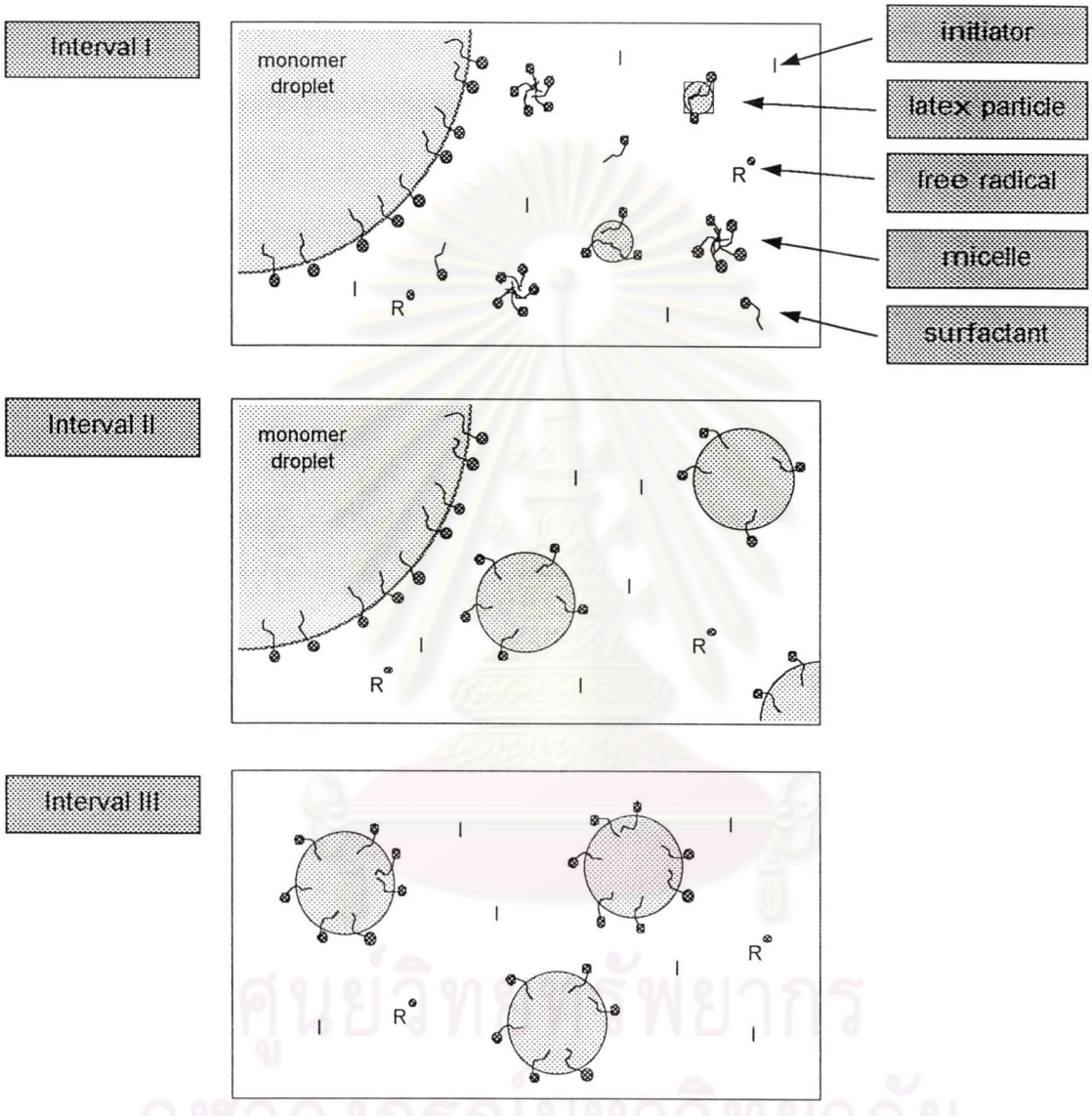

Figure 2-3 Schematic representation of the three intervals in emulsion polymerization.

Interval I

Particle nucleation in emulsion polymerization is a very complex process. Two main mechanisms have been proposed in the literature for particle nucleation mechanism: (a) micellar nucleation (53), (b) homogeneous nucleation (or homogeneous/coagulative nucleation) (55-60).

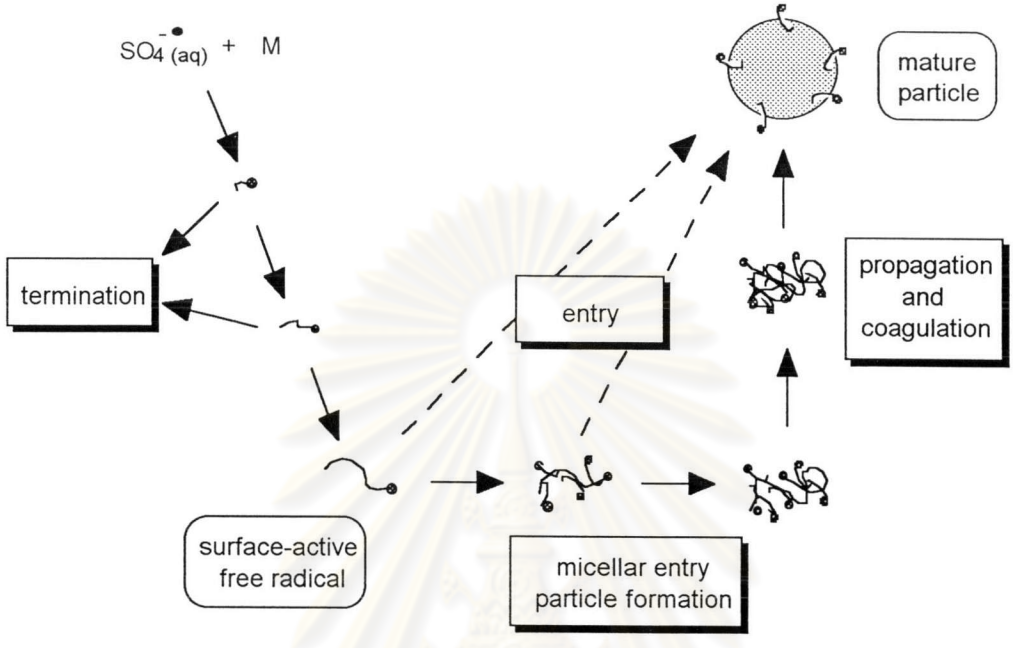

Figure 2-4 Mechanism for particle formation by micellar nucleation.

The first mechanism by micellar nucleation is presented in Figure 2-4. The concentration of surfactant is above the critical micelle concentration (CMC) of the system, and the micelles are thus swollen with monomer. The radicals generated in the aqueous phase will propagate until they reach a sufficient degree of polymerization (z) to become surface active. These species (denoted as z-mer) can then enter a monomer swollen micelle and initiate polymerization or aggregates with surfactant molecules whereupon it becomes a precursor particle (25). This micellar nucleation will eventually stop when the emulsifier concentration drops below its critical micelle concentration due to adsorption onto the newly formed polymer particle surface.

In the second mechanism, particle formation occurs in the absence of added surfactant (surfactant concentration is below the CMC). This mechanism governing particle formation is known as homogeneous nucleation (61). The radicals generated in the aqueous phase add on to a monomer unit until the oligomeric radical reaches a sufficiently high degree of polymerization, denoted as *j*-crit. The *j*-crit-mers then become insoluble in the aqueous phase and "precipitate". The precipitated oligomeric chains absorb more monomer units to form primary particles, which are stabilized by the charged group from the initiator. This model was quantified by Fitch and co-workers (56) and has become known as "HUFT" (Hansen-Ugelstad-Fitch-Tsai) theory (55).

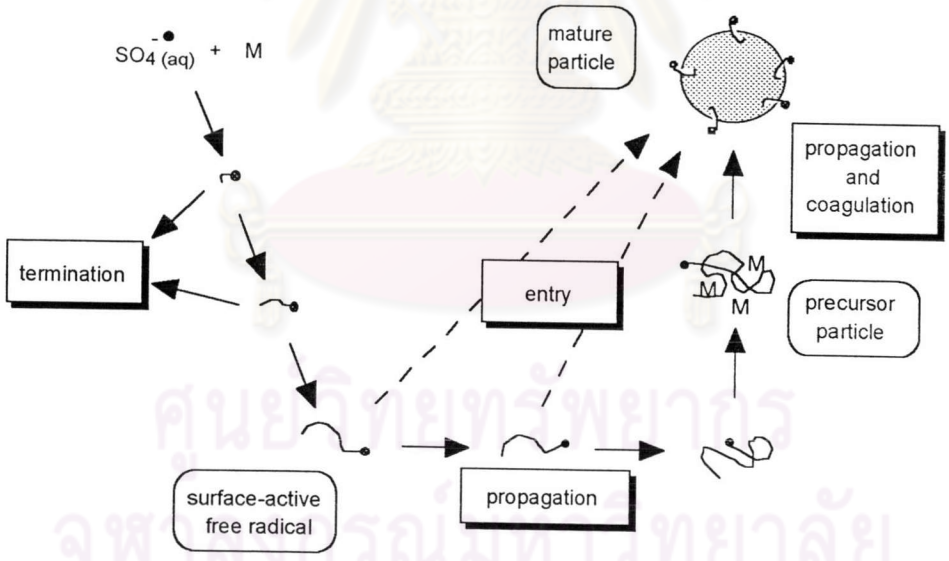

Figure 2-5 Mechanism for particle formation by homogeneous nucleation.

Two modifications later were incorporated in the original HUFT theory (55, 56, 58, 59): (i) propagation of radical chains to attain a sufficient degree of polymerization, *z* (where $z < j$-crit) for entry to occur. (ii) The precursor particles

grow by propagation and also by coagulation with other precursor particles. This version of the modified model is also known as "homogeneous-coagulative nucleation" (25). The "homogeneous-coagulative" nucleation model is described in Figure 2-5.

Interval II

Interval II begins when the particle nucleation ceases. In interval II the presence of monomer droplets acts as a reservoir to replenish the monomer consumption in the particles during the polymerization. The transport of monomer from droplets to the particles is the rate determining, and therefore a constant rate of polymerization is achieved.

Interval III

Interval III begins when the monomer droplets are exhausted. Since there is no constant replenishment of monomer as the polymerization proceeds, the monomer concentration decreases within the particle and the rate of polymerization will decrease in interval III. In some polymerization systems the *Trommsdorff-Norrish* "*gel*" effect is observed during interval III, in which the rate of polymerization increases.

2.3 Natural Rubber Latex

A latex, as defined by Blackley (62), is a stable dispersion of a polymeric substance in an essentially aqueous medium. Based on this definition, he stated that a latex is essentially a two phase system, consisting of a disperse phase and a dispersion medium.

Natural rubber (NR) latex is such a dispersion, consisting of a rubber phase dispersed in an aqueous medium. However, NR latex contains a wide range of constituents, as well as rubber and water. These constituents are distributed throughout the rubber phase, the aqueous phase and the inter-phase boundaries. Freshly-tapped NR latex is a whitish fluid having a density between 0.975×10^3 and 0.980×10^3 kg m^{-3}, a *p*H in the range of 6.5 to 7.0, and a surface free energy ranging 40 to 45 mN m^{-1}. The typical composition of fresh NR latex can vary considerably as shown in Table 2-1.

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Table 2-1 Components in natural rubber latex

Components in NR latex	Concentration, %
Total solid content	32
Dry rubber content	30
Proteinaceous substance	1 – 1.5
Resinous substance	1 – 2.5
Ash	up to 1
Sugars	1
Water	remainder

These constituents are distributed throughout the following principal phase:

(i) The aqueous phase

The aqueous phase accounts for approximately 55% w/w of the latex. It has a density of about 1.02×10^3 kg m^{-3} and contains many chemical species, such as, lipid, carbohydrates and amino acids, and also the serum constituents including free nitrogenous bases such as choline and methylamine, organic acids (rather than amino acids), inorganic anions (principally phosphate), and metallic ions (including potassium, magnesium, iron, sodium and copper).

(ii) The rubber phase

The rubber phase accounts for approximately 35% w/w of the latex. Its presence as particles influences the rubber phase to exhibit a highly asymmetrically distribution of particles sizes ranging from 200 to 20,000 Å. The particles are

sometimes pear-shaped rather than spherical. A typical composition for the rubber phase of NR latex is presented in Table 2-2.

Table 2-2 Components in the rubber phase

Components	Concentration, %
Rubber hydrocarbon	86
Water	10
Proteinaceous substance	1
Lipid substance	3

The presence of proteinaceous substance and lipid substance in the rubber phase plays an important role in storage stability for a long period of time, as they can act as protective layers. The rubber hydrocarbon in NR latex is predominantly *cis*-1,4-polyisoprene,

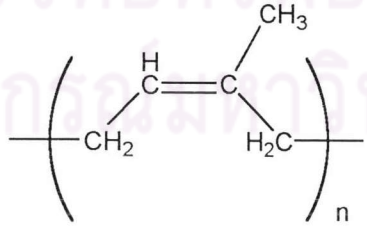

Figure 2-6 Structure of *cis*-1,4-polyisoprene.

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The polyisoprene has a carbon-carbon double bond in each repeat unit. The double bond plays an important role in vulcanization and in the modification of NR by graft copolymerization of a vinyl monomer in either NR latex or dry NR.

(iii) The lutoid phase

The fresh latex also contains ill-defined aggregates, distinct in character from rubber particles. These can be observed as a yellow fraction when the latex is centrifuged. These aggregates are called lutoids. The lutoid phase accounts for approximately 10% w/w of the latex, and contains small quantities of soluble proteins (ca. 3%), insoluble proteins (ca. 2%) and phospholipids (ca. 5%).

2. 4 Modification of NR in NR Latex

Hashim et al. (1) have reported the principal ways in which NR can be chemically modified. The chemical modification of NR can be divided in three main categories:

(i) Rearrangement reactions involving the isoprene repeat unit. These include cyclization, cis-trans isomerization and depolymerization. They do not involve the addition of a new chemical material.

(ii) Addition or substitution reactions to the isoprene unit. These include hydrogenation. These reactions result in the introduction of new chemical atoms or groups into the rubber molecule.

(iii) Graft copolymerization reactions in which other polymer materials become chemically attached to the backbone of a rubber molecule.

The following discussion will concern with the grafting reaction in NR latex only as this grafting is the main reaction in the present investigation. Although the grafting of monomers onto NR appears to be very simple, there are several inherent problems, particularly if grafting is carried out on the polymer in a latex form. The important factors which affect the efficiency of a graft copolymerization reaction are as follows:

(i) Colloidal stability of NR latex. The better the stability of latex against coagulation, the greater are the chances of carrying out successful grafting reactions in the latex.

(ii) Nature of the monomer. The monomer plays an important role in grafting reaction as it can affect the latex stability, the rate of polymerization, the efficiency of grafting, as well as the physical and chemical properties of the end-product.

(iii) Nature of the initiator. The reactivity and solubility of the free radical initiator used affect a graft copolymerization reaction.

2.5 Grafting Reaction to Create Copolymer

Free radical polymerization is the assembly of vinyl monomer units, which contain a carbon-carbon double bond, into larger compounds by the addition of free radicals across the double bonds (Figure 2-7). It is a technique that is used in the synthesis of the majority of polymers produced by industry today. The different properties of a polymer are governed by (among other factors) monomer choice and composition. Creating copolymers - polymers containing more than one type of

monomer units - is one means of creating new materials with new physical properties, while still using monomers that may be readily available and cheaper than a new type of monomer. The physical properties of a copolymer can be varied by the varying the relative proportion of each monomer.

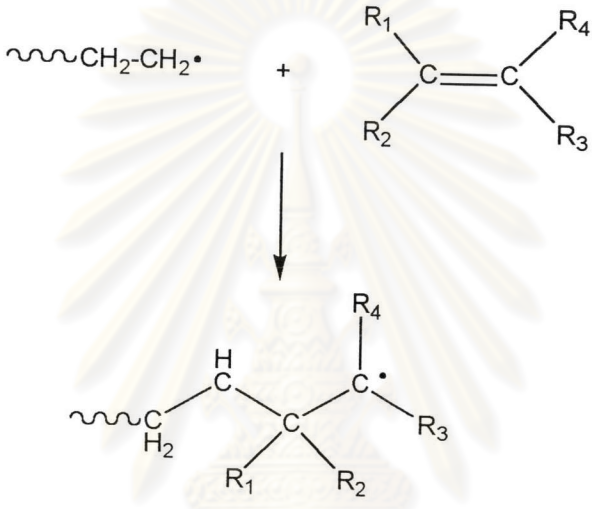

Figure 2-7 Addition of monomer unit to the radical center in free radical polymerization.

There are three basic means of creating copolymers by free radical polymerization. The first means is to perform a polymerization with more than one monomer present and generate an essentially random string of the different monomeric units in each polymer chain. The second way involves keeping the polymer chains from terminating after a complete conversion or polymerization of the monomer, by creation of the more stable radical species on the chain ends, before the polymerization of a second monomer onto these living chain ends; this technique is

generally referred to as "living" free radical polymerization (63) and generates polymer chains with a linear block structure. The third means of creating copolymers, which is used in this work, is the chemical grafting of a monomer onto an existing "dead" polymer at certain position along the polymer chain. This grafting technique can produce polymers with novel properties and a myriad of potential applications.

2.5.1 Reaction Mechanisms

To synthesize a graft copolymer by free radical polymerization, a radical site needs to be created on the existing polymer backbone to initiate the polymerization of a second monomer type. These radical sites can be obtained by either addition or abstraction reaction pathways. The addition reaction (eq 2-13) requires a double bond along the polymer chain, whereas the abstraction reaction (eq 2-14) requires an abstractable proton on the chain (both processes are illustrated in Figure 2-8). These two reactions are followed by the polymerization of monomer (eq 2-15) onto the radical sites to produce a graft copolymer.

$$R^{\bullet} + P \rightarrow R\text{–}P^{\bullet} \qquad (2\text{-}13)$$

$$R^{\bullet} + P \rightarrow R\text{–}H + P^{\bullet} \qquad (2\text{-}14)$$

$$P^{\bullet} + M \rightarrow P\text{-}M^{\bullet} \qquad (2\text{-}15)$$

where $R^{\bullet}$ = initiator radical,

$P^{\bullet}$ = polymeric radical, and

M = monomer.

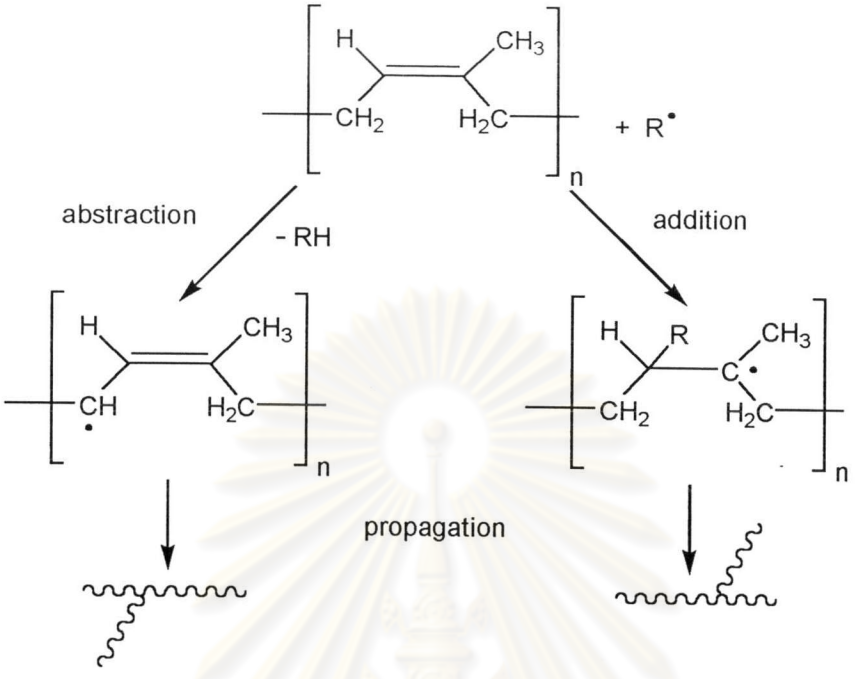

Figure 2-8 Abstraction and addition reactions which can lead to grafting to polydiene system. R• = initiating alkyloxyl radical.

2.5.2 Grafting in Emulsion Polymerization

Emulsion polymerization involves the polymerization of a hydrophobic monomer in water. Monomer, initiator and surfactant are the essential chemical species in any emulsion polymerization and the product of their reaction is a colloidally stable latex consisting of particles generally around 100 nm in size. Often, as is the case in the work presented here, a second stage polymerization is carried out with a seed latex. This is commonly used for the control of latex properties such as particle number. Further polymerization of the monomer can be performed within or around the seed latex particles.

Emulsion polymerization is an important means by which polymers can be created that removes the need for toxic organic solvents, which they are usually required in solution polymerizations of hydrophobic monomers. In addition the technique provides an efficient means of removing the heat generated by the free radical polymerization process through the surrounding water.

2.5.3 Topological Control and "Hairy Layers"

An important advantage of emulsion polymerization is that it enables both hydrophilic and hydrophobic monomers (or polymers) to be used together. This enables some novel systems to be created with unique morphologies and chemical properties that cannot be obtained by other means.

A "hairy layer" is a diffuse layer of hydrophilic polymer chains chemically grafted onto the surface of a hydrophobic polymer colloid (Figure 2-9). This hydrophilic polymer can act as an electrosteric stabilizer for the particles, often giving colloidal stability when the system would usually be unstable. An electrosteric stabilizer is a surface group that acts as both a steric and electrostatic stabilizer. An electrostatic stabilizer provides colloidal stability by electrostatic repulsions between particles that are generated by the like charges of molecules on the particle surfaces. A steric stabilizer achieves colloidal stability by the interparticle repulsion arising from the entropically unfavorable situation of polymer chains on different particles trying to occupy the same space as the particles near each other.

To synthesize the morphology of a hairy layer, two methods can be used. The first is a technique widely used in industry, where a combination of two or more monomers are polymerized with (at least) one monomer being hydrophilic and one hydrophobic. The limited solubility of the hydrophobic monomer enables the copolymer chains to begin growth in solution before becoming surface active, at which point the predominantly hydrophobic section of the polymer partitions into the particle and the predominantly hydrophilic part extends out into the solution. For example systems such as copolymers of styrene and methacrylic acid (64), or acrylic acid and styrene (65) have been documented and their particle surface morphologies are characterized.

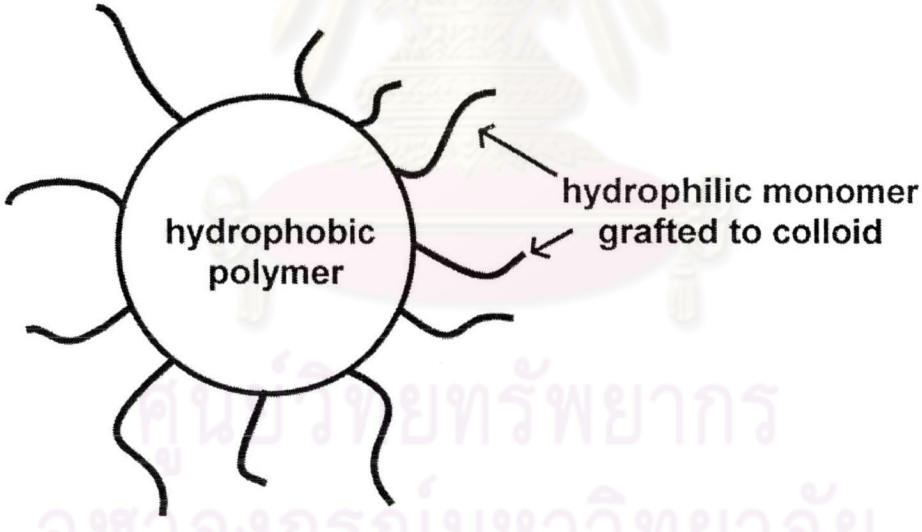

Figure 2-9 Graphical representation of a hairy layer of polymer colloid.

The second means of creating a hairy layer involves taking a seed latex and generating new radical sites on this polymer to polymerize a second monomer. The radical generation and polymerization is easily done with two hydrophobic

components but will not generate a "hairy layer." This second stage polymerization of a hydrophobic monomer inside a polymer latex is an established technique to produce materials with varying morphologies and physical/chemical properties. This form of copolymerization is not dealt with here but has been documented in Subramaniam's work (66). If the radicals are generated near the surface of the particles, (Figure 2-9) and a hydrophilic monomer is used, then a "hairy layer" can result.

2.6 Stability of Colloidal Dispersion

The main interaction involved in the approach of colloidal particles is van der Waals' (London dispersion) forces and repulsion due to electrostatic or steric effects (26).

The particles in dispersion have a natural tendency, as a result of Brownian motion, to reduce in number due to collisions. The forces of attraction between molecules are increased by high solid concentration, agitation, Brownian motion and sedimentation under gravity. Recrystallization by solvent action or by elevated temperature may also cause the particles to settle out. The reduction in particle number is termed "flocculation" if a loose or open network forms or "coagulation" if a compact cluster of particles is formed. Stability is the resistance to flocculation or coagulation. For a colloidal dispersion to remain stable, the repulsive forces should exceed the forces of attraction between the particles.

Two types of repulsive interactions contribute to colloidal stability (67): (i) electrostatic repulsion and (ii) steric repulsion. Electrostatic repulsion is based on the charge of the particles, which may be acquired by the particle by several means. They are: (a) preferential adsorption of ions; (b) dissociation of surface groups; (c) isomorphic substitution; (d) adsorption of charged macro-molecules, e.g. in biopolymers; (e) accumulation of electrons, e.g. in metal-solution interfaces. Dissociation of surface groups is common with polymer lattices which have carboxyl, sulphate or amino groups on the surface which can dissociate. Isomorphic substitution is quite commonly observed in clayey minerals, in which the Si^{4+} ions are substituted by lower valency ions Al^{3+} within the overall crystal lattice, thus conferring upon the entire particle a negative charge, to counterbalance which an excess of positive charge is formed in the dispersion medium.

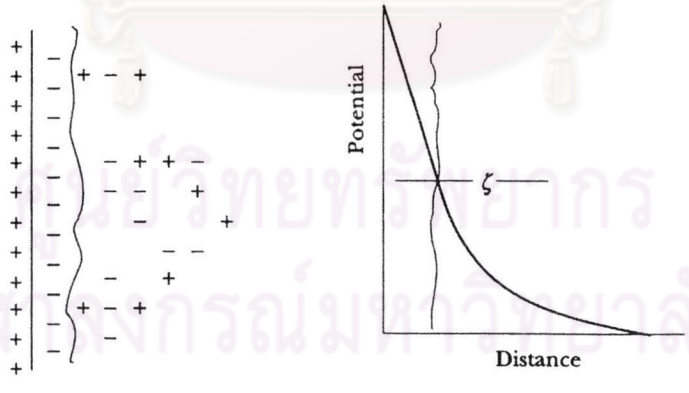

Figure 2-10 Schematic presentation of a diffuse electrical double layer.

A colloidal dispersion of a solid in a liquid, considered as a whole, is electrically neutral. Therefore, a charge that a given particle may possess must be

counterbalanced by ions of opposite charge, i.e. "counter ions" in the solution phase. This results in an electric double layer at the interface between the solid and liquid.

A solid in contact with a liquid tends to develop a difference in potential across the interface between them. An electric double layer is formed with the dissociation of inorganic groups present in the particle surface, e.g. –COOH or –OH groups which would give the particle a negative charge, to counterbalance which positive ions are attracted to the surface to form a double layer of charges, leading to a difference of electric potential between the solid and liquid. The double layer is illustrated in Figure 2-10. From measurements of particle movement within an electric field (elctrophoretic mobility), the potential drop between the stationary compensating layer and the body of the solution can be defined. This is referred to as "zeta potential" (ζ), which is defined by the equation $(\zeta) = \frac{4pd\,q}{D}$, where q is the charge on the particle, d is the thickness of the zone of influence of the charge on the particle, and D is the dielectric constant of the liquid. Measurements of zeta potential can serve as a guide to selection of optimum conditions for coagulation by giving an indication of the effectiveness of added electrolytes in lowering the energy barrier between colloid.

When a d.c. electric field is applied to a colloidal dispersion with charge particles, the double layer is polarized as shown in Figure 2-10 and the particles move with velocity which is proportional to the applied field strength, and the potential of the mobile part of the double layer (zeta potential). This motion is called,

"electrophoresis". This phenomenon is used to study the sign and value of the charge and the potential of the double layer in such colloidal systems. Protein analyses in biochemistry and electro-deposition of paint onto metal e.g. car bodies are examples of the applications of electrophoresis.

The colloidal system maintains electroneutrality on the whole and no net Coloumbic force exists between the charged particles at large distances from each other. However, a repulsive force becomes significant as two particles approach, and the diffuse parts of the electrical double layers interpenetrate and start to influence each other electrostatically. Attraction prevails at both short- and long-distances, but at intermediate distances, repulsion is dominant, and an energy barrier is formed which keeps the particles apart and thus stabilizes the colloidal dispersion. The electric double layer stabilizes colloidal system against coagulation (flocculation) by the potential energy barrier.

A colloidal dispersion may be destabilized by either reducing the magnitude of the energy barrier (i.e. by chemical influences) or by increasing the average kinetic energy of particles (by mechanical influences) so that the energy barrier can be overcome. Increasing the concentration and/or the charge number of the counter-ions in the electrolyte compresses the double layer and eventually eliminates the energy barrier, forcing the particles to agglomerate. The dependence of colloid stability on ion charge (usually called the Schulze-Hardy rule) is very strong.

"Steric repulsion" is particularly important for stabilization in non-aqueous, non polar media. It occurs when the particle surface is covered by adsorption or chemical reaction, by long chain molecules, giving the particles a hairy surface, which causes repulsion between particles in two ways: an osmotic effect caused by the high concentration of chain elements in the region of overlap; and a volume restriction effect due to the narrow space between the two surfaces (e.g. when the colloidal particles are so close as to exclude polymer chains from the interparticle region). Steric repulsion is very strong and such systems may be thermodynamically stable and reversible in contrast to electrostatically stabilized systems which display less thermodynamic stability. Sterically stabilized dispersions can be prepared with polymer melts as the dispersion medium (e.g. dispersion of carbon black particles in rubber).

2.7 Potential Energy of Interaction

The modern view of inter-particle forces dates from Ludwig Seeber's hypothesis (A.D. 1824) that stability must result from a balance between attractive and repulsive forces. The interactions between different forces on colloidal systems may be portrayed by potential energy curves, in which the change in free energy (ΔV) is plotted against the distance between the particles (interparticle separation). Figure 2-11 shows a set of such curves for electrostatic and steric stabilization.

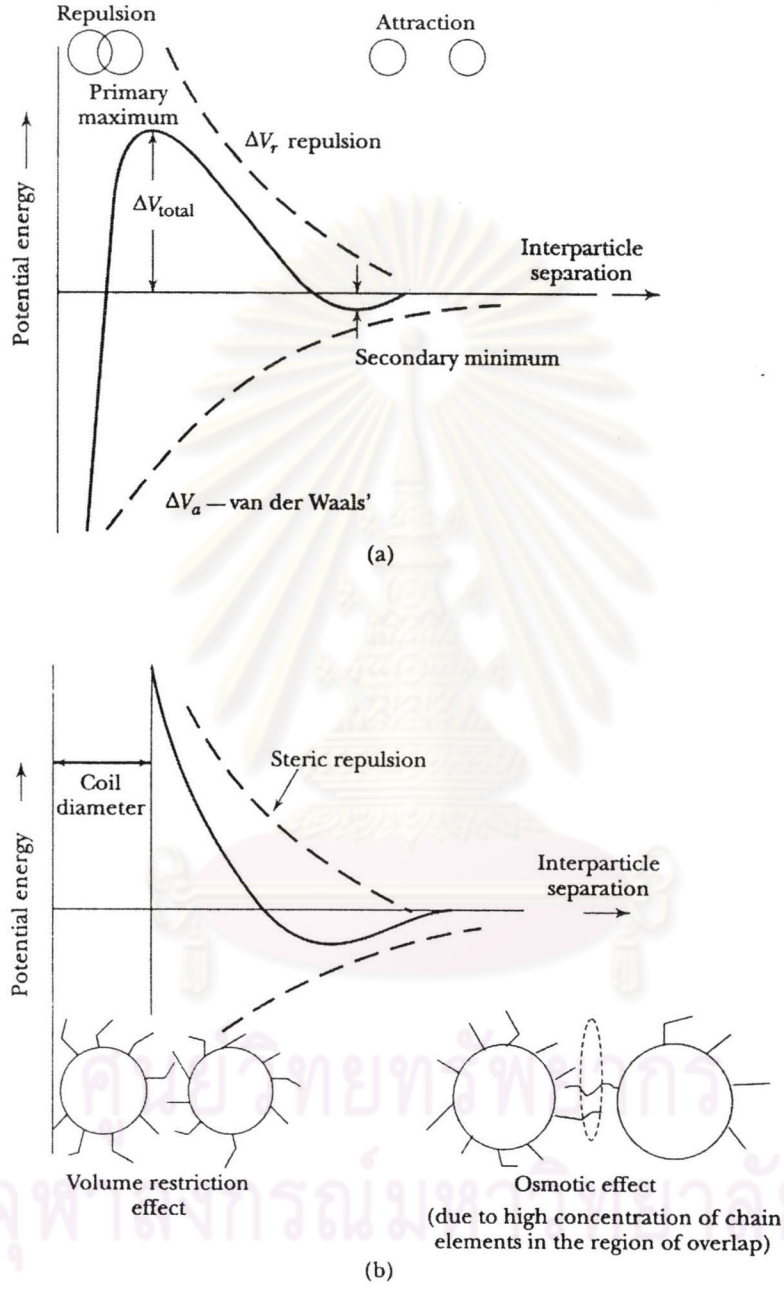

Figure 2-11 Potential energy of interaction between particles as a function of interparticle separation (a) electrostatic repulsion, van der Waals' attraction and combination. and (b) steric stabilization.

In the case of electrostatic stabilization, the height, ΔV_{total} of barrier contributes to stability. If it is desired to coagulate colloidal particles, then they must be given sufficient kinetic energy to overcome the energy barrier that exists, or else the energy barrier must be lowered by some means. These two methods correspond roughly to destabilization by physical and chemical means respectively.

The shallow minimum or the second minimum at larger distances are a temporary trap, such as the occurrence of creaming, from which the particles can be separated by mechanical means of change of composition of the medium. Once a pair of particles have overcome the energy barrier, redispersion will be very difficult.

In steric repulsion, a colloidal particle with absorbed polymer encountering a similarly clad particle will be of approximately similar thermodynamic nature, the barrier to polymer penetration providing a barrier to coagulation of the particles. Frequently, block copolymers are used, one portion of which is readily adsorbed onto the colloidal particles, the other portion of which prefers solvent contact and the freedom to adopt configurations.

2.8 Colloidal Stability of NR Latex

Cookbain (68) has stated that, although NR latex is a very complex physical and chemical system, its colloidal behavior is very similar to that of a large number of other hydrophobic colloidal systems. Cookbain and Philpott (69) defined a stable

latex as one in which no aggregation or coalescence of the rubber particles occurs under the conditions studied.

Blackley (62) stated that, in general, the subject of latex stability has two quite distinct aspects:

(i) the tendency for an individual particle of rubber to undergo changes by interaction with the aqueous phase, for example, the hydrolysis of non-rubber constituents which are associated with the surface of the particle,

(ii) the interaction between rubber particles.

Furthermore, Blackley (62) stated that at least three important and interrelated factors are responsible for the colloidal stability of latex:

(i) the reduction of the free energy associated with the interfacial films surrounding the rubber particle,

(ii) the presence of similar electric charges on the rubber particles giving rise to repulsions between particles,

(iii) the presence of a layer of tightly-bound water molecules around the particles acting as a mechanical barrier preventing the coalescence of two particles.

Cookbain (68) states that stability of a latex depends ultimately upon electric charges associated with the interfacial films surrounding the rubber particles, and also the degree of hydration of the particle surfaces. The rubber particles in ammoniated latex posses an inner core consisting of rubber hydrocarbon, surrounded by a layer of

lipids. An outer film, which is adsorbed on to the lipid layer, contains proteins and fatty-acid soaps. The arrangement of the interfacial region of a rubber particle is shown schematically in Figure 2-12.

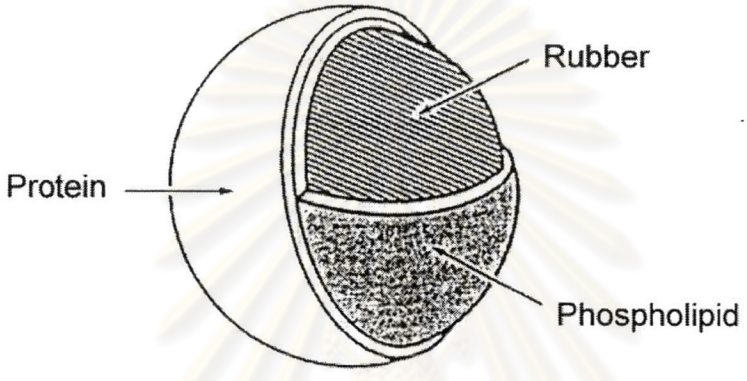

Figure 2-12 Schematic arrangement of interfacial region surrounding a rubber particle.

Due to the nature of fatty-acid soaps, proteins and lipids, the film layers have the properties of a hydrophilic colloid. Consequently, the adsorbed films will have a so-called hydration layer consisting of water molecules bound to the soaps, proteins and lipid. The composition of bath lipids and soap-protein layers, and the degree of hydration of the so-called protective layers, will determine the stability of a latex. For example, the coagulation of latex by solvents such as acetone or alcohol is attributed to the dehydration of the interfacial films.

Flocculation, coagulation, thickening, gel formation, coalescence and creaming are common indication of colloidal instability. Blackley (62) outlined two ways in which a latex can be colloidally destabilized:

(i) By increasing the average kinetic energy of the particles by physical destabilizing agencies such as mechanical stirring.

(ii) By reducing the height of the potential energy barrier between pairs of particles. This reduction can be brought about a) the insolubilization of the adsorbed stabilizer by addition of a coacervant, b) compression of the double layer by ions of opposite polarity to that of the particle side of the double layer, and c) indirect interaction between the precipitated coacervant precipitates and competes with the polymer particles for the colloidal stabilizers adsorbed on the rubber particles.

2.9 Literature Review

The polymerization of hydrophobic monomer in NR latex was first reported in 1928 (70). However, the polymerization of hydrophilic monomers in NR latex was not reported until Redfarn and Schidrowitz applied for a patent in 1937 (71). Here, the inventors used maleic anhydride which is a water-soluble monomer. The process involved simultaneously treating the rubber with maleic anhydride and phenol. The modified rubber was especially suitable for use in moulding compositions giving the products with improved electrical characteristics. The authors did not report any attempts to separate the inherent components of the products.

In 1939, Bacon et al. published the paper which included references for the polymerization of relatively hydrophilic monomers such as acrylonitrile in NR latex. Burlant and Hoffman (72) stated that, although no difficulties arose when attempts were made to polymerize hydrophobic monomers in NR latex, water-soluble monomers were more difficult to polymerize under similar conditions. Notwithstanding this, many workers have attempted to polymerize hydrophilic monomers in NR latex. For example, it has been reported that mixtures of relatively hydrophilic monomers and hydrophobic monomers, such as acrylonitrile/styrene in the ratio of 30/50 phr (73), and acrylonitrile/butadiene in the ratio of 60/60 phr (74), have been successfully graft-copolymerized on to NR in NR latex.

An interesting procedure for graft copolymerizing hydrophilic monomers in NR latex has been reported (75). Two hydrophilic monomers, i.e., methacrylic acid and acrylonitrile, were partially copolymerized in bulk using benzoyl peroxide as an initiator. The product was a milky dispersion and was called a "vinyl resin dispersion". This dispersion was added to NR latex and graft copolymerized at 100°C for two hours to complete the reaction. The polymer obtained was found to be highly resistant to swelling in organic solvents, and to have comparatively high modulus as well as good tensile strength, hardness and abrasion resistance.

Haward et al. (76) have developed polymeric products which are said to be very satisfactory for use in adhesive compositions. The products can be prepared by polymerizing vinyl pyridine in conjunction with another monomer in NR latex. The monomers used consisted of various pairs of methyl methacrylate, styrene, butyl

acrylate and acrylonitrile. The product obtained was reported to be remarkable for its adhesive power, and was used to produce improved rubber-to-metal bond.

Sekhar also investigated the polymerization of hydrophilic monomers, i.e., methacrylic acid and acrylonitrile, in hydroperoxidized NR latex. He reported that the reactive sites, which were probably hydroperoxidic in nature, were formed along the rubber backbone during aeration of the latex over a period of time. In this case, no hydroperoxide initiator was required for the initiation of polymerization. Sekhar merely added the hydrophilic monomers to the latex, followed by a small amount of reducing agents, i.e., iron (II) ions and polyamine. The polymerization was carried out at ambient temperature for 18 hours. The percentage conversion for the monomers polymerized in aerated latex was 89% for methacrylic acid and 55% for acrylonitrile. Although Sekhar was able to establish a high grafting efficiency for methyl methacrylate, with a low free polymer content (less than 10%), he did not report the grafting efficiency for the more hydrophilic monomers.

Burfield and Ng (77) polymerized methacrylamide, a water-soluble hydrophilic monomer, in NR latex. They expected that hydrophilic monomers would show a distinct advantage in self-stabilizing the latex, and that the grafting efficiency could easily determined. Therefore, they did not add any stabilizer to the latex before polymerization. Potassium persulphate (1.3 phr) was used to initiate the polymerization of methacrylamide (13 phr). The DRC of the final latex was 19%. The polymerization was carried out under nitrogen at 60°C for 24 hours under stirring. They found that the rate of polymerization was first-order with respect to monomer

concentration up to at least 70% conversion. They also found that the higher was the monomer concentration was, the higher was the efficiency of grafting. Compared to the ungrafted rubber, the methacrylamide-grafted rubber substantially increased the modulus and hardness, at the expense of tensile strength and elongation at break. The methacrylamide-grafted rubber is superior in resistance to swelling in solvents compared to other modified rubbers such as methyl methacrylate-grafted rubber, methacrylic acid-grafted rubber, acrylonitrile-grafted rubber, and acrylamide grafted rubber. Burfield and Ng (78) further investigated the mechanism of grafting of a hydrophilic monomer on to NR in NR latex. They found that the intrinsic viscosity of the free homopolymer isolated from the grafted system was very close to that of polymer obtained from a control homopolymerization. Based on these results, they believed that the grafting mechanism via transfer reactions with the rubber is negligible. Popham et al. (79) also claimed that the grafting mechanism via transfer reactions using hydrophobic monomers in NR latex is negligible.

Mazam et al. (80) investigated the polymerization of other hydrophilic monomers in NR latex using gamma radiation as an initiator. The hydrophilic monomers polymerized were glycidyl methacrylate (GMA), hydroxyethyl methacrylate (HEMA), and diethylaminomethyl methacrylate (DEAMMA). Up to 15 phr of the monomer was added to the latex, which had a DRC of 35%. The polymerization was carried out by exposing the mixture to a ^{60}Co source of nominal field intensity 0.5 Mrad per hour or more. The conversion obtained was 75 to 95 for lower than 3 Mrad, and 100% for higher than 3 Mrad irradiation dosage. The film-forming properties of both the DEAMMA-NR latex and the GMA-NR latex were

good. However, Mazam et al. (80) reported that the HEMA-NR dry films produced distinct patterns because the monomer HEMA was water soluble, and for this would thus favor polymerization in the aqueous phase and at the surface of the latex particles. As a result, the polymerized monomers were not uniformly distributed throughout the latex particle. Generally, the tensile strength of NR was enhanced after polymerization with these monomers. For DEAMMA-NR, however, there was an optimum DEAMMA monomer concentration (10 phr), which gave the highest tensile strength. The decrease of the tensile strength produced by the monomer concentration of greater than 10 phr was attributed to an increase in the incompatibility between the modified NR, homopolymer and DEAMMA-NR graft rubber components.

Makuuchi and Hagiwara (81) studied the vulcanized NRL by gamma-rays with two polyfunctional acrylate monomers, neopentylglycol diacrylate (NPGDA) and dimethacrylate (NPGDMA). In comparison with NPGDA, NPGDMA was more soluble in rubber particles, but it was less effective as an accelerating agent for the vulcanization because of the smaller rate of polymerization. On the other hand, the colloidal stability of the latex containing NPGDA was low because it was localized on the surface of the NR particles due to its poor solubility to the particles. The solubility of NPGDA was improved by adding NPGDA with solvents. The maximum tensile strength of the irradiated latex film was 350 kg cm^{-2} at 3 Mrad.

The graft copolymerization of methyl methacrylate (MMA) onto NR using various initiator systems, thermal, redox, and radiation was studied by several researchers (5, 82-94). Sundarri and Kadariah (82) investigated the method of

radiation grafting of MMA onto NR latex. Since 1985 several redox systems have been studied by Lenka et al. (83-89) They presented the kinetics of graft copolymerization of complex Mn (III) (85). They also studied the graft copolymerization of MMA onto NR using vanadium ions as the initiators (83). The mechanism of grafting reaction of methyl methacrylate onto natural rubber was also presented by Lenka et al. The free radical ($R^{\bullet}$) might interact with the natural rubber backbone (NR) by hydrogen abstraction producing rubber macroradicals which initiates grafting. The details of the mechanism are given below.

Initiation:

$$\mathrm{NR} + \mathrm{R}^{\bullet} \xrightarrow{k_i} \mathrm{NR}^{\bullet} + \mathrm{RH}$$

$$\mathrm{NR}^{\bullet} + \mathrm{M} \xrightarrow{k'_i} \mathrm{NR\text{-}M}^{\bullet} \qquad (2\text{-}16)$$

Propagation:

$$\mathrm{NR\text{-}M}^{\bullet} + \mathrm{M} \xrightarrow{k_p} \mathrm{NR\text{-}M}^{\bullet}$$

$$\mathrm{NR\text{-}M_n}^{\bullet} + \mathrm{M} \xrightarrow{k_p} \mathrm{NR\text{-}M_{n+1}}^{\bullet} \qquad (2\text{-}17)$$

Termination:

$$\mathrm{NR\text{-}M_n}^{\bullet} + \mathrm{NR\text{-}M_m}^{\bullet} \xrightarrow{k_t} \mathrm{NR\text{-}M_{n+m}\text{-}NR} \qquad (2\text{-}18)$$

Graft copolymerization of the MMA monomer onto crepe NR using potassium peroxydisulfate initiator and catalyzed by silver ions was carried out for various concentrations of the monomer and initiator (87). They found that the grafting reaction was temperature dependent. Enyiegbulam and Aloka (90) reported the graft characteristics and solution properties of the NR-*g*-MMA copolymer in MEK/toluene using benzoyl peroxide as the initiator. Oommen and Thomas (91) prepared the graft copolymer by polymerization of MMA onto NR latex using the cumene hydroperoxide (CHP)–tetraethylenepentamine (TEPA) redox system. Likewise, *tert*-butyl hydroperoxide (*t*-BHP)–TEPA was also studied for grafting styrene (92) and MMA (5) onto highly deproteinized natural rubber (HDPNR) latex. The number of grafting sites for graft copolymer from HDPNR latex was large than that determined for graft copolymer from untreated natural rubber latex. Thiraphattaraphun et al. (93) studied the graft copolymerization of MMA onto NR using potassium persulfate as an initiators and investigated the effect of initiator concentration, reaction temperature, monomer concentration, and reaction time to the conversion and grafting efficiency of the MMA monomer on NR. The different redox systems, CHP–TEPA and *t*-BHP–TEPA used for initiating the graft copolymerization of MMA onto NR latex were studied by Lee et al. (94) The formation of grafting sites on the polyisoprene backbone was promoted by adding vinyl *neo*-decanoate (V*neo*D). The initiator of CHP was observed to be more efficient than *t*-BHP for grafting of secondary polymers in modified natural rubber, grafting was enhanced considerably in the presence of V*neo*D.

Lamb et al. (95) studied the graft copolymerization of DMAEMA monomer onto artificial and natural polymer latexes, polybutadiene, polystyrene, and natural rubber latexes using the CHP–TEPA redox initiator system. Vivaygananthan et al. (96) carried out the graft copolymerization of DMAEMA onto rubber particles in natural rubber latex using CHP-TEPA redox initiator system. Factors influencing the course of reaction were monitored by a microcalorimetric reactor with the computer control (Mettler-Toledo RC1). The relative amount of DMAEMA to natural rubber was varied from 3–16%. The reaction was a semi-continuous process carried out at 15°C. From the heat evolution profile, the reaction proceeded very quickly by adding TEPA to the latex containing the monomer and CHP. The radicals generated were also involved in some crosslinking of the latex particles. Unlike the original rubber latex, the modified latex was stable at low pH. The properties of the modified latex were evaluated. Besides the function of co-initiator in the redox couple, TEPA can also act as a chain terminator due to secondary nitrogen radical formation.

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