

**SYNTHESIS OF POLYMERIC AND CATIONIC SURFACTANTS  
FOR EMULSION POLYMERIZATION OF STYRENE AND  
VINYL ACETATE**

**M. Sc. Thesis by**

**Dürdane ERKAL**

**Department: Chemistry**

**Programme: Chemistry**

**Supervisor: Assoc. Prof. Dr. Bahire Filiz ŞENKAL**

**JUNE 2007**

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Dürdane ERKAL**

**509051205**

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**Supervisor (Chairman) :**

**Assoc. Prof. Dr. Bahire Filiz  
ŞENKAL**

**Members of the Examining  
Committee:**

**Prof. Dr. Candan ERBİL (I.T.U.)**

**Assoc. Prof. Dr. Reha YAVUZ  
(I.T.U.)**

**JUNE 2007**

**STİREN VE VİNİL ASETATIN EMÜLSİYON  
POLİMERİZASYONU İÇİN POLİMERİK VE  
KATYONİK YÜZEY AKTİF MADDELERİN  
SENTEZLENMESİ**

**YÜKSEK LİSANS TEZİ  
Dürdane ERKAL  
509051205**

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**Tez Danışmanı: Doç. Dr. Bahire Filiz ŞENKAL  
Diğer Jüri Üyeleri: Prof. Dr. Candan ERBİL (İ.T.Ü.)  
Doç. Dr. Reha YAVUZ (İ.T.Ü.)**

**HAZİRAN 2007**

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## LIST of ABBREVIATIONS

<b>PS</b>	: Polystyrene
<b>VAc</b>	: Vinyl Acetate
<b>FT-IR</b>	: Fourier Transform Infrared Spectroscopy
<b>NMR</b>	: Nuclear Magnetic Resonance Spectroscopy
<b>UV-VIS</b>	: Ultraviolet Visible Spectroscopy
<b>M<sub>n</sub></b>	: Number Average Molecular Weight
<b>M<sub>v</sub></b>	: Viscosity Average Molecular Weight
<b>AIBN</b>	: Azobisisobutyronitrile
<b>HCl</b>	: Hydrochloride
<b>NaOH</b>	: Sodium Hydroxide
<b>CMC</b>	: Critical Micelle Concentration
<b>NMP</b>	: 2-methyl-1-pyrrolidone
<b>PPS</b>	: Potassium Persulfate
<b>THF</b>	: Tetrahydrofuran
<b>TMED</b>	: Tetramethylene Ethylenediamine

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# **SYNTHESIS OF POLYMERIC AND CATIONIC SURFACTANTS FOR EMULSION POLYMERIZATION OF STYRENE AND VINYL ACETATE**

## **SUMMARY**

Polymer distribution stability is very important in practice. Studies on the polymer distribution stability has gained importance during the last years.

Polymeric surfactants has great importance in industry, plus they have various kinds; anionic, nonionic, cationic and zwitterionic. Predominantly, anionic and nonionic surfactants are used in the emulsion polymerization systems.

In this study, two different surfactants were synthesized.

Starting from poly(vinylbenzyl chloride), polymeric surfactant is synthesized from the modification with N-methyl-D-glucamine.

This surfactant is characterized by analytical and spectroscopic methods. Critical micelle concentration is measured conductometrically.

Cationic surfactant is synthesized by the reaction of N,N,N,N-tetramethylenediamine with decil bromide.

This surfactant is characterized by spectroscopic methods. Critical micelle concentration is measured conductometrically.

The critical micelle concentrations of surfactants are found as  $1.18 \times 10^{-3}$  and  $2.14 \times 10^{-4}$  M respectively.

Surfactant concentrations are changed during polymerization. Potassium persulfate is used as the initiator in the polymerizations. Reactions occurred, during different temperature ranges, at 70°C for vinyl acetate and at 80°C for styrene.

After polymerization processes, surface tension and viscosity of the products were measured. The molecular weights of the synthesized polymers were measured by viscometer.

Synthesized surfactants are very practicable for emulsion polymerization. The reaction time ranges and conditions are suitable than the standard emulsion polymerization processes. The synthesized polymers have very high molecular weights and suitable for industrial uses.

# STİREN VE VİNİL ASETATIN EMÜLSİYON POLİMERİZASYONU İÇİN POLİMERİK VE KATYONİK YÜZEY AKTİF MADDELERİN SENTEZLENMESİ

## ÖZET

Polimerik dağılım kararlılığı uygulamada çok önemli bir yere sahiptir. Bu yüzden yeterli kararlılıkta polimer dağılımı elde etmek için yapılan çalışmalar geçtiğimiz yıllarda önem kazanmıştır.

Polimerik yüzey aktif maddeler endüstriyel açıdan çok önemlidir ve birden çok çeşide sahiptir. Genellikle, anyonik ve non-iyonik yüzey aktif maddelerin geniş bir kullanım alanı vardır.

Bu çalışmamızda iki farklı yüzey aktif sentezlenmiştir.

Polimerik yüzey aktif madde, poli(vinilbenzil klorür)( $M_n=15500$ )den başlayarak N-metil-D-glukaminle modifiye edilerek sentezlenmiştir.

Bu madde analitik ve spektroskopik yöntemler kullanılarak sentezlenmiştir. Kritik misel konsantrasyonu (CMC) kondüktometrik olarak hesaplanmıştır.

Katyonik yüzey aktif madde, N,N,N,N-tetrametilendiamin'le desilbromür'ün reaksiyonu sonucunda sentezlenmiştir. Bu yüzey aktif maddenin karakterizasyonu spektrofotometrik olarak yapılmıştır.

Bu madde analitik ve spektroskopik yöntemler kullanılarak sentezlenmiştir. Kritik misel konsantrasyonu (CMC) kondüktometrik olarak hesaplanmıştır.

Yüzey aktif maddelerin kritik misel konsantrasyonları sırasıyla  $1.18 \times 10^{-3}$  ve  $2.14 \times 10^{-4}$  M olarak bulunmuştur.

Polimerizasyon sırasında yüzey aktif konsantrasyonları değiştirilmiştir. Bu polimerizasyonlarda, başlatıcı olarak potasyum persülfat kullanılmıştır. Reaksiyonlar, farklı zamanlarda, vinil asetat için  $70^\circ\text{C}$ 'de, stiren için  $80^\circ\text{C}$ 'de gerçekleşmiştir.

Polimerizasyon sonrasında, ürünlerin yüzey gerilimi ve vizkoziteleri ölçülmüştür. Sentezlenen polimerlerin molekül ağırlıkları vizkozimetrik olarak ölçülmüştür.

Sentezlenen yüzey aktif maddeler emülsiyon polimerizasyonu sisteminde kullanılabilir yapıdadır. Reaksiyon süresi ve şartları standart emülsiyon polimerizasyonlarından daha rahattır ve endüstriye yatkın çok yüksek molekül ağırlıklı polimerler elde edilmiştir.

## 1. INTRODUCTION

Surfactants are among the most versatile products used in the chemical industry, appearing in such diverse products as motor oils, pharmaceuticals and detergents. More recently, applications have been extended to such high-technology areas like electronic printing, magnetic recording, and biotechnology.

There are four classes of surfactants:

- (a) anionic; where the head group of the molecule has a negative charge,
- (b) cationic; where the head group bears a positive charge,
- (c) zwitterionic; where both positive and negative charges are present, and
- (d) non-ionic; where the head group has no ionic character.

Cationic surfactants, which are most relevant to the present study, usually fall into one of the following categories: long-chain amines or polyamines and their respective salts, quaternary ammonium salts (e.g. hexadecyltrimethyl ammonium bromide), oligo(ethylene oxide) amines and their quaternized derivatives, and amine oxides. Cationic surfactants are used in many applications from fabric softeners and toiletries to adhesion promoters in asphalt and corrosion inhibitors.

Heterophase polymerizations, especially emulsion polymerizations, are important industrial technologies yielding synthetic elastomers, paints, paper coatings, adhesives, etc. In emulsion polymerization, the use, or in situ production, of surfactant is necessary in order to achieve stabilization of the latex particles produced during polymerization and indeed later on in the derived products.

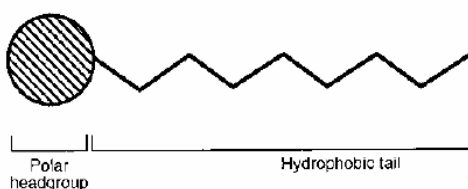
In general, particle stabilization is achieved by the use of various emulsifiers which are employed in emulsion polymerization formulations. The anionic and nonionic emulsifiers are the most widely utilized because of enhanced compatibility with negatively charged latex particles (usually as a result of persulfate initiator fragments) as compared to other emulsifiers. Recent years, particle stabilization can be achieved via novel surfactants.

In the present work, the emulsion homopolymerization system containing vinyl acetate, styrene were studied. The effects of new polymeric emulsifier on the physicochemical properties of obtained latex properties were investigated depending on surfactant percentage in homopolymerization.

## 2. THEORETICAL PART

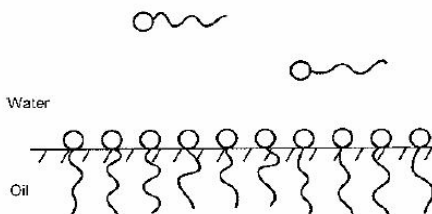
### 2.1. Surfactants

Surfactants are low to moderate molecular weight compounds which contain one hydrophobic part, which is generally readily soluble in oil but sparingly soluble or insoluble in water, and one hydrophilic (or polar) part, which is sparingly soluble or insoluble in oil but readily soluble in water (Figure 2.1).



**Figure 2.1.** Schematic illustration of a surfactant molecule.

Due to this “schizophrenic” nature of surfactant molecules, these experience suboptimal conditions when dissolved molecularly in aqueous solution. If the hydrophobic segment is very large the surfactant will not be water-soluble, whereas for smaller hydrophobic moieties, the surfactant is soluble, but the contact between the hydrophobic block and the aqueous medium nevertheless energetically less favorable than the water-water contacts.



**Figure 2.2.** Schematic illustration of the absorption of surfactants at the oil-water interface.

Alternatives to a molecular solution, where the contact between the hydrophobic group and the aqueous surrounding is reduced, therefore offer ways for these systems to reduce their free energy. Consequently, surfactants are surface active, and tend to accumulate at various interfaces, where the water contact is reduced (Figure 2.2).

Another way to reduce the oil-water contact is self-assembly, through which the

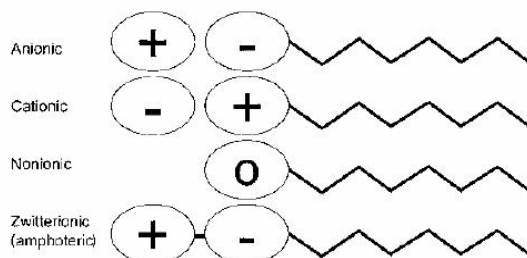


hydrophobic domains of the surfactant molecules can associate to form various structures, which allow a reduced oil-water contact. Various such structures can be formed, including micelles, microemulsions, and a range of liquid crystalline phases (Figure 2.3).



**Figure 2.3.** Schematic illustration of some different self-assembled structures formed in surfactant systems.

The type of structures formed depends on a range of parameters, such as the size of the hydrophobic domain, the nature and size of the polar head group, temperature, salt concentration, pH, etc. Through varying these parameters, one structure may also turn into another, which offers interesting opportunities in triggered drug delivery.



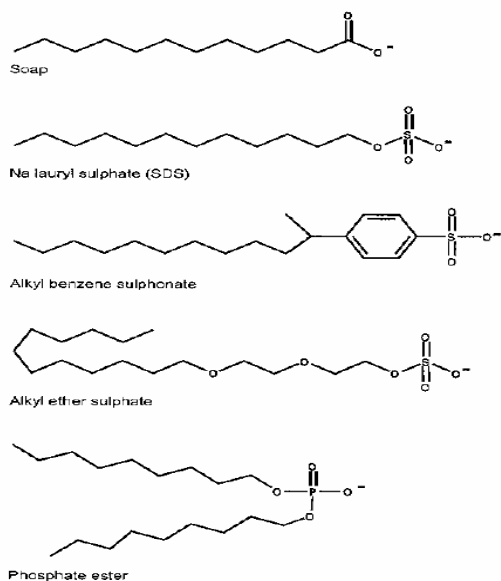
**Figure 2.4.** Schematic illustration of the various types of surfactants.

Surfactants are classified according to their polar headgroup; i.e., surfactants with a negatively charged headgroup are referred to as anionic surfactants, whereas cationic surfactants contain polar headgroups with a positive charge. Uncharged surfactants are generally referred to as nonionic, whereas zwitterionic surfactants contain both a negatively charged and a positively charged group (Figure 2.4).

Anionic surfactants (Figure 2.5) constitute the largest group of available surfactants. Examples of such surfactants include,

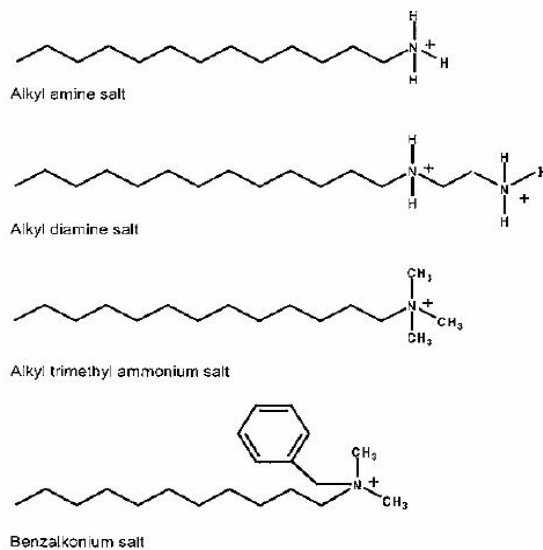
1. Fatty acid salts (“soaps”)
2. Sulfates
3. Ether sulfates
4. Phosphate esters

A common feature of all anionic surfactants is that their properties, e.g., surface activity and self-assembly, are quite sensitive to salt, and particularly divalent or multivalent cations. A commonly experienced illustration of this is poor solubility, foaming, and cleaning efficiency of alkyl sulfate surfactants in salt or hard water. Naturally, this salt dependence also offers opportunities in drug delivery. Sulfates are also somewhat sensitive toward hydrolysis, particularly at low pH.



**Figure 2.5.** Chemical structure of some commonly used anionic surfactants.

Cationic surfactants are frequently based on amine-containing polar headgroups (Figure 2.6).

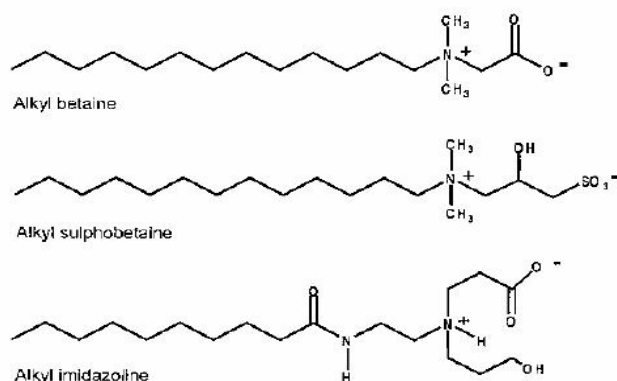


**Figure 2.6.** Chemical structure of some commonly used cationic surfactants.

Due to their charged nature, the properties of cationic surfactants, e.g., surface activity or structure formation, are generally strongly dependent on the salt concentration, and on

the valency of anions present. Cationic surfactants are frequently used as antibacterial agents. However, cationic surfactants are frequently also irritant and some times even toxic.

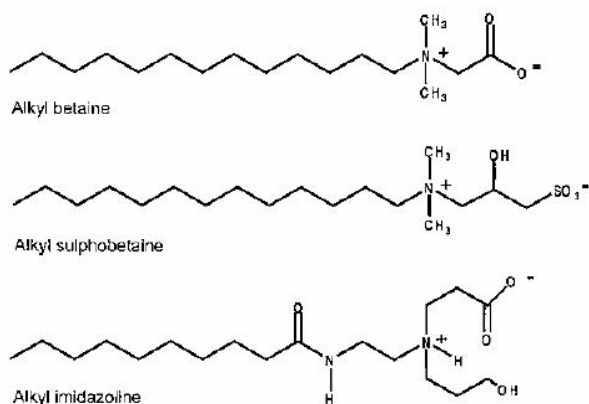
Nonionic surfactants, i.e., surfactants with an uncharged polar headgroup, are probably the ones used most frequently in drug delivery applications, with the possible exception of phospholipids. In particular, nonionic surfactants used in this context are often based on oligo (ethylene oxide)-containing polar head groups (Figure 2.7).



**Figure 2.7.** Chemical structure of some commonly used nonionic surfactants.

Due to the uncharged nature of the latter, these surfactants are less sensitive to salt, but instead quite sensitive to temperature. The critical micellization concentration for such surfactants is generally much lower than that of the corresponding charged surfactants, and partly due to this, such surfactants are generally less irritant and better tolerated than the anionic and cationic surfactants.

Zwitterionic surfactants are less common than anionic, cationic, and nonionic ones. Frequently, the polar headgroup consists of a quarternary amine group and a sulfonic or carboxyl group (Figure 2.8).



**Figure 2.8.** Chemical structure of some typical zwitterionic surfactants.

Due to the zwitterionic nature of the polar headgroup, the surfactant charge changes

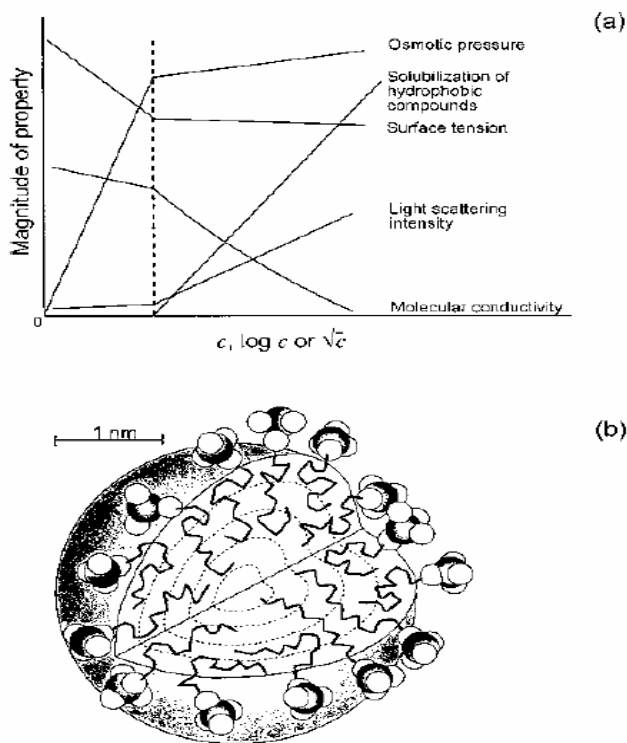
with pH, so that it is cationic at low pH and anionic at high pH. Due to the often low irritating properties of such surfactants, they are commonly used in personal care products.[1-8]

## 2.2 Micelles

### 2.2.1 Structure and dynamics of micellar systems

A notable feature of surfactants is their ability to self-associate to form micelles (Figure 2.9).

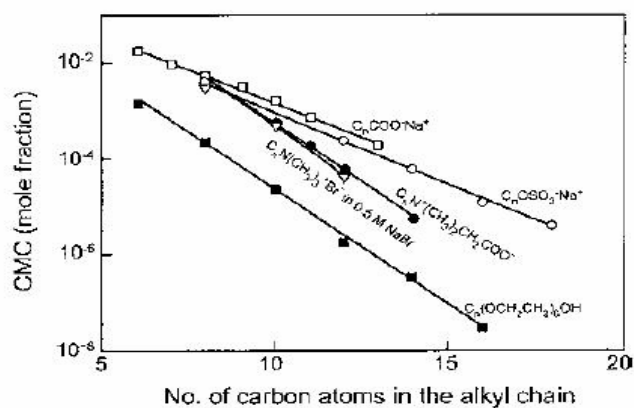
Since micelles consist of surfactant molecules packing in a spacefilling manner numerous parameters of the surfactant solution change at the critical micellization concentration (cmc). For example, since the micelles consist of many individual surfactant molecules, any parameter related to the size or diffusion in surfactant solutions can be used to detect the micellization, e.g., through scattering methods and nuclear magnetic resonance (NMR). Also, the micellar core contains little water (see below); hence solubilization of hydrophobic dyes is initiated at the cmc, and fluorescence investigations with probes sensitive for the polarity of the environment can be used to detect micellization.



**Figure 2.9.** (a) Schematic illustration of how a range of experimentally accessible parameters change with the surfactant concentration and how this can be used to detect the cmc. (b) Schematic illustration of a spherical micelle.

Also, a range of other techniques, such as conductivity (ionic surfactants), osmotic pressure, and surface tension, may be used to determine the cmc. The main driving force for micelle formation in aqueous solution is the effective interaction between the hydrophobic parts of the surfactant molecules, whereas interactions opposing micellization may include electrostatic repulsive interactions between charged head groups of ionic surfactants, repulsive osmotic interactions between chainlike polar head groups such as oligo(ethylene oxide) chains, or steric interactions between bulky head groups.

Given the delicate balance between opposing forces, it is not surprising that surfactant self-assembly is affected by a range of factors, such as the size of the hydrophobic moiety, the nature of the polar head group, the nature of the counterion (charged surfactants), the salt concentration, pH, temperature, and presence of cosolutes. Probably the most universal of all these is the size of the hydrophobic domain(s) in the surfactant molecule. With increasing size of the hydrophobic domain, the hydrophobic interaction increases, thereby promoting micellization. As an illustration of this, Figure 2.9 shows the chain length dependence of the cmc for some different surfactants. As can be seen, the cmc decreases strongly with an increasing number of carbon atoms in the alkyl chain, irrespective of the nature of the polar head group. As a general rule, the cmc decreases a factor of 2 for ionic surfactants and with a factor of 3 for nonionic surfactants on addition of one methylene group to a surfactant alkyl chain. The extent of the decrease also depends on the nature of the hydrophobic domain, in terms of both structure (e.g., single chain vs. double chain surfactants) and composition (e.g., fluorinated surfactants), but qualitatively, the same effect is observed for all surfactants.

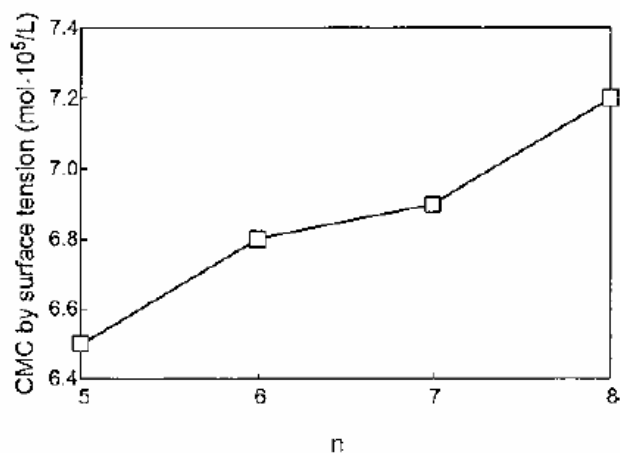


**Figure 2.10.** The dependence of the cmc with the length of the hydrophobic domain for a number of alkyl chain surfactants with different polar head group.

The dependence of the micellization on the nature of the polar head group is less straightforward than that of the alkyl chain length. Nevertheless, the cmc of nonionic

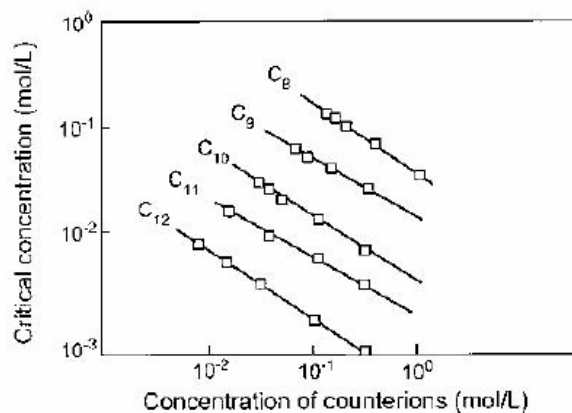
surfactants is generally much lower than that of ionic ones, particularly at low salt concentrations, which is due to the repulsive electrostatic interaction between the charged head groups opposing micellization (Figure 2.10).

For nonionic surfactant of the oligo(ethylene oxide) type, an increasing number of ethylene oxide groups at a constant alkyl chain length results in an increasing cmc as a consequence of an increasing osmotic repulsion between the oligo(ethylene oxide) chains when these grow larger (Figure 2.11). The length of the oligo(ethylene oxide) chains affects also the packing of the surfactant molecules in the micelle. More precisely, with an increasing length of the oligo(ethylene oxide) chain, the head group repulsion increases, which tends to increase the curvature of the aggregates, and hence results in smaller and more spherical micelles. The latter effect can be observed, e.g., from the micellar size or aggregation number.



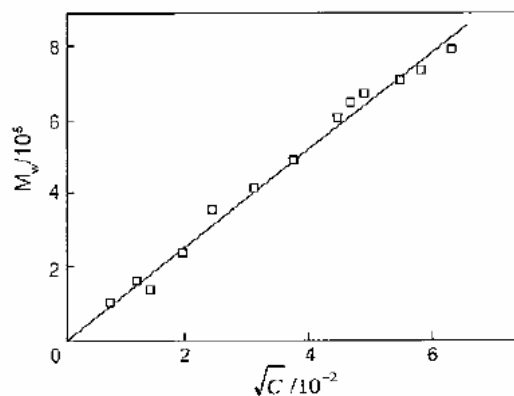
**Figure 2.11.** Effect of the length of the oligo (ethylene oxide) chain  $n$  on the cmc for a series of  $C_{12}E_n$  surfactants.

Cosolutes in general tend to affect the micellization in surfactant systems. Examples of such cosolutes include oils (or other hydrophobic compounds), salt, alcohols, and hydrotropes. Of these, salt plays a particularly important role, particularly for ionic surfactants. Thus, on addition of salt, the electrostatic repulsion between the charged head group is screened. As a consequence, the repulsive interaction opposing micellization becomes relatively less important, and the attractive driving force for micellization therefore dominates to a larger extent. As a result of this, the cmc decreases on addition of salt (Figure 2.12).



**Figure 2.12.** Effect of sodium chloride on the cmc of sodium alkyl sulfate surfactants.

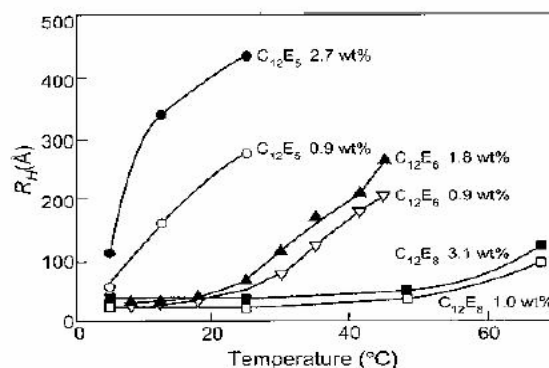
For nonionic surfactants, on the other hand, addition of low or moderate concentrations of salt has little influence on the micellization due to the absence of charges in these systems. At very high salt concentrations ( $\approx 0.1-1 M$ ), so called lyotropic salt effects are typically observed. Depending on the nature of both the cation and the anion of the salt, the presence of the salt may either promote or preclude micellization. For ionic surfactants, the presence of salt also affects the micellar size and aggregation number. In particular, screening of the repulsive electrostatic interaction through addition of salt facilitates a closer packing of the surfactant head groups, and therefore results in a micellar growth (Figure 2.13).



**Figure 2.13.** Effect of added salt on the micellar aggregation number for CTAB.

Again, for nonionic surfactants, little or no such dependence is observed. Instead, many nonionic surfactants, notably those containing oligo(ethylene oxide) groups, display a sensitivity regarding temperature. With increasing temperature, surfactants and polymers containing oligo(ethylene oxide) or its derivatives display a decreased water solubility. At sufficiently high temperature, usually referred to as the lower consolute temperature (LCT) or the cloud point (CP), such molecules phase separate to form one dilute and one more concentrated phase. Note that this behavior is opposite to what is observed for

most other types of surfactants and polymers, which display increasing solubility/miscibility with increasing temperature. The decreased solvency for the oligo(ethylene oxide) moieties with increasing temperature results in a decreased repulsion between the polar head groups in ethylene oxide-based surfactants, and hence micellization is favored at higher temperature. Consequently, the cmc displayed by these surfactants decreases with increasing temperature. For ionic surfactants, on the other hand, the temperature dependence is the opposite for entropic reasons. In parallel, the oligo(ethylene oxide) moieties contract with increasing temperature as a result of the decreasing solvency, and therefore can pack more densely at the interface. Together, this means that micellar growth is facilitated at the higher temperature (Figure 2.14).

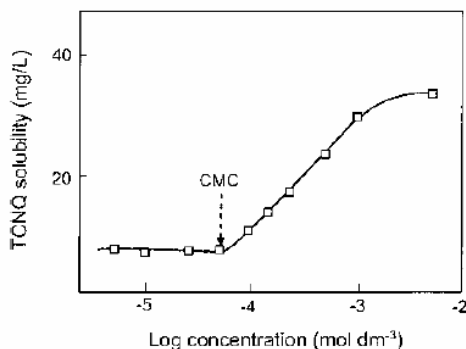


**Figure 2.14.** Effect of temperature on the micellar size  $R_H$  for  $C_{12}E_n$  surfactants.

For ionic surfactants, but also for nonionic surfactants other than those based on oligo(ethylene oxide), the general rule is that the temperature dependence of the micellization and the structure of the micelles formed is rather minor. Organic cosolutes in general play an important role in technical systems containing surfactants. This is the case not the least in drug delivery, where surfactants are used in order to facilitate the efficient and safe administration of a drug. The effect of a cosolute on the micellization in surfactant systems to a large extent depends on the nature of the cosolute. As illustrated above, salts have large effects on the micellization in ionic surfactant systems, but rather weak effects in nonionic surfactant systems. For uncharged cosolutes, the effect on the micellization in surfactant systems depends both on the nature of the cosolute and that of the surfactant, and both an increase and decrease of the cmc on addition of the cosolute is possible. Of particular interest for the use of micellar systems in drug delivery are hydrophobic solutes, which are essentially insoluble in water but readily soluble in oil and therefore also in the hydrophobic core of micelles. As indicated above, the amount of a hydrophobic solute solubilized by a surfactant solution below the cmc is very limited. Above the cmc, on the other hand, the hydrophobic substance is

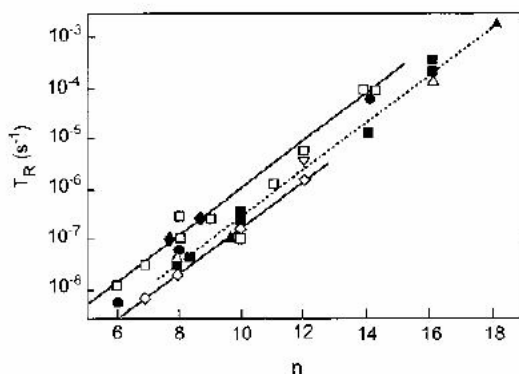


solubilized in the micelles (Figure 2.15). Indeed, the capacity of surfactant systems to solubilize hydrophobic substances constitutes one of the single most important properties of such systems, as this forms the basis for the use of surfactants in numerous industrial contexts.



**Figure 2.15.** Solubility of 7,7,8,8-tetracyanoquinodimethane (TCNQ) in aqueous solution of  $C_{12}E_8$  at  $25^\circ\text{C}$ .

From simple space-filling considerations it is evident that the solubilization of a hydrophobic solute in the core of the micelles causes the latter to grow. At the same time, hydrophobic solutes may promote micellization and cause a decrease in the cmc. This is not entirely unexpected, since reducing the cmc in order to accommodate the oil in a one-phase system may offer an opportunity for free energy minimization for the system as a whole. Finally, it is important to note that surfactant micelles are not static structures, but rather that the schematic illustration shown in Figure 2.9 represents an instant ‘‘snapshot’’ of such a structure.



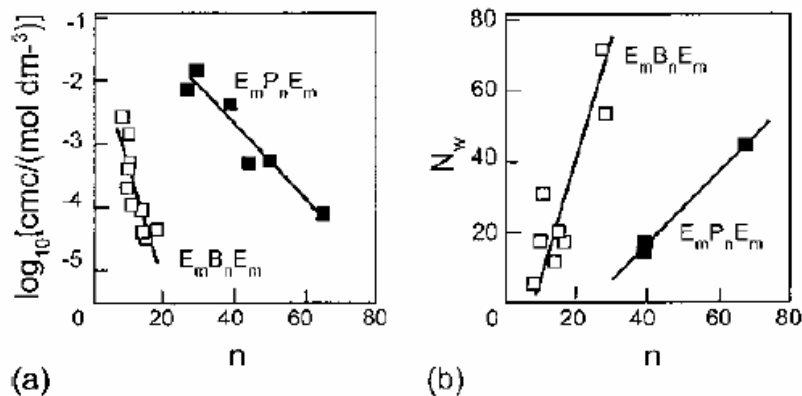
**Figure 2.16.** Effects of the alkyl chain length  $n$  of alkyl-based surfactants on the average residence time  $T_R$  for a surfactant molecule in a given micelle. Open squares: sodium alkylsulfates; filled diamonds: sodium alkylsulfonates; filled squares: sodium alkylcarboxylates; open diamonds: potassium alkylcarboxylates; open square: cesium decylcarboxylate; filled circles: alkylammonium chlorides; Filled triangles: alkyltrimethylamine bromides; open triangles: alkylpyridium chlorides; filled squares: alkylpyridium bromides; reversed open triangle: dodecylpyridium iodine.

Thus, micelles are highly dynamic structures, where the molecules remain essentially in a liquid state. Also, the individual surfactant molecules are freely exchanged between micelles and between micelles and the aqueous solution. The residence time for the surfactant molecules in one given micelle is generally very short, but increasing about one order of magnitude for each ethylene group added to the surfactant hydrophobic tail (Figure 2.16).

### **2.2.2 Block copolymer micelles**

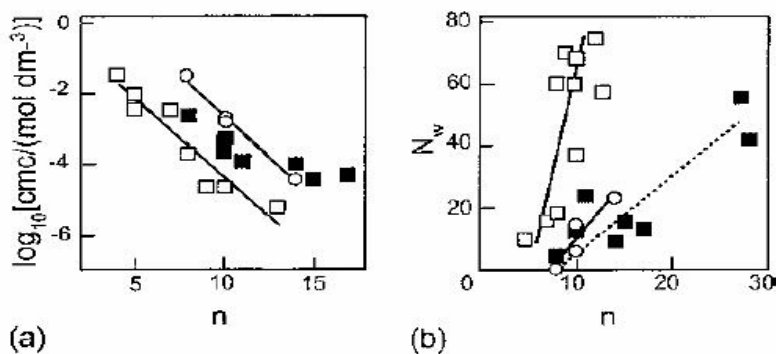
Closely related to low molecular weight surfactants in many ways concerning self-assembly are block copolymers. This is particularly true for simpler block copolymer systems, such as diblock and triblock copolymers, which form not only micelles in dilute aqueous solution but also a range of liquid crystalline phases and microemulsions with oil and water. Such “polymeric surfactants” have found widespread use, not the least in drug delivery, as will be discussed in some detail below.

Although there has been extensive work on a range of block copolymer systems, much of this work has concerned solvent-based systems. During the last decade, however, a number of water-soluble block copolymer systems have been investigated concerning their physicochemical behavior, e.g., regarding self-association. In particular, much of the work has involved PEO-based copolymers [PEO being poly(ethylene oxide)], and these are also the ones of largest interest in the present context. A number of hydrophobic blocks have been investigated for PEO-based block copolymers, including poly(propylene oxide), poly(styrene), alkyl groups, poly(butylene oxide), poly(lactide), and poly(caprolactone). In particular, interest has focused on PEO/PPO block copolymers (PPO being polypropylene oxide), mainly due to their commercial accessibility in a range of compositions and molecular weights. Composition and molecular weight are two of the prime parameters of interest for block copolymer systems. In analogy to low molecular weight nonionic surfactants, micellization is promoted by an increasing length of the hydrophobic block(s) and decreasing length of the hydrophilic one(s) (Figure 2.17). From the slope of the decrease in the cmc and in the micellar aggregation number with an increasing number of hydrophobic groups, the hydrophobicity of the hydrophobic groups may be estimated. Such an analysis yields “hydrophobicity ratios” for propylene oxide (P), lactide (L), caprolactone (C), butylene oxide (B), and styrene (S) of 1:4:5:6:12.



**Figure 2.17.** Effect of the length of the hydrophobic block  $n$  on the cmc (a) and micellar aggregation number  $N_w$  (b) of  $E_m B_n E_m$  and  $E_m P_n E_m$  triblock copolymers.

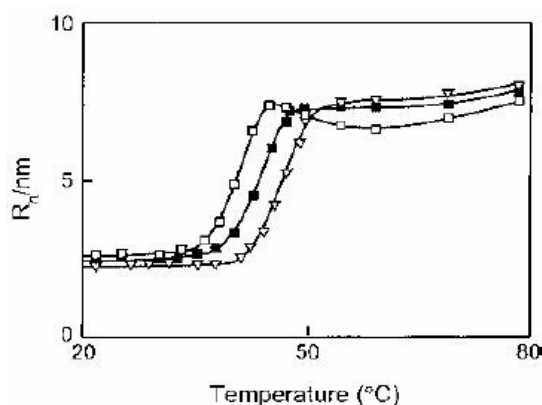
Also, the molecular architecture affects micellization in block copolymer systems. As can be seen in Figure 2.18, diblock ( $E_m B_n$ ) copolymers self-associated more readily than triblock ( $B_n/2E_m B_n/2$  and  $E_m/2B_n E_m/2$ ) copolymers of the same total molecular weight and composition. The origin of this is that less efficient packing is achieved with the triblock copolymers, in the case of the BAB copolymer due to the hydrophilic block being a loop rather than a tail, and in the ABA case due to the presence of two rather than one hydrophilic tail.



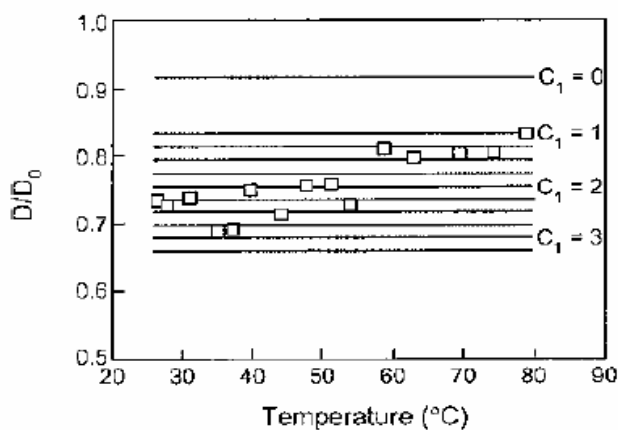
**Figure 2.18.** Effect of the number of butylene oxide groups  $n$  on the cmc (a) and micellar aggregation number  $N_w$  (b) for  $E_m B_n$  (open squares),  $B_n/2E_m B_n/2$  (circles), and  $E_m/2B_n E_m/2$  (filled squares) copolymers.

The micellization of PEO-containing block copolymers is promoted by increasing temperature. As with the low molecular weight surfactants, this is due to a decreased solvency of the PEO domain(s). However, for PEO/PPO copolymers, the decreased aqueous solubility of the PPO domain(s) with increasing temperature also contributes to this behavior. Quantitatively, the temperature dependence of the cmc is quite strong for many PEO/PPO block copolymers. The concentration-induced aggregation at a fixed temperature, on the other hand, is frequently quite gradual, and the determination of the cmc in the traditional manner therefore difficult. The cmc values so determined

frequently span widely, e.g., between different experimental methods used, but also display batch-to-batch variations. Therefore, the onset of self-assembly in such systems is often identified by a critical micellization temperature at a fixed polymer concentration (cmt), rather than by a cmc at fixed temperature (Figure 2.19).



**Figure 2.19.** Temperature-dependent hydrodynamic radius  $R_h$  of Pluronic F68 at a bulk concentration of 51.7 (open squares), 25.0 (filled squares), and 12.5 (open triangles)  $\text{mg}\cdot\text{ml}^{-1}$ .

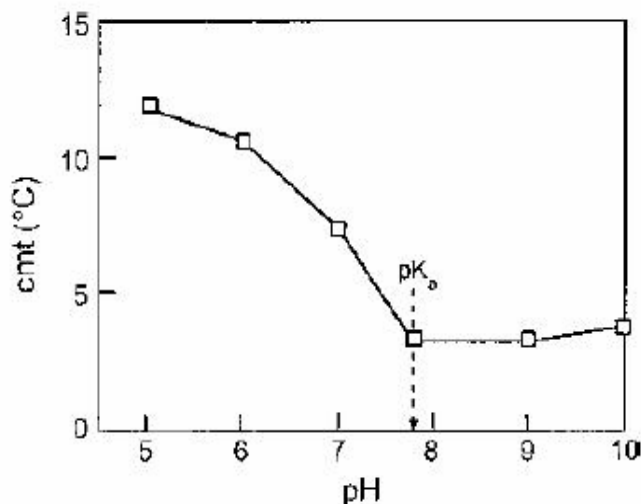


**Figure 2.20.** Effects of temperature on the number of water molecules bound per monomer  $C_1$  in Pluronic F127 micelles, determined from the water self-diffusion ( $D/D_0$ ).

There is also micellar growth with increasing temperature. However, in the general case, the increase in the micellar aggregation number is significantly stronger than that in the micellar radius, which indicates that the block copolymers pack more efficiently with increasing temperature. As with the  $E_0$  containing low molecular weight surfactants, this is an effect of the decreasing solvency of the polymer with increasing temperature. This also means that the hydration of the polymer molecules decreases with increasing temperature (Figure 2.20).

The effects of cosolutes on the self-assembly of PEO/PPO block copolymers are quite similar to those on low molecular weight PEO-containing surfactants. Thus, effects of salts on the micellization in these block copolymer systems are minor at low to

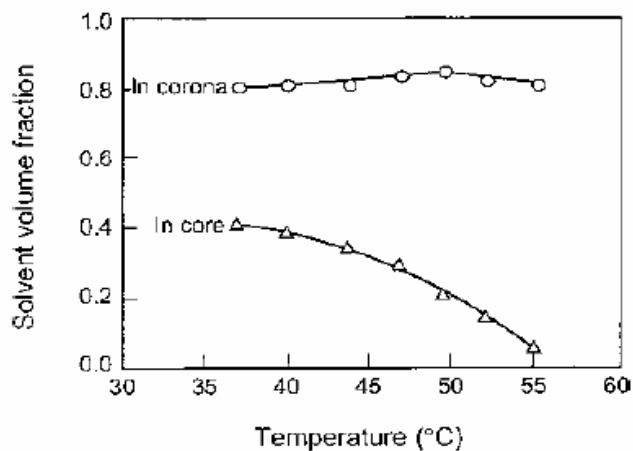
medium salt concentration, whereas at high salt concentration ( $\approx 0.1\text{--}1\text{M}$ ), lyotropic salt effects are observed. Furthermore, hydrophobic solutes may induce micellization. An illustration of this is given in Figure 2.21.



**Figure 2.21.** cmt as a function of pH from a formulation containing 5 wt% of active ingredient (50/50 mol/mol of lidocaine and prilocaine), 15.5 wt% Lutrol F127, and 5.5 wt% Lutrol F68.

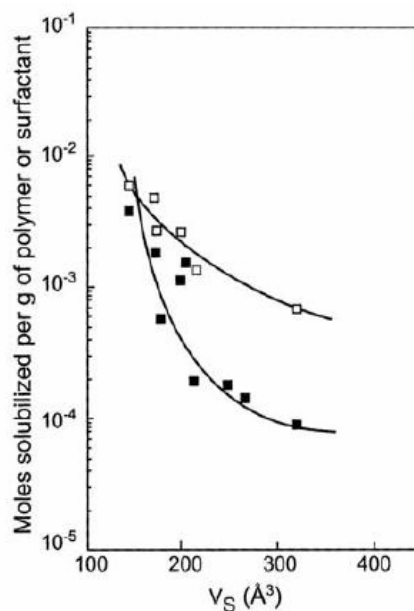
As can be seen, the presence of lidocaine/prilocaine has little effect on the cmc for this copolymer system at  $\text{pH} \ll \text{pKa}$  (7.86 and 7.89 for lidocaine and prilocaine, respectively), i.e., where these compounds are fully ionized and readily soluble in water, and therefore behaving as ordinary salt. On increasing pH, on the other hand, lidocaine and prilocaine become less soluble in water as a result of deprotonation, and at  $\text{pH} \geq \text{pKa}$  behave essentially as sparingly soluble oils, thus promoting micellization and lowering cmt. The localization of the solubilized molecule depends on the properties of the solubilize, notably its hydrophobicity. The more hydrophobic the solubilize, the more it tends to be localized in the core of the micelles. More amphiphilic molecules, on the other hand, tend to be located preferentially in the micellar interfacial layer.

An interesting difference between alkyl-based surfactants, on one hand, and PEO/PPO block copolymer, on the other, is that the hydrophobic moiety is significantly more polar in the latter case. This means that there is intermixing between the PEO and PPO blocks, but also that there is a significant amount of water present also in the core of the micelles formed by PEO/PPO block copolymers (Figure 2.22). With increasing temperature, however, there is a decreased hydration of the polymer.

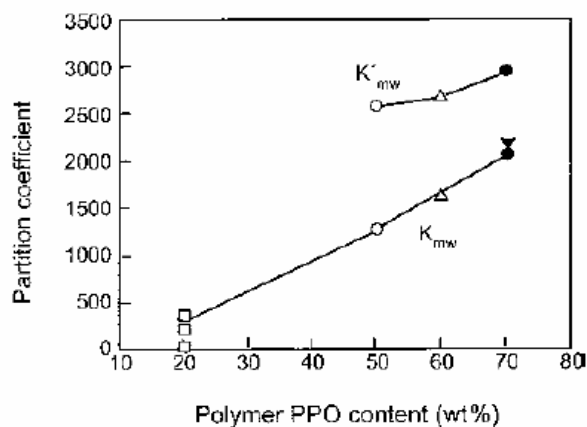


**Figure 2.22.** Volume fraction of water in the micellar core (triangles) and corona (circles) for a 2.5 wt% Pluronic L64 in  $D_2O$ .

Due to the partial polarity of the PPO block and the presence of water also in the micellar core, the solubilization capacity of PEO/PPO block copolymers differs somewhat from that of alkyl-based low molecular weight surfactants, where the water penetration to the micellar core is negligible. More specifically, while the solubilization of aromatic hydrocarbons may be significant in micelles formed by PEO/PPO block copolymers, that of aliphatic hydrocarbons is more limited. The amount solubilized also depends on the molecular volume of the solubilize, and the larger the solubilized molecule, the lower the solubilization (Figure 2.23). Also, the structure of the copolymer affects the solubilization, and the solubilization capacity increases with an increasing molecular weight and an increasing PPO content of the block copolymer (Figure 2.24).



**Figure 2.23.** Effect of the molecular volume  $V_s$  on the extent of solubilization of hydrocarbons in SDS (open symbols) and Pluronic F127 (filled symbols) micelles.



**Figure 2.24.** Relation between the micelle-water partition coefficient  $K_{mw}$  for naphthalene in PEO/PPO block copolymer micelles and the PPO content of the block copolymer. Shown also is  $K'_{mw}$ , the partition coefficient normalized with the polymer PPO content.

As with micelle formation as such, the solubilizing capacity of block copolymers also depends on the molecular architecture, with a lower degree of solubilization in tetrabranched PEO/PPO copolymers (Tetronics) than in PEO-PPO-PEO copolymers (Pluronic). There are several reasons for the observed dependence of the polymer molecular weight, composition, and architecture on its solubilizing capacity, all relating to the micelle formation and structure. For solubilization to be efficient, the micelles formed should preferably be of a sufficiently high aggregation number and contain a sufficiently large and hydrophobic micellar core. Since micellization is promoted by an increasing PPO content and precluded by branching of the copolymer, the solubilization is improved with an increased PPO content, and is poorer for tetrabranched than for linear block copolymers. As long as spherical micelles are formed, higher molecular weight block copolymers form larger micelles than low molecular weight ones, and are therefore expected to be more efficient solubilizers. However, spherical micelles are not always formed, and both the aggregation number and the shape of the micelles may change on solubilization, which affect the latter. As a general rule, however, larger micelles are more efficient solubilizers than small ones. For PEO/PPO block copolymers, where the block segregation is incomplete, and where also the micellar core contains some water, increasing the molecular weight also has another effect, in that the segregation between the blocks increases with the polymer molecular weight. This, in turn, results in a decreased polarity of the micellar core, thereby facilitating solubilization.

A striking difference between low molecular weight surfactants and many (unfractionated) block copolymers is that while the former are usually well defined and

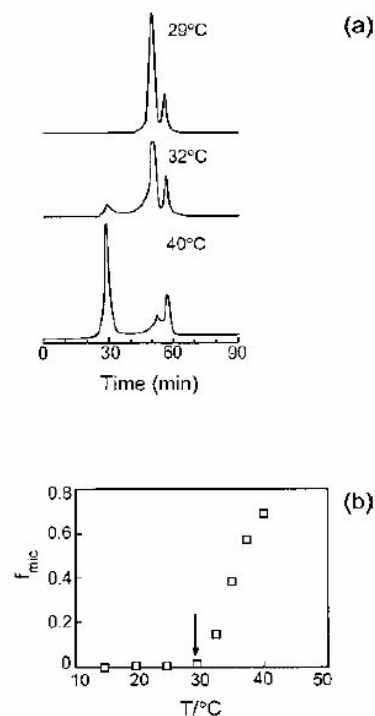
reasonably homogeneous and monodisperse, the latter frequently contain a range of molecular weights and compositions. Since fractions containing different molecular weights and compositions display different self-assembly, the overall micellization process for such systems is gradual. Furthermore, the composition of the micelles changes during this process, e.g., with an increasing polymer concentration. Thus, in the early stages of micellization, the micelles are dominated by the fractions which have the highest tendency to self-assemble (e.g., those with the highest content of the hydrophobic block, or diblock impurities in the case of triblock copolymers), whereas at higher total polymer concentration, the micellar composition approaches that of the overall average of the system. From an experimental point of view, this gradual transition makes the micellization more difficult to investigate for technical block copolymer (and surfactant) systems, and the cmc loses its strict meaning. Most likely, this has contributed to the rather widely differing cmc values reported for commercial block copolymers (e.g., the Pluronics) over the years.

Another difference between low molecular weight surfactants and block copolymers concerns the dynamics in micellar systems. As discussed above, the average residence time for surfactant molecules in micelles increases strongly with the number of methylene group in the hydrophobic tail(s). Due to the very large hydrophobic group(s) frequently present in block copolymers, block copolymer micelles are characterized by much slower kinetics than those formed by low molecular weight surfactants. For example, high molecular weight Pluronic copolymers display an exceedingly slow micellar dynamics. Thus, micelles can, at least in certain cases, be separated from the unmicellized molecules in size exclusion chromatography experiments typically spanning over more than an hour. This is an astonishing result since it shows that the micelles do not disintegrate over the time of the experiment despite the free polymer concentration surrounding the micelles being below cmc. In fact, the possibility of separating micelles from unmicellized polymers for at least some block copolymer systems offers a way to follow the micellization process, and to determine the cmt (Figure 2.25).

From a practical drug delivery perspective, this slow disintegration kinetics offers some possibilities. For example, while micelles formed by low molecular weight surfactants disintegrate rapidly after parenteral administration of a surfactant solution unless the surfactant concentration is very high, drug-loaded block copolymer micelles may be administered in a similar way without disintegrating over an appreciable time period. Without any doubt, the slow disintegration kinetics of the micelles formed by at least



some block copolymers has contributed significantly to their successful use in drug delivery. Although the vast majority of the work performed on block copolymer micelles in both basic studies and drug delivery work has been performed with PEO/PPO block copolymers, there is a current development to find new block copolymers for such uses. Over the last few years in particular, this has involved the development of biodegradable hydrophobic blocks, such as poly(lactide), poly (caprolactone), poly( $\beta$ -benzyl-L-aspartate), poly( $\gamma$ -benzyl-L-glutamate), poly(aspartic acid), and poly(L-lysine). Such systems offer possibilities in drug delivery in that the degradation allows control of the drug release rate and other drug formulation performances, and the elimination of the polymer from the body is facilitated.



**Figure 2.25.** (a) Size exclusion chromatography trace for an aqueous Pluronic F127 solution at different temperatures. The peak appearing at an elution time of 30 min corresponds to micelles, whereas the peaks at 50–60 min correspond to the nonmicellized polymers (with impurities). (b) Temperature dependence of the relative intensity of the peak corresponding to micelles  $f_{mic}$ . The arrow indicates the cmt.

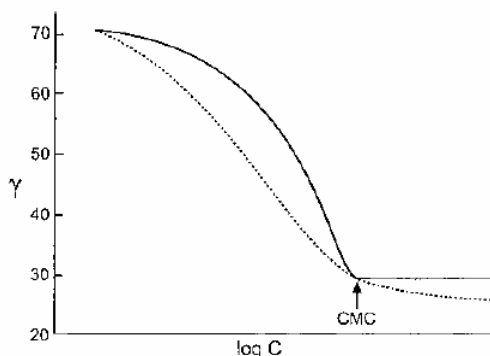
### 2.2.3 Characterization of micellar systems

There are a number of aspects of surfactant and block copolymer micelles which are interesting to characterize in order to learn more about a particular system. The main one of these is without doubt the onset of micellization, i.e., the cmc or cmt. Once this has been determined, one may proceed to determine the size of the micelles formed, and the micellar aggregation number. In some cases, it may also be interesting to investigate other parameters, such as the shape of the micelles, the state of hydration,

microviscosity in the micellar core, and the micellar dynamics. As indicated above, there are numerous methods to determine the cmc or the cmt, including surface tension measurements, scattering experiments, NMR, fluorescence spectroscopy, calorimetry, osmometry, conductivity, and solubilization experiments (Figure 2.9). Of these, three are discussed here, i.e., surface tension because this is the most frequently used method for cmc determinations, and scattering and NMR techniques because these are very versatile, and may provide information also about other aspects of micellar systems, such as the micellar size, the micellar aggregation number (scattering methods), the state of hydration (NMR), the counterion binding (NMR), and the location of solubilized molecules in micelles (NMR).

### 2.2.3.1 Surface tension measurements

Seemingly very simple surface tension measurements probably constitute the most frequently employed method for determining the cmc of surfactant and block copolymer systems. The origin behind this is that surfactants/block copolymers are surface active, and tend to adsorb at numerous surfaces, and so also at the air-water interface. On increasing the surfactant/block copolymer concentration (below cmc) the adsorption increases, which results in a surface tension reduction. Once the cmc is reached, all additionally added surfactant/copolymer molecules go to the micelles, whereas the free surfactant/ copolymer concentration is essentially constant, as is the adsorption and the surface tension. Ideally, therefore, a plot of the surface tension vs. the surfactant/copolymer concentration displays a clear breakpoint, from which the cmc is readily identified (Figure 2.26).



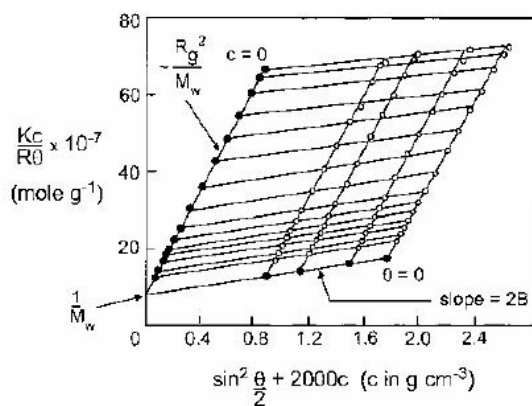
**Figure 2.26.** Schematic illustration of the surface tension  $\gamma$  of a surfactant/block copolymer versus the concentration  $c$  for a monodisperse and homogeneous sample (solid line) and a polydisperse and/or heterogeneous sample (dashed line).

In the case of polydisperse and/or heterogeneous surfactants/block copolymers the strict meaning of the cmc is lost, and also from a practical perspective determination of an

effective cmc becomes more difficult. This is illustrated in Figure 2.26, where it is shown that the polydisperse/heterogeneous compound displays a more gradual decrease in the surface tension vs. concentration. Surface tension measurements are also very sensitive to the presence of hydrophobic impurities, and only an impurity level of the order of 0.1% of the surfactant may well cause a drastic deviation from the “ideal” curve displayed in Figure 2.26. The reason for this is that typical surface tension methods are based on the use of a macroscopic air-water surface (e.g., in a trough), and hence the bulk volume to surface area is large, and even minute amounts of impurities are sufficient to cause a dramatic accumulation at the interface, and hence large effects on the surface tension. From a more positive perspective, surface tension measurements constitute a critical test of the surfactant purity. If the surface tension curve looks nice, then the risk of any hydrophobic impurities is generally limited.

### 2.2.3.2 Light scattering

Scattering of radiation from a surfactant solution offers possibilities to characterize the solution in a number of ways. In principle, both light, X-rays, and neutrons can be used for investigations of surfactant and block copolymer micelles, but due to its simplicity, light scattering is the technique most extensively used for such investigations. In so-called static light scattering, the scattering intensity is collected at different scattering angles for a series of samples of different concentrations. Frequently, the results are summarized in a so-called Zimm-plot, and information about the molecular weight  $M_w$ , radius of gyration  $R_g$  size, and second virial coefficient  $B$  (a measure of intermolecular interactions) is extracted from the reciprocal of the scattering intensity extrapolated to zero concentration, the angular dependence of the scattering intensity, and the concentration dependence of the scattering intensity, respectively (Figure 2.27).



**Figure 2.27.** Typical Zimm-plot for static light scattering data, in which the scattering intensity is plotted as a function of concentration  $c$  and scattering angle  $\theta$ .

In dynamic light scattering (often called also photon correlation spectroscopy), the time dependence of the light intensity fluctuations is analyzed in order to yield information about the diffusion coefficient, which in turn can be used to extract a micellar hydrodynamic radius. Frequently, static and dynamic light scattering experiments are combined for a given system, which allows information to be extracted on both the micellar size, shape, and aggregation number.

### 2.2.3.3 NMR

Since both the microenvironment of a nucleus of a surfactant molecule and the overall mass transport properties change on micellization, NMR offers many opportunities when it comes to investigating both micellization and the properties of micellar systems. Probably the most extensively used of these is NMR self diffusion measurements. Such measurements have several advantages:

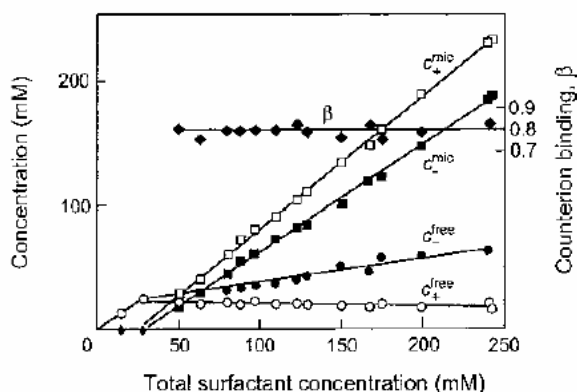
1. A true self-diffusion coefficient is obtained.
2. No chemical labeling is required, and possible artefacts relating to fluorescence or radioactive labels can therefore be avoided.
3. The self-diffusion of essentially any number of components in a mixture can be followed simultaneously.
4. In contrast to, e.g., light scattering, there are no restrictions relating to optical clarity of the sample and use of dilute samples.
5. In contrast to experiments where the diffusion coefficient is determined

through following the concentration gradient of the diffusing species, NMR self-diffusion measurements are fast. In the case of micellizing surfactants, self-diffusion measurements contain information on both free molecules and molecules in the micellar state. For low molecular weight surfactants, the micellar residence time is generally very short on the NMR time scale ( $\approx 100$  ms), which means that there is extensive molecular exchange during an NMR experiment, and therefore the observed diffusion coefficient  $D_{\text{obs}}$  determined by NMR constitutes an average over the two states, i.e.,

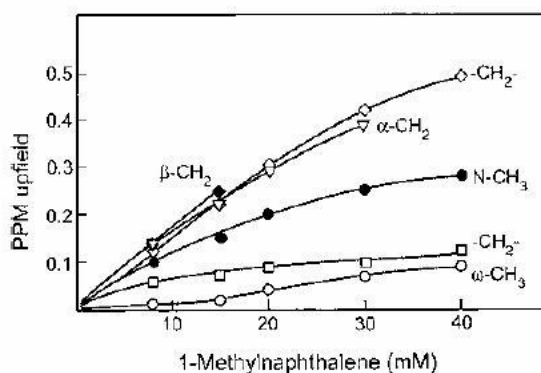
$$D_{\text{obs}} = p_{\text{mic}}D_{\text{mic}} + p_{\text{free}}D_{\text{free}} \quad (2.1)$$

where  $D_i$  and  $p_i$  are the diffusion coefficient and the fraction in state  $i$ . Since the diffusion coefficients of the free surfactant molecules can be determined from measurements below the cmc, since the diffusion coefficient of the micelles may be

obtained through measurement of the diffusion coefficient of a hydrophobic molecule solubilized in the micellar core, and since the total concentration is known, the concentration of micelles and free surfactant micelles can be extracted. Furthermore, by simultaneously measuring the surfactant and counterion self-diffusion in the case of ionic surfactants, information about the degree of counterion binding, i.e., the fraction of counterions bound to the micelles, can be estimated. A typical result from such an analysis is shown in Figure 2.28.



**Figure 2.28.** Concentrations of micellar (squares) and free (circles) surfactant molecules (open symbols), and counterions (filled symbols), as well as the degree of counterion binding (filled diamonds), as a function of the total surfactant concentration. The surfactant used was decylammonium dichloroacetate.



**Figure 2.29.** Effect of 1-methylnaphthalene on the chemical shift of CTAB protons.

From the latter type of measurement one can conclude that:

1. Above the cmc, the concentration of micelles increases largely linearly with the total surfactant concentration, whereas the free monomer concentration is either constant (nonionic surfactants) or decreases somewhat (ionic surfactants).
2. Below the cmc, all surfactant molecules are in a nonmicellized form.
3. The degree of counterion binding for ionic surfactants is generally quite high ( $\approx 70\text{--}90\%$ ).

Apart from self-diffusion measurements, there are also several other NMR techniques which may be used in order to characterize micellar systems. For example, measuring the chemical shift of surfactant molecules may provide information about both the extent of water penetration into the micellar core, and the precise location of solubilized molecules in micelles. As an example of the latter, Figure 2.29 shows the effect of an aromatic solubilisate, 1-methylnaphthalene, on the chemical shift of cetyltrimethylammunium bromide (CTAB) protons. As can be seen, the protons in the polar head group ( $\alpha$ -,  $\beta$ -) of the surfactant experience a larger chemical shift than protons closer to the micellar core ( $\omega$ -), which shows that the solubilizate is located close to the polar head groups, i.e., close to the micellar surface.[9-27]

### **2.3. Emulsion polymerization**

Emulsion polymerization refers to a unique process employed for some radical chain polymerizations. It involves the polymerization of monomers in the form of emulsions (i.e., colloidal dispersions). The process bears a superficial resemblance to suspension polymerization but is quite different in mechanisms and reaction characteristics. Emulsion polymerization differs from suspension polymerization in the type and smaller size of the particles in which polymerization occurs, in the kind of initiator employed, and in the dependence of polymer molecular weight on reaction parameters.

#### **2.3.1 Description of process**

##### **2.3.1.1 Utility**

Emulsion polymerization was first employed during World War II for producing synthetic rubbers from 1,3-butadiene and styrene. This was the start of the synthetic rubber industry in the United States. It was a dramatic development because the Japanese naval forces threatened access to the natural-rubber (NR) sources, which were necessary for the war effort. Synthetic rubber has advanced significantly from the first days of “balloon” tires, which had a useful life of 5000 mi to present-day tires, which are good for 50,000 mi. Emulsion polymerization is presently the pre-dominant process for the commercial polymerizations of vinyl acetate, chloroprene, various acrylate copolymerizations, and copolymerizations of butadiene with styrene and acrylonitrile. It is also used for methacrylates, vinyl chloride, acrylamide, and some fluorinated ethylenes.

The emulsion polymerization process has several distinct advantages. The physical state

of emulsion (colloidal) system makes it easy to control the process. Thermal and viscosity problems are much less significant than in bulk polymerizations. The product of an emulsion polymerization, referred to as a *latex*, can in many instances be used directly without further separations. (However, there may be the need for appropriate blending operations, e.g., for the addition of pigments.) Such applications include paints, coatings, finishes, and floor polishes. Aside from the physical difference between the emulsion and other polymerization processes, there is one very significant kinetic difference. For the other processes there is an inverse relationship between the polymerization rate and the polymer molecular weight. This drastically limits one's ability to make large changes in the molecular weight of a polymer, from 25,000 to 100,000 or from 100,000 to 25,000. Large decreases in the molecular weight of a polymer can be made without altering the polymerization rate by lowering the initiator concentration or lowering the reaction temperature. Emulsion polymerization is a unique process in that it affords the means of increasing the polymer molecular weight without decreasing the polymerization rate. Because of a different reaction mechanism, emulsion polymerization has the advantage of being able to simultaneously attain both high molecular weights and high reaction rates.

### **2.3.1.2 Qualitative picture**

#### ***Components and Their Locations***

The physical picture of emulsion polymerization is based on the original qualitative picture of Harkins [1947] and the quantitative treatment of Smith and Ewart [1948] with subsequent contributions by other workers. Table 2.1 shows a typical recipe for an emulsion polymerization. This formulation, one of the early ones employed for the production of styrene-1,3-butadiene rubber (trade name: GR-S), is typical of all emulsion polymerization systems. The main components are the monomer(s), dispersing medium, emulsifier, and water-soluble initiator. The dispersing medium is the liquid, usually water, in which the various components are dispersed by means of the emulsifier. The ratio of water to monomer(s) is generally in the range 70/30 to 40/60 (by weight).

The action of the emulsifier (also referred to as surfactant or soap) is due to its molecules having both hydrophilic and hydrophobic segments. Various other components may also be present in the emulsion system. Thus, a mercaptan is used in the above formulation as a chain transfer agent to control the polymer molecular weight. The initiator is the hydroperoxide-ferrous ion redox system and the function of

fructose is probably to regenerate ferrous ion by reducing the ferric ion produced in the initiation reaction. The sodium pyrophosphate acts to solubilize the iron salts in the strongly alkaline reaction medium. The emulsion system is usually kept in a well-agitated state during reaction.

**Table 2.1.** Composition of a GR-S Recipe for Emulsion Polymerization of Styrene-Butadiene<sup>a</sup>

Component	Parts by Weight
Styrene	25
Butadiene	75
Water	180
Emulsifier (Dresinate 731)	5
n-Dodecyl mercaptan	0.5
NaOH	0.061
Cumene hydroperoxide	0.17
FeSO <sub>4</sub>	0.017
NA <sub>4</sub> P <sub>2</sub> O <sub>7</sub> .10 H <sub>2</sub> O	1.5
Fructose	0.5

<sup>a</sup>Data from Vanderberg and Hulse [1948].

The locations of the various components in an emulsion system will now be considered. When the concentration of a surfactant exceeds its critical micelle concentration (CMC), the excess surfactant molecules aggregate together to form small colloidal clusters referred to as micelles. The transformation of a solution to the colloidal state as the surfactant concentration exceeds the CMC occurs to minimize the free energy of solution (heat is liberated) and is accompanied by a sharp drop in the surface tension of the solution. Electrical conductivity, ion activities, viscosity, and other solution properties also show marked changes at CMC. CMC values are in the range 0.001-0.1 mole/liter, with most surfactants having values in the lower end of the range. Since surfactant concentrations in most emulsion polymerizations (0.1-3 wt % based on the aqueous phase) exceed CMC by one or more orders of magnitude, the bulk of the surfactant is in the micelles. Typical micelles have dimensions of 2-10 nm (1 nm: 10<sup>0</sup> = 10<sup>-3</sup> μm) with each micelle containing 50-150 surfactant molecules. Most authors show the shape of micelles as being spherical, but this is not always the case. Both spherical and rodlike micelles are observed depending on the surfactant and its concentration. The surfactant molecules are arranged in a micelle and their ionic ends outward toward the aqueous phase. The number of micelles and their size depends on the amount of emulsifier. Large amounts of emulsifier yield larger numbers of smaller sized particles.

When a water-insoluble or slightly water-soluble monomer is added, a very small fraction dissolves in the continuous aqueous phase. The water solubilities of most



monomers are quite low, although the spread is large; for example, styrene, butadiene, vinyl chloride, methyl methacrylate, and vinyl acetate are soluble to the extent of 0.07, 0.8, 7, 16, 25 g/liter, respectively, at 25<sup>0</sup>C. An additional but still small portion of the monomer enters the interior hydrocarbon portions of the micelles. This is evidenced by X-ray and light-scattering measurements showing that the micelles increase in size as monomer is added. The amount of monomer in micelles compared to that in solution is much greater for the water-insoluble, nonpolar monomers. For example, the amount of micellar monomer is 2-, 5-, and 40-fold larger for methyl methacrylate, butadiene, and styrene, respectively, than the amount in solution. For vinyl acetate, the amount of micellar monomer is only a few percent of that in solution.

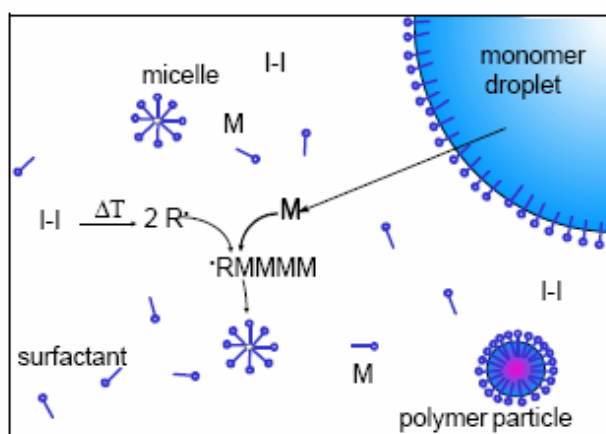
The largest portion of the monomer (>95%) is dispersed as monomer droplets whose size depends on the stirring rate. The monomer droplets are stabilized by surfactant molecules absorbed on their surfaces. Monomer droplets have diameters in the range 1-10  $\mu\text{m}$  ( $10^3$ - $10^4$  nm) or larger. Thus, in a typical emulsion polymerization system, the monomer droplets are much larger than the monomer-containing micelles. Consequently, while the concentration of micelles is  $10^{17}$ - $10^{18}$  per millimeter, there are at most  $10^{10}$ - $10^{11}$  monomer droplets per millimeter. A further difference between micelles and monomer droplets is that the total surface area of the micelles is larger than that of the droplets by more than two orders of magnitude. The size, shape, and concentration of each of the various types of particles in the emulsion system are obtained from electron microscopy, light scattering, ultracentrifugation, photon correlation spectroscopy, and other techniques.

### ***Site of Polymerization***

The initiator is present in the water phase and this is where the initiating radicals are produced. The rate of radical production  $R_i$  is typically of the order of  $10^{13}$  radicals per millimeter per second. (The symbol  $\rho$  is often used instead of  $R_i$  in emulsion polymerization terminology.) The locus of polymerization is now of prime concern. The site of polymerization is not the monomer droplets since the initiators employed are insoluble in the organic monomer. Such initiators are referred to as oil-insoluble initiators. This situation distinguishes emulsion polymerization from suspension polymerization. Oil-soluble initiators are used in suspension polymerization and reaction occurs in the monomer droplets. The absence of polymerization in the monomer droplets in emulsion polymerization has been experimentally verified. If one halts an emulsion polymerization at an appropriate point before complete conversion is achieved, the monomer droplets can be separated and analyzed. An insignificant amount

(approximately  $< 0.1\%$ ) of polymer is found in the monomer droplets in such experiments. Polymerization takes place almost exclusively in the micelles. Monomer droplets do not complete effectively with micelles in capturing radicals produced in solution because of the much smaller total surface area of the droplets.

Polymerization of the monomer in solution doubtedly takes place but does not contribute significantly, since the monomer concentration is low and propagating radicals would precipitate out of aqueous solution at very small (oligomeric) size. The micelles act as a meeting place for the organic (oil-soluble) monomer and the water-soluble initiator. The micelles are favored as the reaction site because of their high monomer concentration (similar to bulk monomer concentration) compared to the monomer in solution. As polymerization proceeds, the micelles grow by the addition of monomer from the aqueous solution whose concentration is replenished by dis-solution of monomer from the monomer droplets. A simplified schematic representation of an emulsion polymerization system is shown in Fig. 2.30. The system consists of three types of particles: monomer droplets, inactive micelles in which polymerization is not occurring, and active micelles in which polymerization is occurring. The latter are no longer considered as micelles but are referred to as polymer particles. An emulsifier molecule is shown as o- to indicate one end (o) is polar or ionic and the other end (-) nonpolar.



**Figure 2.30.** Simplified representation of an emulsion polymerization system.

The mechanism for particle nucleation (i.e., formation of polymer particles) proceeds by two simultaneous processes. One is the entry of radicals (either primary radicals or, more likely, oligomeric radicals formed by solution polymerization) from the aqueous phase into the micelles (micellar nucleation). The other, homogeneous nucleation, involves solution-polymerized oligomeric radicals becoming insoluble and precipitating onto themselves (or onto dead oligomer). The precipitated species become stabilized by absorbing surfactant (from solution, monomer droplets, and micelles) and on

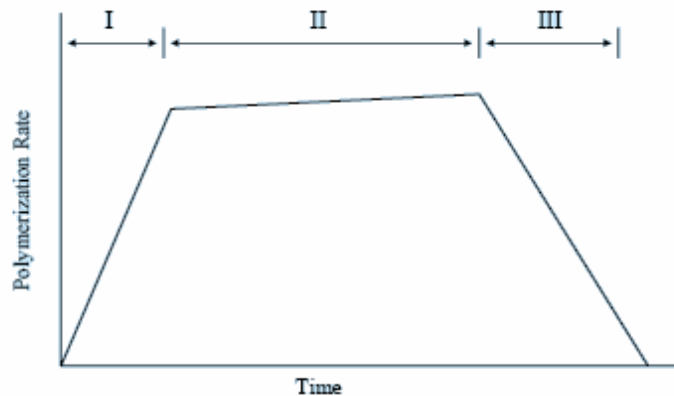
subsequent absorption of monomer are the equivalent of polymer particles formed by micellar nucleation. The relative extents of micellar and homogeneous nucleation are expected to vary with the water solubility of the monomer and the surfactant concentration. Higher water solubility and low surfactant concentration favor homogeneous nucleation; micellar nucleation is favored by low water solubility and high surfactant concentration. (That is homogeneous nucleation occurs is evidenced by the occurrence of emulsion polymerization of systems where the surfactant concentration is below CMC). Micellar nucleation is probably the predominant mechanism for a highly water-insoluble monomer such as styrene with homogeneous nucleation the predominant mechanism for a water-soluble monomer such as vinyl acetate.

It has been suggested that the major growth process for the first-formed polymer particles, sometimes referred to as precursor particles, is coagulation with other particles and not polymerization of monomer. This coagulation, referred to as coagulative nucleation, is then considered as part of the overall nucleation sequence for the formation of mature polymer particles whose subsequent growth occurs entirely by polymerization. The experimental evidence for the coagulative nucleation process is the positive skewness of the polymer particle size distribution determined at short reaction times. This indicates that the rate of formation of polymer particles is an increasing function of time that is incompatible with a one-step mechanism but compatible with the two-step process of micellar and/or homogeneous nucleation followed by coagulative nucleation. The driving force for coagulation of precursor particles is their relative instability compared to larger-sized particles. The small size of a precursor particle (several nanometers) with its high curvature of the electrical double layer precludes the high surface charge density required for high colloidal stability. Once the particles reach a larger size with high colloidal stability, there is no longer a driving force for coagulation and further growth occurs only by polymerization.

### ***Progress of Polymerization***

A variety of behaviours are observed for the polymerization rate versus conversion depending on the relative rates of initiation, propagation, and termination, which are in turn dependent on the monomer and reaction conditions (Fig. 2.31).

Irrespective of the particular behaviour observed, three intervals (I, II, III) can be discerned in all emulsion polymerizations based on the particle number  $N$  (the concentration of polymer particles in units of number of particle per millimeter) and the existence of a separate monomer phase (i.e., monomer droplets).



**Figure 2.31.** Different rate behaviours observed in emulsion polymerization.

There is a separate monomer phase in intervals I and II but not in III. The particle number increases with time in Interval I and then remains constant during Intervals II and III. Particle nucleation occurs in Interval I with the polymerization rate increasing with time as the particle number builds up. Monomer diffuses into the polymer particles to replace that which has reacted. The reaction system undergoes a very significant change during Interval I. The particle number stabilizes at some value which is only a small fraction, typically about 0.1%, of the concentration of micelles initially present. ( $N$  is in range  $10^{13}$ - $10^{15}$  particles per millimeter.) As the polymer particles grow in size and contain polymer as well as monomer, they absorb more and more surfactant (in order to maintain stability) from that which is in solution. The point is quickly reached at which the surfactant concentration in solution falls below its CMC, the inactive micelles become unstable and disappear with dissolution of micellar surfactant. By the end of Interval I or very early in Interval II all or almost all of the surfactant in the system has been absorbed by the polymer particles. As a consequence the monomer droplets are relatively unstable and will coalesce if agitation is stopped. Interval I is generally the shortest of the three intervals, its duration varying in the range 2-15% conversion. Interval I is longer for low initiation rates as more time is needed to attain the steady-state particle number. The more water-soluble monomers such as vinyl acetate tend to complete Interval I faster than the less water-soluble monomers. This is probably a consequence of the significant extent of homogeneous nucleation occurring simultaneously with micellar nucleation, resulting in achieving the steady-state particle number sooner. The predicted maximum in Fig. 2.31 (interval I), arising from a transient high particle number and/or high proportion of particles containing propagating radicals, is often not distinguishable experimentally, since it is not a high maximum. The maximum is observed for many monomers when the initiation rates are sufficiently high. Polymerization proceeds in the polymer particles as the monomer concentration in

the particles is maintained at the equilibrium (saturation) level by diffusion of monomer from solution, which in turn is maintained at the saturated level by dissolution of monomer from the monomer droplets. The monomer concentration in the polymer particles is high; the volume fraction of monomer  $\Phi_m$  is 0.2, 0.3, 0.5, 0.6, 0.71, and 0.85 for ethylene, vinyl chloride, butadiene, styrene, methyl methacrylate, and vinyl acetate, respectively. The polymerization rate either is constant or increases slightly with time during Interval II. The latter behaviour, which may begin immediately as shown in Fig. 2.31 or after a constant rate period, is a consequence of the gel or Trommsdorff effect. The polymer particles increase in size as the monomer droplets decrease. Interval II ends when the monomer droplets disappear. The transition from Interval II to III occurs at lower conversions as the water solubility of the monomer increases and the extent of swelling of the polymer particles by monomer increases. For monomers (e.g., vinyl chloride) with low water solubility and low  $\Phi_m$ , the transition occurs at about 70-80% conversion. The transition occurs at progressively lower conversion as the proportion of the total monomer in the system that is contained in the droplets decreases; styrene and butadiene at 40-50% conversion, methyl methacrylate at 25%, and vinyl acetate at 15%.

The particle number remains the same in Interval III as in Interval II but the monomer concentration decreases with time, since monomer droplets are no longer present. The decrease in  $\Phi_m$  is slower with the more water-soluble monomers as the monomer in solution acts as a reservoir. The presence of a gel effect continues in Interval III. The quantitative interplay of a decreasing monomer concentration with the gel effect determines the exact behaviour observed in this interval. Polymerization continues at a steadily decreasing rate as the monomer concentration in the polymer particles decreases. Final conversions of essentially 100% are usually achieved. The final polymer particles, spherical in shape, usually have diameters of 50-200 nm, which places them intermediate in size between the initial micelles and monomer droplets. (Polymer particles as small as 10 nm and as high as several  $\mu\text{m}$  have been produced in emulsion polymerization.)

### **2.3.2. Quantitative aspects**

#### **2.3.2.1. Rate of polymerization**

An expression for the rate of polymerization can be obtained by considering first the rate in a single polymer particle in which propagation is occurring (i.e., a particle containing a radical) and then the number of such particles. At the start of polymerization in a typical system where the concentration of micelles is  $10^{18}$  per millimeter and the initiation rate

is  $10^{13}$  radicals per millimeter-second, a radical diffuses into a micelle every  $10^5$  sec at the start of Interval I. As the system progresses through Interval I, this time period decreases sharply, since the concentration of micelles is decreasing. A radical enters each particle on an average of every 10 sec during Intervals II and III, where  $N$  is typically  $10^{14}$  particles per millimeter. Once inside the micelle or polymer particle, a radical propagates in the usual manner at a rate  $r_p$  dependent on the propagation rate constant  $k_p$  and the monomer concentration  $[M]$  in the particle.

$$r_p = k_p[M] \quad (2.2)$$

The monomer concentration is usually quite high since in many cases the equilibrium swelling of the particle by monomer is of the order 50 – 85 % by volume. Values of  $[M]$  as high as 5M are common.  $[M]$  varies only weakly with the size of the polymer particles.

Consider now what occurs on the entry of a radical into a particle that already has a radical. For most reaction systems, the radical concentration in a polymer particle is  $10^{-6}$  M or higher. This is a higher radical concentration than in the homogeneous polymerization systems and the radical lifetime here is only a few thousandths of a second. The entry of a second radical into the polymer particle results in immediate bimolecular termination. Thus the polymer particle will have either one or zero radicals. The presence of two radicals in one particle is synonymous with zero radicals, since termination occurs so quickly. The particle is then dormant until another (the third) radical arrives. The particle is again activated and propagation proceeds until the next radical. The cycle of alternate growth and inactivity of the polymer particle continues until the monomer conversion is essentially complete.

The rate of polymerization  $R_p$  at any instant is given by the product of the concentration of active particles  $[P\cdot]$  and the rate of propagation in a particle.

$$R_p = k_p[M][P\cdot] \quad (2.3)$$

$[P\cdot]$  is conveniently expressed by

$$[P\cdot] = \frac{10^3 N' n}{N_A} \quad (2.4)$$

where  $N'$  is the concentration of micelles plus particles,  $n$  is the average number of radicals per micelle plus particle, and  $N_A$  is the Avagadro number. The use of  $10^3 / N_A$  in Eq. 2.4 and in the subsequent equations expresses  $[P\cdot]$  in moles/liter and  $R_p$  in

moles/liter-sec. Combination of Eqs. 2.3 and 2.4 yields the polymerization rate as

$$[P\cdot] = \frac{10^3 N' n k_p [M]}{N_A} \quad (2.5)$$

$N'n$  is zero at the start of Interval I, since  $n = 0$ .  $N'$  decreases,  $n$  decreases and the product  $N'n$  increases with time during Interval I. At the start of Interval II,  $N'$  has reached its steady-state value  $N$ .  $n$  may or may not reach an absolutely constant value. Behaviour D in Interval II usually involves a slow increase in  $n$  with conversion.  $n$  will remain approximately constant or increase in Interval III although a decrease will occur if the initiation rate decreases sharply due to exhaustion of the initiator concentration. Most texts show

$$[P\cdot] = \frac{10^3 N n k_p [M]}{N_A} \quad (2.6)$$

For the polymerization rate instead of the more general Eq. 2.5. Equation 2.6 applies to Intervals II and III where only polymer particles exist (no micelles). It is during Intervals II and III that the overwhelming percent of monomer conversion to polymer takes place.

The value of  $n$  during Intervals II and III is of critical importance in determining  $R_p$  and has been the subject of much theoretical and experimental work. Three cases can be distinguished – Cases 1, 2, and 3. The major differences between the three cases are the occurrence of radical diffusion out of the polymer particles (desorption), the particle size, modes of termination, and the rates of initiation and termination relative to each other and to the other reaction parameters. The quantitative interplay of these factors leading to Case 1, 2, or 3 behavior has been discussed. Our discussion will be in qualitative terms.

Case2:  $n = 0.5$ . This is the case usually described in texts as applicable to most emulsion polymerizations. It occurs when desorption of radicals does not occur or is negligible compared to the rate of radicals entering particles (absorption) and the particle size is too small, relative to the bimolecular termination rate constant, to accommodate more than one radical. Under these conditions, a radical entering a polymer particle will be active half of the time and dormant the other half of the time. In other words, at any given moment half of the polymer particles contain one radical and are growing while the other half are dormant. The number of radicals per particle  $n$  averaged over all the particles is 0.5. Case 2 behaviour also requires the initiation rate not be excessively low and negligible termination of radicals in the aqueous phase.

Case 1:  $n < 0.5$ . The average number of radicals per particle can drop below 0.5 if radical desorption from particles and termination in the aqueous phase are not negligible. The decrease in  $n$  is larger for small particle sizes and low initiation rates.

Case 3:  $n > 0.5$ . Some fraction of the polymer particles must contain two or more radicals per particle in order for  $n$  to be larger than 0.5, since there will always be a fraction (a very significant fraction) that has zero radical per particle. This occurs if the particle size is large or the termination rate constant is low while termination in the aqueous phase and desorption are not important and the initiation rate is not too low.

Although most texts indicate that Case 2 is the predominant behaviour for all monomers, this is not true. Certain monomers, especially vinyl acetate and vinyl chloride, follow Case 1 behaviour under a variety of reaction conditions. For example,  $n$  is approximately 0.1 or lower for vinyl acetate and vinyl chloride. Values of  $n$  are calculated from Eq. 2.6 using the  $K_p$  value from bulk polymerization at the appropriate percent conversion, that is, at the conversion corresponding to the volume fraction of monomer in the polymer particles. The monomers which show strong Case 1 behaviour are those with high monomer chain-transfer constants. Chain transfer to monomer results in a small-sized monomer radical that can desorb from the polymer particle much more readily than the large-sized propagating radical. This was verified by carrying out emulsion polymerizations with intermittent ionizing radiation. The polymerization rate decays to zero after irradiation ceases but before all of the monomer would be exhausted. The polymerization rate decays to zero after irradiation ceases but before all of the monomer has polymerized. If desorption of monomer radicals did not occur, polymerization should continue until monomer would be exhausted. The polymerization rate decays for all monomers but at very different rates. The decay rate, which follows the desorption rate, increased as the monomer chain transfer constant increased.

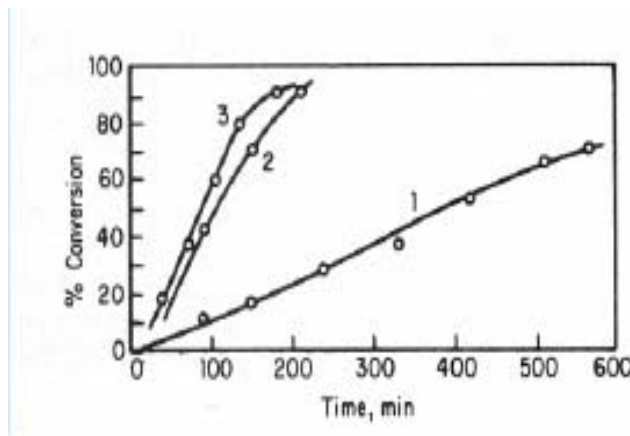
The effect of reaction conditions on  $n$  (and  $R_p$ , of course) can be observed even with styrene, which shows a very strong tendency toward Case 2 behaviour under a wide range of reaction conditions. Seed polymerization, involving the addition of monomer and initiator to a previously prepared emulsion of polymer particles, is especially useful for this purpose since it allows the variation of certain reaction parameters while holding  $N$  constant. Thus,  $n$  in seeded styrene polymerization drops from 0.5 to 0.2 when the initiator concentration decreases from  $10^{-2}$  to  $10^{-5}$  M. At sufficiently low  $R_i$ , the rate of radical absorption is not sufficiently high to counterbalance the rate of desorption. One also observes that above a particular initiation rate ( $[I] = 10^{-2}$  M in this case), the system maintains Case 2 behaviour with  $n$  constant at 0.5 and  $R_p$  independent of  $R_i$ . A



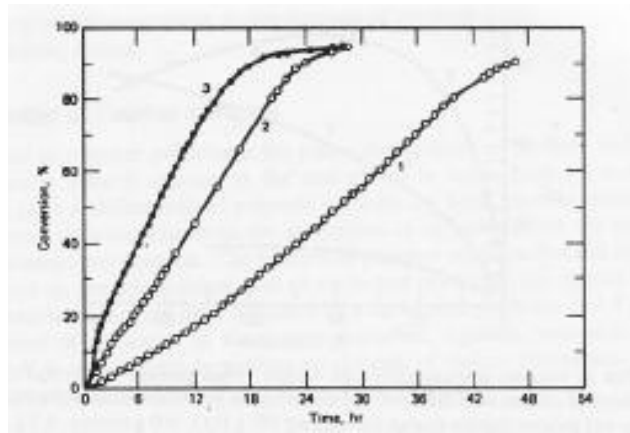
change in  $R_i$  simply results in an increased rate of alternation of activity and inactivity in each polymer particle. Similar experiments show that  $n$  drops below 0.5 for styrene when the particle size becomes sufficiently small. The extent of radical desorption increases with decreasing particle size since the travel distance for radical diffusion from a particle decreases.

Case 3 behaviour occurs when the particle size is sufficiently large (about 0.1-1  $\mu\text{m}$ ) relative to  $k_t$  such that two or more radicals can coexist in a polymer particle without instantaneous termination. This effect is more pronounced as the particle size and percent conversion increase. At high conversion the particle size increases and  $k_t$  decreases, leading to an increase in  $n$ . The increase in  $n$  occurs at lower conversions for the larger-sized particles. Thus for styrene polymerization  $n$  increases from 0.5 to only 0.6 at 90 % conversion for 0.7- $\mu\text{m}$  particles. On the other hand, for 1.4- $\mu\text{m}$  particles,  $n$  increases to about 1 at 80 % conversion and more than 2 at 90 % polymerization. Much higher values of  $n$  have been reported in other emulsion polymerizations.

Consider now the implications of Eq. 2.6. The values of  $k_p$ ,  $[M]$  and, to a large extent,  $n$  are specified for any particular monomer. The polymerization rate is then determined by the value of  $N$ . Increasing the surfactant concentration and increasing  $R_i$  increases  $N$  and, therefore,  $R_p$ . These trends are shown in Figs. 2.32 and 2.33.



**Figure 2.32.** Plot of percent conversion vs time for emulsion polymerizations of styrene with different concentrations of potassium laurate at 60°C. The moles of emulsifier per polymerization charge (containing 180 g H<sub>2</sub>O, 100 g styrene, 0.5 g K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) are 0.0035 (plot 1), 0.007 (plot 2), and 0.0014 (plot 3).



**Figure 2.33.** Plot of percent conversion vs time for emulsion polymerizations of vinyl chloride at 50°C for monomer/water ratio of 26/74 and 0.883% surfactant. The initiator concentrations are 0.0012% (plot 1), 0.0057% (plot 2), and 0.023% (plot 3).

It should be noted that the polymerization rate is unaffected by changes in  $R_i$  once particle nucleation has ceased at the end of Interval I. Such changes would only result in changing the rate of alternation of activity and inactivity in each polymer particle.

### 2.3.2.2 Degree of polymerization

The number-average degree of polymerization in an emulsion polymerization can be obtained by considering what occurs in a single polymer particle. The rate  $r_i$  at which primary radicals enter a polymer particle is given by

$$r_i = \frac{R_i}{N} \quad (2.7)$$

This is the same as the rate of termination  $r_t$  of a polymer chain for Case 2 behaviour, since termination occurs immediately on the entry of a radical into a polymer particle in which a polymer chain is propagating. The degree of polymerization is then the rate of growth of a polymer chain divided by the rate at which primary radicals enter the polymer particle, that is, Eq. 2.2 divided by Eq. 2.6.

$$X_n = \frac{r_p}{r_i} = \frac{Nk_p[M]}{R_i} \quad (2.8)$$

It should be noted that the degree of polymerization in an emulsion polymerization is synonymous with the kinetic chain length. Although termination is by bimolecular coupling, one of the radicals is a primary (or oligomeric) radical, which does not significantly contribute to the size of a dead polymer molecule. The derivation of Eq. 2.8 assumes the absence of any termination by chain transfer. If chain transfer occurs the degree of polymerization will be given by

$$X_n = \frac{r_p}{r_i + \sum r_{tr}} \quad (2.9)$$

where  $\sum r_{tr}$  is the sum of the rates of all transfer reactions. The rate of a chain transfer reaction in a polymer particle would be given by an equation of the type

$$r_{tr} = k_{tr}[X_A] \quad (2.10)$$

analogous to the case of transfer in homogeneous polymerization.

The degree of polymerization, like the polymerization rate, varies directly with  $N$ , but the degree of polymerization also varies indirectly with  $R_i$ . A consideration of Eqs. 2.6 and 2.8 with their analogues for homogeneous, radical chain polymerization shows the significant characteristics of the emulsion process. In homogeneous polymerization, one can increase the polymerization rate by increasing the rate of initiation, but the result is a simultaneous lowering of the polymer molecular weight. No experimental variable is available to increase  $R_p$  without decreasing  $X_n$ . The situation is quite different in emulsion polymerization. The rate and degree of polymerization can be simultaneously increased by increasing the number of polymer particles at a constant initiation rate.

Equations 2.8 and 2.9 require modification to be applicable to Case 3 behaviour where a significant fraction of the polymer particles have 2 or more radicals per particle. For such particles, one still has  $r_i = r_t$  (assuming a steady-state  $n$ ) but the degree of polymerization will be twice that for Case 2, since termination is by coupling between propagating radicals instead of propagating and primary (or oligomeric) radicals. Thus, the overall degree of polymerization for Case 3 behaviour will be between  $X_n$  as calculated from Eq. 2.8 and twice that value, the exact value being the average between the two weighted in proportion to the fraction of particles which contain more than one propagating radical.

### 2.3.2.3. Number of polymer particles

The number of polymer particles is the prime determinant of the rate and degree of polymerization since it appears as the first power in both Eqs. 2.6 and 2.8. The formation (and stabilization) of polymer particles by both micellar nucleation and homogeneous nucleation involves the adsorption of surfactant from the micelles, solution, and monomer droplets. The number of polymer particles that can be stabilized is dependent on the total surface area of surfactant in the system (micelles, solution, monomer droplets). However,  $N$  is also directly dependent on the rate of radical generation. The quantitative dependence of  $N$  on  $S$  and  $R_i$  has been derived as

$$N = k \left( \frac{R_i}{\mu} \right)^{2/5} (a_s S)^{3/5} \quad (2.11)$$

where  $\mu$  is the rate of volume increase of a polymer particle (which can be determined from  $r_p$  and geometric considerations). The same result has been derived for both micellar and homogeneous nucleations – each in the absence of coagulative nucleation. The value of  $k$  is between 0.37 and 0.53 depending on the assumptions made regarding the relative efficiencies of radical capture by micelles versus polymer particles and which geometric parameter of the particle (radius, surface area or volume) determines the rate at which polymer particles capture radicals. We should note that high particle numbers are associated with small particle size and low particle numbers with large particle size. Equation 2.11 leads to the prediction that the particle radius will be inversely dependent on the 0.20- and 0.13- order of  $S$  and  $R_i$ , respectively.

A consideration of Eq. 2.11 together with Eqs. 2.6 and 2.8 shows that both  $R_p$  and  $X_n$  depend on the  $\frac{3}{5}$ -power of the total surfactant concentrations. The polymerization rate varies with the  $\frac{2}{5}$ -power of  $R_i$  while the degree of polymerization varies inversely with the  $\frac{3}{5}$ -power of  $R_i$ . The dependence of  $R_p$  on  $R_i$  does not contradict the earlier conclusion regarding the independence of the polymerization rate on the rate of radical production. The rate of radical generation affects the number of polymer particles formed, which in turn determines the polymerization rate. However, once an emulsion polymerization system has reached a steady state with regard to  $N$ , the rate of radical generation no longer has any effect on the polymerization rate as long as initiation is taking place. Further and very significantly, it should be noted that the number of polymer particles can be increased by increasing the emulsifier concentration while maintaining a constant rate of radical generation. Thus from the practical viewpoint one can simultaneously increase  $R_p$  and  $X_n$  by increasing  $N$ . Increasing  $N$  by increasing  $R_i$  increases  $R_p$  but at the expense of decreasing  $X_n$ .

The predicted dependence of  $N$  on  $S$  and  $R_i$  for the formation of polymer particles by micellar and homogeneous nucleation followed by coagulative nucleation is given by Eq. 2.12.

$$N \propto R_i^{2/5} S^{0.4-1.2} \quad (2.12)$$

The occurrence of coagulative nucleation does not alter the  $\frac{2}{5}$ -power dependence of  $N$  on  $R_i$ . However, the coagulative nucleation mechanism indicates a more complex dependence of  $N$  on  $S$ . The exponent of  $S$  decreases monotonically from 1.2 to 0.4 with increasing  $S$ . The concentration of polymer particles is higher and the nucleation time is no longer for systems with high surfactant concentrations. Polymer particle formation becomes less efficient at longer times as there is a greater tendency for capture of precursor particles by polymer particles when the latter concentrations are high. Within the overall behaviour predicted by Eq. 2.12, there is no compatibility with the  $\frac{3}{5}$ -power dependence of  $N$  on  $R_i$  by the Eq. 2.11.

Nonpolar monomers such as styrene, with little tendency toward radical desorption, generally show  $\frac{3}{5}$ - and  $\frac{2}{5}$ -power dependencies of  $N$  on  $S$  and  $R_i$ , respectively. This result, however, cannot be taken to exclude coagulative nucleation since one cannot preclude the exponent of the dependence of  $N$  on  $S$  being larger and smaller, respectively, than  $\frac{3}{5}$  at lower and higher concentrations of surfactant than those studied.

Monomers such as vinyl acetate and vinyl chloride, which show Case 1 behaviour, tend to show a dependence of  $N$  on  $S$  in line with that predicted by Eq. 2.12, indicating the presence of coagulative nucleation. Simultaneously, the dependence of  $N$  on  $R_i$  deviates markedly from Eq. 2.12. When extensive radical desorption occurs, the large fraction of nucleation is initiated by desorbed radicals with the result that  $N$  is little affected by  $R_i$ . Thus, the order of dependence of  $N$  on  $S$  is 0.64 for styrene, 0.86 for methyl methacrylate, 1.0 for vinyl acetate, while the orders of dependence on  $R_i$  are 0.36, 0.20, 0, and 0, respectively. The emulsion copolymerization of acrylonitrile and butyl acrylate shows a decrease in the exponent of the dependence of  $N$  on  $S$  from 0.67 to 0.40 with increasing surfactant concentration when an anionic surfactant was used. The exponent was close to one for polymerization in the presence of a cationic surfactant.

Anomalous results have been observed in some emulsion polymerizations – inverse dependencies of  $N$ ,  $R_p$ , and  $X_n$  on surfactant concentration. Some surfactants act as inhibitors or retarders of polymerization, especially of the more highly reactive radicals from vinyl acetate and vinyl chloride. This is most apparent with surfactants possessing unsaturation (e.g., certain fatty acid soaps). Degradative chain transfer through allyl hydrogens is probably quite extensive.

The polymer particles decrease in stability during Intervals II and III since the total polymer particle surface area increases and the coverage of the surface with surfactant decreases. The relative decrease in particle stability appears to be insufficient to cause coalescence as long as stirring is maintained since  $N$  is generally observed to be constant. In some systems, however, the stability decreases sufficiently to cause the particles to coalesce and  $N$  decreases with conversion.

### **2.3.3 Other characteristics of emulsion polymerization**

#### **2.3.3.1 Initiators**

The initiators used in emulsion polymerization are water-soluble initiators such as potassium or ammonium persulfate, hydrogen peroxide, and 2,2'-azobis(2-amidino-propane) dihydrochloride. Partially water-soluble peroxides such as succinic acid peroxide and t-butyl hydroperoxide and azo compounds such as 4,4'-azobis(4-cyanopentanoic acid) have also been used. Redox systems such as persulfate with ferrous ion are commonly used. Redox systems are advantageous in yielding desirable initiation rates at temperatures below 50°C. Other useful redox systems include cumyl hydroperoxide or hydrogen peroxide with ferrous, sulfite, or bisulfite ion.

#### **2.3.3.2 Surfactants**

Anionic surfactants are the most commonly used surfactants in emulsion polymerization. These include fatty acid soaps (sodium or potassium stearate, laurate, pelmitate), sulfates, and sulfonates (sodium lauryl sulfate and sodium dodecylbenzene sulfonate). The sulfates and sulfonates are useful for polymerization in acidic medium where fatty acid soaps are unstable or where the final product must be stable toward either acid or heavy-metal ions. Nonionic surfactants such as poly(ethylene oxide), poly(vinyl alcohol) and hydroxyethyl cellulose are sometimes used in conjunction with anionic surfactants for improving the freeze-thaw and shear stability of the polymer or to aid in controlling particle size and size distribution. The presence of the nonionic surfactant imparts a second mode of colloidal stabilization, in addition to electrostatic stabilization by the anionic surfactant, via steric interference with the Van der Waals attraction between polymer particles. Nonionic surfactants are also of use where the final polymer latex should be insensitive to changes in pH over a wide range. Nonionic surfactants are only infrequently used alone, since their efficiency in producing stable emulsions is less than that of the anionic surfactants. Anionic surfactants are generally used at a level of 0.2 - 3 wt% based on the amount of water; nonionic surfactants are used at the 2 - 10 % level.

Cationic surfactants such as dodecylammonium chloride and cethyltrimethylammonium bromide are much less frequently used than anionic surfactants because of their inefficient emulsifying action or adverse effects on initiator decomposition. Also, cationic surfactants are more expensive than anionic surfactants.

Surfactants increase particle number and decrease particle size as their concentration in the initial reaction charge is increased. However, one can use delayed addition of surfactant after nucleation is complete to improve particle stability, without affecting the particle number, size and size distribution.

#### **2.3.3.3. Other components**

The quality of the water used in emulsion polymerization is important. Deionized water may be used since the presence of foreign ions or ions in uncontrolled concentrations can interfere with both the initiation process and the action of the emulsifier. Antifreeze additives are used to allow polymerization at temperatures below 0°C. These include inorganic electrolytes as well as organics such as ethylene glycol, glycerol, methanol, and monoalkyl ethers of ethylene glycol. The addition of inorganic electrolytes often affects the polymerization rate and stability of the emulsion. Sequestering agents such as ethylenediamine tetraacetic acid or its alkali metal salts may be added to help solubilize a component of the initiator system or to deactivate traces of calcium and magnesium ions present in the water. Buffers such as phosphate or citrate salts may be used to stabilize the latex toward pH changes.

#### **2.3.3.4. Propagation and termination rate constants**

Emulsion polymerization proceeds in a polymer particle where the concentration of polymer is quite high throughout the reaction. This type of system is then similar to a bulk polymerization in the later stages of reaction and one would anticipate the occurrence of the Trommdorff effect. The propagation rate constant for an emulsion polymerization can be obtained for Case 2 systems from the polymerization rate using Eq. 2.6, where  $n = 0.5$ . One can ascertain that Case 2 behavior is present by observing whether the polymerization rate in Interval II is insensitive to changes in the initiation rate. The value of  $k_p$  can also be obtained from the degree of polymerization using Eq. 2.6. This is often a more reliable measure of  $k_p$  since there is no need to make any assumption on the value of  $n$ . The propagation rate constant is generally found to have the same value in emulsion polymerization as in the corresponding bulk polymerization at high conversion – more specifically, at a conversion corresponding to the volume

fraction of polymer in monomer that exists in the emulsion system.

### 2.3.3.5. Energetics

The heat of an emulsion polymerization is the same as that for the corresponding bulk of solution polymerization, since  $\Delta H$  is essentially the enthalpy change of the propagation step. Thus, the heats of emulsion polymerization for acrylic acid, methyl acrylate, and methyl methacrylate are  $-67$ ,  $-77$  and  $-58$  kJ/mole, respectively, in excellent agreement with the  $\Delta H$  values for the corresponding homogeneous polymerizations (Table 2.2).

**Table 2.2.** Enthalpy and Entropy of Polymerization at 25°C <sup>a</sup>

Monomer	- $\Delta H$	- $\Delta S$
Ethylene <sup>b</sup>	93	155
Propene	84	116
1-Butene	83.5	113
Isobutylene	48	121
1,3-Butadiene	73	89
Isoprene	75	101
Styrene	73	104
$\alpha$ -Methylstyrene	35	110
Vinyl Chloride	72	-
Vinylidene chloride	73	89
Tetrafluoroethylene	163	112
Acrylic acid	67	-
Acrylonitrile	76.5	109
Maleic anhydride	59	-
Vinyl acetate	88	110
Methyl acrylate	78	-
Methyl methacrylate	56	117

<sup>a</sup>  $\Delta H$  refers to the conversion of liquid monomer to amorphous or (slightly) crystalline polymer.  $\Delta S$  refers to the conversion of monomer (at a concentration of 1 M) to amorphous or slightly crystalline polymer. The subscripts *lc* often used with  $\Delta H$  and  $\Delta S$  to show the initial and final states (that is,  $\Delta H_{lc}$  and  $\Delta S_{lc}$ ). The units of  $\Delta H$  are kJ/mole of polymerized monomer; the units of  $\Delta S$  are J/K.mole.

<sup>b</sup> Data are for conversion of gaseous monomer to crystalline polymer.

The effect of temperature on the rate of emulsion polymerization, although not extensively studied, is generally similar to that on homogeneous polymerization with a few modifications. The overall rate of polymerization increases with an increase in temperature. Temperature increases the rate by increasing both  $k_p$  and  $N$ . The increase in  $N$  is due to the increased rate of radical generation at higher temperatures. Opposing this trend to a slight extent is the small decrease in the concentration of monomer in the particles at higher temperatures. Thus, the value of  $[M]$  for styrene decreases  $\sim 15\%$  in going from 30 to 90°C. The overall activation energy for emulsion polymerization is, thus, a combination of the activation energies for propagation, radical production, and  $[M]$ . For the few systems studied, the overall activation energies for emulsion polymerization are approximately the same or less than those for the corresponding



homogeneous polymerization.

Carrying out an emulsion polymerization requires an awareness of the Kraft point of an ionic surfactant and the cloud point of a nonionic surfactant. Micelles are formed only at temperatures above the Kraft point of an ionic surfactant. For a nonionic surfactant, micelles are formed only at temperatures below the cloud point. Emulsion polymerization is carried out below the cloud temperature of a nonionic surfactant and above the Kraft temperature of an ionic surfactant.

### **2.3.3.6. Molecular weight and particle size distribution**

Theoretical considerations indicate that compartmentalization of radicals in polymer particles does not change the polydispersity index PDI ( $= X_w / X_n$ ) in emulsion polymerization from its value of 2 in homogeneous polymerization when termination takes place by transfer to monomer, chain-transfer agent, or other substance. However, emulsion polymerization results in molecular - weight broadening when termination involves the bimolecular reaction between radicals. While short propagating chains are likely to couple or disproportionate with longer chains in homogeneous polymerization (PDI = 1.5 and 2 for coupling and disproportionation, respectively), any two chains that undergo bimolecular termination in emulsion polymerization are not random. The broadening of PDI in emulsion polymerization is greater for disproportionation than for coupling. For Case 2 behaviour, coupling of the propagating chain in a polymer particle with the low – molecular - weight entering radical does not greatly affect PDI. Such coupling is equivalent to termination by chain transfer and PDI has a value of 2 compared to 1.5 for homogeneous polymerization. When termination is by disproportionation, PDI has a value of 4 at  $n = 0.5$  compared to 2 for homogeneous polymerization. Low – molecular - weight radicals entering the polymer particles disproportionate with propagating radicals and increase the number of low – molecular - weight molecules;  $X_n$  is decreased while  $X_w$  is essentially unchanged and  $X_w/X_n$  increases. When  $n > 0.5$  (Case 3), the tendency toward molecular-weight broadening decreases as the sizes of the radicals undergoing coupling or disproportionation become more nearly the same size. PDI tends toward the values in homogeneous polymerization (1.5 and 2 for coupling and disproportionation, respectively) as  $n$  increases from 0.5 to 2.

Although the preceding discussion indicates that PDI is generally larger in emulsion polymerization compared to homogeneous polymerization, the opposite is usually observed because of different trends in PDI as a function of conversion. The molecular weight of the polymer produced during a batch emulsion polymerization remain

reasonably constant during a large part (i.e., Interval II) of the overall reaction, since  $N$ ,  $[M]$ ,  $k_p$  and  $R_i$  are relatively constant. This is different from homogeneous batch polymerization where substantial changes occur in the molecular weight and PDI with conversion throughout the whole conversion range.

In addition to the molecular-weight distribution, there is a particle size distribution in emulsion polymerization. The particle size distribution PSD is expressed, analogously to the molecular weight distribution, as the ratio of the weight-average particle size to number-average particle size. (Different particle sizes are calculated depending on whether one uses the particle radius, diameter, or volume as the measure of particle size.) The particle size distribution is a consequence of the distribution of times at which different polymer particles are nucleated. The polydispersity is maximum during Interval I and narrows considerably during the subsequent period. There has been an effort to produce narrow – particle - size distributions (PSD) by controlling the nucleation process, choice and amount of surfactant, and the use of seed emulsion polymerization, temperature, and other reaction variables. Narrow – particle - size distributions are useful in applications such as calibration of electron microscope, ultracentrifuge, aerosol counting, and light-scattering instruments and the measurement of pore sizes of filters and membranes. Narrow particle distributions, with PSD values of 1.1 and lower, have been obtained by choosing reaction conditions with short nucleation times (short Interval I relative to Intervals II and III), increased latex stability (to prevent coagulation), and decreased Interval III times.

#### **2.3.3.7. Surfactant-free emulsion polymerization**

The presence of surfactant is a disadvantage for certain applications of emulsion polymers such as those involving instrument calibration and pore size determination. The presence of adsorbed surfactant gives rise to somewhat variable properties since the amount of adsorbed surfactant can vary with the polymerization and application conditions. Removal of the surfactant, on the other hand, can lead to coagulation or flocculation of the destabilized latex. Surfactant-free emulsion polymerization, involving no added surfactant, is a useful approach to solving this problem. The technique requires the use of an initiator yielding initiating species that impart surface-active properties to the polymer particles. Persulfate is a useful initiator for this purpose. Latices prepared by the surfactant - free technique are stabilized by chemically bound sulfate groups of the  $SO_4^-$  · initiating species derived from persulfate ion. Since the surface-active groups are chemically bound, the latices can be purified (freed of unreacted monomer, initiator,

etc.) without loss of stability, and their stability is retained over a wider range of use conditions than the corresponding latices produced using surfactants. A characteristic of surfactant-free emulsion polymerization is that the particle number is generally lower by up to about two orders of magnitude compared to the typical emulsion polymerization, typically  $10^{12}$  versus  $10^{14}$  particles per millimeter. This is simply a consequence of the lower total particle surface area that can be stabilized by the sulfate groups alone relative to that when added surfactant is present.

#### **2.3.3.8 Core-shell model**

Several groups have suggested that emulsion polymerization does not occur homogeneously throughout a polymer particle but follows a core-shell model in which polymerization takes place within the outer periphery (shell) of a particle. The strongest evidence for this model comes from experiments in which radioactive styrene was added at various times after the start of a styrene emulsion polymerization. Analysis of the resulting latex particles showed that radioactive (new) polymer was formed on the outer shell of the polymer particles. Two different mechanisms have been proposed to explain preferential polymerization in the shell layer. One mechanism invokes a nonuniform distribution of both monomer and polymer in the polymer particles – an outer monomer-rich shell surrounding an inner polymer-rich core. The other mechanism suggests that radicals derived from water-soluble initiators, such as  $\text{SO}_4^{\cdot -}$ , are not able to penetrate into the central core of polymer particles because of their hydrophilic character.

#### **2.3.3.9 Inverse emulsion polymerization**

In the conventional emulsion polymerization, a hydrophobic monomer is emulsified in water and polymerization initiated with a water-soluble initiator. Emulsion polymerization can also be carried out as an inverse emulsion polymerization. Here, an aqueous solution of a hydrophilic monomer is emulsified in a nonpolar organic solvent such as xylene or paraffin and polymerization initiated with an oil-soluble initiator. The two types of emulsion polymerization are referred to as oil-water (o/w) and water-oil (w/o) emulsions, respectively. Inverse emulsion polymerization is used in various commercial polymerizations and copolymerizations of acrylamide as well as other water-soluble monomers. The end use of the reverse latices often involves their addition to water at the point of application. The polymer dissolves readily in water, and the aqueous solution is used in applications such as secondary oil recovery and flocculation (clarification of waste water, metal recovery).

Nonionic surfactants such as sorbitan monooleate yield more stable emulsions

than do ionic surfactants. However, the latices from inverse emulsion polymerizations are generally less stable than those from conventional emulsion polymerizations and flocculation is a problem. Stable latices can be obtained by inverse microemulsion polymerization. Inverse microemulsion polymerization involves systems devoid of droplets, in which only micelles are present. Microemulsions are obtained by using larger amounts of surfactant and continuous phase relative to monomer compared to the amounts used for conventional emulsions. The term macroemulsion is sometimes used to refer to a “conventional-sized” emulsion system. (The micelle size is the same in macroemulsions and microemulsions). Both water-soluble and oil-soluble initiators have been used in inverse microemulsion polymerizations. The polymer particles produced from inverse microemulsion polymerization have much smaller sizes than do those from the corresponding macroemulsion polymerization and, in the presence of a considerable amount of surfactant, are well stabilized against flocculation. Oil-in-water microemulsion polymerizations have also been studied. Miniemulsion polymerization systems are somewhere in between macro and micro systems. They contain both micelles and monomer droplets but the monomer droplets are smaller than in macro systems. Such systems, although labeled “emulsion”, may involve a combination of emulsion and suspension polymerizations. Also, the reader is cautioned that some systems referred to in the literature as microemulsion polymerizations may actually be microsuspension polymerizations. This confusion results when the reaction system is inadequately characterized in terms of the presence or absence of micelles and monomer droplets and their relative numbers and the size of monomer droplets. For both micro and mini reaction systems in which the initiator is soluble in the continuous phase, the mechanism for polymerization is determined by the relative surface areas of micelles versus monomer droplets (if both types of particles are present). Emulsion polymerization occurs if only micelles are present; suspension polymerization occurs if only monomer droplets are present [28].

### **3. EXPERIMENTAL**

#### **3.1 Materials**

All the chemicals, Vinylbenzyl chloride (VBC) (Fluka), Vinyl acetate (Fluka), TMED (Fluka), Decyl bromide (Fluka) were analytical grade chemicals. They were used as supplied.

#### **3.2 Instruments**

KSV model 701 Tensiometer, Pt ring

Brookfield viscometer model DVII (programmable-spindle)

FT-IR (Perkin Elmer spectrum one)

Conductometer (WTW)

GPC (Water 996; Stationary phase is 3 ultrastaygel column with HR 4, 3, 2, moving phase is THF with the speed of 0.3 mL/min)

#### **3.3 Preparation of Polymeric Surfactant**

This material was prepared starting from poly(vinylbenzyl chloride) and modified with N-methyl-D-glucamine.

##### **3.3.1 Preparation of Polyvinyl benzyl Chloride**

5 g of vinylbenzyl chloride was placed in 15 mL of N-methyl pyrrolidone in a 100 mL of flask. 0.05 gr AIBN was used as an initiator. The reaction mixture was placed in a thermostated oil bath at 70<sup>0</sup>C. Polymerization reaction was preceded for 5 h.

After the reaction, viscous solution was poured into 250 mL of water and dried overnight under vacuum for 48 h. the yield was 4.8 g.

##### **3.3.2 Modification of polyvinylbenzyl chloride with N-methyl-D-glucamine**

N-Methyl-D-glucamine (6.4 g) was dissolved in 30 mL of 2-methyl-1-pyrrolidone (NMP) by heating to reflux in a 250 mL three-neck roundbottomed flask equipped with a condenser, thermometer, and overhead stirrer. Poly vinyl benzyl chloride (2 g)

( $M_n=15500\text{g/mol}$ ) was dissolved in 20 mL of 2-methyl-1-pyrrolidone (NMP) and then added to the hot N-methyl-D-glucamine solution. The mixture was refluxed for 2 h. The modified polymer was precipitate in 100 mL of ethanol and dried overnight under vacuum for 24 h. The yield was found 4 g.

Characterization of the modified polymer was performed by using titrimetric method and FT-IR spectra.

### 3.3.3. Determination of the amine content

To determine the amine content, 0.116 g of the polymer sample was left in contact with 15 mL of HCl (0.1M) for 10 h. After filtration, 10 mL of the filtrate was taken, and the acid content of the solution was determined by titration with a 0.1 M NaOH solution in the presence of phenolphthalein as a color indicator.

### 3.3.4. Determination of the critical micelle concentration (CMC)

For this purpose, 0.324 g polymer sample was dissolved in 30 ml water. This solution was placed in thermostat bath at  $25^{\circ}\text{C}$ . 1 mL of water at a time was added to the surfactant solution until the volume reaches up to 250 mL and conductivity of the solution was measured after every addition continuously.

### 3.3.5 Emulsion polymerization of vinyl acetate

The stability of the latexes was achieved by polymeric surfactant consisting of N-methy-D-glucamine based polymer which its chemical structure was given in Figure 4.1. This substance was acted like a protective colloid because of given viscose solution even very low concentration. All substances were used as received. Deionized water was used in all studies.

**Table 3.1.** Recipe for the emulsion polymerization of vinyl acetate using the polymeric surfactant

Substance	Use
Vinyl acetate	Monomer
Polymeric surfactant	Achieving the stability of latexes
Potassium persulfate	Thermal initiator
Sodium bicarbonate	Adjusting the pH value
Water	Media

The polymerization was performed at 70°C for different time depending of the surfactant value.

After polymerization, surface tension and viscosity measurements of the latex were investigated (Table 4.1).

Polyvinyl acetate was precipitated adding salt and the polymer was filtered and washed with excess of hot water to remove salt and surfactant.

### 3.3.6. Emulsion polymerization of styrene

Semicontinuous emulsion polymerization was carried out in a 1 L three neck glass reactor equipped with a condenser, a dropping funnels and a mechanical stirrer having a constant speed of 400 rpm and a reflux condenser in a total batch period of 3 h. Only 10% of the total monomer was introduced at the beginning of the reaction at 70°C and the remaining monomer was added dropwise at 81±2°C from dropping funnels during the remaining time. Initiator was dissolved in a small amount of water and these freshly prepared initiator portions were added at 30 minute intervals throughout the reaction.

**Table 3.2.** Recipe for the emulsion polymerization of styrene using the polymeric surfactant

Substance	Use
Styrene	Monomer
Polymeric surfactant	Achieving the stability of latexes
Potassium persulfate	Thermal initiator
Water	Media

Other procedures were repeated according to the procedure giving above.

### 3.3.7. Measurements

New synthesized polymeric surfactant was characterized by FT-IR and its critical micelle concentration was determined by conductometric methods. Latexes were characterized by measuring Brookfield viscosity, viscosity average molecular weight ( $M_v$ ), and surface tension of latexes to air.

Conversion was monitored gravimetrically. The original viscosities of the homopolymer latexes were determined by Brookfield Programmable DV-II model viscometer with spindle number 4 at 20°C. Viscosity average molecular weights

( $M_v$ ) of polymers were determined by capillary intrinsic viscometry at 30°C.  $M_v$  values of the polymers were determined using a Ubbelohde-type viscometer in an acetone solvent for polyvinyl acetate and a toluene solvent for polystyrene at 30°C. Mark–Houwink constant values of VAc were used as  $a= 0.73$  and  $K= 1.01 \times 10^{-4}$  (dL/g) and St were used as  $a= 0.73$  and  $K= 1.55 \times 10^{-4}$  (dL/g) in the calculations. The surface tension measurements were done with ring-detachment method by torsion tensiometer and a platinum ring at 23.7°C. [29-30]

### 3.3.8. Determination of the molecular weight of polymers

Stable latexes were precipitated by adding salt and obtained polymers were filtered and washed excess of hot water and were dried under vacuum at room temperature for 48 h.

Dried polymers were dissolved in different concentrations by using toluene for polystyrene and acetone for poly (vinyl acetate).

Molecular weight of the polymers were determined viscosimetrically by using Mark – Houwink – Sakurada equation:

$$[\eta] = K M_v^a \quad (3.1)$$

All results were given in Table 4.1 and Table 4.2.

## 3.4 Preparation of the cationic surfactant

In this study, 10 ml of TMED (tetramethylene ethylenediamine) was added 20 ml of ether and 27.5 ml of decyl bromide was added to this solution. The reaction was proceeded for 24 hour at room temperature. Precipitated solid product was filtered and was washed excess of ether. The product was dried under vacuum for 24 hour at room temperature. Reaction yield was found 33.3 g (90%).

The surfactant was characterized by using FT-IR spectrophotometer.

### 3.4.1. Determination of the critical micelle concentration (CMC)

For this purpose 0.513 g surfactant sample was dissolved in 20 ml water. This solution was placed in thermostat bath at 25°C. 1 mL of water at a time was added to the surfactant solution until the volume reaches up to 200 mL and conductivity of the solution was measured after every addition continuously.



### 3.4.2 Emulsion polymerization of vinyl acetate

Polymerization procedure was conducted according to the above. In this system potassium bicarbonate was not used.

**Table 3.3.** Recipe for the emulsion polymerization of vinyl acetate using the cationic surfactant

Substance	Use
Vinyl acetate	Monomer
Cationic surfactant	Achieving the stability of latexes
Potassium persulfate	Thermal initiator
Water	Media

After polymerization, surface tension and viscosity measurements of the latex were investigated (Table 4.2).

### 3.4.3. Emulsion polymerization of styrene

Polymerization procedure was conducted according to the above.

**Table 3.4.** Recipe for the emulsion polymerization of styrene using the cationic surfactant

Substance	Use
Styrene	Monomer
Cationic surfactant	Achieving the stability of latexes
Potassium persulfate	Thermal initiator
Water	Media

### 3.4.4. Measurements

New synthesized polymeric surfactant was characterized by FT-IR and determining critical micelle concentration. Latexes were characterized by measuring Brookfield viscosity, viscosity average molecular weight ( $M_v$ ), and surface tension of latexes to air.

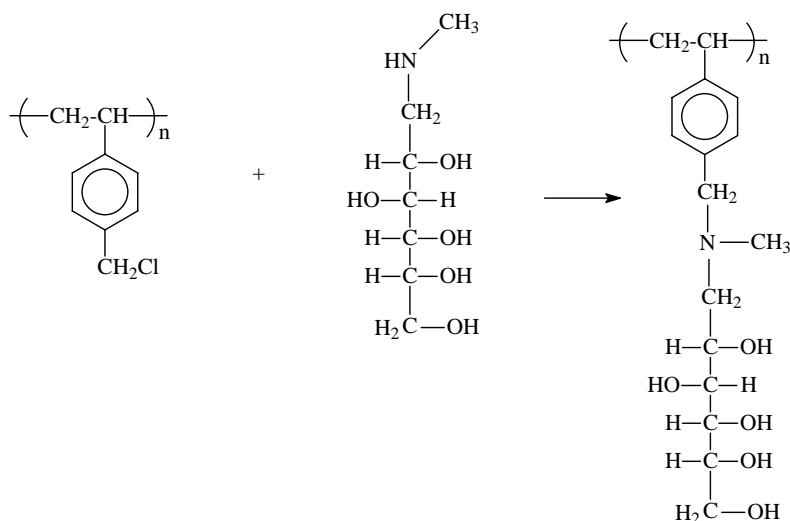
Conversion was monitored gravimetrically. The original viscosities of the homopolymer latexes were determined by Brookfield Programmable DV-II model viscometer with spindle number 4 at 20°C. Viscosity average molecular weights ( $M_v$ ) of polymers were determined by capillary intrinsic viscosity measurements at 30°C.  $M_v$  values of the polymers were determined using a Ubbelohde-type

viscometer in an acetone solvent for polyvinyl acetate and a toluene solvent for polystyrene at 30°C. Mark–Houwink constant values of VAc were used as  $a= 0.73$  and  $K= 1.01 \times 10^{-4}$  (dL/g) and St were used as  $a= 0.73$  and  $K= 1.55 \times 10^{-4}$  (dL/g) in the calculations. The surface tension measurements were done with ring-detachment method by torsion tensiometer and a platinum ring at 23.7°C. [29-30]

## 4. RESULTS AND DISCUSSION

### 4.1. Preparation of the Polymeric Surfactant

In this study, two different surfactants were prepared accordingly. Polymeric surfactant was prepared by starting from polyvinyl benzylchloride. This polymer was synthesized by radical polymerization method in THF. Polyvinylbenzyl chloride ( $M_n=15500$  g/mol) was modified by N-methyl-D-glucamine.



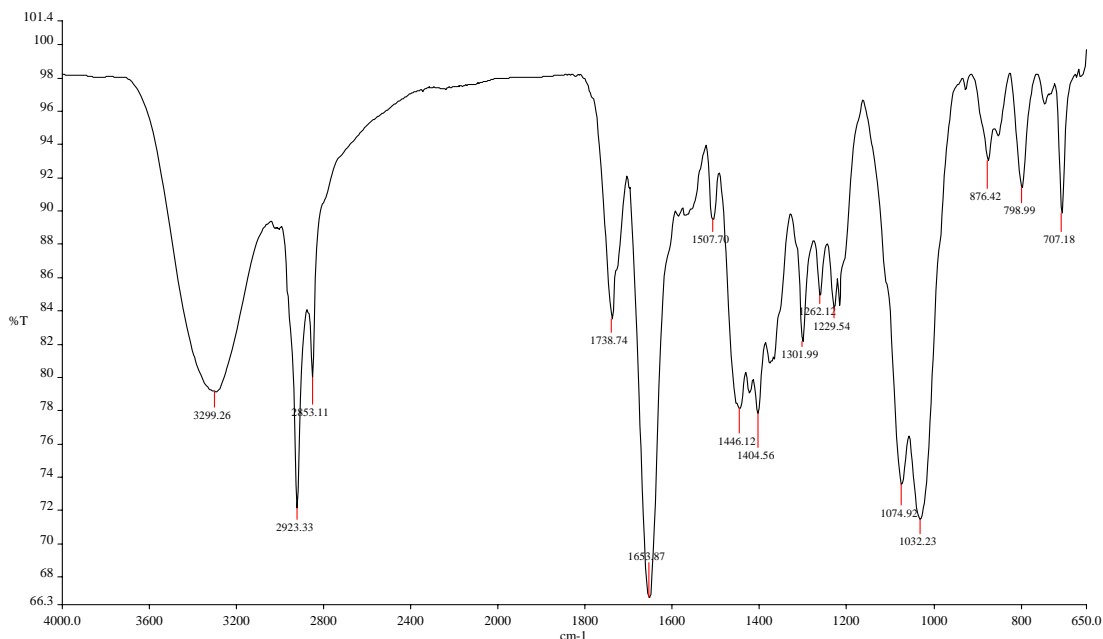
**Figure 4.1.** The preparation reaction of the polymeric surfactant

#### 4.1.1. Measurements of the Polymeric Surfactant

##### 4.1.1.1. Characterization of the Polymeric Surfactant

Modified polymer was characterized by FT-IR spectroscopy and determination of amine content.

The characterization of the polymeric surfactant was performed by using FT-IR spectroscopy. The FT-IR spectrum (Figure 4.2) was as expected, with bands for the N-H, O-H, C-O, and C-N stretch evident at  $3200\text{-}3500$  and  $1033\text{-}1074$   $\text{cm}^{-1}$ .



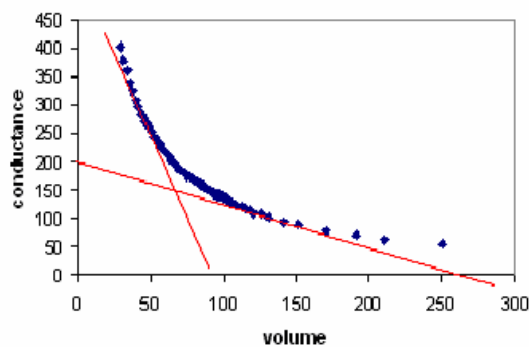
**Figure 4.2.** The IR spectrum of the polymeric surfactant.

#### 4.1.1.2. The Amine Content of the Polymeric Surfactant

Amine content of the polymer was found as 3.06 mmol/g. This indicated 95.3 % conversion.

#### 4.1.1.3. Determination of CMC of the Polymeric Surfactant

Critical micelle concentration of the water soluble modified polymer was determined by conductometric measurements. This value was calculated as  $1.18 \times 10^{-3}$  g/mL (Figure 4.3).



**Figure 4.3.** The CMC graph of the polymeric surfactant.

#### 4.1.2. Viscosity

Increasing emulsifier in the polymer recipe does not effect very seriously on the viscosities of poly(VAc) latexes and poly(St) (Table 4.1 and 4.2). There were not any differences between viscosity data of both series of latexes because of very low amounts of emulsifier in the polymerization medium.

### 4.1.3. Surface Tension

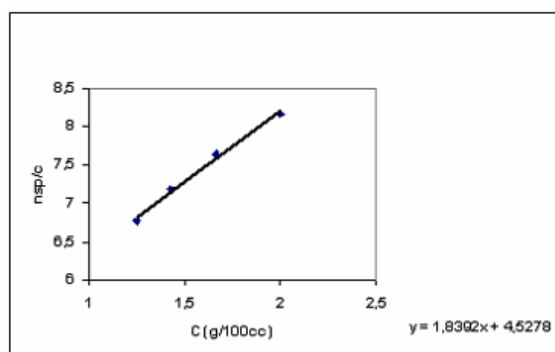
The surface tension studies were carried out for surface characterization of latex films. The measurements shown in Table 4.1 and the results obtained shown in Table 4.2.

It was determined that the surface tensions of the poly(VAc) latexes increased regularly with increasing emulsifier concentration in the polymerization.

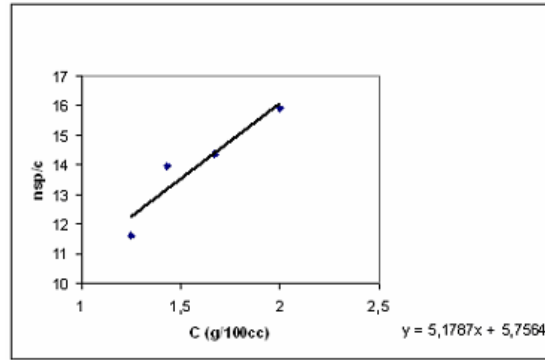
Polymeric surfactant can stabilize latexes even if it is used in small amounts. Therefore, there is no big difference in the Brookfield viscosity and molecular weight results

**Table 4.1:** The results from the viscometric measurements of the emulsion polymerization of styrene and vinyl acetate by using the polymeric surfactant.

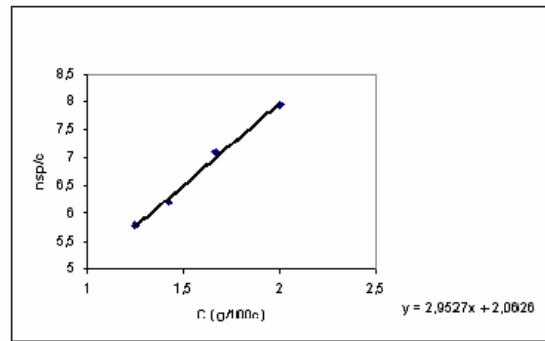
Polymer	Solvent	t (sec)	$\eta_r$	$\eta_{sp}$	c	$\eta_{sp}/c$
<i>PS</i> (0.0067 g/mL)	+ 0 mL	797	17.33	16.33	2	8.17
	+ 3 mL	634	13.78	12.78	1.67	7.65
	+ 6 mL	519	11.28	10.28	1.43	7.19
	+ 9 mL	436	9.48	8.48	1.25	6.78
<i>PS</i> (0.0027 g/mL)	+ 0 mL	1512	32.87	31.87	2	15.94
	+ 3 mL	1149	24.98	23.98	1.67	14.36
	+ 6 mL	966	21	20	1.43	13.99
	+ 9 mL	714	15.52	14.52	1.25	11.62
<i>VAc</i> (0.0013 g/mL)	+ 0 mL	776	16.87	15.87	2	7.94
	+ 3 mL	590	12.83	11.83	1.67	7.08
	+ 6 mL	454	9.87	8.87	1.43	6.20
	+ 9 mL	378	8.22	7.22	1.25	5.78
<i>VAc</i> (0.0007 g/mL)	+ 0 mL	410	8.91	7.91	2	3.96
	+ 3 mL	329	7.15	6.15	1.67	3.68
	+ 6 mL	269	5.85	4.85	1.43	3.39
	+ 9 mL	233	5.07	4.07	1.25	3.25
<i>VAc</i> (0.0003 g/mL)	+ 0 mL	1047	22.76	21.76	2	10,88
	+ 3 mL	818	17.78	16.78	1.67	10,05
	+ 6 mL	631	13.72	12.72	1.43	8,89
	+ 9 mL	512	11.13	10.13	1.25	8,10



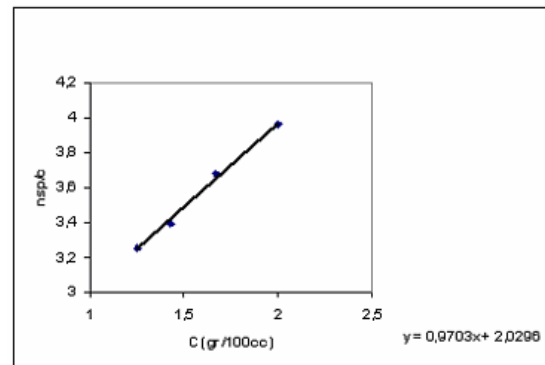
**Figure 4.4.** Viscosity graph of PS (0.0067 g/mL).



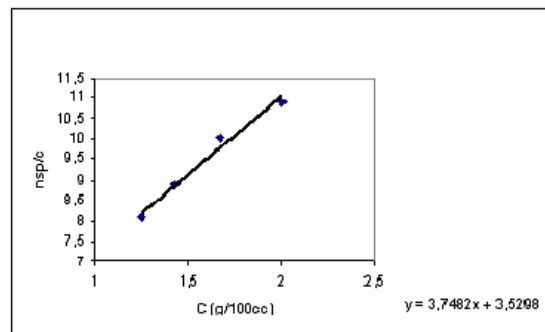
**Figure 4.5.** Viscosity graph of PS (0.0027 g/mL).



**Figure 4.6.** Viscosity graph of PVAc (0.0013 g/mL).



**Figure 4.7.** Viscosity graph of PVAc (0.0007 g/mL).



**Figure 4.8.** Viscosity graph of PVAc (0.0003 g/mL).

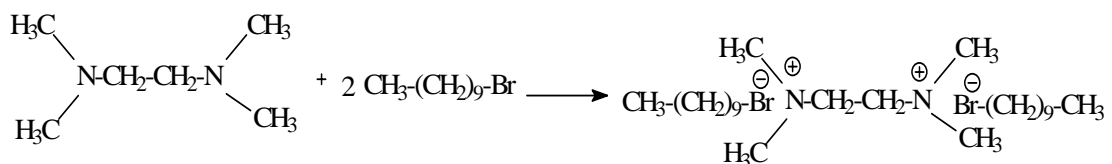
By the help of the intercept values of the graphs, we determined the molecular weights of the polymers using Mark – Houwink – Sakurada equation (Table 4.2).

**Table 4.2.** The results from the experiments of the emulsion polymerization of styrene and vinyl acetate by using the polymeric surfactant.

Polymer	Surfactant Quantity	Brookfield Viscosity (cP)	Surface Tension (mN/m)	M <sub>v</sub>
PS (1.75 M)	0.1 g	Highly viscose	-	1.3·10 <sup>6</sup>
	0.04 g	Highly viscose	-	1.8·10 <sup>6</sup>
	0.02 g	0.22	54.7	-
PVAc	0.02 g	0.10	49.0	0.8·10 <sup>6</sup>
	0.01 g (polymer conc. 2.2 M)	0.10	48.7	0.8·10 <sup>6</sup>
	5x10 <sup>-3</sup> g (polymer conc. 3.2 M)	0.10	48.1	1.7·10 <sup>6</sup>

## 4.2 Preparation of the Cationic Surfactant

Cationic surfactant was prepared by the reaction between TMED and decil bromide (Figure 4.9).

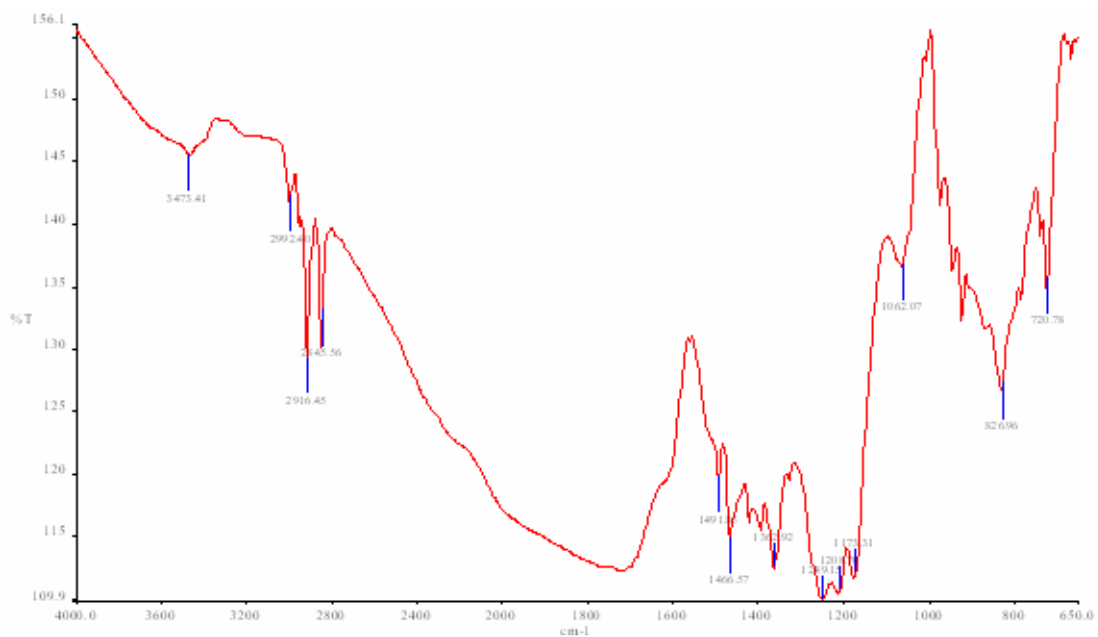


**Figure 4.9.** The production reaction of the cationic surfactant

### 4.2.1. Measurements of the Cationic Surfactant

#### 4.2.1.1. Characterization of the Cationic Surfactant

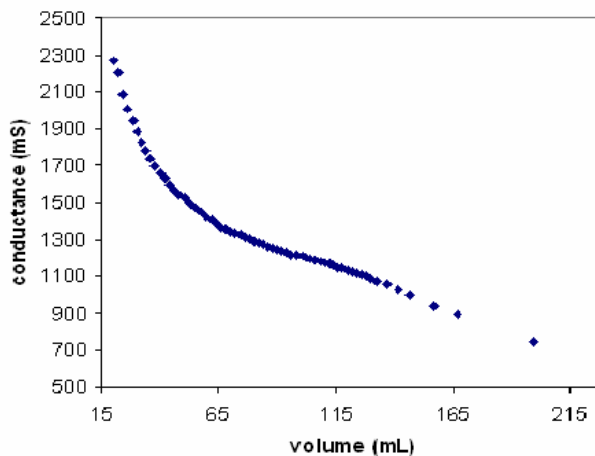
Characterization of the cationic surfactant was achieved mainly by FT-IR spectroscopy and critical micelle determination. The FT-IR spectrum of cationic emulsifier (Figure 4.10) was as expected, with bands for the alkyl group at 2900-2800 cm<sup>-1</sup>. If FT-IR spectrum of surfactant was compared with TMED [31] new bands were observed at 1170cm<sup>-1</sup> and 2992 cm<sup>-1</sup> because of quaternization.



**Figure 4.10.** The IR spectrum of the Cationic Surfactant

#### 4.2.1.2. Determination of CMC of the Cationic Surfactant

Critical micelle concentration of the cationic surfactant was determined as  $2.14 \times 10^{-4}$  g/mL (Figure 4.11).



**Figure 4.11.** The CMC graph of the Cationic Surfactant

#### 4.2.2. Viscosity

Increasing emulsifier in the polymer recipe does effect very seriously on the viscosities of poly(VAc) latexes and poly(St) (Table 4.3 and 4.4). Also increasing emulsifier in the polymer recipe favors in higher molecular weighted polymers.



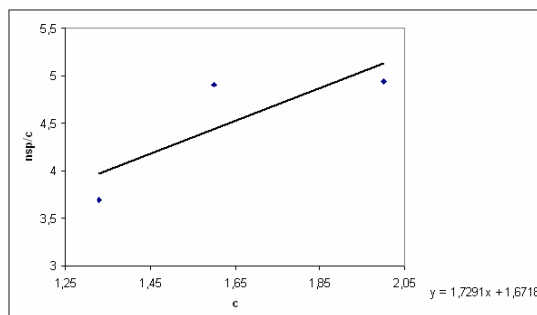
### 4.2.3. Surface Tension

The surface tension studies were carried out for surface characterization of latex films. The measurements shown in Table 4.3 and the results obtained shown in Table 4.4.

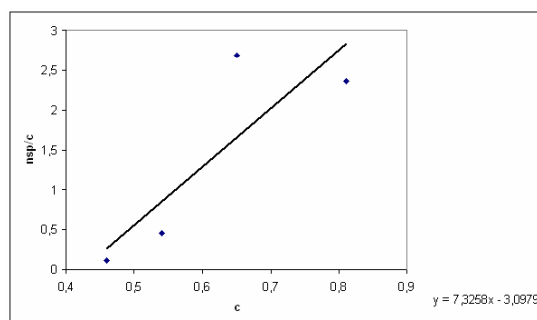
It was determined that the surface tensions of the poly(VAc) latexes increased regularly with increasing emulsifier concentration in the polymerization.

**Table 4.3:** The results from the viscometric measurements of the emulsion polymerization of styrene and vinyl acetate by using the cationic surfactant.

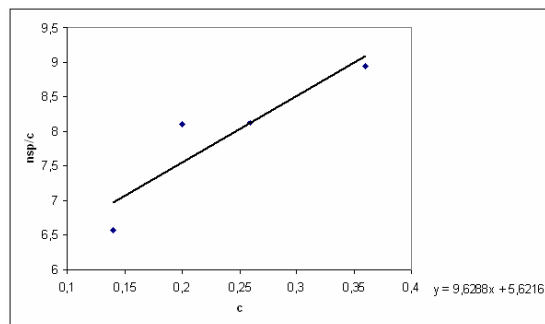
Polymer	Solvent	t (sec)	$\eta_r$	$\eta_{sp}$	c	$\eta_{sp}/c$
<i>PS</i> (8 mL)	+ 0 mL	1034	10.88	9.88	2	4.94
	+ 2 mL	843	8.87	7.87	1.6	4.91
	+ 4 mL	561	5.91	4.91	1.33	3.69
<i>VAc(I)</i> (8 mL)	+ 0 mL	190	2.92	1.92	0.81	2.37
	+ 2 mL	179	2.75	1.75	0.65	2.69
	+ 4 mL	146	1.25	0.25	0.54	0.46
	+ 6 mL	133	1.05	0.05	0.46	0.11
<i>VAc(II)</i> (5 mL)	+ 0 mL	274	4.22	3.22	0.36	8.94
	+ 2 mL	202	3.11	2.11	0.26	8.12
	+ 4 mL	170	2.62	1.62	0.20	8.10
	+ 8 mL	125	1.92	0.92	0.14	6.57



**Figure 4.12.** Viscosity graph of PS (1.75 M).



**Figure 4.13.** Viscosity graph of PVAc (2.2 M; conc. 0.2 g)



**Figure 4.14.** Viscosity graph of PVAc (2.2 M; conc. 0.4 g)

**Table 4.4.** The results from the experiments of the emulsion polymerization of styrene and vinyl acetate by using the cationic surfactant.

<b>POLYMER</b>	<b>Concentration</b>	<b>Brookfield Viscosity (cP)</b>	<b>Surface Tension (mN/m)</b>	<b>M<sub>v</sub></b>
<b>PS (1.75 M)</b>	0.4 g	0.78	31.107	$0.4 \cdot 10^6$
<b>PVAc (2.2 M)</b>	0.2 g	0.30	27.298	$1.4 \cdot 10^6$
<b>PVAc (2.2 M)</b>	0.4 g	0.95	39.776	$3.2 \cdot 10^6$

## 5. CONCLUSION

There are four different type of surfactants. Anionic and non-ionic surfactants are used extensively. Polymers which contain hydrophilic and hydrophobic groups like amphiphilic block copolymers can be used as surface active materials.

In this study, polystyrene based N-methyl-D- Glucamine pendant surfactant has been prepared and characterized.

This surfactant has been used in emulsion polymerization of vinyl acetate and styrene successfully.

Critical micelle concentration of the surfactant is higher than commercially available surfactants. It can be used small amount to obtain stable latex.

Cationic surfactants are not used extensively.

In this study, cationic surfactant has been prepared by reaction between TMED and decyl bromide.

This surfactant has been used in emulsion polymerization of vinyl acetate and styrene.

Characterizations of latex have been performed by surface tension and viscosity measurements.

Molecular weights of the polymers have been determined by using viscosimetric methods.

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## AUTOBIOGRAPHY

- 1. Name Surname:** Dürdane ERKAL
- 2. Date of Birth:** 14.03.1983
- 3. Academic Title:** Research Assistant
- 4. Academic Background:**

Degree	Department	University	Year
B.S.	Chemistry	İstanbul Technical University	2005
M.S.	Chemistry	İstanbul Technical University	--

### 5. Academic Qualifications

Research Assistant Faculty of Arts and Science University of Bahçeşehir 2006 - ...

### 7. Publications

#### 7.1 Articles published in international arbitroral journals

- 1) Bahire Filiz Şenkal, Erdem Yavuz, Dürdane Erkal, Removal of Dyes from Water by Polyvinyl Pyrrolidone Hydrogel, *Polymers for Advanced Technologies*, 2006, 17, 924-927.

#### 7.2 Presentations presented in International Scientific Meetings and published in proceedings books

- 1) Bahire Filiz Şenkal, Erdem Yavuz, Dürdane Erkal, Removal of Dyes from Water by Polyvinyl Pyrrolidone Hydrogel, Proceeding of the *8th Polymers for Advanced Technologies International Symposium*, Budapest, Hungary, 13-16 September 2005.
- 2) Bahire Filiz Şenkal, Erdem Yavuz, Dürdane Erkal, Ayfer Saraç, Yeşim Gürsel, Preparation of a new polymeric surfactant for emulsion polymerization, Abstract Book of *1st European Chemistry Congress*, Budapest, Hungary, 27-31 August 2006.

### 8. Projects

- 1) Synthesis of new Reactives and Polymers for Removal of Dyes, 2006, TÜBİTAK, project number: 106T406.