

## CHAPTER I

### INTRODUCTION

Surfactant molecules in aqueous solution, as well as in polar and non-polar solvents, can self-assemble into micellar aggregates at concentrations greater than their critical micelle concentration (CMC). A variety of aggregate structures can be formed such as spheres, rods, vesicles, or lamellar structures (Laughlin, 1994). These microstructures can change due to changes in temperature, salinity, pH, etc. (Israelachvili, 1992). These microstructures can be utilized during polymerization to produce polymers with unique shapes and special applications, such as microencapsulation for controlled drug delivery, etc. (Paleos, 1992). There are two methods; (1) the polymerization of monomers previously solubilized in the microstructure, and (2) the polymerization of microstructure made with polymerizable surfactants to stabilize the micro structure of these micelles (Thundathil, 1980; McGrath, 1996; Guyot, 1996). One approach to the stabilization of microstructures is through the emulsion polymerization of monomer solubilized in surfactant micelles (McKelvey *et al.*, 2000). The polymerized surfactant structures are in general similar in physical structure to polymer-surfactant complexes (Kline, 1999).

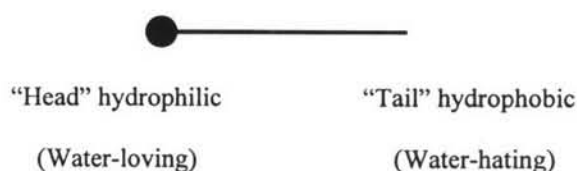
Emulsion polymerization is a heterogeneous reaction process in which unsaturated monomers or monomer solutions are dispersed in a continuous phase with the aid of an emulsifier system and polymerized with free-radical initiators. The product, a colloidal dispersion of the polymer or polymer solution, is called a latex. Emulsion polymerization is one of the most important techniques for the commercial production of polymers. Monomers polymerized by way of emulsion processes include styrene, butadiene, acrylics, chloroprene, vinyl chloride, vinyl acetate, acrylonitrile, acrylamide, ethylene, and many others. Emulsion polymers have found a much broader range of application, especially in water-based surface coatings and adhesives.

Few papers have reported the impact of surfactant aggregate structure on that of the formed polymer (Thundathil, 1980; McGrath, 1996; Guyot, 1996,

Becerra, 2003). This work will focus on characterization and morphology of polystyrene that is polymerized from the emulsion polymerization of the styrene monomer solubilized in CTAT wormlike micelles under various polymerization conditions. The effect of the amount of surfactant, monomer, and initiator and polymerization temperature on the properties of the obtained polystyrene and on morphology of wormlike micelles would be examined. Comparison between characteristic of polymer and morphology of polystyrene stabilized wormlike micelle, obtained from transmission electron microscope (TEM), were made. Effects of these parameters on the properties of the obtained polystyrene were characterized by fourier transform infrared (FTIR), gel permeation chromatography (GPC), thermogravimetric analyzer (TGA), differential scanning calorimeter (DSC).

### 1.1 Surfactant

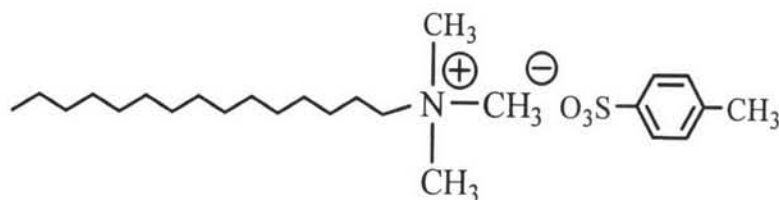
A surfactant (a contraction of surface active agent) is a substance that, when present at low concentration in a system, has the properties of (1) adsorbing onto surfaces or interfaces of system, (2) of altering to a marked degree the surface or interfacial free energies of those surfaces or interfaces, and (3) of forming aggregates in solution. Surfactants are used in such fields as detergency; enhanced oil recovery, and pharmaceuticals. Surfactants have a characteristic molecular structure consisting of a structural group that has very little attraction for the solvent (lyophobic, nonpolar, or in the case of water, hydrophobic) together with a group that has strong attraction for the solvent, (lyophilic, polar, or in the case of water, hydrophilic). Depending on the nature of the hydrophilic group, surfactants are classified into four categories-anionic, cationic, nonionic and zwitterionic (Rosen, 2004).



**Figure 1.1** Structure of a surfactant molecule.

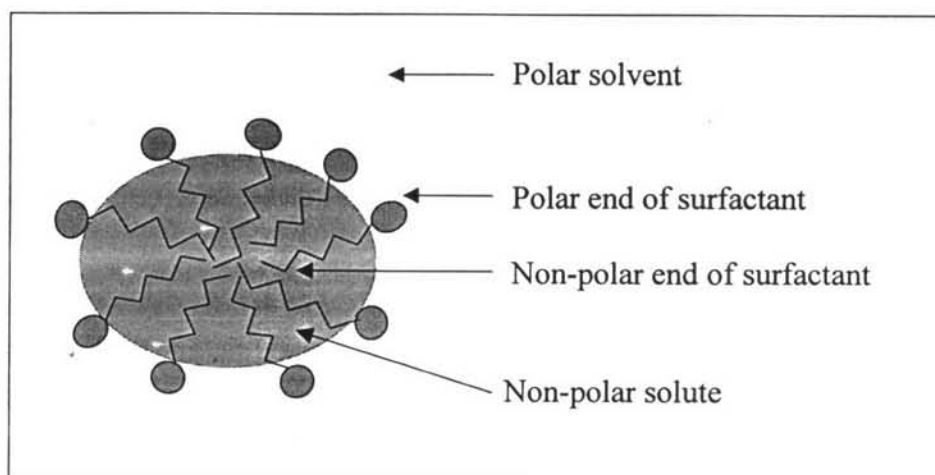
Almost invariably, the head group of a cationic surfactant is centered on one or more nitrogen atoms. Although corresponding analogs are to be found that contain sulfur, phosphorus, or arsenic, they are considerably more expensive than their nitrogenous counterparts and are used relatively rarely (Cross, 1994).

Quaternary ammonium surfactants retain their cationic character at any pH (unless molecular breakdown occurs), with common examples including, cetyltrimethylammonium bromide (CTAB), cetyltrimethylammonium tosylate (CTAT), distearyldimethylammonium chloride, dialkylmethylimidazolium methylsulfate. CTAT is a familiar cationic surfactant salt in the neutral sub-group (see Figure 2.2). The quaternary ammonium nitrogen in CTAT 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 tosylate, the molecular structure of this salt is independent of pH (Rubingh and Holland, 1990).



**Figure 1.2** The structure of cetyltrimethylammonium tosylate (CTAT).

Above certain concentrations in water, surfactant molecules tend to cluster into a spherical geometry with their nonpolar ends on the inside of the sphere and their polar ends on the outside. These clusters are called micelles and an example is shown in Figure 1.3.

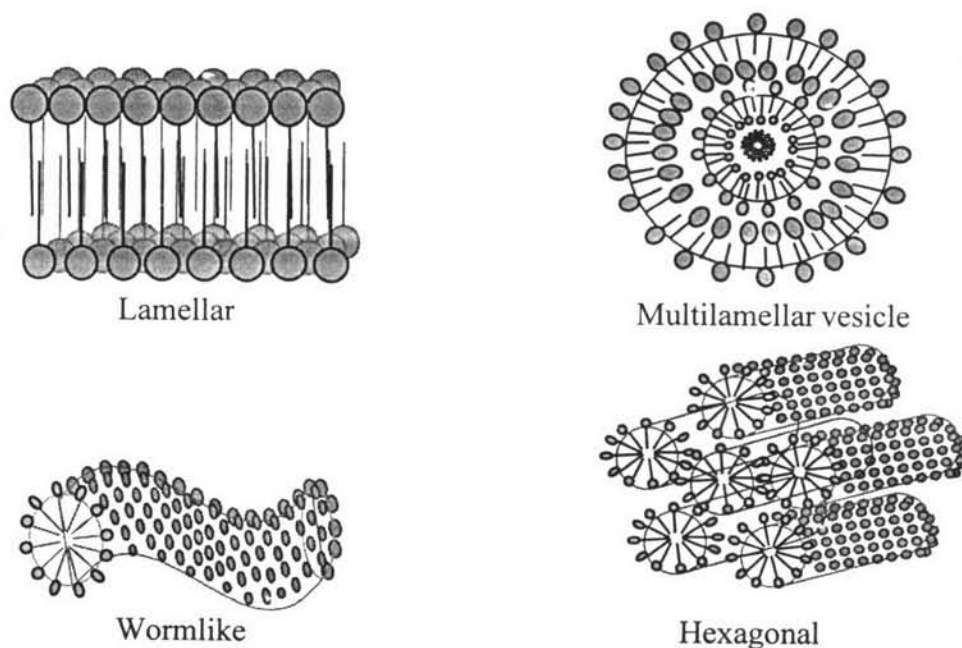


**Figure 1.3** Formation of surfactant micelle in aqueous media.

## 1.2 Micelle Formation

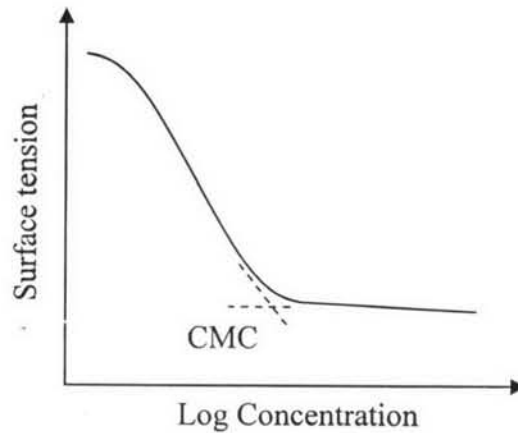
Micelle formation, or micellization, is an important phenomenon not only because a number of important interfacial phenomena such as detergency and solubilization depend on the existence of micelles in solution, but also because it affects other interfacial phenomena, such as surface or interfacial tension reduction. Several types of surfactant aggregates can be synthesized under varying bulk concentrations, the major types of micelles appear to be (1) relatively small, spherical structures, (2) elongated cylindrical, rodlike micelles with hemispherical ends (prolate ellipsoids), (3) large, flat lamellar micelles (disklike extended oblate spheroid), and (4) vesicles- more or less spherical structures consisting of bilayer lamellar micelles as shown in Figure 2.4. Changing the size, shape, and aggregation number of the micelle, with the structure varying from spherical through rod- or disklike to lamellar in shape (Winsor, 1968 ), are caused by changes in the temperature, concentration of surfactant, additives in the liquid phase, and structural group (Laughlin, 1994). The physical properties, phase behavior, and rheology of aqueous solutions of cationic surfactant are sensitive to changes in the molecular structure of the counterions. Also, large organic counterions (i.e. salicylate or tosylate) usually include formation of long elongated micelles and viscoelasticity in dilute regime ( $\leq 1\text{wt}\%$  surfactant). Some ionic surfactants can form long, wormlike

micelles in aqueous media, especially in the presence of electrolyte or other additives that decrease the repulsion between the ionic head groups (Raghavan, 2001). These wormlike micelles give rise to unusually strong viscoelasticity because of the entanglement of these structures.



**Figure 1.4** Structure of the micelle.

The concentration at which this phenomenon occurs is called the critical micelle concentration (CMC). The determination of the value of the CMC can be made by use of the physical properties, but most commonly breaks in the electrical conductivity, surface tension, light scattering, or fluorescence spectroscopy versus concentrations plots have been used for this purpose. In some cases, particularly where the hydrophobic group is long (e.g.  $>C_{16}$ ), a second break in the conductivity-surfactant concentration curve has been observed. It has been suggested that this indicates change in the micellar structure (Treiner, 1992).

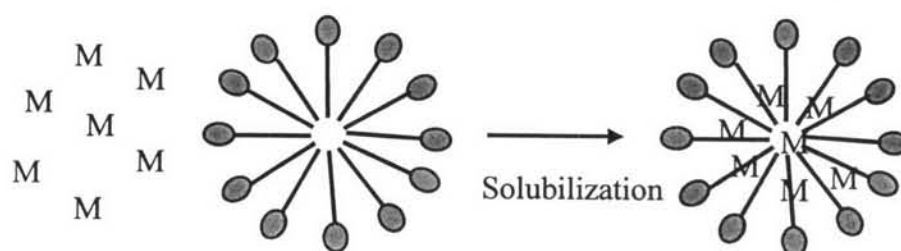


**Figure 1.5** Plot of surface tension versus log of the bulk phase concentration for an aqueous solution of a surfactant (Rosen, 2004).

The factors affect the CMC in aqueous solution are (1) the structure of the surfactant, (2) the presence of added electrolyte in the solution (3) the presence in the solution of various organic compounds, (4) the presence of a second liquid phase, and (5) temperature of the solution (Rosen, 2004).

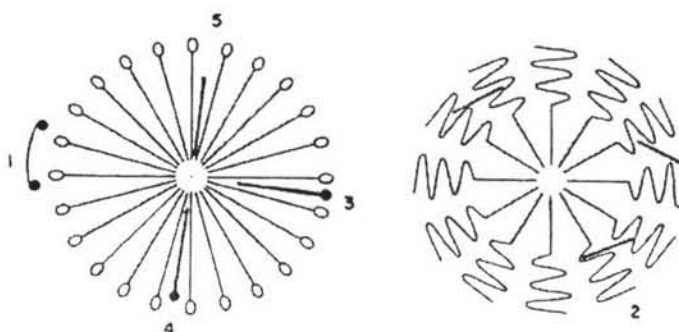
### 1.3 Solubilization

Solubilization is an important property of surfactants that is directly related to micelle formation. Surfactant solutions above the CMC can dissolve considerably larger quantities of organic materials than pure water or surfactant solution with concentrations below the CMC. The additional capacity is obtained by solubilizing solute in the micelle. 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 material” (Rosen, 2004) as shown in figure 1.6.



**Figure 1.6** Phenomenon of solubilization.

The location of the solubilize (solubilized material) occurs at different sites in the micelle: (1) on the surface of the micelle, at the micelle- solvent interface, (2) between the hydrophilic head groups, (3) in the so-called palisade layer of the micelle between the hydrophilic groups and the first few carbon atoms of hydrophobic groups that comprise the outer core of the micellar interior, (4) more deeply in the palisade layer, and (5) in the inner core of the micelle (Rosen, 2004).



**Figure 1.7** Loci of solubilization of material in a surfactant micelle.

#### 1.4 Emulsion Polymerization

Ingredients for a typical emulsion-polymerization system include the continuous phase normally water; monomer; monomer mixture, or monomer solution, emulsifiers and/or stabilizers, and initiator system. The product of the emulsion-polymerization reaction is a colloidal dispersion of polymer particles or polymer-solvent droplets.

In conventional emulsion polymerization, a hydrophobic monomer, such as styrene, is dispersed in an aqueous continuous phase with an oil-in-water emulsifier. The polymerization is usually carried out with a water-soluble initiator system. The Harkin model of emulsion polymerization is based on monomers such as styrene and butadiene, water-soluble initiators such as persulfate ion, and anionic surfactants which form micelles in water. The course of a batch reaction is described in term of three intervals (Herman, 1986).

Interval 1: The reaction mixture at the beginning of Interval 1 consists of a continuous water phase and dispersion of monomer droplets. The water phase contains the initiator, buffer or other electrolytes, small quantities of dissolved monomer and the emulsifier. Most of the the monomer is located in the large droplets, but some is solubilized within the micelles and some dissolved in the water. It was proposed that the polymerization reaction starts when the water-borne free radicals migrate into the monomer-swollen micelles. Polymerization within these micelles depletes the monomer and establishes a thermodynamic driving force which causes mass transfer from the monomer droplets through the water phase to the newly formed and growing polymer particles.

Interval 2: At the end of Interval 1, the reaction mixture is comprised of monomer-swollen polymer particles and monomer droplets. Most of emulsifier is on the surface of the polymer particle. The reaction proceeds by polymerization within the particles. Monomer is supplied by diffusion from the shrinking monomer droplets. As the particles grow during Interval 2, the total interfacial area increases, usually to values higher than can be saturated with the emulsifier used in the initial charge. Interval 2 ends when the monomer is depleted from the droplets. At this point in the reaction, the degree of saturation of the particle surfaces by emulsifier is at or near its lowest value.

Interval 3: Overall monomer conversion at the beginning of Interval 3 varies considerably among different monomer system; for styrene, it is typically about 40%. Continuing polymerization during Interval 3 reduces the monomer concentration in the particles. In Interval 3, polymerization takes place with higher polymer concentrations at the reaction loci, and thus more branching and cross-linking reactions are expected. This is particularly important with some synthetic



elastomers. Product quality in such system is controlled by lower polymerization temperatures, chain-transfer agents and limitation of conversion. In the last case, polymerization is stopped at the desired conversion, and the unreacted monomer is recycled.