

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEWS

2.1 Surfactant

A surfactant or surface-active agent is a substance that, when mixed with a solvent, will preferentially partition at interfaces rather than in the bulk of the solution (Cross, 1994). Surfactants have a characteristic molecular structure consisting of a structural group that has very little attraction for the solvent (lyophobic, or in the case of water, hydrophobic) together with a group that has strong attraction for the solvent, (lyophilic, or in the case of water, hydrophilic) as shown in Figure 2.1. For surface activity in a particular system the surfactant molecule must have a chemical structure that is amphipathic in that solvent under the conditions of use. Depending on the nature of the hydrophilic group, surfactants are classified into four categories-anionic, cationic, nonionic and zwitterionic. (Rosen, 1989)

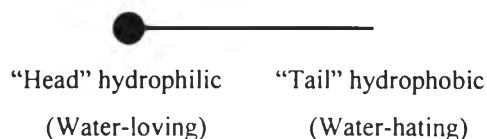


Figure 2.1 Structure of a surfactant molecule.

Most natural surfaces are negatively charged. Therefore, if the surface is to be made hydrophobic by use of a surfactant, then the best type of surfactant is positively charged hydrophilic head group (cationic surfactant) oriented toward the negatively charged surface (because of electrostatic attraction) and its hydrophobic group oriented away from the surface, making the surface water-repellent (Rosen, 1989). Often, the head group of a cationic surfactant is centered on one or more nitrogen atoms. Although corresponding analogs are to be found that contain sulfur, phosphorus, or arsenic, they are considerably more expensive than their nitrogenous counterparts and are used relatively rarely (Cross, 1994).

Quaternary ammonium surfactants such as cetyltrimethylammonium bromide (CTAB), distearyldimethylammonium chloride, dialkylmethylimidazolium methylsulfate, retain their cationic character at any pH (unless molecular breakdown occurs). CTAB is a common cationic surfactant (see Figure 2.2). The quaternary ammonium nitrogen in CTAB displays sp^3 bonding. This cationic molecule lacks both acidic protons and nonbonding electron pairs; therefore, it is “neutral in water”. If the anionic partner in such a salt is also neither acidic nor basic, as is true of bromide, the molecular structure of this salt is independent of pH (Rubingh and Holland, 1990).

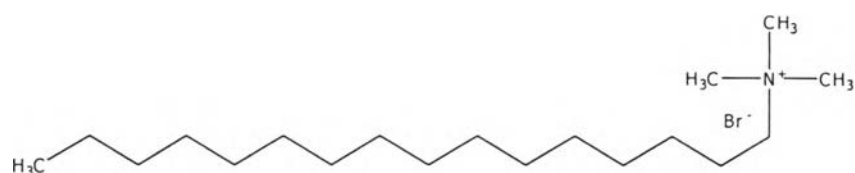


Figure 2.2 The structure of cetyltrimethylammonium bromide (CTAB).

Several types of surfactant aggregates can be formed under varying bulk concentrations as shown in Figure 2.3. At low concentration, surfactants are in molecular form in the solution. An admicelle or hemimicelle structure can be formed on surfaces or other interfaces of the system as the concentration increases. Micelle formation occurs when the concentration of surfactant reaches the critical concentration (CMC).

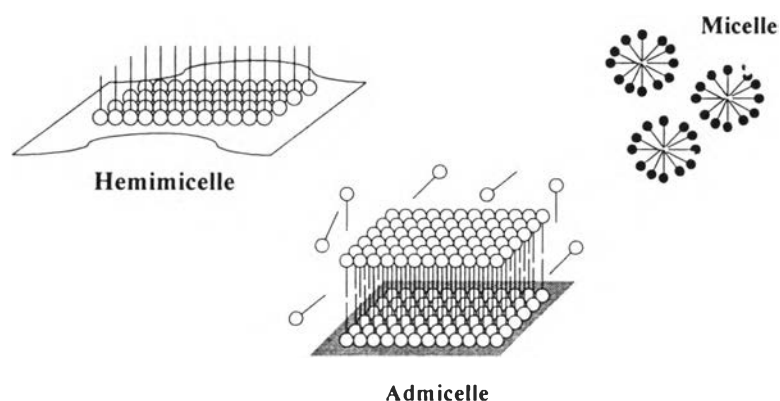


Figure 2.3 The types of surfactant formation.

Similar in nature to a micelle, the admicelle is characterized by three regions as shown in Figure 2.4. The outer region is the most polar, consists of the surfactant head groups, and forms the admicelle/water and admicelle/solid interfaces. The inner region is referred to as the core region. This region consists of the hydrocarbon chains and is nonpolar in nature. The region between the head groups and the core is the palisade region. This region is intermediate in polarity, consists of the carbons near the head groups, and is also characterized by water molecules that have penetrated the admicelle. It is thought that organic solutes will partition into the regions of the admicelle that possess similar polarity. Thus, alkanes or other nonpolar solutes partition primarily to the core region, while polar components partition to the palisade region and the head group region (Dickson and O'Haver, 2002).

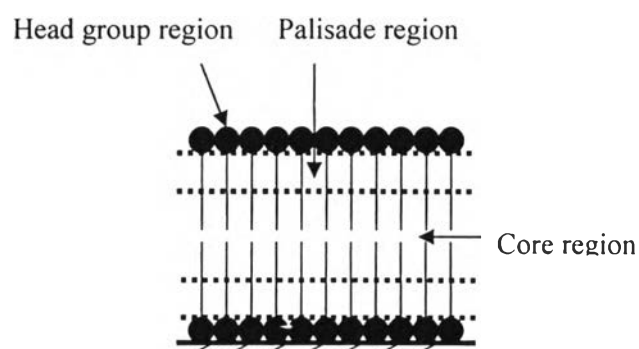


Figure 2.4 Model showing the assumed bilayer structure of an admicelle.

2.2 Surfactant Adsorption

The adsorption of surfactants at solid surfaces provides the key to a wide spectrum of applications. Factors that influence the adsorption of surfactant include (1) the nature of the structural groups on the solid surface-whether the surface contains highly charged sites or essentially nonpolar groupings, and the nature of the atoms of which these sites or groupings are constituted; (2) the molecular structure of the surfactant being absorbed (the adsorbate); and (3) the environment of the aqueous phase such as pH, electrolyte content, the presence of any additives, and temperature.

These factors determine the mechanism by which adsorption occurs, and the efficiency and effectiveness of adsorption.

It is interesting to determine (1) the amount of surfactant adsorbed per unit mass or unit area of the solid adsorbent since this a measure of how much of the surface of the adsorbent has been covered by adsorption; (2) the equilibrium concentration of surfactant in the liquid phase which allows one to calculate the efficiency of surfactant adsorption; (3) the concentration of surfactant on the adsorbent at surface saturation at a given temperature, which is a measure of the effectiveness of the surfactant; (4) the orientation of the adsorbed surfactant; and (5) the effect of adsorption on other properties of the adsorbent.

The adsorption isotherm is the usual method of describing adsorption at the liquid-solid interface, since most of the information that we desire can be obtained from the isotherm. Data from adsorption experiments are normally expressed in an adsorption isotherm, which shows the relationship between the amount of adsorbed surfactant and the equilibrium concentration of the surfactant in the liquid phase. The adsorption isotherm for an ionic surfactant onto an oppositely charge substrate is typically S-shaped which can be separated into four regions (Rosen, 1989) as shown in Figure 2.5.

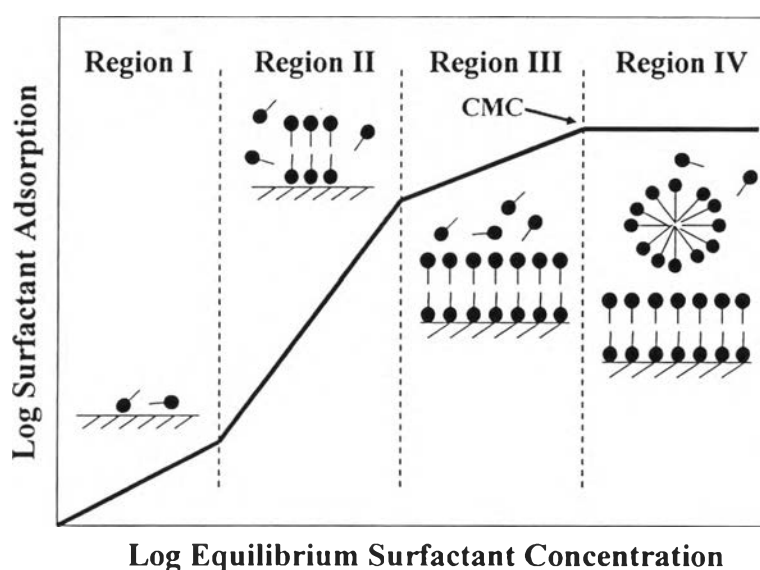


Figure 2.5 Adsorption isotherms for an ionic surfactant on an oppositely charged substrate.

In region I, surfactant adsorption is mainly by ion exchange and the amount of surfactant adsorption increases linearly with an increase in surfactant concentration

In region II, there is a marked increase in the slope of the graph resulting from interaction of the hydrophobic chains of oncoming surfactant with those previously adsorbed to form admicelles or hemimicelles depending upon whether the aggregates are viewed as bilayer or monolayer. The admicelle is a local bilayer structure with a lower layer of head groups adsorbs on the substrate surface and an upper layer of head groups exposed to the solution. The hemimicelle is a monolayer structure having the head groups adsorb on the surface while the tail groups expose to the solution. The transition point from region I to region II, representing the equilibrium concentration at which the first formation of adsorbed surfactant aggregates, is called the critical admicelle concentration (CAC) or the hemimicelle concentration (HMC). During aggregate formation, the original charge on the solid surface is often neutralized and may eventually be reversed with sufficient adsorption. In many case, by the end of region II, the solid surface has the same sign on its overall charge as does the surfactant ion.

In region III, the slope of the isotherm is reduced because adsorption now must overcome electrostatic repulsion between the oncoming ions and the like-charged head groups of surfactants on the surface. The critical micelle concentration (CMC) is the transition point from region III to region IV, representing the equilibrium concentration at which micelles first forms. Surfactant surface coverage can be limited either by the attainment of the CMC below complete coverage at low surface charge densities or by the attainment of complete coverage below the CMC at high surface charge densities (Scamehorn *et al.*, 1982).

In either case, the adsorbed surfactants reach equilibrium in region IV where the amount of surfactant adsorption remains constant with a further increase in surfactant concentration. In admicellar polymerization, the surfactant concentration is chosen to be in region III to obtain maximum admicelle formation with no micelles in the solution to avoid emulsion polymerization.

Many studies have examined surfactant adsorption isotherms of all types. In 1988, Yeskie and Harwell found that while there are conditions under which a

second layer of surfactant will always form simultaneously with the first layer of surfactant (admicelle formation), there is also a wide range of conditions under which hemimicelle will form, i.e., under certain conditions, surfactants will aggregate to form a first layer without the simultaneous formation of second layer. This was shown to be because the electrostatic contributions to the free energy of transferring a monomer from a hemimicelle to an admicelle are potentially much larger in magnitude than the largest possible hydrophobic contributions to the free energy of transfer. In addition, when admicelles do form, there is little if any interpenetrating of the hydrocarbon tails of the second layer of surfactant monomers between the hydrocarbon tails of the first layer, because the electrostatic repulsion between two layers of head groups is larger than the largest possible gain in hydrophobic bonding that could result from the interpenetrating.

The adsorption of cationic surfactants is of much interest and has been studied on many substrates. O'Haver *et al.* (1994) investigated the adsorption isotherm of cetyltrimethylammonium bromide ($C_{16}TAB$), octylphenoxypoly(ethoxy)ethanol (MACOL[®] OP10SP), and methyltri (C_8-C_{10}) ammonium chloride aggregates on Hi-Sil[®] 233 silica. The maximum adsorption of $C_{16}TAB$ on Hi-Sil[®] 233 was found to be approximately 270 $\mu\text{mol/g}$ of silica.

In 1996, Kitiyanan *et al.* studied $C_{16}TAB$ adsorption isotherm on Hi-Sil[®] 255. The isotherm illustrated the characteristics of regions II, III, and IV. The slope is greater than one from a concentration of $C_{16}TAB$ in the aqueous solution of 70 μM to a concentration of 120 μM . This indicated that the onset of $C_{16}TAB$ aggregate on the surface of the silica occurs either at or below 70 μM . The maximum adsorption of $C_{16}TAB$ on Hi-Sil[®] 255 is approximately 550 $\mu\text{mol/g}$. The comparison of $C_{16}TAB$ adsorption (molecules/nm^2) on Hi-Sil[®] 255 and Hi-Sil[®] 233, having specific surface areas of 170 and 145 m^2/g , respectively showed that the increase in adsorption of $C_{16}TAB$ is not linear with respect to specific surface area.

Arayawongkul *et al.* (2002) investigated the adsorption of $C_{16}TAB$ on nonporous silica (Aerosil[®] OX50), fumed silica with a N_2 BET surface area of 53.5 m^2/g . The isotherm showed only three of the typical regions (II, III, and IV) of the standard adsorption isotherm. Plateau adsorption of $C_{16}TAB$ was 130 $\mu\text{mol/g}$. The

results suggest that the bilayer does not completely cover the silica surface. Thus, it is possible that there was electrostatic repulsion between adjacent C₁₆TAB groups which caused a looser packing on this silica. If one assumes that C₁₆TAB formed a perfect bilayer and completely covers the silica surface, the C₁₆TAB will have the average of 1.37 nm²/molecule.

2.3 Adsolubilization

Solubilization is an important property of surfactants that is directly related to the micelle formation. Surfactant solutions above the CMC can dissolve considerably larger quantities of organic materials than pure water or surfactant solutions with concentrations below the CMC. Solubilization may be defined as "*the spontaneous dissolving of a substance (solid, liquid, or gas) by reversible interaction with the micelles of a surfactant in a solvent to form a thermodynamically stable isotropic solution with reduced thermodynamic activity of the solubilized material*" (Rosen, 1989). Consequently, a water insoluble material in a dilute surfactant solution could appreciably increase its solubility when the surfactant concentration surpasses the CMC. Solubility increases approximately linearly with the concentration of surfactant above the CMC.

Similar to the solubilization of organics into micelles, organic molecules will be incorporated into surfactant aggregates adsorbed at the solid-liquid interface. This phenomenon is termed adsolubilization. Adsolubilization is defined as "*the incorporation of compounds into surfactant aggregates adsorbed on surfaces, of which compounds would not be in excess at the solid solution interface in the absence of the surfactant*" (Scamehorn and Harwell, 1988). This phenomenon is analogue of solubilization, with adsorbed surfactant bilayers playing the role of micelles as shown in Figure 2.6.

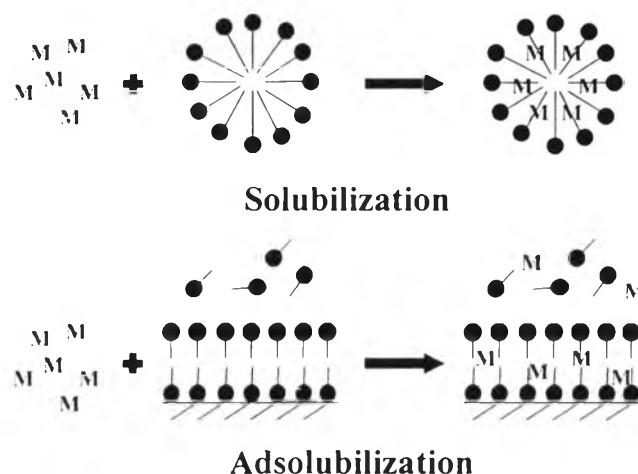


Figure 2.6 Phenomena of solubilization and adsolubilization.

In 1994, O'Haver *et al.* studied the adsolubilization isotherm of styrene in cetyltrimethylammonium bromide ($C_{16}TAB$) on Hi-Sil[®] 233. The maximum measured adsolubilization of styrene is approximately $155 \mu\text{mol/g}$ of silica. This measurement was determined for the experimental runs in which surfactant adsorption was $267 \mu\text{mol/g}$ of silica, similar to that reported by the previous work by Wu *et al.* (1987). This gives a ratio of adsorbed surfactant molecules to adsolubilized monomer molecules of approximately 2. They also concluded that cationic surfactants tend to have a greater solubilizing power than anionics.

The adsolubilization of styrene, isoprene, and mixtures of styrene and isoprene into $C_{16}TAB$ bilayers (admicelles) on precipitated silica (Hi-Sil[®] 255) was investigated by Kitiyanan *et al.* (1996). The adsolubilization constant is nearly unchanged with increasing styrene equilibrium concentration in the aqueous phase, while the isoprene adsolubilization constant increases with increasing isoprene partial pressure. The adsolubilization constants suggest that styrene adsolubilizes into both the palisade layer and the core of the admicelle, while isoprene adsolubilizes into the palisade layer. In the comonomer system styrene adsolubilization is slightly increased in the presence of isoprene but isoprene adsolubilization is significantly enhanced in the presence of styrene; however, the adsolubilization isotherms of both monomers have increasing slopes in the

comonomer system and show that there is a synergistic effect, possibly due to swelling of the admicelle due to the addition of adsolubilize. Arayawongkul *et al.* (2002) studied the adsolubilization of styrene in C₁₆TAB at two levels of C₁₆TAB adsorption. The result showed that the adsolubilization of styrene increased with increasing styrene equilibrium concentration at both adsorption levels. When comparing the two, styrene adsolubilization at higher C₁₆TAB level is higher than at the low C₁₆TAB adsorption.

See and O' Haver (2004) studied the adsolubilization of styrene by C₁₆TAB admicelle at the mica/ water interface. When the feed concentration of styrene is lower than the surface concentration of C₁₆TAB, styrene molecules adsolubilized as individual molecules concentrate at the admicelle-water interface which leads to the slow transition to a patchy cylindrical structure. At higher feed concentrations, styrene molecules start to partition inside the core region of the admicelle, coalescing the admicelle to swell.

2.4 Admicellar Polymerization

The method utilized for the modification of inorganic powers by admicellar polymerization is based on the formation of micelle-like surfactant aggregates, which will be called admicelle or adsorbed micelle (Harwell *et al.*, 1985 and Wu *et al.*, 1987), at a solid solution interface. Just as in the phenomenon of solubilization for micelles, the analogous behavior of partitioning of organic solutes into admicelles has been termed adsolubilization form the basis of a four-step process to construct a polymeric thin film on a solid substrate via a low-energy process, as illustrated in Figure 2.7.

Step 1: Admicelle Formation

First step consists of admicelle formation by the adsorption of a surfactant bilayer onto the surface of the substrate. Adsorption is accomplished through the use of a suitable surfactant under appropriate system conditions. The choice of surfactant is influenced by the point of zero change (PZC) of the substrate, the chemical nature of the polymer to be formed, and the chosen polymerization initiator system. The adsorption of surfactant on the substrate surface is controlled by several parameters

including the electrochemical nature of the substrate, the type of surfactant molecule, the pH of solution, and added counterion. Charge on the substrate surface can be manipulated to be either positive or negative by adjusting the pH of the contacting aqueous solution because both hydronium and hydroxide ions are potential determining ions for substrates. The solution pH at which the surface exhibits a net surface charge of zero is called the point of zero charge (PZC). A study of the PZC for the substrate provides information on the pH ranges in which cationic or anionic surfactants may readily be utilized. At pH values below the PZC, the surface becomes protonated and more positively charged; above the PZC the surface is negatively charged. Consequently, anionic surfactants adsorb well below the PZC and cationic surfactants above the PZC. For example, silica having $3 < \text{PZC} < 2$ (Iler, 1979) and minimum solubility in water at a pH between 7 and 8, is negatively charged when the pH of the aqueous solution exceeds 3. In this study, therefore, a feed pH of 8 is chosen; this maximized the negative charge on the surface while dissolving a negligible amount of the silica. Cationics such as CTAB adsorb readily on the surface of silica when the pH of the contacting aqueous phase is greater than 3 (pH 8). The feed concentration of the surfactant is chosen so that at equilibrium the bulk concentration of the surfactant is below the surfactant's critical micelle concentration (CMC) in order to prevent the formation of micelles in the bulk solution or to avoid emulsion polymerization during Step 3. In the absence of micelles, the organic interior of the surfactant bilayer became the only locus for the adsolubilization of organic monomers.

Step 2: Monomer Adsolubilization

Monomer is solubilized into the admicelle, a process called adsolubilization. In the absence of micelles, the bilayer acts as a two-dimensional solvent to concentrate the monomer near the surface of the substrate (Wu *et al.*, 1987). Many organic monomers are nearly insoluble in water. Thus, at equilibrium, they preferentially partition into the hydrophobic interior of the admicelle. This process can occur either after the formation of the admicelles or concurrently with surfactant adsorption. Addition of monomer and surfactant solution may be simultaneous or sequential.

Step 3: In situ Polymerization of adsolubilized monomer

In this step, initiator is added to start the polymerization in the admicelle. For free-radical polymerization, this is accomplished through the generation of radicals capable of initiating polymerization. Once the polymerization reaction has been initiated and the monomer in the bulk solution can begin to re-equilibrate by diffusing into the admicelle. If the reaction is continued for a sufficient time period, essentially all of the monomer can be converted into polymer.

Step 4: Surfactant Removal

After polymerization is complete, the upper layer of surfactant (or the accessible surfactant) can be removed by washing of the treated powder to remove as much the excess surfactant as possible in order to expose the layer of polymer on the substrate surface. The powder is then dried in an oven at a suitable temperature to vaporize unreacted monomer and excess solvent, but not affect the properties of the polymer. The need for this step is optional, depending upon the application.

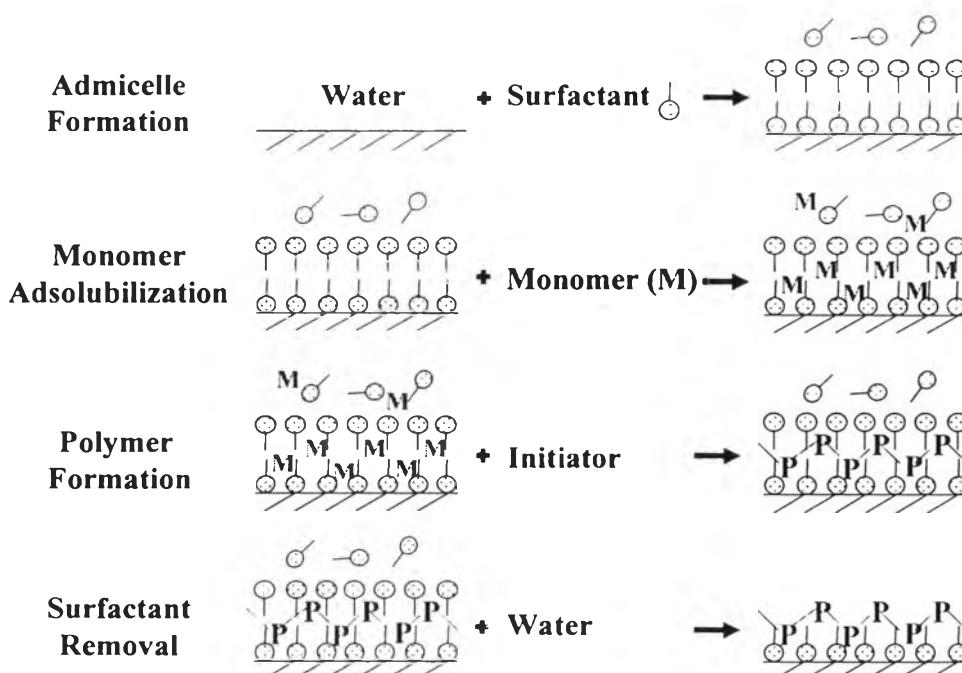


Figure 2.7 Schematic of the four-step process for admicellar polymerization: (1) adsorption; (2) adsolubilization; (3) polymerization; (4) washing.

The formation of thin films on solid surfaces has the object of intense study in recent years because of a wide variety of possible applications for these films. In particular, the surface modification of substrates using admicellar polymerization, polymerization of monomers solubilized in adsorbed surfactants bilayers (admicelle), has been examined since 1987 and improved over the years. Wu *et al.* (1987) manipulated the formation of admicelles on the solid surface, and the adsolubilization of organic monomer of interest into admicelles, and developed a novel method of ultra-thin film formation using the organized structure of admicelles as a chemical reaction solvent. The polymerization of styrene which adsolubilized monomer in sodium dodecyl sulfate (SDS) bilayers was observed on alumina. The results show that 75% conversion of adsolubilized monomer to polymer occurred after 25 minutes. The presence of a polymeric film was confirmed by UV and FTIR.

Other substrate types (i.e. silica, clay, nonporous silica) can be modified by admicellar polymerization. O'Haver *et al.* successfully formed a polystyrene thin film on silica surface in 1994. They studied the effect of various surfactant types including CTAB, water-insoluble cationic surfactant ADOGEN[®] 464 (methyltriethylammonium chloride) and nonionic surfactant, MACOL[®] OP10SP (octylphenoxy poly(ethoxy) ethanol with an average of 10 mol of ethylene oxide), to form thin film polymer films of styrene on amorphous precipitated silica substrates. The results from the polymerization showed effective conversion of adsolubilized styrene monomer to polystyrene. The extractable polymer has been characterized using photoacoustic FTIR, UV, and GPC. Only approximately 25% of the polymer was extractable after refluxing for 4 hr in THF. This study has also showed that, on precipitated silica substrates at least, the organic polymer produced is quite firmly attached to the substrates even though not chemically bonded.

Applications of the modified silica have been studied since 1995 by Waddell and co-workers. Silica was surface modified with polymerized styrene, isoprene, butadiene, and copolymers in order to improve the physical properties in a silica-filled tire compound. Polystyrene-modified silica caused reduction in overall physical properties while polyisoprene-modified silica showed a decreasing in compound cure time, reinforcement, and hysteresis, but does maintain compound

tear strength and cut resistance compared to use of the control silica. It also showed that modification of silica by polymerization a styrene-butadiene, styrene-isoprene, or isoprene-butadiene copolymer onto the silica surface decreases the compound cure time and hysteresis, and increases tear energy and the ratio of the modulus values measured at 300% elongation and 100% elongation.

In 1996, O'Haver *et al.* expanded the synthetic method to include the copolymerization of polar monomers with 1, 3-butadiene and isoprene by utilizing redox initiation of polymerization at both 5°C and ambient conditions and thermal initiation of reactions at 70°C. Silica was thus modified using copolymers of isoprene or 1,3-butadiene with vinyl acetate, acrylonitrile, 4-methoxy-styrene, 4-chlorostyrene, and methyl methacrylate on silica surface. The physical testing results showed that cure times were decreased, and break strength, tear energy, elongation to break, and cut growth resistance were increased. Further study in the same period. Thammathadanukul *et al.* (1996) and Chinpan (1996) compared the reinforcement of a natural rubber compound by various surfaced-modified precipitated silicas. Silica modified with styrene-butadiene and styrene-isoprene copolymers were studied. The results found that all copolymer-treated silicas offered greater improvements in the rubber performance than the silica modified by the silane coupling process. And it was also found that those lower loading of monomer and surfactant achieved the greatest improvement in the largest number of rubber properties.

The attempt to improve the properties of rubber compounds by reinforcing with non-black filler (e.g. silica, clay) was tested. Kudisri (1997) formed styrene-isoprene copolymer on clay by *in situ* polymerization. The research studied the effect of the amount of surfactant and monomer on physical properties compared with unmodified clay. The results show that this process increases the compound cure rate, decreased t_{90} cure time, and improved tensile property, tear strength, hardness, flex cracking resistance, and compression set.

In 1998, the application of admicellar polymerization was expanded by Grady *et al.* who studied the modification of glass cloth used in composite manufacturing by admicellar polymerization. The formed thin polymeric film of polystyrene-isoprene on glass cloth was achieved using SDS as the surfactant. The treated glass cloths were combined with epoxy and polyester resin to make a

composite. The composite shows improvement in flexural strength and physical properties when compared to the untreated glass cloth composite.

More recently a variety of studies have examined polymer thin film formation via admicellar polymerization. A continuous reactor for admicellar polymerization was developed by Chaisirimahamorakot (2001). CTAB, styrene, isoprene, and porous silica were used to form thin film polymer by admicellar polymerization. FTIR proved the existence of styrene-isoprene copolymer on the modified silica. The effect of reaction time and monomer loading on the amount of formed polymer were studied. It was concluded that the 5 g comonomer per kilogram silica and 60 minutes polymerization time provided the largest amount of polymer on silica surface. From the Chaisirimahamorakot's results, Nonthasorn (2002) improved natural rubber properties by modification of silica surface using a continuous admicellar polymerization system. CTAB, styrene and isoprene were used as surfactant and comonomer, respectively. The results showed that modification of the silica surface reduced the BET surface area and increased the mean agglomerate particle size for all samples. SEM showed the increase in the particle agglomeration. The use of the modified silica in rubber compounds significantly reduced t_{90} cure times and improved modulus, abrasion resistance, and compression set.

The presence of polymer on the substrate surfaces was indirectly confirmed by various techniques, including SEM, UV analysis of tetrahydrofuran-extracted polymer, nitrogen adsorption, ellipsometry, FTIR, contact angle analysis, evaluation of properties of the composites produced, x-ray photoelectron spectroscopic (XPS), thermogravimetric analysis (TGA), gel permeation chromatography (GPC) and scanning tunneling microscopy. Recent advances in atomic force microscopy (AFM) have allowed researchers to study the nanometer scale surface characteristic of substrates modified via admicellar polymerization. See and O'Haver (2003) examined the structure and locations of the formed polystyrene film under tapping mode atomic force microscopy (TMAFM) as a function of surfactant and monomer feed concentrations. Amorphous silicas and silica disks were modified by the admicellar polymerization process by using styrene adsolubilized in C_{16} TAB aggregates. The thickness of the polymer film on precipitated silica is directly

proportional to the styrene feed level. At high styrene loadings, the polymer tends to form aggregates, whereas at lower loadings of both surfactant and styrene, a thin film forms. The morphology of the polymer film does not change significantly when the surfactant feed is kept constant. Whereas the structure of the polystyrene film formed on smooth silica disk was very dependent on the amount of the surfactant feed to the system; this contrasted with the results on precipitated silica. When the coverage of the adsorbed surfactant is low, the polymer film will be less stable, and aggregations will occur immediately. At maximum coverage, a uniform thin film will form when there is enough styrene monomer. The stability of the polymer film is thought to be caused by the presence of a monolayer of C₁₆TAB at the polystyrene–silica interface. The morphology of the polymer formed may be the result of uneven adsolubilization of the monomer(s) or the interaction between the silica substrate and polymer surface during the dewetting mechanism.

The characterization of polystyrene produced by admicellar polymerization was studied by Arayawongkul (2002). The polymerization reactions were carried out on nonporous silica (Aerosil[®]OX50) in CTAB aggregates using styrene monomer. This research also focused on the effects of surfactant loading, monomer loading, and reaction time on the polystyrene thin film on silica surface. The polystyrene was extracted from the surface of the modified silica using THF solvent. The modified silica has been examined by TGA and AFM. The extracted polystyrene was characterized by FTIR, TGA, and GPC. The results showed that the reaction time for conducting admicellar polymerization should not shorter than two hours to obtain relatively high molecular weight polystyrene. The extent of the polystyrene film and amount of polystyrene forming on silica particles increased with increasing CTAB adsorption and adsolubilized styrene.

Aumsuwan (2003) also studied the effect of the amount of initiator on formed polystyrene film on nonporous silica. The results showed that the ratio of initiator concentration to styrene for an admicellar polymerization time of two hours should not be less than 1:15 to obtain relative high molecular weight polystyrene.

In 2004, Sam Hom studied the characteristic of polystyrene film formed on precipitated nonporous silica Aerosil[®]OX50 surface using CTAB surfactant, and both water soluble (VA-044) and insoluble (AIBN) initiator via admicellar

polymerization. The initiator to monomer ratio which formed the highest molecular weight polystyrene was 1:15 for AIBN and 1:7 for VA-044. The water soluble initiator (VA-044) could form much higher molecular weight polymer than that of the water insoluble initiator (AIBN), with M_w that were as high as $\sim 1,300,000$.