



## CHAPTER II

### BACKGROUND AND LITERATURE REVIEW

#### 2.1 Silica Filler

Silica is widely used reinforcing filler for polymer matrices. Natural and synthetic silica come in several forms. Precipitated amorphous silica may be produced to form various particle sizes and specific surface areas for different applications. Silica makes up 90% of the reinforcing fillers used in rubber (Hewitt, 2000) as its properties, particle size and extent of hydration; make it versatile in reinforcing rubber compounds. Using AP modified silicas in rubber compounds can improve its physical and cure properties (O'Haver, 2002).

#### 2.2 Surfactant

A surfactant is a molecule composed of both hydrophilic (head) and hydrophobic (tail) sections. Four general types of surfactants exist, cationic, anionic, non-ionic and zwitterionic surfactants, classified according to the nature of the hydrophilic group. Surfactants can form various types of aggregates, micelles in solution and admicelles and hemimicelles on surfaces.

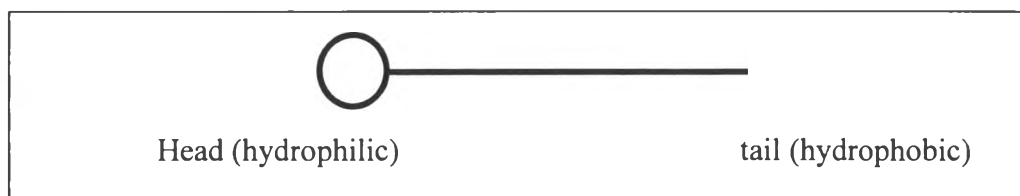


Figure 2.1 Structure of surfactant molecule

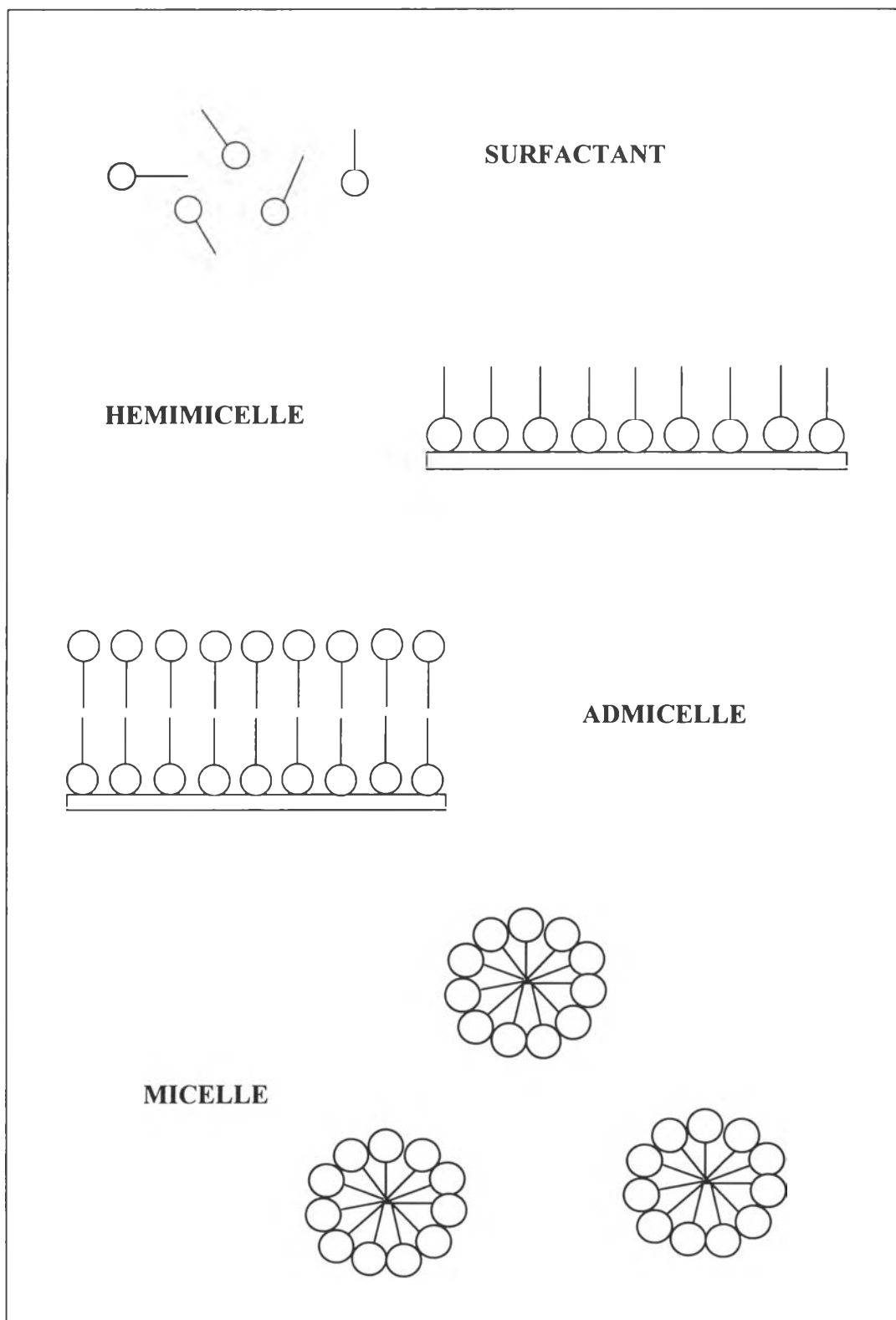


Figure 2.2 Types of surfactant formation.

### 2.3 Surfactant Adsorption

Surfactants in aqueous solution containing a solid substrate will partition to all interfaces, air-solution, solution-vessel, and solution-substrate, as well as form micelles if the concentration is sufficiently high. Surfactant adsorption is usually plotted in terms of the amount of adsorbed surfactant as a function of the equilibrium surfactant concentration in a plot called an adsorption isotherm. Figure 3 represents a typical adsorption isotherm for an ionic surfactant onto an oppositely charged substrate, a graph which is typically divided into four regions (Rosen, 1989).

Region one, corresponding to low bulk concentrations and low levels of surfactant adsorption, is sometimes called the Henry's law region as the adsorbed surfactant is considered to be very diluted on the surface and the interaction between surfactant molecules is negligible. Adsorbed surfactant aggregates are not thought to be present in this region.

The slope of the isotherm increases significantly at the beginning of Region two. This is thought to be due to interactions of the hydrophobic chains as surface aggregates, whether admicelle (bilayer) or hemimicelle (monolayer), begin to form. The transition from region one to region two, representing the equilibrium concentration at which adsorbed surfactant aggregates begin to form, is called critical admicelle concentration (CAC) or critical hemimicelle concentration (CHC).

A marked decrease in the slope of the isotherm indicates the beginning of region 3. This decrease is thought to be caused by neutralization of the solid surface or the beginning of adsorption onto lower energy surface patches, thus making additional adsorption less favourable.

Region 4 is the plateau region, having almost constant surfactant adsorption with increasing surfactant concentration. The transition from region 3 to region 4 is at the critical micelle concentration (CMC).

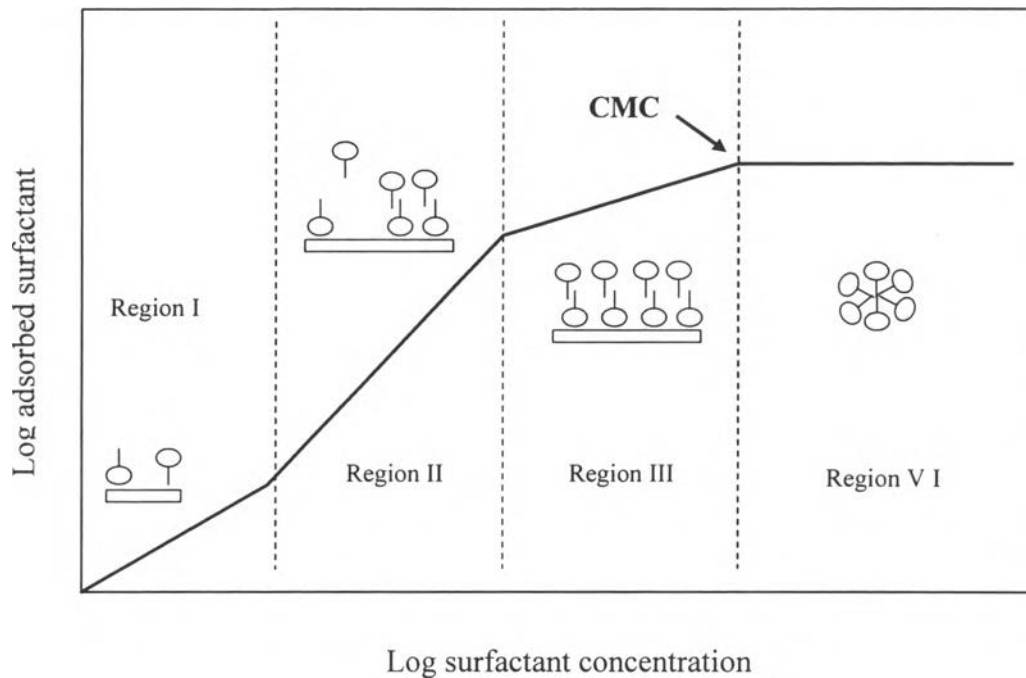


Figure 2.3 Schematic of an adsorption isotherm.

## 2.4 Solubilization and Adsolubilization

Solubilization is the dissolving of solutes into micelles. Adsolubilization is the surface analogue with adsorbed surfactant aggregates taking the place of micelles. By definition, solubilization can be defined as “the spontaneous dissolving of a substance (solid, liquid or gas) by reversible thermodynamically stable isotropic solution with reduced thermodynamic activity of solubilized materials” (Rosen, 1989). And adsolubilization is defined as “the incorporation of compounds into surfactant aggregates adsorbed on surfaces, of which compound would not be in excess at the interface without surfactant” (Scamehorn, 1988).

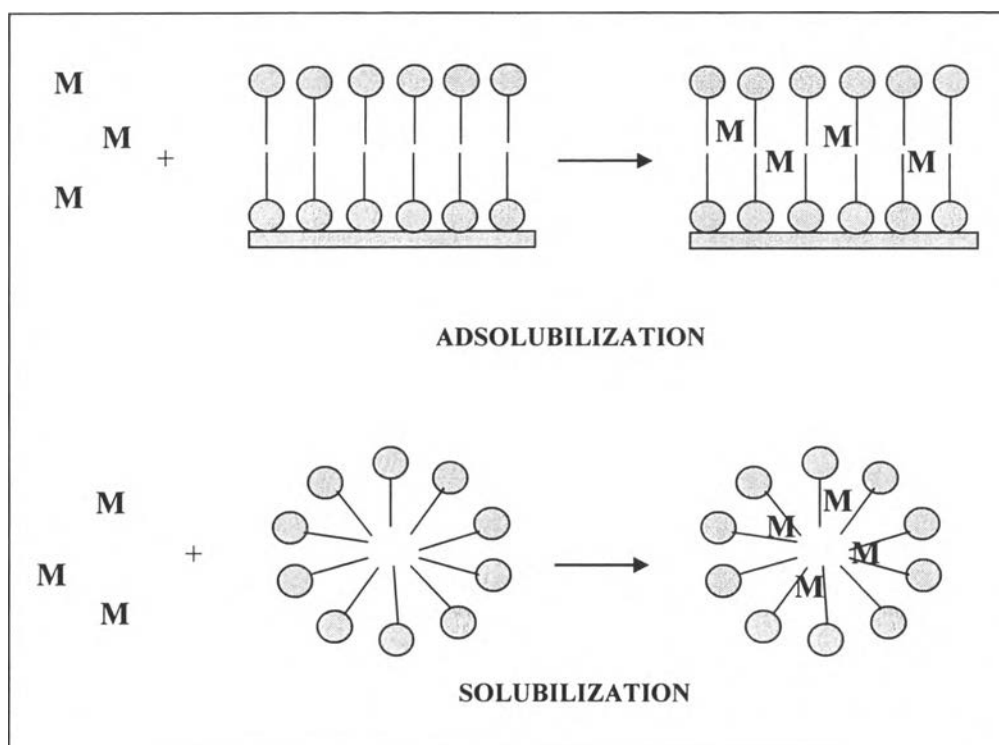


Figure 2.4 Schematic of solubilization and adsolubilization.

## 2.5 Admicellar Polymerization

The process can be divided into four steps as shown in Figure 2.5.

### *Step 1 Surfactant adsorption/ admicelle formation*

To obtain admicelle formation on the solid surface, the choice of surfactant is influenced by the chemical and electrostatic nature of the substrate as well as by the chosen initiator system. They must also be chemically similar to the selected monomers in order to promote adsolubilization. Admicelle formation, for ionic surfactants, is promoted by adjusting the surface charge on the substrate to be opposite that of the surfactant head group. The surface charge depends on pH. The pH value at which the surface charge is completely neutralized is called the point of

zero charge (PZC). The substrate surface will be negatively charged at above the PZC and positively charge at pH below the PZC.

Figure 3 shows the adsorption isotherm of surfactant adsorbed onto the solid surface from aqueous solution. At the plateau adsorption region, the surfactant adsorption is nearly constant and reaches this maximum at a bulk concentration equal to the critical micelle concentration (CMC). The bulk concentration of surfactant must be below the CMC during AP or emulsion polymerization will also occur.

### *Step 2 Monomer adsolubilization*

Adsolubilization is the solubilization of monomer into the adsorbed surfactant aggregates (admicelle). The partition coefficient has been defined by-

$$K = \frac{X_{admicelle}}{C_{bulk}}$$

where K is the partition coefficient,  $X_{admicelle}$  the mole fraction of monomer in the admicelle, and  $C_{bulk}$  the bulk concentration of the monomer. The partition coefficient may stay constant with increasing amounts of adsolubilization, or may increase or decrease. In typical AP, the molar concentration ratio of monomer to surfactant may be as high as 3:1 while in emulsion polymerization it is 100:1.

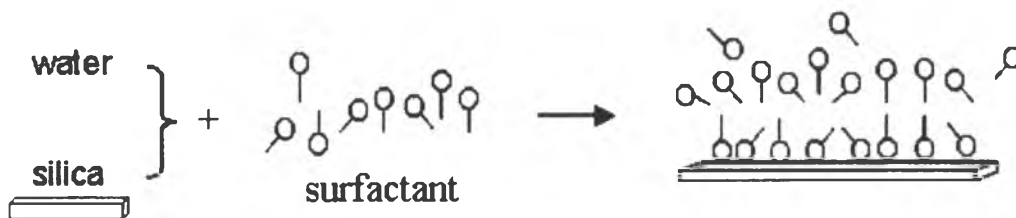
### *Step 3 Polymerization*

Initiator is added to the system to start polymerization in the admicelle. Reaction times vary depending on reaction conditions and decrease with increasing initiator concentration.

### *Step 4 Washing/Removal of surfactant*

Excess surfactant is removed by multiple washings with water to expose the thin polymer film.

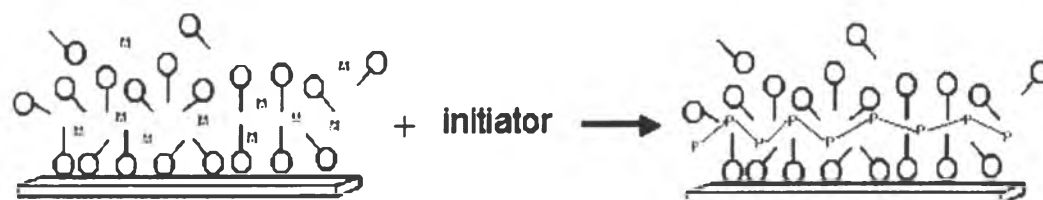
### Admicelle formation



### Monomer adsolubilization



### Polymerization



### Surfactant removal

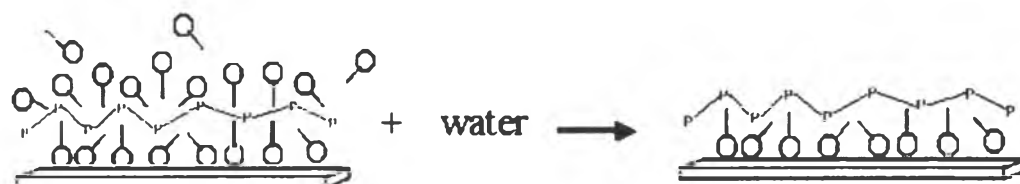


Figure 2.5 Schematic of admicellar polymerization

## 2.6 Reversible Addition-Fragmentation Chain Transfer Polymerization (RAFT)

There are several methods of controlled free radical polymerizations which can take place in heterogeneous aqueous systems (emulsions and miniemulsions), reversible addition-fragmentation chain transfer (RAFT), degenerative transfer (DT), atom transfer radical polymerization (ATRP), and stable free radical polymerization. Since admicellar polymerization is similar to emulsion polymerization, an obvious extension is to apply RAFT polymerization to AP. RAFT was chosen because it is suitable to a wide range of monomers and can be practiced in both organic solvents and aqueous media under a broad range of experimental conditions.

The RAFT mechanism differs from the normal free radical polymerization mechanism by having a chain transfer agent (CTA) such as di-thioesters and xanthates. The key to successful RAFT polymerization is to select highly efficient CTAs (Cheng, 2001.). The CTA is added into a propagating chain to form intermediate radicals that fragment into new initiating radicals and an end-capped dormant chain. The reaction can be controlled through the chain equilibration step. The propagating chain reversibly reacts with a dormant chain and can reactivate the dormant chain. The process is called RAFT polymerization as its mechanism consists of addition-fragmentation, re-initiation/propagation, chain equilibrium between chain radical and the reaction is reversible. The mechanism of RAFT polymerization is as shown in figure 2.6.

RAFT is an advanced method for synthesizing well-controlled water-soluble polymers and copolymers with low polydispersity index ( $\sim 1-1.25$ ) as compared to that of normal free radical polymerization.

This study will examine the characterization of polystyrene formed in RAFT polymerization via AP. The RAFT agent, cumyl dithiobenzoate (CDB) will be used together with AIBN water insoluble initiator.



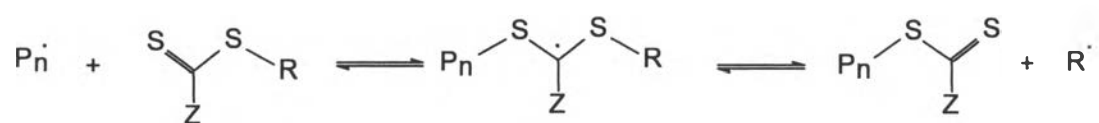
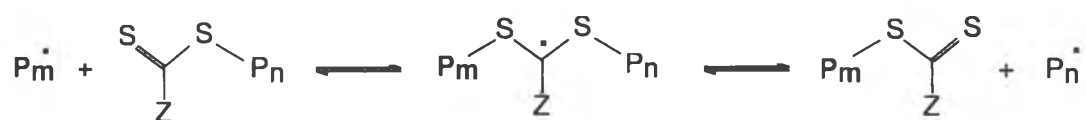
**Initiation****Addition-Fragmentation****Chain equilibrium****Termination**

Figure 2.6 Schematic of RAFT polymerization.

## 2.7 Literature Review

### 2.7.1 Admicellar Polymerization

The structure of self-assembled surfactant aggregates on metal oxide surfaces has interested researchers for many years. The technique of specular reflection of neutrons has been used to study the structure of cetyltrimethylammonium bromide ( $C_{16}TAB$ ) adsorbed at the interface between a plate of amorphous silica and  $C_{16}TAB$  solutions by Rennie (1990). He found out the thickness of the surfactant layer was equal to that of two extended  $C_{16}TAB$  molecules.

Wu *et al.* (1988) first investigated the use of AP for the formation of ultra-thin polystyrene films. They used adsorbed SDS admicelles on alumina and a sodium persulfate initiator. The results showed 75% monomer conversion after 25 minutes. Wu used ellipsometry to determine that the film thickness ranged from 1.8 to 0.4 nm.

In 1991, Lai *et al.* examined the polymerization of gas-phase tetrafluoroethylene (TFE) monomer in perfluorosurfactant admicelles. The reaction was carried out in a high-pressure reactor. It was found that the adsolubilization of TFE in admicelle can be controlled by pressure and the effective initiator concentration was in the range of 0.25-2.5 wt%.

The field was advanced when O'Haver *et al.* successfully formed a polystyrene thin film on silica by AP in 1993. CTAB surfactant and a water-insoluble initiator, 2,2'-azobis-2-methylpropionitrile (AIBN) were used in this polymerization. The result showed the polymeric film on porous silica increased particle size and decreased the silica BET surface area. In 1994, O'Haver formed polystyrene films in octylphenoxypoly (ethoxy) ethanol and in methyltri (C8-C10) ammonium chloride on amorphous precipitated silica, expanding the process to new surfactants.

Waddell *et al.* (1995) examined silica surfaces modified by AP with styrene, isoprene, and butadiene homo and copolymers. The modified silicas improved the physical and cure properties of a silica-filled tire compound (rubber

compound). Silicas modified by a copolymer of styrene-butadiene gave better results compared to any of the homopolymers, especially in regards to in cure time, tear modulus and good cut growth resistance values.

Sakhalkar, S.S. and Hirt, D.E. (1995) observed polystyrene formed on glass fibers by AP. The films were not uniform, and they showed that the polymer formed both in the surface aggregates and in the bulk.

The adsolubilization of styrene, isoprene and mixtures of these two solutes was examined by Kitiyanan *et al.* in 1996. The results showed that styrene adsolubilizes into both the palisade layer and the core of the admicelle while isoprene adsolubilizes into the palisade layer. In the copolymer system, the adsolubilization of styrene decreases with increased isoprene adsolubilization and vice-versa.

Fragneto *et al.* (1996) studied on the structure of C<sub>16</sub>TAB bilayer on smooth and rough silica surfaces by neutron reflection. The rough surface had a much more significant effect on the properties of the layer than the smooth one and they concluded that the thickness of bilayer on both rough and smooth silica is the length of two extended C<sub>16</sub>TAB molecules.

Kudisri (1997) examined the formation of styrene-isoprene copolymer on clay by in-situ polymerization. He found increases in the compound cure rate, decreases in cure time and improvements in tensile strength, hardness, flex cracking resistance, and compression set.

In 1998, Grady modified glass cloth with styrene-isoprene thin copolymeric film using SDS surfactant. The treated glass cloths were combined with epoxy and polyester resin to make a composite. That composite had improvements in flexural strength and physical properties compare to the untreated one.

Polyethylene composites treated with polypyrrole (PPy) coating of nickel flake was developed by Genetti, W.B. *et al.* (1998). His results led to a three-order-of-manitude increase in conductivity at concentrations well above the percolation threshold without significantly changing the thermal or mechanical properties of the composite.

The polystyrene thin film formed on porous silica via AP was confirmed by See and O'Haver using AFM in 2001. Normal tapping and phase contrast modes in air were used to image the topography of the polystyrene modified

silica. The formed polystyrene was found in the pores of the silica and patches on the surface of the particles. The thickness of the polystyrene formed was varied from less than 1 nm to 10 nm.

Polystyrene thin film can be coated on nonporous silica via AP was examined by Arayawongkul in 2001, using CTAB surfactant and AIBN initiator. The impact of surfactant adsorption, amount of adsolubilized monomer and different polymerization times were studied. The maximum CTAB adsorption on the nonporous silica was approximately 130  $\mu\text{mol/g}$  of silica and the molecular weight and extent of polymer coverage increased with increased CTAB adsorption and adsolubilized styrene. Moreover, it was found that the reaction time should not be less than two hours in order to obtain complete conversion and relatively high molecular weight polystyrene.

Aumsuwan continue studies on the effect of initiator loading at low and high level of CTAB adsorption under varying monomer loadings. The monomer to initiator ratio should be approximately 1:15 if the goal is to obtain high molecular weight in both surfactant adsorption levels. In addition, the molecular weight of formed polystyrene increased with increasing styrene loading.

Yuan *et al.* (2002) formed electrically conducting poly(pyrrole) ultrathin films on silica and graphite. The film thickness is less than 5 nm and dependant upon reaction conditions initial monomer concentration.

Polystyrene thin films formed in anionic alkylbenzenesulfonate (LAS) surfactant coated on cotton fabric were studied by Pongprayoon *et al.* in 2002. The film formed was characterized by SEM, FTIR and GPC. The hydrophobicity of the treated cotton surface was also examined by the drop test. Results showed that polystyrene thin film was successfully formed on cotton and that the treated cotton can resist wetting for longer than 30 minutes.

This study was expanded by Methachan *et al.* in 2002. Testing of treated fabric showed the improving of water repellency and resistance to water impact penetration while retaining good air permeability in the fabric.

Conductive PPy on natural rubber (NR) latex in SDS surfactant was investigated by Boufi, S. *et al.* 2002. The conductivity of the treated NR latex film formed by AP without salt was the lowest while that of salt addition film improved

significantly. According to the result, oxidative polymerization techniques gave higher conductivity than oxidative AP.

Bunsomsit, K. *et al.* studied a three-step process for the formation of polymerized films on the surface of cellulosic fibers in 2002, absorption, adsorption and addition initiator to in situ polymerization. However, treatment did not lead to a uniform surface modification.

### 2.7.2 RAFT Polymerization

Chiefari studied the choice of Z and R group of RAFT agent in 1998. The choice of Z and R in the reagent is crucial to the success of the RAFT process. The Z group should activate the C=S double bond toward radical addition to ensure a high transfer constants or at least prevent deactivation. The R group should be a good free-radical producing group and R' should be effective in reinitiating free-radical polymerization.

The use of dithiocarbamates as RAFT agents in living radical polymerization was achieved by Mayadunne in 1999. Dithiocarbamates, which have nonbonded electron pairs on the nitrogen included as part of an aromatic system have been shown to be highly effective in the RAFT polymerization of styrene and (meth)acrylate esters while simple dialkyl dithiocarbamates are ineffective as RAFT agents in these systems. The produced polymer using dithiocarbamates provided polymers with controlled molecular weight and narrow polydispersity.

Moad (2000) studied the living character of RAFT polymerization, the controlling of the activity of thiocarbonylthio compounds in RAFT polymerization, the difference of polymerization rate from that of conventional polymerization and the using of RAFT in emulsion polymerization.

The retardation of the RAFT process was described by Monteiro (2000). The termination of the intermediate radical/ dormant chain retarded the speed of the entire mechanism. Apparently, only a few percent of dead chains causes a broad molecular weight distribution to occur with this process. Consequently, the loss of RAFT (dormant) species at only a few percent such that there will be little or

no effect on the molecular weight distribution and controlled polymer architecture with narrow polydispersity will be maintained.

Mayadunne (2000) demonstrated living polymers by the use of trithiocarbonates as RAFT agents. Homopolymers and block copolymers of controlled molecular weight as well as narrow polydispersity can be performed by using effective trithiocarbonate RAFT agent. The research discovered the important ABA triblock copolymers of predetermined molecular weight are accessible by radical polymerization in two steps from these compounds.

RAFT is a new and robust method to synthesize well-controlled water-soluble polymers and copolymers with low polydispersity index. According to a review by Cheng (2001), the advantages of synthesis of water-soluble polymer via RAFT over other normal free radical polymerization and controlled polymerization (NMP, ATRP or living ionic polymerization) are:

1. mild conditions, fast reaction
2. reaction can be conducted in aqueous media as well as organic solvent.
3. a broad range of monomers can be chosen.
4. RAFT is a controlled polymerization. The resultant polymer has low polydispersity index ( $\sim 1-1.25$ ).
5. di-block copolymer, tri-block copolymer, star polymer have been synthesized.

In 2002, Kwak discovered RAFT polymerization of styrene using polystyryl dithiobenzoate. The study carried out by electron spin resonance spectroscopy to determine the concentration of the intermediate radical produced by the addition of polystyryl radical to the dithiobenzoate. The polymerization was also followed by dilatometry to estimate the concentration of the growing radical. The results showed that the fragmentation of the intermediate radical is a fast process with a relevant rate constant on the order of  $10^4 \text{ s}^{-1}$  (at  $60^\circ\text{C}$ ) and that the intermediate radical undergoes the cross-termination with polystyryl radical to form a 3-arm star chain, thus causing a retardation in the rate of polymerization.

Prescott, *et al* (2002) indicated that the RAFT agent most suited for the emulsion polymerization of styrene is 2-phenylpropyl-2-phenyldithioacetate (PPPDTA). Its use led to long induction periods and was difficult to eliminate.

RAFT polymerization of styrene had been successfully performed in miniemulsion by using 1-phenylethylphenyldithioacetate (PEPDTA) as a RAFT agent. Lansalot (2002) studied on the comparison of the performance of PEPDTA with those of cumyl dithiobenzoate (CDB) and 1-phenylethyl dithiobenzoate (PEDB) in bulk. Miniemulsion polymerizations mediated by PEPDTA were found to proceed at a considerably higher rate than those mediated by CDB or PEDB mediated ones. All three systems showed a significantly decrease in polymerization rate as compared to a conventional miniemulsion polymerization. Additionally, the result suggests that the main factor controlling the polymerization rate in miniemulsion RAFT polymerization is the possible escape of the radical leaving group  $R^{\cdot}$  from the initial RAFT agent to the aqueous phase.

The RAFT-mediated graft-polymerization of styrene on a silica particle was first studied by Tsujii, *et al* (2002), by using 1-phenylethyl dithiobenzoate (PDB) as a RAFT<sup>†</sup> agent. The study proved that the enhanced recombination is specific to the RAFT-mediated graft polymerization and is due to the effective migration of radical on the surface by sequential degenerative (exchange) chain transfer. And the reaction took place as diffusion process. The result from GPC showed  $M_n$  increased linearly with increasing monomer conversion.

In 2003, Michelle concluded via high-level ab initio molecular orbital calculations that the presence of the phenyl substituent at the radical center of the RAFT adduct radical significantly retards the fragmentation rate compared with the corresponding benzyl substituted adduct. Their conclusion was that the polymerization rate depends on Z and R substituted group.