Modification and characterization of novel polymeric surfactants

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Modification and characterization of novel polymeric surfactants

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School of Materials Science and Engineering

**A thesis submitted to the Nanyang Technological University
in fulfillment of the requirement for the degree of Doctor of
philosophy**

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Abstract

Poly (ethylene oxide)-poly (propylene oxide)-poly (ethylene oxide) (PEO-PPO-PEO) triblock copolymers (Pluronic F127) have been extensively studied because of their thermal responsive aggregation behavior that can be used for a variety of biomedical applications. On top of its unique surfactant behavior, its low toxicity and minimal immune response also make this polymer highly attractive for such application. In this work, the objective is to incorporate the thermal responsive aggregation behavior of such a polymer into another water-soluble, biocompatible and relatively amphiphilic polymer, polyvinyl pyrrolidone (PVP). This is achieved by grafting of the PVP on PEO-PPO-PEO triblock copolymers. This modified polymer with both thermal responsiveness and remarkable capacity to interact with a wide variety of hydrophilic and hydrophobic pharmaceutical agents is very attractive for medical applications.

These novel graft copolymers were synthesized by free-radical polymerization. Polymerization conditions such as types of initiators, concentrations of reactants, reaction times and temperatures, are critical to obtain the graft copolymers with high grafting efficiency. It is found that ideal feeding ratio, reaction time and reaction temperature are 2.5, 6 hours and 70 °C respectively. PVP was also grafted onto either PEO block (F127(PEO)-g-PVP) or PPO block (F127(PPO)-g-PVP) of F127 successfully.

The copolymers were characterized by means of infrared spectroscopy, gel permeation chromatography and nuclear magnetic resonance spectroscopy. The structures, molecular weights and molecular weight distribution of three kinds of graft copolymers, which are F127-g-PVP, F127(PPO)-g-PVP and F127(PEO)-g-PVP, have been obtained and verified.

The molecular weights are found to be 26,000, 52,400 and 70,000, respectively. Their distribution is approximately 1.9, which is reasonable for graft systems.

The solution behaviors of three graft copolymers were also studied. The critical micellization concentration has been obtained through fluorescence spectroscopy and surface tension measurement at room temperature. The effect of the different concentrations of the copolymers on the critical micellization temperature was also investigated and the size and aggregation number of the aggregate were measured using dynamic light scattering, intrinsic viscosity and static light scattering measurements. It was found that the graft copolymers still have the thermal reversible property. The CMT decreased with an increase in the polymer concentrations. The aggregation numbers increased when the temperature increased.

Binary surfactant systems which contain normal surfactants and polymeric surfactants were investigated systematically and thoroughly. Three typical normal surfactants were studied. They are anionic surfactant, SDS, cationic surfactant, TTAB, and non-ionic surfactant, C₁₂EO₆. The two graft copolymers that were synthesized in a controlled manner, showed more synergistic interaction with the normal surfactants as compared to the ungrafted F127. In particular, F127(PEO)-g-PVP showed very favorable interaction with the normal surfactants. Regular solution theory (RST) was used to model these binary surfactant systems and found to be applicable to the mixed surfactant systems of graft polymer with cationic, anionic and non-ionic surfactants.

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Chapter 1 Introduction

1.1 Background

Surface-active agent, called surfactant or amphiphiles, tends to segregate to an air-water interface and consequently lower the surface tension of the solution. Jekyll and Hyde character of surfactants (Hamley, 2000) refers to the opposite nature of surfactants - solvent liking and solvent hating nature. The solvent liking and solvent hating nature of surfactants result in their self-assembly into ordered structures in both organic solvents and aqueous solutions. There are two primary categories of surfactants. Ionic surfactants has an ionic hydrophilic head group (can be cationic, anionic or both) attached to a hydrophobic tail. Non-ionic surfactants usually consist of a short poly (ethylene oxide) chain attached to a hydrocarbon tail. There are a lot of non-ionic polymeric surfactants. They form ordered structure such as micelles, cylinder, lamellar and so on. Micelles can be either spherical or extended into an ellipsoidal or rod-like shape. In this thesis, the author focuses her discussion mainly on spherical micelles since this structure is most commonly formed at moderate concentration solution just above critical micelle concentration.

At a particular temperature, the critical micelle concentration (CMC) is the concentration at which micelles are formed. CMC can be determined using surface tension measurement techniques. Micellization can also occur upon varying the temperature at a fixed concentration. It is predominantly driven by an increase in the entropy of the system when the molecules associate into micelles due to the hydrophobic effect. This

Chapter 1: Introduction

reduced ordering effect is due to the gain in entropy by the water molecules upon micelle formation. Micellization is a very complicated process that is influenced by many factors.

For equal hydrophobic chain length, the CMC of non-ionic surfactants is much lower than that of ionic ones because the electrostatic repulsions between the head groups of the ionic surfactants have to be overcome to form micelles. The longer is the hydrophobic chain, the lower is the CMC. The CMCs of most surfactants are essentially independent of temperature. An exception is the non-ionic surfactants with oxyethylene units as the hydrophilic group. The CMCs of surfactants, which have oxyethylene units, decrease strongly with increasing temperature. Increasing temperature for ionic surfactants usually opposes micellization due to enhanced molecular motion. At the same time, when the temperature increases, the association number increase up to the cloud point, when phase separation occurs because poly (ethylene oxide) becomes insoluble in water. Due to this special thermal property of amphiphilic surfactants containing oxyethylene group the author chooses a non-ionic polymeric surfactant consists of oxyethylene units - Pluronic F127 as the starting material.

Pluronic F127 is a triblock copolymer made up of poly(oxyethylene) and poly(propylene oxide) units (PEO-PPO-PEO). F127 consists of 70% oxyethylene block and the molecular weight is 12,600. Increasing the chain length of hydrophobic part beyond 16 carbons does not lead to a significant decrease in the CMC, possibly due to the coiling of long hydrocarbon chains in the unimers to minimize the hydrophobic interactions of unassociated molecules. Hence, most of the modifications of Pluronic are done by adding the new groups to the main chain. For ionic surfactants, it is found that the CMC decreases by approximately a factor of two for each additional $-\text{CH}_2$ unit, whereas for non-ionic surfactants the increase is larger, typically by a factor of three. In

pharmaceutical and industrial practice, non-ionic surfactants and ionic surfactants are usually employed together in the system to obtain the synergistic effect. Hence, the investigation of interactions between the surfactants in binary surfactants systems is very important.

1.2 Problems

The delivery of commonly used potent drugs in cancer treatment is currently done mostly through intravenous drug infusions. The infusions, or injections, lead to an initial rapid increase and subsequent decay, below therapeutic levels, of the drug concentration in blood. Thus, the infusions need to be performed frequently, exacerbating the potential for side effects. Therefore, the therapeutic potential for protracted infusions is still confined to a subset of patients. Toxicity side effects have led to numerous attempts at the development of new formulations for drug delivery such as long-circulating liposomes and micelles, water soluble polymer-drug conjugates, biodegradable gels and microparticles, and drug formulations more suitable for oral administration. Oral treatment with cytotoxic anticancer drugs is preferred as this delivery route is convenient for patients, economical, and adaptable to more chronic treatment regimens. However, low oral bioavailability has usually limited the development of cancer treatment by the oral route.

As PEO-PPO-PEO triblock copolymers have attractive temperature-sensitive and biocompatible properties, they are potential candidates for biomedical application such as drug delivery system. In most applications, a mixture of copolymers is used. In the case of PEO-PPO-PEO triblock copolymer, it shows synergistic effect when interacting with

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anionic surfactants, but interacts weakly with the other kinds of surfactants. In this work, the author attempts to improve the synergism of the interactions between different surfactants systems.

1.3 Objectives

The objective of this project was to synthesize and characterize a novel polymer, Pluronic –g-Poly(vinyl pyrrolidone) that gives rise to novel phase structures in a selective solvents and change in physical conditions such as concentration and temperature. Pluronic F127 has unique thermal reversible property, but it can only interact with a few surfactants such as anionic surfactant. Poly(vinyl pyrrolidone), PVP, which has been largely used in pharmaceutical field, has wonderful biocompatibility and interact with various additives. A combination of these two classes of molecules is investigated to extend the synergistic interactions of Pluronic with other complimentary surfactants.

In this research, the conditions for the grafting of PEO-PPO-PEO copolymer and different polymerization routes were studied. The structure, molecular weight and the components of the graft copolymers were characterized. Interesting work on solution properties of the copolymers such as the study of CMC, CMT, association number, the interaction with additives, and the modeling of mixed surfactants interaction were studied in detail.

1.4 Outline of this Work

This thesis consists of nine chapters. In this chapter, an introduction to the system, the problem and objective of this research were presented. Chapter Two will review the

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research that has been published on Pluronic triblock copolymer, poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide), and polyvinyl pyrrolidone. The review will include work on interaction of such copolymers with additives, the chemical modifications of both Pluronic block copolymers and PVP and the synthesis of graft copolymers.

A detailed experimental techniques and different synthesis routes of Pluronics-g-PVP are given in Chapter Three and Chapter Four respectively. The results and discussion of the characterization and association studies of the polymeric surfactants are presented in Chapter Five, Six and Seven. A comparison is also made between the modified and the unmodified copolymer in all chapters. Some of results in those chapters have been published. Following this, Chapter Eight gives a conclusion of the characterization and the solution property of Pluronic-g-PVP. Finally, the recommendations for future studies are presented in Chapter Nine.

Chapter 2 Literature Review

2.1 Poly(ethylene oxide)–poly(propylene oxide)-poly(ethylene oxide)

Water-soluble triblock copolymers of the EPE-type [P and E represent poly (propylene oxide) and poly (ethylene oxide), respectively], often abbreviated as PEO-PPO-PEO (or $(EO)_m(PO)_n(EO)_m$ with m, n representing the number of repeat units), are commercially available non-ionic macromolecular surfactants and have many uses. Refer to Figure 2.1. Pluronic[®] or Poloxamer[®] (BASF) and Synperonic[®] (ICI) polyols are the commercial names that find widespread industrial applications in their uses as emulsifying, wetting, thickening, coating, solubilizing, stabilizing, dispersing, lubricating and foaming agents. Chu (1995) has reviewed the main physical methods used in studying Pluronic polyols.

The Pluronic polyols with an average molecular weight which contains different ratio of ethylene oxide to propylene oxide by weight, are the most commonly used gel-forming polymer matrix to deliver proteins, especially Pluronic F-127 ($PEO_{99}-PPO_{69}-PEO_{99}$) (Gombotz, 1995). This polymer exhibits a reversible thermal gelation in aqueous solutions at a concentration of 20% or more. Thus, the polymer solution exists as liquid at a room temperature but gels rapidly in the body. Although the polymer is not degraded by the body, the gels dissolve slowly and the polymer is eventually cleared. This polymer has been utilized in protein delivery (Jushasz, 1989; Morikawa, 1987) and skin burn treatments (Pautian, 1993).

Figure 2.1 The structures of Pluronic and its components.

2.1.1 Types of Pluronic Block Copolymers and their Physical Properties

There are more than twenty kinds of Pluronic block copolymers available commercially, with molecular weights ranging from 1000 to 20000 g mol⁻¹. The copolymers with different molecular weights and PEO contents have different characteristics. Some of the characteristics of Pluronic copolymers are summarized in Table 2. 1 (Alexandridis, 1994). In the nomenclature of Pluronic copolymers, the letters L, P or F represent liquid, paste or flakes respectively. The first one or two numbers denote the molecular weight of the PPO block and the last number is indicative of the weight fraction of PEO block. The cloud point corresponds to the temperature at which phase separation of the copolymer from water occurs. For Pluronic copolymers, clouding is observed at moderately high temperatures. It can be seen that the cloud point increases with the PEO content and may even exceed 100 °C.

PEO-PPO-PEO copolymers are non-ionic, water-soluble macromolecular surface-active agents. It can be synthesized by two step process shown in Figure 2.2. Both PEO and

PPO homopolymers have a lower critical solution temperature (LCST) in water. Below this temperature, the solution exists as an isotropic single phase system. Above this temperature, the isotropic single phase polymer solution phase- separates into a two phase mixture. It is due to this unique solution behavior that the phase transition of PEO-PPO-PEO block copolymer is both concentration and temperature dependent.

Table 2.1 Properties of the Pluronic copolymers.

polymer	MW	PPO	PO units	EO units	Lot no.
Segm wt					
L64	2900	1740	30	2×13	WPWN-505A
P65	3400	1700	29	2×18	WPAN-605B
F68	3400	1680	29	2×76	WPON-611B
P84	4200	2520	43	2×19	WPTN-561B
P85	4600	2300	40	2×26	WPAN-628B
F88	11400	2280	39	2×103	WPDN-616B
P103	4950	3465	60	2×17	WPHM-539B
P104	5900	3540	61	2×27	WPAN-503B
P105	6500	3250	56	2×37	WPDI-522A
P108	14600	2920	50	2×132	WPDN-564B
P123	6750	4025	69	2×19	WPYM-569B
F127	12600	3780	65	2×100	WPON-593B
25R4	3600	2500	2×21	25	WPMN-515B

Figure 2.2 Reaction scheme for Pluronic copolymers PEO-PPO-PEO.

2.1.2 Self-assembly of Pluronic Copolymers in Aqueous Solutions

The defining property of Pluronic is the ability of individual block copolymer molecules, often termed as ‘unimers’, to self-assemble into micelles in aqueous solutions. These unimers form a solution in water at block copolymer concentrations below the critical micelle concentration (CMC). CMC is the concentration at which stable micelles form. When the concentration of the block copolymer reaches above CMC, the unimer molecules aggregate, forming micelles through a process called ‘micellization’. One of the driving forces for the micellization is the hydrophobic interaction of the PO blocks. Above CMC, the hydrophobic PO blocks aggregate to form the inner core of the micelles surrounded by the hydrophilic EO blocks that constitute the corona. Hence, Pluronic micelles are commonly pictured as spheres composed of a PO core and an EO corona. However, some results from small angle neutron scattering on Pluronic L64 in D₂O show that the core-shell boundary in the PEO-PPO-PEO micelles is not sharp (Zhou, 1988). Some miscibility of the PO and EO groups may exist and the water penetration into the PPO core may also occur.

Depending on the type of Pluronic, the spherical micelles have an average hydrodynamic diameter ranging from about 20 to about 80 nm. The number of block copolymer unimers aggregated to form one micelle is referred to as the aggregation number. Usually this number ranges from several tens to over a hundred (Mortensen, 1993a; Mortensen, K., 1993b; Linse, P., 1993b; Nagarajan, 1999). This portrayal is correct for most block copolymers, which have an EO content above 30%, especially in relatively dilute solutions at body temperature. However, other morphologies, such as lamellar and rods (cylinders), can also be formed in aqueous Pluronic systems.

Nagarajan and coworkers (1999) was first to compute the aggregation properties of the block copolymers and the results are summarized in Table 2.2. L represents lamellar, S represents spheres and C represents cylinders. The calculations show that the lamellar aggregates are favored when the ratio of PEO/PPO is small whereas spherical aggregates are favored when the ratio of PEO/PPO is large. Typically, for block copolymers containing 40 or more weight percent PEO, only spherical aggregates will be formed at 25 °C. For block copolymers containing 30 wt% PEO, cylindrical aggregates are possible. Block copolymers containing 20 or less wt% PEO give rise to lamellae. The phase diagram for a purified Pluronic P94 sample (which contains about 40wt% EO) at concentrations up to 40% is shown in Figure 2. 3 (Hvidt, 1994).

Figure 2.3 The combined concentration and temperature conditions where P-94 is found as unimers, micelles, and gels in water, as determined by use of viscoelastic, scanning calorimetry, and cloud point techniques.

Table 2.2 Core size R (Å), corona thickness D (Å), shape and/or aggregation number g of solubilize-free micelles.

Trade name	Structure	R (Å)	D (Å)	g for spheres	Shape
L62	E ₆ P ₃₅ E ₆	7.5	19.2		L
L63	E ₉ P ₃₂ E ₉	14.5	13.9		L
L64	E ₁₃ P ₃₀ E ₁₃	34.1 (38–46 ^a)	16.6 (37–44 ^a)	57 (39–70 ^a)	S
P65	E ₁₉ P ₂₉ E ₁₉	30.7	22.1	43	S
F68	E ₇₇ P ₂₉ E ₇₇	21.3 (25 ^b)	51.0 (53 ^b)	15 (22 ^b)	S
P84	E ₁₉ P ₄₃ E ₁₉	42.2	22.5	75	S
P85	E ₂₆ P ₄₀ E ₂₆	36.3 (37 ^c)	28.3 (36 ^c)	53 (57 ^c , 37–78 ^d)	S
F88	E ₁₀₄ P ₃₉ E ₁₀₄	25.0	63.9	17	S
F98	E ₁₁₈ P ₄₅ E ₁₁₈	26.7	70.3	18	S
P103	E ₁₇ P ₆₀ E ₁₇	38.6	21.5		C
P104	E ₂₇ P ₆₁ E ₂₇	51.0	29.8	94	S
P105	E ₃₇ P ₅₆ E ₃₇	43.9	37.3	65	S
F108	E ₁₃₃ P ₅₀ E ₁₃₃	28.3 (25.0 ^c)	76.6 (150 ^c)	20 (13 ^c)	S
P123	E ₂₀ P ₇₀ E ₂₀	42.1	24.4		C
F127	E ₁₀₀ P ₆₄ E ₁₀₀	37.5	70.2	35 (15–45, 30 ^f)	S

^a 8–32 wt% polymer and between 23 and 35 °C using SANS (Wu, 1995).

^b From Ref. (Zhou, 1987) as interpreted and reported in Ref. (Kabanov, 1995).

^c Based on light scattering and ultracentrifugation at 37 °C (Kabanov, 1995).

^d Measurements using SANS in the range 20–40 °C (Mortensen, K., 1993a).

^e In the range 30–40 °C (Rassing, 1982).

^f At 25 °C (Wanka, 1990).

2.1.3 PEO-PPO-PEO Copolymers in Aqueous Solutions

2.1.3.1 Thermodynamics

The micellization mechanism of Pluronic copolymers was studied and reported (Kositza, 1999; Nivaggioli, 1995). There are two possible association models for block copolymers, namely the closed association model and the open association model. The closed association model is characterized by the equilibrium between the free polymers (unimers) and macromolecular micelles. A critical micelle concentration exists for this model. The open association model is characterized by a stepwise association resulting in a distribution of unimers, dimmers, trimers. A series of corresponding equilibrium constants exist between the respective species for this kind of model. The mechanism of micellization of Pluronic copolymers belongs to the first model (Chu, 1996).

The aggregation process of Pluronic copolymers is driven strongly by entropy. For a 1wt% copolymer solution at the critical micelle temperature, the reported ΔH° , ΔG° and ΔS° values are in the range of 169 to 339 kJmol⁻¹, -24.5 to -28.8 kJmol⁻¹ and 0.638 to 1.244 kJmol⁻¹K⁻¹ range respectively (Alexandridis, 1994). The positive values of the standard enthalpy (ΔH°) indicate that the micellization of the polymers are an unfavorable endothermic process. The free energy (ΔG°) is negative indicating the formation of micelles is spontaneous. Therefore, the positive standard entropy (ΔS°) is the main driving force for the aggregation of the Pluronic copolymers.

2.1.3.2 Effect of Architecture

The composition and molecular weight of Pluronic copolymers affect the CMC and CMT (Zhou, 1994). Critical Micelle Temperature, CMT, means above this temperature, the formation of micelle happens. At a given temperature, the CMC values increase with decreasing PPO block lengths and increasing PEO block length. For a constant PPO/PEO ratio, the CMC and CMT values decrease with increasing molecular weights of the Pluronic copolymers. The CMT values decreased with increasing the content of the PPO block at a given concentration. Figure 2. 3 shows the CMC-CMT micellization boundary of a typical Pluronic, Pluronic P-94, in aqueous solution. The free polymer chains (unimer) exist in solutions at the copolymer concentrations and the temperatures lower than the CMC-CMT boundary. The micelles in equilibrium with unimers exist above the boundary.

The PPO segment of Pluronic copolymers plays an important role on their temperature-sensitive properties because the dehydration of the PPO block with increasing temperature is responsible for the micelle formation. The effect of the PPO block on micelle formation is more pronounced than that of PEO block. The CMC and CMT values increase marginally with increasing PEO block length.

2.1.3.3 Effect of Temperature and Concentration

In general, the hydrodynamic radius, R_h , which is a value to indicate the *apparent* size of the dynamic hydrated/solvated particle, is used to describe the structure and shape of the micelles. The R_h of Pluronic copolymers is between 2nm and 15nm in the temperature range from 20 to 80 °C and the aggregation number varies from 4 to 400 in the same

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temperature range (Brown, 1991; Almgren, 1991; Pandya, 1993). The core radius r_c can be estimated by the following equation:

$$\frac{4\pi r_c^3}{3} = N_{po} n_w M_0 / \rho N_A \quad (2.1)$$

where M_0 is the molar mass of oxypropylene monomer, ρ is the density of liquid oxypropylene, n_w is the aggregation number and N_A is the Avogadro's number. Hence, the thickness of outer corona can be roughly estimated by the difference between R_h and r_c ($R_h - r_c$).

The effect of temperature and concentration on the aggregation number, the size and the shape of micelles formed from Pluronic copolymers have been studied by many research groups (Schillen, 1994; Linse, P., 1993a; Linse, P., 1993b; Linse, P., 1994a; Linse, P., 1994b). The CMC values of Pluronic copolymers decreases with increasing temperature. The hydrodynamic radius, R_h , of Pluronic L64 in aqueous solution remained constant over a wide concentration range at 35 °C. This is more likely to be represented by a closed association model. Nolan (1997) established that the aggregation number related to chain length of Pluronic.

The shape of PEO-PPO-PEO micelles was also studied by many research groups (Mortensen, 1996; Jeon, 2002). Mortensen (1996) studied the phase diagram for Pluronic P85 solution in D_2O . The Pluronic copolymers exist as unimers at low concentration and temperature. In the low concentration range, with increasing temperature, spherical micelles are formed. The transition from spherical to rod-like micelles occurs with increasing the temperature. The morphology of Pluronic P85 micelles changed from sphere to rod when the temperature increased to about 70 °C. This change in morphology is due to the fact that the PPO chains in the micellar core are fully stretched at high temperature. Further increase in the aggregation number must result in the transition

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from spherical to rod-like micelles. The transition from micelles to “gel” occurs when the concentration of Pluronic copolymers is increased beyond a critical threshold.

The water-soluble and hydrophilic polymer in aqueous solution shows an extended chain conformation below its LCST (lower critical solution temperature). Above the LCST, the polymer undergoes a phase transition to an insoluble and hydrophobic aggregate. This phase transition occurs in a narrow temperature range through the LCST and is reversible corresponding to temperature changes. Figure 2. 4 (Jeon, 2002) shows the typical gelling behavior of Pluronic F127. From the figure, it is evident that gel is only formed at concentration higher than 18wt%. This indicates that high concentration is a necessary condition for gel formation. At a given concentration, the gels exist within a certain temperature range. The temperature for gel formation decreases with increasing concentration of F127 solution. The sol-gel transitions are thermoreversible.

Figure 2.4 Phase behavior of Pluronic F127 in aqueous solution.

2.1.3.4 Effect of Additives

The interactions of polymer and surfactant, especially those in oppositely charged polymer-surfactant systems, have received significant attention over the past two decades (Tanaka, 1998; Tsianou, 1999; Moren, 1998). Such mixed amphiphilic systems are present in diverse industrial fields such as paints, coatings, pharmaceuticals, cosmetics, foods, paper and oil processing. The effects of electrolytes and surfactants on the micellization of the Pluronic copolymers solution have been studied by viscosity, cloud point and light scattering methods. A thorough understanding of such mixed systems is essential for an efficient industrial development. Among the many water-soluble polymers and surfactants available, the non-ionic ones, such as Pluronic, are receiving increasing attention recently as they are milder and environmentally friendlier. There are some groups that have published work relating to the study of the interactions in surfactant systems (Hecht, 1994; Zhang, 1995). Most of the studies are limited to the dilute concentration regions of the copolymer and the surfactant.

Many researchers (Almgren, 1991; Hecht, 1995) studied the effect of anionic surfactant, sodium dodecyl sulfate (SDS), on Pluronic block copolymer micellization. The results obtained from adding SDS into the Pluronic copolymer solutions indicate that SDS can interact with both Pluronic unimers and micelles. At the saturation condition, several SDS molecules bind to one F127 molecule. The binding between the SDS and F127 begins to occur at a concentration lower than the CMC of SDS.

In comparison, cationic surfactants are more selective and only interact with those polymers which have flexible backbones and hydrophobic side groups to form polymer/surfactant complex by weak hydrophobic and/or electrostatic interactions (Li,

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1999, Ghoreishi, 1999). Li and coworkers (2001b) investigated how the cationic surfactant, tetradecyltrimethyl-ammonium bromide (TTAB) interacts with F127. The experiments have shown that TTAB binds to both monomeric and micellar F127. TTAB forms a polymer/micellar TTAB complex with monomeric F127. In addition, TTAB binds to F127 micelles leading to the transformation of the aggregated F127 into mixed micelles followed by a breakdown of these aggregates into smaller mixed F127/TTAB aggregates as more TTAB is added. This process continues until all the aggregated F127 are dissociated. DSC measurements have also shown that small amounts of TTAB can decrease the critical micelle temperature (CMT) of F127.

Electrolytes with different sizes and polarizabilities are often used as additives (Elisseeva, 2005; Bahadur, 1992; Ivanova, 2001). Addition of salts such as KBr, KCl and KF decreases the CMT of L64 and F68 solutions. However, addition of KSCN results in the increase of CMT. A linear change in the cloud point with increasing salt concentration is also observed. The effect of electrolytes is discussed in terms of “salting in” and “salting out” (Alexandridis, 1997). Most of the inorganic salts decrease the water solubility of organic solutes, called salting-out phenomenon, while some of them (NaI, NaSCN) have an opposite action, called salting-in. The organic solutes, depending on their relative polarities, locate preferably either in the PEO-rich or the PPO-rich domains of the microstructure. Some solutes, however, independent of their polarities (e.g. ethanol and glycerol triacetate), may show amphiphilic behavior and act as cosurfactants locating preferably at the interface between the PEO-rich and the PPO-rich domains.

2.1.4 The Applications of Pluronic Copolymers

Block copolymer micelles are of interest for drug delivery applications for a number of reasons. First of all, hydrophobic drugs can be physically entrapped in the copolymer at

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the concentrations that exceed their intrinsic water-solubility. Secondly, the hydrophilic blocks, which are often composed of poly (ethylene oxide) (PEO), can form hydrogen bonds with the aqueous surroundings and form a tight shell around the micellar core. Diblock copolymer micelles with a PEO corona resist protein adsorption and cellular adhesion. As a result, the contents of the hydrophobic core are effectively protected against hydrolysis and enzymatic degradation. In addition, the PEO corona prevents recognition by the reticuloendothelial system and, therefore, prevents the preliminary elimination of the micelles from the blood stream. Thus, these so-called “stealth” properties of the PEO corona result in increased blood circulation times and allow the drugs to be administered over prolonged periods of time. A final feature that makes amphiphilic block copolymers attractive for drug delivery applications is the fact that their chemical composition, total molecular weight and block length ratios can be easily changed, which allows the control of the size and morphology of the micelles (Desnoyer, 2003).

The process of transferring water-insoluble compounds into the PO core of the micellar solution is referred to as solubilization. Pluronic micelles containing solubilized low molecular mass drugs, such as polypeptides, are being actively investigated as potential drug delivery systems (Marin, 2002; Muniruzzaman, 2002; Marin, A., 2001a; Marin, A., 2001b; Hussein, 2000). The core-shell architecture of polymeric micelles is essential for their use in these applications. The core formed by the PO chains is a water-incompatible compartment that is segregated from the aqueous exterior by the hydrophilic chains of the EO corona, thereby forming, within the core, a ‘cargo hold’ for the incorporation of various therapeutic reagents. As a result, polymeric micelles can be used as efficient carriers for compounds, which alone exhibit poor solubility, undesired pharmacokinetics and low stability in a physiological environment. The hydrophilic shell contributes greatly to the pharmaceutical behavior of block copolymer formulations by maintaining

the micelles in a dispersed state, as well as by decreasing undesirable drug interactions with cells and proteins through steric-stabilization effects.

Pluronic micelles can also be used to protect microorganisms. Mammalian cells are very useful in the biotechnology industry for the production of complex proteins, but they are easily destroyed by high shear. It was observed that Pluronic F68 can protect them from destruction. Miksik and coworkers (2002) found that Pluronic copolymers have the potential to be used as an effective separation medium in capillary electrophoresis (CE) for the separation of biomacromolecules such as DNA and proteins.

Pivitera (1995) suggest that Pluronic block copolymers can be useful as the components of novel self-assembling gene delivery systems. Gebhart and coworkers (2002) evaluated several non-viral transfection systems based on the complexes of DNA and polycations with respect to their effectiveness, toxicity and cell type dependence in a variety of in vitro models. High stability of the block-graft copolymer-based complexes is evidently due to the formation of micelle-like structures, which include the DNA, polycation and block copolymer chains.

2.1.5 Chemical Modification of PEO-PPO-PEO Copolymers

There are some disadvantages in the use of Pluronic copolymers for various applications. The CMC of Pluronic copolymers is too high due to the weak hydrophobicity of PPO block and the strength of gels formed from Pluronic copolymers is weak because they are only cross-linked physically; hence, chemical modifications of Pluronic copolymers will not only improve the properties of the polymers but also impart new and more attractive properties to them.

Bromberg, L. (1998a) has synthesized the PEO-PPO-PEO block copolymers with poly (acrylic acid) (PAA), thereby imparting a dual responsive property (i.e. pH and temperature) to the polymer by dispersion/emulsion polymerization. The PEO-PPO-PEO-g-PAA graft polymer has high molecular weight and extreme temperature sensitivity. Compared with Pluronic copolymers, the graft copolymers can form reversible gels with significant elastic moduli in water at lower concentration above a certain temperature. Pluronic F127 can form gels at body temperature in aqueous solution only above 16wt%, but F127-PAA exhibits enhanced viscosity in moderately low aqueous solution (1-3wt%). The strength of the gel increases with pH until a critical pH value, above which the PAA segments expand with increasing pH due to the repulsive interactions between the ionized carboxylic groups. Thus, PAA chain has the ability to participate in the increase of the size of the aggregates, which results in the enhanced viscoelasticity of the gels.

Ha and coworkers (1999) studied the Pluronic copolymers which have also been hydrophobically modified with polycaprolactone (PCL). The copolymers PCL-Pluronic-PCL are synthesized by the ring opening polymerization of the monomer ϵ -caprolactone using the Pluronic copolymers as the initiator and stannous octoate ($\text{Sn}(\text{Oct})_2$) as the catalyst. The PCL-Pluronic-PCL copolymers can self-assemble into micelles in water at lower CMC than the Pluronic copolymers. The structure of the micelle consists of a core-shell structure, with the inner core containing PCL and the outer shell comprising PEO-PPO-PEO segments. It is surprising to find that the size of micelle decreased with increasing the temperature. This may be attributed to the hydrophobicity of PPO block which increases with increasing temperature. Kim and coworkers (2000) also studied the interaction between PCL block in the core and PPO block in the shell.

2.2 Water-soluble Polymer----Polyvinyl Pyrrolidone

2.2.1 Background and Basic Properties of PVP

Polymers represent a growing and promising field of therapeutics. One such a polymer is polyvinyl pyrrolidone, which was first developed by Rappe (1949) in 1930 in his pioneering work in acetylene chemistry. Polyvinyl pyrrolidone (PVP) is a macromolecular polymer of N-vinylpyrrolidone. Chemically, PVP is a polymeric lactam. Polyvinyl pyrrolidone, brand name Povidone, is known as one of the major additives to gastrointestinal pharmaceutical preparations. This polymer has a lot of interesting properties. Some of these properties, such as water solubility, low toxicity, and physiological compatibility, led to its first use in 1940 as a plasma extender. Later clinical and chemical experience suggested other important therapeutic and scientific benefits.

2.2.2 Amphiphilic Poly(vinyl pyrrolidones)

PVP is a well-known water-soluble, biocompatible and relatively amphiphilic polymer. The highly polar amide confers hydrophilic and polar attracting properties to the polymer while the apolar methylene group in the backbone and the methine group in the ring contribute to its hydrophobic properties (Rothschild, 1972). PVP is more hydrophobic than PEO. And the modification of Poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) using PVP can be taken in certain degree as the hydrophobic modification of PEO-PPO-PEO by PVP. Homopolymer PVP can interact well with many

kinds of surfactants, such cationic surfactants, anionic surfactants and nonionic surfactants (Shannigrahi, 2005; Yuan, 2005; Khan, 2005; Shen, 2004; Feng, 2003).

2.2.2.1 PVP Synthesis

PVP is usually synthesized by the free-radical polymerization of vinyl pyrrolidone with some amphiphilic water-soluble polymers, such as amphiphilic derivatives of PVP. The polymerization of VP is carried out under dry argon atmosphere in the dioxane solution in the presence of an initiator. To prepare PVP with different molecular weight, chain-transferring agent sometime should be added to the system. Different ended PVPs use different chain transferring agents. Molecular weight of the polymers depends on the concentration of the corresponding chain-transferring agent. The molecular weight decreases with an increase in the amount of chain-transferring agent, such as mercaptan, added to the system.

Torchilin and coworkers (2001) have studied the formation of S-PVP and P-PVP which are amphiphilic PVP with the end stearyl or palmityl residues respectively. They indicated that to attach stearyl or palmityl groups, a corresponding polymer was dissolved in dry dioxane, and then excessive amounts of triethylamine and stearyl chloride or palmitoyl chloride in the same solvent was added. The mixture was then purified from any precipitate by filtration, and modified polymers were precipitated into diethyl ether, repeatedly washed with ether, and dried in vacuum until a constant weight. In all the experiments, the actual polymer yield was close to the theoretical yield.

Michalakis and coworkers (1999) investigated the influence of different chain length polyvinyl pyrrolidone-palmityl conjugates on the thermotropic phase behavior of 1,2

dipalmitoyl-sn-glycero-3-phosphatidylcholine bilayer which is a self-assembled colloidal structure composed of concentric phospholipid bilayers enclosing an aqueous space. Their results indicated that chemical conjugation of PVP to a lipophilic acyl anchor that directs grafting of the polymer to the liposomes surface is not able to inhibit interaction of the polymer backbone with liposomes.

2.2.2.2 PVP Applications

Since PVP discovery, the applications of PVP have increased tremendously. Murnper and coworkers (1998) reported the use of PVP as a protective agent during plasmid delivery to muscle. Ziebell and coworkers (2001) studied the extent of the binding affinity of PVP toward small molecules in aqueous solution. Polson and coworkers (1964) took advantage of certain PVP properties, such as water solubility and formation of complexes with anion and neutral organic molecules.

Mohr and coworkers (2002) showed that PVP is metabolically inert in rat, dog and man as shown by experiments using ^{14}C labeled PVP. It has been widely used as plasma expander. The excretion of PVP is inversely related to molecular weight. The glomerulus can excrete all PVP of molecular weight 40 000 or below within a few days. Baritaki and coworkers (2002) showed that Low molecular weight PVP adsorbs various substances, e.g. bacterial toxins, inorganic poisons, barbiturates, vitamins and hormones in the blood, either reducing their toxicity or prolonging their activity.

As a binder in the preparation of tablets through the process of granulation, PVP remains the prefer recipients. Its inclusion in dry form pharmaceuticals offers enhancement of the dissolution rates and bioavailability of drugs with low solubility. Stubberud and

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coworkers (1996) examined the relationship between the moisture sorption and compaction properties of microcrystalline cellulose, MCC, and the binary mixtures of MCC with a completely amorphous PVP. MCC contains various fractions of amorphous structure depending not only on the quantity used but also on the pharmaceutical processing. The tensile strength of tablets of MCC is dependent on the relative humidity, prior to compaction.

Chou and coworkers (2000) studied the effects of protective agents such as PVP on the synthesis of nanosized silver particles by chemical reduction using formaldehyde in aqueous solution. The products were mainly characterized by its particle size distribution to provide information on the optimal conditions of synthesis and sufficient stability against coagulation. The changing of the PVP/Ag weight ratio could produce silver colloids having the different sizes, between 7 and 20 nm.

2.2.2.3 Interaction of PVP Copolymer with Additives in Aqueous Solution

The interaction between polymers and surfactants in aqueous solution has attracted much interest in recent years due to the application of these systems in many industrial products such as paints, coatings, cosmetic products and medical field (Esumi, K., 1993a; Esumi, K., 1993b; Lin, 1999). The most extensively studied systems have been those consisting of uncharged polymers and ionic surfactants or polyelectrolytes and oppositely charged surfactants. In the first category, a strong interaction between uncharged polymers, such as poly (vinyl pyrrolidone) and anionic surfactants like sodium dodecyl sulfate (SDS), has been observed by Shannigrahi, (2004). At the same time, cationic surfactant interacts only weakly, if at all, with PVP, while for more hydrophobic polymers such as PPO, significant interactions were detected.

Roscigno and coworkers (2001) investigated the interaction of anionic surfactants, sodium alkylsulfonate, with nonionic polymers, poly(vinylpyrrolidone) using many methods such as surface tension, viscosity, intradiffusion, and interdiffusion measurements. The results showed the absence of detectable specific short-range interactions between PVP and the longer alkyl chain surfactants of the sodium alkylsulfonate. He verified the different behavior between alkyl sulfate and alkylsulfonate in the presence of PVP.

Misselyn-Bauduin and coworkers (2001) also investigated the interaction of PVP with an anionic surfactant (SDS), a non-ionic surfactant (pentaethylene glycol monodecyl ether, $C_{10}E_5$), and a zwitterionic surfactant (lauryl amido propyl betaine, LAPB). The results confirm the strong interaction prevailing in the PVP/SDS system. And the mixing PVP with two surfactants, namely SDS and $C_{10}E_5$ or SDS and LAPB, results in the formation of ternary aggregates between the polymer and the mixed micelles.

Benrraou and coworkers (2003) also studied the interaction between poly(ethylene oxide) or poly(vinylpyrrolidone) and cesium and tetraalkylammonium dodecylsulfate by means of electrical conductivity. He found the interaction between PVP and anionic surfactants is stronger than that of PEO with anionic surfactants. He also studied the relationship between the value of CMC of mixture and the radius of the counterion in the surfactant which means the strength of the interaction depends on the counterion radius.

Olofsson and Wang (1994) used the method of the titration microcalorimetry to investigate the interaction between ionic surfactants and uncharged polymers in dilute aqueous solution. The resulting enthalpic titration curves give detailed information about

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polymer-surfactant interactions. He concluded: although the experimental data showed there is no obvious interaction of the polymers, PEO and PVP with cationic surfactants, there is no significant difference between the interaction of the anionic and cationic surfactants with PEO and PVP in theory. At the same time, he also confirmed PVP interact with SDS stronger than PEO because it is more hydrophobic.

Gharibi and coworkers (1998) studied the interaction between a series of n-alkyl trimethyl ammonium bromides and polyvinyl pyrrolidone by a potentiometric method using a surfactant-selective electrode. The investigation showed the binding isotherms can be measured which were used to calculate an apparent Gibbs energy of binding per surfactant cat ion. It was also found that the aggregation of PVP-surfactant complexes is concentration dependent.

Sesta and coworkers (1997) investigated the interaction of polymer, poly(vinyl pyrrolidone) with a special surfactant, lithium heptafluorononanoate (LiPFN) using the methods such as proton NMR, surface tension, viscosity and volume evidence. The results confirmed that there is hydrophobic interaction in LiPFN-PVP system.

2.3 Graft Copolymerization

Graft and block copolymers contain long sequences of two or more different monomers in the copolymer chain. In general, a graft copolymer contains a long sequence of one monomer with one or more branches consisting of long sequences of a second monomer. A variety of techniques for synthesizing these structures have been studied (Colombani, 1997 and Forster, 1998). Some of the more useful or promising methods will be reviewed here.

2.3.1 Synthesis of Graft Copolymer

The synthesis of a graft copolymer requires the formation of a reactive center on a polymer molecule in the presence of a polymerizable monomer. Most methods of synthesizing graft copolymers involve the use of radical graft polymerization, although ionic graft polymerizations are receiving increasing attention. Graft polymerizations are carried out successfully in either homogeneous or heterogeneous systems depending on whether the polymer being grafted to is soluble or insoluble in the monomer. There are a lot of techniques used to proceed radical graft polymerization, such as chain transfer and copolymerization, ionizing radiation, ultraviolet radiation, redox initiation and so on. Chain transfer and copolymerization system is used mostly to obtain the graft copolymers. The author also employed this system to achieve the graft copolymerization. The range of radical grafting systems has been studied. Almost all of the common monomers such as styrene, methyl methacrylate, vinyl chloride, and acrylonitrile have been grafted to almost all of the commercially available addition and condensation polymers by Wang, W. X. (2003), Mondal (2003) and Zhang (2003).

The radical polymerization of a monomer using an initiator such as benzoyl peroxide can result in grafting via radical formation on the polymer backbone.

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Although chain transfer usually involves hydrogen abstraction, some polymers contain groups more labile than hydrogen. Abbasi and coworkers (2002) studied the chlorine abstraction which occurs with chlorinated rubber. Polymeric radicals such as I are also formed by attack on the polymer by primary radicals from the initiator. For the polymers containing double bonds such as 1, 4-polybutadiene, graft polymerization involves copolymerization between the polymerizing monomer and the polymer, in addition to the chain transfer sequence described by Equations 2.2 and Equation 2.3.

Egboh and coworkers (2002) discussed the grafting copolymer N-vinyl pyrrolidone on polyurethane. This grafting was done directly under vacuum, N₂ or air by using γ -ray or accelerated electrons. Aydinli and coworkers (2001) used monomers of some water-soluble polymers such as 1-vinyl-2 pyrrolidone, grafted on ultra-high molecular weight polyethylene (UHMWPE) powders by a direct grafting method in an aqueous medium in air. At the same time, various concentrations of Fe²⁺ or Cu²⁺ ions were added to inhibit homopolymerization.

Brunius and coworkers (2001, 2002) designed a novel family of hydrosoluble biomaterials: PVP-based graft copolymers. The route was elaborated in which functionalized PVP is prepared via chain-transfer radical polymerization, and subsequently grafted onto a polyhydroxylated backbone, dextran. The finished graft copolymer which is degradable biomaterials has a stronger potential for plasma expansion.

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Eguiburu and coworkers (1996) synthesized the biodegradable-biocompatible comb-like copolymers with different hydrophilic characteristics via grafting N-vinyl pyrrolidone, methyl methacrylate, methyl acrylate N, N'-dimethyl acrylamide onto Poly(L-lactide) macromonomers. He concluded the compatibility between the growing chain and the macromonomer plays the main role in the copolymerization behaviour.

2.3.2 Graft Copolymer and its Applications

Many graft copolymers are designed to integrate the benign nature of several polymers and have many important applications in the polymer industry, mainly as surface modifiers in the coatings, adhesives, dispersants, as compatibilizing agents in polymer blends, and also biomedical applications (Jeong, 2003; Yu, 1998; Radhakrishnan, 1997; Lin, 1992; Fujioka, 2003; Razzak, 1992; Bogdanov, 1995; Iguchi, 1996; Ringrose, 1999; Li, 2003). The polymers and copolymers prepared by the polymerization of poly(ethylene oxide) macromonomers with acrylic and vinyl comonomers have been extensively studied as semi-permeable membranes for biomedical applications, as well as support systems for the preparation of microcapsules and nanoparticles that are being used in drug delivery systems

Gao and coworkers (1998) studied the graft copolymerization of N-vinylpyrrolidone (VP) onto gelatin using different initiator systems such as AIBN, $K_2S_2O_8$ and so on. The relationships between the rate of grafting and the concentration of initiator, monomer, and gelatin were established experimentally. They also find that the adding of the graft copolymers Gel-g-PVP into the coating films can improve the prewetting ability of the film.

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Polymer and polymer solutions can be characterized using a variety of techniques. The selection of these techniques is primarily based on the type of properties to be studied and the state of the polymer. In this thesis, the author is interested in the structure and components of the copolymers and the micellization properties of copolymers in aqueous solution. The structure of graft copolymer chains and the molecular weight of graft copolymer were studied using Fourier Transform Infrared Spectroscopy (FTIR), nuclear magnetic resonance (NMR) and size exclusion chromatography (SEC). To determine the transition temperature and concentration, differential scanning calorimetry (DSC) and surface tension measurement (ST) were used. To determine the micellar size, dynamic light scattering (DLS) was used. The association number is determined using both the intrinsic viscosity and the micellar size. This chapter will give a brief description of the materials used and cover the techniques which are used later in the discussion namely Chapter 4, 5 and 6. This chapter will provide an overview of the various techniques and how they were applied.

3.1 Raw Materials

Pluronic F127 was purchased from Fluka and used without further purification. It has a formula of $\text{EO}_{100}\text{PO}_{65}\text{EO}_{100}$ and a nominal molecular weight of 12,600. The molecular weight of PPO segment is 3780 and 70 wt% of the chain is made up of EO. The cloud point of F127 is above 100 °C. N-Vinyl pyrrolidone (VP) was obtained from Fluka and

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distilled at 100 °C before use. PVP (poly vinyl pyrrolidone) with a molecular weight of 10,000 was obtained from Sigma-Aldrich. Dioxane (HPLC grade) and diethyl ether (HPLC grade) were purchased from Fisher company and used without further purification. Acetone (HPLC grade) and ethanol (HPLC grade) were obtained from J. T. Baker and used as received. Figure 3.1 shows the chemical structures of some of the materials used.

Figure 3.1 Molecular structures of some of the materials used.

Four initiator systems were used. Lauroyl peroxide (97%, LP) was obtained from Lancaster and used as received. 2, 2'-azobisisobutyronitrile (98%, AIBN) was bought from Tee hai and recrystallized from methanol before being used. Initiator 1, 1'-azobiscyclohexanecarbonitrile (Vazo 88) was purchased from Dupont Specialty chemicals and was recrystallized from cold acetone. Lastly, benzyl peroxide (BP) was obtained from Fluka.

3.2 Characterization of Graft Copolymers

3.2.1 Nuclear Magnetic Resonance (NMR)

NMR spectroscopy is well established as one of the most useful techniques for characterizing polymeric materials. It has been developed since the first discovery of a

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signal from the protons of water by Bloch and co-workers and a signal from paraffin wax by Purcell and coworkers in 1945. Significant developments in the instrumentation and experimental techniques have occurred over the past twenty years resulting in improvements in sensitivity and spectral resolution. Polymer scientists and technologists have taken full advantage of these developments and important strides have been made in our understanding of the detailed chain structure of polymers and copolymers. NMR has also provided a means for identifying intermediate structures. A comprehensive treatment of the theory and experimental aspects has been made available by Pople (1959) and Slichter (1978).

3.2.1.1 The NMR Spectrometer

There are many nuclei that are suitable for NMR. The choice of the nuclei should be based on its abundance and whether the resonance condition is satisfied, that is, the quantum number is non-zero. Nuclei with $I = \frac{1}{2}$ are most suitable because they satisfy the resonance condition and can interact with other similar nuclei to give rise to splitting patterns.

Figure 3.2 Schematic of NMR spectrometer.

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The typical arrangement of an NMR spectrometer is shown in Figure 3.2 (Campbell, 1989). It consists of 5 main components: high field strength magnet, radio frequency source, NMR probe, sweep system and amplification and recording system. The magnet is required to have high homogeneity and may be a permanent magnet, an electromagnet or a superconducting magnet. Field strengths are normally in the range 1.4 to 2.3 T corresponding to operating frequencies of 60 and 100 MHz respectively. The radio frequency source is a crystal controlled oscillator having high stability (1 in 10^9). The NMR probe consists of transmitter and receiver coils which surround the sample and act to couple the incident radio frequency and the receiver signal to the sample. When the resonance condition is satisfied, the sample absorbs energy from the transmitter and the change in the coil is detected by the receiver coil and is then amplified as the NMR signal. The sweep system may be operated by either varying the magnetic field or varying the frequency. The NMR signal is recorded by sweeping through the resonance position from low to high field. The samples are contained in glass tubes (about 5-12 mm diameter), located in an air driven rotating spinner. The higher the spinning frequency, the higher the intensity of the signal and the smaller the spinning side band signals which result from sample spinning. Rates of up to about 200 rpm are used. It is common practice to locate a reference standard in a small capillary tube within the sample tube. The NMR studies were carried out on a Bruker 400MHz instrument, operating at 400 MHz (^1H). CDCl_3 was used as the solvent and TMS was used as the internal zero reference. The ^1H -NMR spectra were recorded.

3.2.1.2 Interpreting the Spectrum

The NMR spectroscopy is concerned with the detection of the absorption or the emission of electromagnetic radiation by stimulated transitions between energy levels in the system

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under investigation. Since the energy levels are influenced by the environment of the nuclei, the resulting spectrum gives more or less direct evidence regarding the chemical nature of interacting atoms, both qualitatively and quantitatively. A NMR spectrum arises from the interaction of the applied electromagnetic radiation with the nuclear spins when the energy levels in the latter are split by an external magnetic field. The ^1H -NMR can also be used in polymer characterization to determine branching, tacticity, structural defects, the sequence of comonomer units in a copolymer chain and chemical changes such as oxidation states. In this work, the structural of the graft copolymer, that is branching of copolymer under different synthesis condition, is investigated. To do that, some signs of changes in structure, namely chemical shifts and spin-spin couplings, will be studied.

In the absence of other interactions, for a given applied frequency and nuclear spin type, NMR resonance would only be observed at a single value of field strength and this would result in a single absorption peak. In fact, the field experienced by the nucleus is modified due to magnetic shielding by electrons orbiting the nucleus Figure 3.3. In effect, induced electric currents produce magnetic fields which oppose the applied magnetic field. The higher the electron density around the nucleus and the higher the applied field, the greater the extent of shielding.

Figure 3.3 Induced secondary field, B_s , opposing the applied field, B_0 , hence reducing the impact of the field on the nucleus.

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Chemical shift is the result of nuclear shielding by the electron cloud surrounding the positive nucleus. When an atom/molecule is placed in a magnetic field, the induced motion of the electrons around the nucleus set up a secondary, opposing magnetic field and shield it from the full impact of the magnetic field. The resonant frequency for a given type of nucleus is directly proportional to the magnetic field felt at the nucleus. The result of the shielding is that the applied field has to be increased to compensate for the reduction due to this effect. The chemical shift is given by

$$\delta = \frac{(\nu_{reference} - \nu_{sample})}{\nu_{spectrometer}} \times 10^6 \text{ ppm} \quad (3.1)$$

Where $\nu_{reference}$ is resonant frequency of reference, ν_{sample} is resonant frequency of sample and $\nu_{spectrometer}$ is spectrometer frequency. If a proton is bonded to a carbon atom with a substituent atom, X, more electronegative than carbon, the proton is going to be deshielded, resulting in a downfield shift and the chemical shift is going to increase. This shift is known as paramagnetic shift. This is what happens in proton chemical shifts. If the substituent atom, X, is less electronegative than carbon, then the proton is going to be more shielded, resulting in a decrease in the chemical shift, and, hence, an upfield shift.

The electron withdrawing inductive effect affects predominantly the nearest proton and is

known as the geminal effect (, germinal hydrogen) and the electron-donating conjugative effect, which affects mainly the vicinal protons, is known as vicinal effect

(, vicinal hydrogen).

One important implication of these shifts is in the case of the presence of hydrogen bonding between X and another H-atom. When a H-bond is formed, the hydrogen

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becomes more positive and the proton becomes deshielded and moves to a lower field, hence higher δ (Massiah, 2001).

3.2.2 Fourier Transform Infrared Spectroscopy (FTIR)

In attempting to identify and characterize polymeric materials, almost invariably recourse will be made to some form of vibrational spectroscopy. When used either alone or in conjunction with other physicochemical techniques, vibrational spectroscopy is capable of providing detailed information on polymer structure (Siesler, 1980; Maddams, 1982).

Vibrational spectroscopy is concerned with the detection of transitions between energy levels in molecules which is a result from the vibrations of interatomic bonds. The vibrational frequencies are shown to be characteristic of particular functional groups in molecules. They are sensitive to the molecular environment, chain conformations and morphology and, hence, afford a useful method for polymer analysis.

At room temperature, most molecules exist in their ground vibrational states and, in order to excite them to higher vibrational states, energy must be absorbed. The two experimental techniques which are used to detect changes in vibrational energy states are infra-red spectroscopy (IR) and Raman spectroscopy. In this work, infrared spectroscopy is used to study the chemical structure of the graft copolymers.

3.2.2.1 Fundamentals of Vibrational Spectroscopy

When molecular vibrations result in a change in the bond dipole moment, as a consequence of change in the electron distribution in the bond, it is possible to stimulate

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transitions between energy levels by interaction with electromagnetic radiation of the appropriate frequency. In effect, when the vibrating dipole is in phase with the electric vector of the incident radiation, the vibrations are enhanced and there is transfer of energy from the incident radiation to the molecule. It is the detection of this energy absorption which constitutes IR spectroscopy.

In practice, the spectral transitions are detected by scanning through the frequency whilst continuously monitoring the transmitted light intensity. The energies of molecular vibrations of interest for analytical work correspond to electromagnetic wavelengths in the range 2.5-25 μm or, when expressed conventionally in terms of wavenumber, 4000-400 cm^{-1} .

The Perkin Elmer system 2000 Fourier Transform Infrared Spectrometer was used to characterize the polymer. First, a background spectrum was run. The copolymer sample was then thoroughly mixed with KBr powder upon careful grinding and then the mixture is pressed into pellets. The spectrum of the mixed pellet was then collected against the spectrum of the background. A total of ten scans at a resolution of 4 cm^{-1} (in the Mid IR region of 4000-400 cm^{-1}) were obtained to achieve a good signal-to-noise ratio.

3.2.2.2 Fourier Transform Spectrometers

Fourier transform spectroscopy was used to investigate the whole IR region of the spectrum. The interferogram is an intensity function of the path difference, x . The absorption spectrum is derived from the interferogram by a Fourier transform of the form

$$G(\nu) = \int_{-x_1}^{+x_1} I(x) \cos 2\pi\nu x dx \quad (3.2)$$

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where $G(\nu)$ is the spectral distribution at a given frequency (ν). The transformation is carried out on a range of intensity values $I(x)$ at different path lengths x to give the spectral intensity at the given frequency. The signal must be sampled at precise path differences. This is achieved by using a He/Ne laser whose beam traverses the same optical path and the interference produced by the laser is used to trigger the sampling of the IR signal. Typical detectors include Golay cells. The Fourier transformation is usually carried out by means of a built-in dedicated microprocessor, enabling the absorption spectrum to be produced in a relatively short time.

The movement of the mirror determines the resolution of the spectra in different IR frequency ranges. Rapid scan speeds (3 mm s^{-1}) are used for the middle infra-red region (4000 to 400 cm^{-1}), whereas much lower scan speeds (0.005 mm s^{-1}) are necessary in the far IR region. Rapid scan speeds were used for all the samples in this study.

3.2.2.3 Group Frequencies

Although it is possible to predict the expected vibrational spectra of molecules, most spectroscopic investigations rely on a much more empirical approach, that is the concept of group frequencies. It is based on the fact that the vibrational frequencies of particular chemical groups in molecules such as C=O, C-O-C, tend to behave largely independently of the rest of the molecule. In other words, the degree of mechanical or electrical coupling between vibrations of atoms in the group in question to those in neighbouring groups is minimal. Consequently, the absorption frequencies for a particular chemical group are essentially constant and the absorption bands appear in roughly the same region of the spectra. This means that it is possible in most cases to assign particular absorption

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bands to vibrations in the groups by reference to standard correlation tables (Haslam, 1980).

3.2.2.4 Quantitative Analysis

The variation of light intensity on passing through an absorbing medium may be expressed in terms of the Beer-Lambert Law,

$$A = \log \frac{I_0}{I} = abc \quad (3.3)$$

where A is the absorbance, I_0 is the incident light intensity, I the intensity at a depth b in the absorbing medium, c the concentration of the absorbing species, and a is a constant for the material termed the absorptivity or extinction coefficient. Transmittance is defined as $T=I/I_0$ so that percentage transmittance is $100I/I_0$ and absorbance, A is $\log I/T$. In principle, determination of the concentration of the absorbing species can be made by direct application of the Beer-Lambert Law, provided that the extinction coefficient for the species at the particular wavelength is known. It is more common, however, to use comparative methods for quantitative analysis of polymers. Quantitative analysis is best carried out in solution, but usually, there is a need to examine polymers in the solid state, e.g. as thin films or in the form of KBr discs. Some problems arise with uniform film thickness or homogeneous distribution of absorbing species and optical effects such as extraneous light scattering means that there is a need for great care when attempting absolute measurements.

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More reliable results are usually obtained when it is possible to compare the sample under investigation with a standard reference material located in the reference beam of dual beam spectrometers. In general, it is possible to use internal reference standards.

3.2.2.5 Specimen Preparation

Polymers are usually examined in the solid state and the nature of the technique imposes some limitations on the form of sample which may be examined. In general solids have strong IR absorptions which means that the samples have to be relatively thin or the absorbing species only present in low concentration when dispersed in a transparent medium.

Standard sample preparation techniques used for IR examination of non-polymeric materials including filled KBr discs are also employed in this study when examining polymeric materials. The KBr and the polymer samples were finely ground, dispersed to give an approximately 1% concentration of the polymer then pressed in a die using a combination of pressure to produce a thin disc.

3.2.3 Size exclusion Chromatography (SEC)

The molecular weight (M_w) and molecular weight distribution (M_wD) of the polymers were determined using an Agilent series 1100 gel permeation chromatograph. The equipment consists of an isocratic pump, an online degasser, an auto-sampler, a thermostat column compartment and a refractive index detector. A mixed bed column (PLGel Mixed Bed C, 5 μ m, 300 x 7.5 mm, Polymer Laboratories), along with a guard

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column (50 x 7.5 mm, Polymer Laboratories) was used. The mobile phase was a mixture of tetrahydrofuran (THF) and dichloromethane (DCM) in a volume ratio of 80:20. The molecular weights of the samples were obtained relative to the polystyrene (PS) standards. The flow rate was 1 mL/min and the temperature (both the column compartment and the flow cell of the refractive index detector) was 35 ± 0.1 °C.

The samples were dissolved in the mobile phase and filtered through 0.22 µm disposable syringe filters into 2 mL glass vials. These vials were then put into the auto-sampler tray. The typical injection volume was 20 µL.

Although SEC is fast and rapid method to obtain the weight average molecular weight and molecular weight distribution, it has its own limitation. If the structure of the sample is largely different from that of PS, which is used to do the calibration and comparison in SEC, SEC results are not reliable.

3.3 Solution Behavior of the Graft Copolymers

3.3.1 Sample Preparation in Aqueous Solution

Pluronic-g-PVP copolymers were dissolved in distilled water. The solutions were allowed to equilibrate for more than 24 hours at room temperature. The sample solutions were centrifuged in order to remove any dust that may exist in the test solutions.

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3.3.2 Differential Scanning Calorimetry (DSC)

In the study of the material properties, the term ‘thermal analysis’ is frequently used to describe the experimental techniques that are used to study materials response to temperature or variation of material properties as a function of temperature. In polymer science, preliminary investigation of sample transition temperatures and decomposition characteristics are routinely performed using thermal analysis. Some methods, such as differential thermal analysis (DTA) and differential scanning calorimetry (DSC) are specifically designed to measure the thermal properties of the material under examination. In this work, since the phenomena of interest is micellization which is an endothermic process, the heat flow into the system will give an indication of when micellization takes place. DSC is the technique that can be used for heat flow measurements.

3.3.2.1 Principle of DSC and Instrumentation

Power compensation DSCs are the most commonly used in recent years. The sample and reference are heated separately and the power supplied to the heaters is adjusted continuously to keep the sample and reference at the same temperature. The differential power required to achieve this condition is recorded. To do this accurately and to remove any instrumental effects, baseline setting is critical.

Essential features of a DSC apparatus are shown in Figure 3.4. The sample is placed in cell S, located in a block that can be heated or cooled at a programmed rate. A reference sample in an identical cell is located close to the sample cell. The sample and the reference are provided with independent heater. Background heating of the block may be provided separately to give approximate adherence to the programmed rate, but the individual heaters are used to maintain the sample and reference cells at the programme

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temperature. The temperature of each cell is measured continuously and compared with the instantaneous value of the programme temperature. The power delivered to the sample and the reference cells via the individual heaters is a function of the departure from the programme temperature respectively. The differential power requirement is the quantity plotted and can be presented as a function of temperature.

Figure 3.4 Schematic of a DSC apparatus: r is reference; s is specimen.

Our studies were conducted using a DSC (DSC 2920, TA Instruments, USA), equipped with refrigerated cooling system (RCS), under a constant flow of nitrogen (50 mL/min). The aqueous solutions of copolymers (5-15 mg), were hermetically sealed in aluminum pans under dry conditions. To test the thermal responsiveness of the sample, the sample was cooled down to 2 °C and equilibrated for 10 minutes. The sample is then heated up to 50 °C at 5° Cmin⁻¹. Following that, the sample was cooled to 2 °C at 5 °C/min. Figure 3.5 shows a typical scan where a endothermic peak, indicating the micellization transitions can be observed. The apparent critical micellization temperature is taken to be the minimum point of the endothermic signal, T_p.

Figure 3.5 Typical DSC curve.

3.3.2.2 Quantitative Analysis in DSC

Enthalpy of transition can be determined by using the area under a DSC curve. The most common method is to calibrate the energy scale of the instrument with a standard reference material whose enthalpies of melting are well characterized and whose melting temperatures extend over a wide temperature range. Using a certain peak area corresponding to a known value of the standard enthalpy and under identical experimental conditions, the enthalpy of transition can be estimated as its area is proportional to the integral of $d(\Delta H)/dT$ with respect to temperature. The peak area is related to ΔH by the following equation:

$$PeakArea = mk\Delta H \quad (3.4)$$

where m is the mass of the sample and k is a calibration constant, which is found by calibrating with a sample such as indium with a known enthalpy of fusion peak.

3.3.3 Fluorescence Spectroscopy

The fluorescence studies were carried out by RF-5301 fluorescence spectrophotometer (SHIMADZU). The essence of fluorescence analysis is sensitivity. The high throughput

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optical system in the RF-5301PC employs a blazed holographic grating, photomultiplier and digital signal processing to provide the highest level S/N ratio attainable. The advantages of this technique are high speed scanning and high resolution and extended spectral range.

Pyrene has been extensively used as a fluorescence probe to investigate the formation of hydrophobic microdomains by surfactants. Its structure is shown in Figure 3.6. In particular, the pyrene spectrum shows several vibronic peaks, and the ratio I_1/I_3 of the intensities of the first and third peak is a sensitive indicator of the polarity of the pyrene microenvironment. The apparent critical micelle concentration (CMC) of the polymers was estimated by a steady-state pyrene fluorescence method, which is based on the shift in the (0,0) band of pyrene in the excitation spectra from 373 to 383 nm due to its incorporation in the hydrophobic core of the micelles. In general, a 2 mL aqueous solution of pyrene (2×10^{-7} M) was added to a 2 mL polymer solution with increasing concentrations (0.005-150g/L). This solution was kept at room temperature in the dark and stirred gently for one night. Their excitation spectra were recorded. The CMC was determined from the intersection of two straight lines (one line with an almost constant value of the ratio $I_{373\text{nm}}/I_{383\text{nm}}$ and the other line with a steady decrease in the ratio value) on the graph of the fluorescence intensity ratio $I_{373\text{nm}}/I_{383\text{nm}}$ vs log polymer concentration.

pyrene

Figure 3.6 The structure of pyrene.

3.3.4 Surface Tension (ST) Measurement

The molecules at the surface of a liquid have potential energies greater than those in the interior of the liquid. This is because attractive interactions of molecules at the surface with those in the interior of the liquid are greater than those widely separated molecules in the gas phase. Because the potential energies of molecules at the surface are greater than those in the interior of the phase, an amount of work equal to this difference in potential energy must be expended to bring a molecule from the interior to the surface. The surface free energy per unit area, or surface tension, is a measure of this work; it is the minimum amount of work required to bring sufficient molecules to the surface from the interior to expand it by unit area.

The FTA200 is a general purpose laboratory instrument for measuring surface tension, contact angles, and indirectly, surface energy and adhesion characteristics. The instrument uses “drop shape” analysis to make its measurements. It captures video images of droplets and analyzes their shape and size to determine surface tension, etc. It is capable of extremely accurate results if the experiments are carefully conducted. On a practical basis, the limitation on accuracy is the care the user takes in setting up and running the experiments.

Many different parameters can be determined from drop shape analysis. The more commonly used experiments are pendant drop surface tension. The author generally uses the Laplace-Young equation to fit the shape of a drop (John, 2002). A hanging pendant drop can be analyzed more reliably than can a sitting sessile drop, since one can safely assume axial symmetry for the pendant drop but not for the sessile drop. Unfortunately, the Laplace-Young equation can not be solved analytically in the general case. Therefore, all solution methods rely on numerical techniques and interpolations.

Figure 3.7 (Abrahmsen, 2002) illustrates a pendant drop and the Bashforth-Adams technique for solving the Laplace-Young equation. Surface tension is derived from drop shape. When measured manually, as with a ruler on a photograph, it suffers from the difficulty in finding S_E , the equatorial diameter, because many points have to be measured to determine the true maximum width. When measured automatically, it suffers from errors introduced by noise at the specific measurement points. The FTA200 extends this technique by optimally fitting curves to the regions of interest in the pendant drop in order to minimize noise effects. The various distances are then determined by solving the equations analytically. An alternative technique is to determine a drop shape parameter by interpolating the drop shape against a set of reference shapes. After the shape parameter is known, the solution follows the classical Bashforth-Adams technique. Given fluid density and the value of S_W/S_E (where S_E is the equatorial diameter of pendant drop, the relationship between S_W and S_E is shown in Figure 3.7), surface tension can be derived easily.

Figure 3.7 Pendant drop surface tension measured by the Bashforth-Adams technique.

3.3.5 Dynamic Light Scattering

Successful applications of scattering techniques, such as light scattering and neutron scattering, often involved a considerable amount of interdisciplinary knowledge.

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Chemists and physicists have utilized light scattering, small angle x-ray scattering (SAXS) and small-angle neutron scattering (SANS) to study the size and shape of macromolecules in solution as well as in a whole range of materials including colloidal suspensions and solid polymers. Wave interference yields information on particle size whenever the wavelength of the electromagnetic radiation is of the same order of magnitude as the size of the scatterer. In our work, the measurement of the particle size and its distribution was carried out by BI-MAS (multi angle sizing option on the Zetaplus, Brookhaven Instruments Corporation).

3.3.5.1 Theory of Dynamic Light Scattering

A typical light-scattering geometry is shown in Figure 3.8,

Figure 3.8 A typical light-scattering geometry.

where the incident beam (I_{INC}) impinges on the scattering medium (particles), with most of the radiation being transmitted (I_t) and a small portion being scattered (I_s). Laser light scattering study not only the changes in number (intensity) and the direction (momentum) of each type of photon in the incident and the emerging light beams, but also the corresponding frequency (energy) changes. Whereas the scattered intensity can be related to the structure of the particles, the optical spectra reveal the dynamical motions of the particles. The word ‘laser’ is used to emphasize its essential role in obtaining effective measurements of potential spectral where wavefront matching of scattered light must be accomplished. Thus, a laser source is needed in dynamic light scattering. Furthermore,

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‘laser light scattering’ is retained as the title so as to remind us of the importance of time-averaged light-scattering intensity measurements.

Figure 3.9 Scatter light intensity change with the time.

Particles that are suspended in a liquid are subject to Brownian motion. Small particles diffuse “faster” and large particles diffuse “slower”. The time variation of the scattered intensity is analyzed by examining their auto-correlation. From this a diffusion coefficient can be derived. From the measured diffusion coefficient, particle size is calculated.

When a beam of laser light is focused on the sample, particles in the scattering volume scatter light in all directions. The scattered photons are measured by a photomultiplier tube. The intensity appears to fluctuate randomly as shown in Figure 3. 9. The random motion of small particles in a liquid gives rise to fluctuations in the time intensity of the scattered light. The fluctuating signal is processed by forming the autocorrelation function, $C(t)$, t being the time delay. As time increases, the delay correlation is lost and the function approaches the constant background term B . For a short time the correlation is high. In between these two limits, the function decays exponentially for a monodisperse suspension of rigid, globular particles and is given by

$$C(t) = A \cdot e^{-2\Gamma t} + B \quad (3.5)$$

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where A is an optical constant determined by the instrument design, and Γ is related to the relaxation of the fluctuations by,

$$\Gamma = q^2 D \quad (3.6)$$

$$q = \frac{4\pi \sin(\frac{\theta}{2})}{\lambda} \quad (3.7)$$

where q is the line width, D is the Z-averaged diffusion coefficient, λ is the wavelength and θ is the scattering angle. The hydrodynamic diameter, R_h , can be calculated by using the following equation:

$$R_h = \frac{k_B T}{3\pi\eta D} \quad (3.8)$$

where k_B is the Boltzmann's constant, T is the absolute temperature and η is the viscosity index of the solvent.

3.3.5.2 Instrumentation

Figure 3.10 Overview of DLS Instrument.

An overview of the instrumentation is shown in Figure 3.10. High power 35 mW diode laser was used as the light source. Laser diodes emit electromagnetic radiation mainly beyond the visible range, but visible-light laser diodes have now become readily available.

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The size range of this instrument is 3nm to 3mm. All measurements were conducted at a measurement angle of 90°. The sample volume was 1 to 3 ml and contained in the disposable rectangular cell. The flat entrance and exit windows tend to reduce stray light scattering in the scattering cell. The temperature of the cell can be controlled from 8 °C to 75 °C. After the light passes through the sample in the cell, the scattering light was detected by the photomultipliers.

3.3.6 Capillary Viscosity

Relatively small amounts of dissolved polymer may cause tremendous increases in viscosity. If all the conditions are kept equal, larger molecules will impede flow more than smaller ones and give a higher viscosity. The interactions between the polymer and solvent are determined by the conformations of polymer molecules and the extent of entanglements between molecules in solution. Hence, the solvent viscosity, the temperature, the solute concentration and the type of polymer and solvent influence the viscosity of the polymer solution.

In this work, intrinsic viscosity of copolymers with and without additives at different temperature was measured. Using both the intrinsic viscosity of copolymer solution, $[\eta]$, and micellar size, R_h , the association number can be calculated using the following

equation $R_h^3 = \frac{3[\eta]M_m}{10\pi N}$ (Pandya, 1993), where M_m is the micellar molecular weight and N

is Avogadro's number.

3.3.6.1 Viscosity Measurements for Diluted Polymers

In this work, the viscosity measurements were done using the Ubbelodhe viscometer and the viscosity was calculated from the flow time of the polymer solution. To obtain the intrinsic viscosity, various viscosities are calculated. The definitions of the various viscosity quantities are as follows:

(i) Relative Viscosity, η_{rel}

As the absolute value of the viscosity is usually not important, relative viscosity is calculated instead and it is defined as

$$\eta_{rel} = \eta / \eta_s \quad (3.9)$$

where η is the viscosity of the solution and η_s is the viscosity of the pure solvent. In this work, the pure solvent is water. For dilute solutions and solutions containing solute with density close to that of water, the relative viscosities are evaluated using an extremely simple relation,

$$\eta_{rel} = t / t_0 \quad (3.10)$$

where t is the outflow time for solution, and t_0 is the outflow time for the pure solvent, water.

(ii) Specific Viscosity, η_{sp}

This viscosity refers to the relative increment of the viscosity of the solution over the viscosity of the solvent and can be found by,

$$\eta_{sp} = (\eta - \eta_s) / \eta_s = \eta_{rel} - 1 \quad (3.11)$$

Both the relative viscosity and the specific viscosity are dimensionless.

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(iii) Reduced Specific Viscosity, η_{red}

The specific viscosity in this case is taken as per unit concentration, c ,

$$\eta_{red} = \eta_{sp} / c = (\eta_{rel} - 1) / c \quad (3.12)$$

where c is the concentration of polymer in grammes per millilitres, that is weighed in 100ml of solution. The reduced viscosity has a dimension that is the inverse of concentration.

(iv) Intrinsic Viscosity, $[\eta]$

To eliminate the influence of entanglements on viscosity, the reduced viscosity is extrapolated to zero concentration giving the intrinsic viscosity $[\eta]$.

$$[\eta] = \lim_{c \rightarrow 0} \frac{(\eta / \eta_s) - 1}{c} \quad (3.13)$$

Huggins proposed a relation between reduced viscosity and concentration for dilute polymer solutions:

$$\eta_{red} = \eta_{sp} / c = [\eta] + k' c [\eta]^2 \quad (3.14)$$

Plots of the reduced viscosities are linear with concentration, at least at low concentrations, and have a common intercept, the intrinsic viscosity.

3.3.6.2 Instrumentation

The viscosity of polymer solution, η , is usually measured using capillary viscometer. This has some advantages such as high accuracy, easy operation, speed and low cost as compared with a rotational viscometer.

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The principle of the measurement is based on Poiseuille equation relating time, t , necessary for volume, V , of a liquid to flow through a capillary with radius, r , and length L , to the viscosity of the liquid, η , and the pressure difference ΔP between the ends of the capillary that is causing the flow (Munk, 1989). $t = \frac{8LV\eta}{\pi r^4 \Delta P}$, where $\Delta P = \rho gh$ where h is the height of the liquid level, ρ is the density of the liquid and g is the gravitation acceleration.

Therefore 3.10 can be expressed as $t = K \left(\frac{\eta}{\rho} \right)$, where K is an instrumental constant.

3.3.7 Static Light Scattering

The weight-average molecular weight can only be obtained directly by scattering experiments. The most commonly used technique is light scattering from dilute polymer solution. It is also possible to determine M_w by using small angle neutron scattering of specially prepared solid samples. Although this technique has great current importance in polymer research, it is not routinely used for molecular weight determination because of the difficulty and expense of sample preparation and the specialized facilities required. Hence, in this work, static light scattering is used to determine the molecular weight of the aggregates. The basic principles of light scattering measurements of dilute polymer solution are described next.

3.3.7.1 Theory and Instrumentation

The fundamental relationship for light scattering is given as

$$\frac{Kc}{R(\theta)} = \frac{1}{M_w P(\theta)} + 2A_2VC + \dots \quad (3.15)$$

where M_w is micellar weight, $R(\theta)$ is Rayleigh ratio, $P(\theta)$ is particle scattering function, A_2 is the second virial coefficient in the virial expansion of the osmotic pressure, C is

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polymer concentration and V the second virial coefficient in the virial expansion of the osmotic pressure (Todriguez, 1989).

$$K = \frac{2\pi^2 n_0^2}{N_A \lambda^4} \left(\frac{dn}{dc} \right)^2 \quad (3.16)$$

Where n_0 is the refractive index of the pure solvent; dn/dc is the specific refractive increment of the dilute polymer solution; λ is and the wavelength of the incident light and N_A is Avogadro's number (6.023×10^{23} molecules mol^{-1}).

Rayleigh ratio, $R(\theta)$, which is giving by

$$R(\theta) = \frac{i(\theta)r^2}{I_0 V} \quad (3.17)$$

Where I_0 is the intensity of the incident light beam and $i(\theta)$ is the intensity of the scattered light measured at a distance of r from the scattering volume, V , and at an angle θ with respect to the incident beam. $P(\theta)$ is the particle scattering function, which incorporates the effect of chain size and conformation on the angular dependence of scattered light intensity. Spherical particles smaller than the wavelength of light act as independent scattering centers generating a symmetrical envelope of scattered light intensity. In this case of small particles, $P(\theta)$ is unity, but in the case of polymer chains whose dimensions are $> \lambda/20$, scattering occur from different points along the same chain and $P(\theta) < 1$. For this reason, diminution of scattered light intensity can occur due to interference, and the scattering envelope is no longer spherically symmetrical, as seen in Figure 3.11. In this case, the angular dependence of scattered light intensity is given by the particle scattering function, which, for a monodisperse system of randomly-coiling molecules in dilute solution, is given by the expression (Todriguez, 1989)

$$P(\theta) = \frac{2}{v^2} [e^{-v} - (1 - v)] \quad (3.18)$$

where

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$$\nu = 16 \left(\frac{\pi m}{\lambda} \right)^2 \langle s^2 \rangle \sin^2 \left(\frac{\theta}{2} \right) \quad (3.19)$$

and $\langle s^2 \rangle$ is called the mean-square radius of gyration. For linear-chain polymers, $\langle s^2 \rangle$ is related to the mean-square end-to-end distance as

$$\langle s^2 \rangle = \frac{\langle r^2 \rangle}{6} \quad (3.20)$$

Basic instrumentation for light scattering measurements is illustrated in Figure 3.12. Light from a high-intensity mercury lamp is polarized and filtered before passing through a glass cell that contains a filtered, dilute polymer solution. Scattered light intensity at an angle θ is recorded as a signal from a movable high-voltage photomultiplier tube.

To determine M_w from Equation 3.15, it is necessary to know the value of $P(\theta)$ at each angle for which $R(\theta)$ has been measured. When the molecular weight distribution of a polymer is polydisperse, as it usually is, $P(\theta)$ is not precisely given by Equation 3.18, but by a summation of similar equations from polymer chains of different sizes weighted by the amount of variously sized chains present in the polymer sample. Since this information is generally not known, it is customary to treat the data in a way that does not require explicit knowledge of $P(\theta)$. The Zimm methods were used in this study.

Figure 3.11 Intensity distribution of light scattering at various angles for a small particle (dashed line), symmetric distribution, and a large polymer molecule (solid line), asymmetric distribution (Todríguez, 1989).

Figure 3.12 Conventional light-scattering instrumentation showing incident and scattered light, sample cell, and photomultiplier (Todríguez, 1989).

3.3.7.2 Zimm Method

The most rigorous approach to determine M_w from light scattering data is a Zimm plot. This procedure has the advantage that chain conformation need not be known in advance; however, Zimm plots require tedious measurements of scattered light intensity at a many more angles than needed by the dissymmetry technique. A double extrapolation to both zero concentration and zero angle is used to obtain information concerning molecular weight, second virial coefficient, and chain dimensions. In the limit of small angles where $P(\theta)$ approaches unity, it can be shown by means of a series expansion of $1/P(\theta)$ that Equation 3.15 becomes

$$\frac{Kc}{R(\theta)} = \frac{1}{M_w} \left[1 + \frac{16}{3} \left(\frac{\pi n}{\lambda} \right)^2 \langle s^2 \rangle \sin^2 \left(\frac{\theta}{2} \right) \right] + 2A_2c \quad (3.21)$$

Figure 3.13 Idealized Zimm plot of light-scattering data (●) taken at different angles (θ) and solution concentrations (c). Double extrapolations to zero concentration and zero scattering-angle are represented by broken lines (Todríguez, 1989).

As illustrated in Figure 3.13, data is plotted in the form of $Kc/R(\theta)$ versus $\sin^2(\theta/2) + kc$ for different angles and concentrations (where k is an arbitrary constant added to provide spacing between curves). A double extrapolation to $\theta=0^\circ$ and $c=0$, for which the second and third terms on the right of Equation 3.21 become zero, yields M_w as the reciprocal of the intercept. As inspection of Equation 3.21 indicates, A_2 is then obtained as one-half of the slope of the extrapolated line at $\theta=0$; then the mean-square radius of gyration is obtained from the initial slope of the extrapolated line at $c=0$ as given below.

$$\langle s^2 \rangle = \frac{3\overline{M}_w}{16} \left(\frac{\lambda}{\pi n} \right)^2 \times slope \quad (3.24)$$

Chapter 4 Synthesis and Characterization of Graft Copolymers

In this work, three different routes of graft polymerization using free radical polymerization were carried out. These three routes were designed to obtain products of different structures. In Route 1, the factors influencing the graft polymerization such as effect of different initiators, feeding ratio and reaction time were studied. During free radical polymerization, the formation of reactive centers is the rate controlling step of the polymerization in the homogeneous system. Route 2 and Route 3 are controlled synthesis routes whereby the location of the grafting is more controlled as compared to Route 1. Using spectroscopy, Pluronic, initially present in the reaction mixture, appeared to be attached to the poly(vinyl pyrrolidone), PVP.

4.1 Mechanism of Graft Copolymerization

The initiation of the vinyl pyrrolidone monomers was done using different initiators. This resulted in the generation of radicals. There are two steps in the initiation stage. Step 1 is the dissociation of the initiators when the temperature is high enough. Step 2 is the initiation of the monomer using the free radicals formed in Step 1. For example, if lauroyl peroxide is used as initiator in Step 1, the dissociation step is

(4.1)

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Radicals ($\text{R}^\bullet$) have been shown to effectively initiate the polymerization of N-VP (Bromberg, 1998a; Bromberg, 1998b),

At the same time, the radicals also initiate PEO-PPO-PEO copolymers, producing macroradicals due to hydrogen abstraction,

X is H or CH_3 .

During the propagation stage as in step 2, the new radical will react with other monomers rapidly.

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Another possible initiation reaction is that shown in Reaction 4.6. Given the high speed of Reaction 4.6, a more likely scenario is the chain transfer of the VP radicals to Pluronic molecules that is present in high concentrations, resembling those of a solvent in more conventional polymerization processes.

Reaction 4.7 represents chain transfer followed by branching. In the case of reactive propagating radicals, such as Pluronic copolymers, multiple branches on one chain are likely, leading to the appearance of the brush structure as shown in reaction 4.8.

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(4.8)

The most likely termination reactions are shown as follows:

(4.9)

(4.10)

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It is noted that the recombination of VP and Pluronic radicals produced in reactions 4.3 and 4.5 would also produce graft copolymer.

In general, there are other termination reactions. For example, the active centers on the macro-Pluronic radicals or VP radicals transfer to VP monomers or to the initiators left in the system. At the same time, the chain growth is terminated on these radicals and new radicals are formed. The amount of radicals in the reaction system do not changed. However, the newly formed radicals such as VP radical or initiator radical are less active than original radicals. Most of them cannot continue the reaction and, hence, will not contribute to the chain growth. In radical polymerization, these reactions are generally not desirable. They will influence the molecular weight of products and the efficiency of the initiators.

No quantitative data has been published on the chain transfer involving PVP, arguably because of both the complexity of the system and the significant commercial interest that leads to few publications about the polymerization rate.

4.2 The Definition of Various Terms

In order to describe the procedures of the graft polymerization well, the effectiveness or percentage of the grafting, the effective degree of conversion, the degree of bonding and the graft efficiency were determined either during the reaction or after the reaction. These various terms are defined in this section.

The effective degree of conversion of vinyl pyrrolidone (VP) into the polymer, F, is defined as follows,

$$F\% = \frac{\text{Weight of polymerized VP}}{\text{Initial weight of VP in the reaction mixture}} \times 100 \quad (4.12)$$

The degree of bonding between Pluronic and poly (vinyl pyrrolidone), B, is defined as follows,

$$B\% = \frac{\text{weight of Pluronic bonded}}{\text{initial weight of Pluronic in reaction mixture}} \times 100 \quad (4.13)$$

The percentage of grafting, PG, and the grafting efficiency (%), GE, were estimated from the following equation,

$$PG\% = \frac{\text{Weight of grafted PVP}}{\text{Weight of graft copolymer}} \times 100 \quad (4.14)$$

$$GE\% = \frac{\text{Weight of grafted PVP}}{\text{Weight of grafted PVP} + \text{Weight of homoPVP}} \times 100 \quad (4.15)$$

4.3 Synthesis Route 1

Pluronic F127 was purchased from Fluka and was used without further purification. It has a formula of EO₉₉PO₆₅EO₉₉ and a nominal molecular weight of 12,600. The molecular weight of PPO segment is 3780 and 70 wt% of the chain is made up of EO. The cloud point of F127 is above 100 °C. N-Vinyl pyrrolidone (VP) was distilled at 100

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°C before use. Lauroyl peroxide (LP) (97%, redox initiator) was obtained from Lancaster and 2,2'-azobisisobutyronitrile (98%, AIBN) was bought from Teehai and recrystallized from methanol. 1,1'-azobiscyclohexanecarbonitrile (Vazo 88) was purchased from Dupont Specialty chemicals and was recrystallized from cold acetone and benzyl peroxide (BP). PVP with a molecular weight of 10,000 was obtained from Sigma-Aldrich. Dioxane (HPLC grade) were first distilled at 100 °C and then kept in sealed bottles. Diethyl ether (HPLC grade) was purchased from Fisher and used without further purification. The rest of the chemicals were used as received unless specified.

Poly (ethylene oxide)-b-poly (propylene oxide)-b-poly (ethylene oxide)-g-poly (vinyl pyrrolidone) was synthesized by free radical polymerization of vinyl pyrrolidone along with simultaneous grafting of poly(vinyl pyrrolidone) onto the Pluronic backbone. A known amount of vinyl pyrrolidone and Pluronic was charged into a 125 ml flask. The polymerization was carried out in dioxane solution under dry nitrogen atmosphere. In the presence of initiator, such as azobisisobutyronitrile (AIBN) or V88, the resulting solution was deoxygenated by nitrogen flow for 24 hours while being stirred.

The reactor was equilibrated for 1 hour while being stirred at room temperature under nitrogen atmosphere. After that, the heating began and the timing commenced. The reactor was heated to a certain temperature at a desired rate (typically 1-2 °C/min) under constant nitrogen flow and it was kept at this temperature for a number of hours while being stirred. The reactor was then allowed to equilibrate at room temperature. After equilibration, the nitrogen flow was discontinued. The resulting solution was repeatedly added to excess heptane and excess cyclohexane to precipitate the product. The resultant white powder was dried under vacuum (10^{-3} Torr) at 40 °C for 24 hours. After that, the crude product was washed by acetone and THF to get rid of PVP homopolymer and

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Pluronic respectively. Then, the resultant powder was dried under vacuum at 40 °C for another 24 hours.

4.3.1 Factors Influencing Graft Copolymerization

Various factors can affect the grafting of the copolymer. They are:

- Types of initiators and their concentration
- Feeding ratio of VP and Pluronic copolymer
- Reaction time

In the following discussion, a systematic study of the effect of the factors is presented.

4.3.1.1 Effect of Initiators and Their Concentrations

To investigate the effect of one factor, the other factors need to be fixed. The effect of initiators and their concentration was studied first. The reaction was carried out in dioxane with 2 g of Pluronic copolymer and 5 g VP using several initiators and different concentrations for each initiator at 70 °C for 6 hours.

As outlined in the introduction, the role of the initiator in this system may be two fold: initiators result in the formation of the radicals that initiate VP polymerization and also participate in the chain transfer to Pluronic (an agent with readily abstractable hydrogen atoms). Therefore, the strength of the initiator in the hydrogen abstraction reactions should be considered.

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Azonitriles are generally regarded as weaker chain transfer agents compared to peroxides, although they are also capable of chain transfer via displacement reactions. An azo initiator may successfully polymerize VP, and the growing PVP radicals may abstract hydrogen from Pluronic backbones. This process will only result in a PVP homopolymer and Pluronic radical. Thus, the efficiency of the bonding between Pluronic and PVP would be lowered overall. Acyl peroxides have higher transfer constants than the alkyl peroxides due to a weaker O-O bond. Several syntheses utilizing the four different initiators were carried out (Table 4.1).

Table 4.1 Free-radical initiators used in the synthesis and their effect on grafting efficiency of Vinyl pyrrolidone and Polyether bonding.

Initiator	abbreviation	Mw	half-life (h) ^a	F% ^b	B% ^c	GE% ^d
lauroyl peroxide	LP	398.63	3.5	92	80	71
2,2'-azobisisobutyronitrile	AIBN	164.21	4.8	87	20	20
benzoyl peroxide	BP	242.23	7.3	84	85	50
1,1'-azobiscyclohexane carbonitrile	V88	244.34	143	81	12	33

^a At 70 °C in toluene. ^b Degree of VP conversion (initiator concentration 2 mM, after 10 hours of graft polymerization.) ^c Effective degree of Pluronic bonding ^d Grafting efficiency of PVP

Parameters evaluated were the effective degree of VP conversion (F%) and degree of bonding of Pluronic to the resulting copolymer (B%) and the grafting efficiency of VP (GE%). Table 4.1 shows that the F values were high for all initiators except for V88, which possesses a very long half-life. F% value greater than 92% is desirable in this synthesis for the minimization of the residual monomer content. It is also important that the initiator and propagating radicals be spent as fully as possible since radical species remaining in the polymer will result in the formation of hydroperoxides upon contact with air. Hydroperoxides formation will cause chain scission reactions and polymer degradation. Therefore, initiators with a shorter half-life (LP and AIBN) are more suitable for the synthesis.

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However, azonitriles yielded much lesser B values than the peroxy initiators, in agreement with the above discussion on the effect of the initiator strength on hydrogen abstraction reactions. While BP resulted in the highest B value, some researchers showed that it also contributed to the appearance of the permanently cross-linked fraction which is probably due to multiple branches on one Pluronic chain (Bromberg, 1998). Another reason why BP is not selected is that it has a lower grafting efficiency to VP monomer. Hence the initiator that is most suitable for this grafting polymerization system is LP.

After the best initiators were chosen, the optimal quantity of the initiators was studied. The amount of initiators in the system is one of the important factors that influenced the grafting efficiency of the copolymerization and the molecular weight of graft copolymers.

Figure 4.1 Grafting efficiency as a function of initiator concentration.

The effect of initiator on the graft copolymerization is shown in Figure 4.1. The grafting efficiencies increased as the concentration of the initiator LP is increased up to 2 mM, but

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the grafting efficiency decreased when the concentration increased beyond 2 mM. The phenomenon is due to the fact that the homopolymer is more favourable to form than the graft copolymer at a high concentration of the initiator. This confirms previous argument that with an increase in the radical concentrations, the recombination of radicals becomes dominant over the grafting reaction.

In general for free radical polymerization, there is an optimum ratio of initiator concentration to the monomer concentration at a specific temperature. If the concentration is low at a particular temperature, it will influence both the initial rate of polymerization and the number of radicals formed. There will not be enough initiator to initiate the monomers to become the radicals whether for homopolymerization or chain transfer reaction. Hence, some of the monomer in the system will remain. Above the optimal initiator concentration, the grafting efficiency decreases with further increase in the initiator concentration as shown in Figure 4.1. High initiator concentration usually keeps the rate of polymerization high for a relatively long time. At the same time, it also increases the chances of the other reactions such as chain decomposition and oxidation processes. These reactions will decrease the molecular weight of products as this generally happens on the ether backbone of Pluronic copolymer. On top of this, if more initiator is left in the final system, the purification of the product becomes more difficult.

To summarize, both the type and the concentration of the initiators are important factors that will influence the graft polymerization. Peroxide initiator (LP) is more effective for the graft polymerization of this system. The maximum grafting efficiency occurred at an initiator concentration of 2 mM.

*Chapter 4: Synthesis and Characterization of graft copolymers***4.3.1.2 Effect of Monomer Feeding Ratio**

Graft polymerizations were carried out in dioxane with 2 g Pluronic F127 and 2 mM lauroyl peroxide at 70 °C for 6 hours using several feeding ratio of VP to F127 such as 1, 1.5, 2, 2.5, 3 and 3.5 g. Figure 4. 2 shows the effect of the monomer concentration on the grafting efficiency.

Figure 4.2 Effect of feeding ratio of monomers on grafting efficiency.

The feeding ratio of VP and Pluronic copolymers is one of the most important factors that influence the grafting polymerization. The grafting efficiency reached a maximum at 2.5 feeding ratio of VP to Pluronic copolymers. The increase in the grafting efficiency at a higher monomer concentration is ascribed to the fact that the formation of the homopolymer is easier as the monomer concentration increases and more of them were grafted onto the Pluronic backbone. At higher ratio of VP to F127, there are more VP radicals available to react with a Pluronic chain. Hence, the graft efficiency increased. The grafting efficiency decreased after a critical concentration is reached. A possible reason for such trend is the homopolymerization of VP. As the concentration of VP

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radicals increases, the recombination of VP radicals comes into play. The concentration of the initiator also plays a role. Thus, the tendency for the chain transfer to Pluronic copolymer decreased as the concentration of VP goes to higher values.

Figure 4.2 shows a slight change of feeding ratio produced a large change in the grafting efficiency for this grafting polymerization system. It confirms the principle of graft polymerization, that is, there is an optimal feeding ratio of the materials.

4.3.1.3 Effect of Reaction Time

The graft polymerizations were conducted with 2g of Pluronic copolymer and 5 g of VP, and 2 mM LP for several reaction times at 70 °C. The effect of reaction time on the grafting process is shown in Figure 4.3.

Figure 4.3 Effect of reaction time on the grafting polymerization.

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Percentage of grafting over time was determined using FTIR. A typical spectra is shown in Figure 4.4. Generally, if the solid sample has just one component, potassium thiocyanate, KSCN, is often used as an internal reference. The pellet was prepared by mixing 1mg of graft copolymer in 100 mg of potassium bromide, KBr, with 1wt% KSCN. The component of all samples was weighed accurately. The calculation of the proportion of the component is determined by comparing to the internal reference KSCN.

Figure 4.4 Typical FTIR spectra of F127-g-PVP with 1 wt% KSCN added in KBr.

In a binary system, the area under each special peak relating to each component can be used to calculate the relative concentration in the sample. The thickness of the pellets also influences the accuracy of the results. The weight of every pellet should be same. Each sample was measured three times to increase the accuracy of the results. The spectra were corrected for the background in an interactive manner and then analyzed. Areas under $1600\text{--}1800\text{ cm}^{-1}$ is due to the vibration of carbonyl bonds of PVP and the area under $1200\text{--}1000\text{ cm}^{-1}$ is due to ether bonds of Pluronic copolymer. They were averaged and compared to the area of the reference SCN band which is centered at about

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2100 cm⁻¹. The ratio of the peak areas were changed into the weight ratio (ζ) of Pluronic and PVP components in the copolymer:

$$\frac{A_1}{A_2} = \frac{a_1 c_1 b}{a_2 c_2 b} = K \cdot \frac{C_1}{C_2} = K \cdot (k \cdot \frac{W_1}{W_2}) = K \cdot \frac{W_1}{W_2} = K \cdot \zeta \quad (4.16)$$

where a , b , c have been shown in Chapter 3 and K is an instrumental constant. A_1 is the intensity of the peak near 1100 cm⁻¹ spectral region (ether bond) that is the ether bands of Pluronic F127. A_2 is the intensity of the peak around 1650 cm⁻¹ obtained from the carbonyl bonds of PVP. C_1 and C_2 are the concentration of F127 and PVP in the pellets, respectively. W_1 and W_2 are the weight of F127 and PVP, respectively. Hence,

$$\zeta = \frac{1}{K} \cdot \frac{A_1}{A_2} \quad (4.17)$$

$$PG\% = \frac{100 \times W_1}{W_1 + W_2} \% = \frac{100 \times (W_1 / W_2)}{W_1 / W_2 + 1} \% = \frac{100\zeta}{\zeta + 1} \% \quad (4.18)$$

These values were compared to the results obtained using NMR in a later section. According to other researchers, the deviation between the content of Pluronic in the copolymer determined using FTIR and HPLC is less than 5%-10% (Bromberg, 1998).

Figure 4.3 shows that when the degree of the conversion of VP reached the maximum value, the grafting efficiency and the percentage of grafting also reached maximum value. This means that the polymerization of VP monomer to form the homopolymer PVP and grafting of the VP onto the Pluronic backbone occur at the same time. As seen in Table 4.1, the degree of the conversion of VP using LP as the initiator is near 92%. The percentage of grafting reached a peak and then with further increase in the reaction time, it decreased slightly. Since the concentration of the VP monomer is relatively lower than that of Pluronic copolymer in the system at this time, Pluronic will have higher chances of becoming the reactive center than VP monomer. Hence, the weight of graft copolymer will increase more than that of PVP. Based on Equation 4.14, the percentage of grafting, PG, ought to decrease.

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Reaction time also has an effect on the molecular weight of the graft copolymer. SEC is one of the methods to get information on molecular weight of polymers. The effect of the reaction time on the molecular weight of the samples is shown in Figure 4.5. The molecular weight determined using SEC is different to those obtained from ^1H -NMR. ^1H NMR results will be presented in the following section. The distribution of molecular weight was found to range from 1.80 to 2.00 for the graft copolymer using SEC. This is reasonable since graft copolymer generally has high polydispersity. Simultaneous polymerization of VP and Pluronic-g-PVP bonding increase the molecular weights of the product. After the molecular weight of the graft copolymer reaches the maximum value, the weight start to decrease with increasing reaction time. From Figure 4.5, one can observe that the molecular weight of the graft copolymer starts to decrease slightly after 8 hours, the main reason may be prolonged reaction time can lead to more oxidation and decomposition reactions. There may still be some unfavorable chain transfer reactions in the synthesis system after 8 hours. Hence, the optimal reaction time is 6 hours.

Figure 4.5 Effect of reaction time on M_w of graft polymer.

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As discussed, most of the information about the grafting process can be obtained through investigating the changes in the conversion of the monomer VP, the grafting efficiency of VP and the percentage of grafting of VP with increasing reaction time. By studying the effect of reaction time on these percentages, the process of the grafting of VP onto Pluronic copolymer can be understood. With this understanding, the percentage of grafting can be controlled by controlling the reaction time.

4.3.2 Characterization of the Graft Copolymers

The structure of the graft copolymers synthesized in the previous section was characterized using Fourier Transform Infrared Spectroscopy (FTIR) and Nuclear magnetic Resonance (NMR). The molecular weight of the products can also be studied using NMR. The following sections present the results of the characterization.

4.3.2.1 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR was used to study the chemical structure of polymer. Its spectra were recorded in a water-free atmosphere using the Perkin Elmer system 2000 Fourier Transform Infrared Spectrometer. Figure 4.6 shows the spectra for homopolymer PVP, Pluronic F127 and Pluronic F127-g-PVP. The VP carbonyl peak occurred at around 1650 cm^{-1} . The ether bands of the Pluronic F127 can be found near 1100 cm^{-1} spectral region. Since the graft copolymer, Pluronic-g-PVP, consists of both carbonyl bond of VP and ether bond of F127, the peaks in both two areas can be observed in the spectra.

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To determine whether the materials obtained were graft copolymer with covalent bond or mere blends where the two polymers are physically mixed, a mixture of PVP and Pluronic F127 was dissolved and cast from chloroform solution at room temperature. The blend was characterized before and after the extraction procedure. The extraction procedure consists of acetone extraction at room temperature. The spectra obtained for the graft copolymer was compared to the spectra obtained for the mixture of PVP and Pluronic F127 before and after the acetone extraction. Looking at Figure 4.7, a strong reduction of the carbonyl peak of PVP after the acetone extraction for the blend was observed. These findings strongly indicate that when there is no covalent bond between PVP and Pluronic copolymer chain, such as in the case of the blend, both components of the system could be easily separated by a selective solubilization procedure. After the graft copolymer was extracted twice using acetone, the PVP carbonyl peak could clearly be seen. This indicates that the PVP is chemically bonded to the Pluronic backbone.

Figure 4.6 FTIR spectra of (1) copolymer F127-g-PVP, (2) VP and (3) Pluronic F127 in KBr.

Figure 4.7 FTIR spectra of (1) blend of PVP and F127 and (2) blend of PVP and F127 after extraction procedure.

4.3.2.2 Nuclear Magnetic Resonance (NMR)

The major features of NMR spectra of Pluronic F127-g-PVP copolymer in CDCl_3 are shown in Table 4.2. Figure 4.8, Figure 4.9 and Figure 4.10 shows the spectrum for the various components. ^1H -NMR was used to determine the composition of the copolymer. The copolymer was prepared by radical polymerization of 2 g of Pluronic copolymer and 5 g VP using 2 mM LP as initiator at 70 °C for 6 hours in the dioxane.

As seen in Figure 4.8, the peak at 3.4-3.3 ppm and 1.1-1.0 ppm due to the protons of methine and methyl groups in PO can be observed, respectively. The integration ratio of these two peaks is 1/3 which corresponds well with their real ratio. The ratio of the methine in graft copolymer/methyl in PO is about 0.17. This value is lower than that of Pluronic, indicating VP radicals have been grafted onto the methine groups of PO. Also, peaks for PVP backbone protons $-\text{CH}-$ (p_2) and ring $-\text{CH}_2-$ (p_3) near to N are seen around 3.7 and 3.5 ppm, respectively. Peak for PVP backbone protons $-\text{CH}_2-$ (p_1) are shown around 1.7 ppm. The broaden peak emerged around 2.5 ppm belongs to $-\text{CH}_2-$ (p_4 , p_5). This peak is the typical peak that can be used to tell whether PVP has been grafted onto

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F127. The VP/Pluronic unit ratios can be obtained from the integration ratio of resonances arising from the protons due to methyl group in Pluronic and P₃ hydrogen in PVP shown in Figure 4.10. Hence, the mole ratio of PVP in the whole graft copolymer can be obtained. This mole ratio can be converted to weight fraction for the calculation of the percentage of grafting.

The percentage of grafting can be calculated using the following equations,

$$\frac{W_{vp}}{W_{F127}} = 1.5 \times \frac{M_{vp}}{\left(\frac{198}{69}M_{EO} + M_{PO}\right)} \times \frac{I_{CH_2CO}}{I_{CH_3}} = 1.16$$

$$PG \% = W_{vp}/(W_{vp} + W_{F127}) = 52\%$$

From the percentage of grafting, the molecular weight of the graft copolymer can also be obtained since the molecular weight of Pluronic F127 is known to be 12,600. The molecular weight is found to be approximately 26,000.

Table 4.2 Major features of ¹H NMR spectra of Poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide)-g-P(vinyl pyrrolidone) in CDCl₃.

Assignment	δ, ppm
methine HC-OC in EO, PO	
methylene H ₂ C-OC in EO, PO	3.5-3.3
methyl in PO	3.8-3.4
	1.1-1.0
P ₁ *	
P ₂ *	1.8-1.6
P ₄ , P ₅ *	3.8-3.7
P ₃ *	2.5-1.5
	3.5-3.4

* PVP

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Figure 4.8 ^1H NMR spectrum of F127.

Figure 4.9 ^1H NMR spectrum of PVP.

Figure 4.10 ^1H NMR spectrum (CDCl_3) of the graft copolymer.

The results are listed in Table 4.3.

Table 4.3 PG% obtained using different methods.

	FTIR	Chemical method ^b	NMR
PG% of F127-g-PVP copolymer ^a	57	67	52

^a the conditions of polymerization described in the former part.

^b mass reduction method which was described in section Synthesis Route 1.

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In this grafting reaction, another question to be answered is: where are most of PVP grafted on, PPO or PEO? Researchers who studied the structure of Pluronic-g-PAA observed a 3-fold increase in the overall PPO content in the reaction mixture with L121 (PEO₄-PPO₆₉-PEO₄)-g-PAA versus that with F127 (PEO₉₉-PPO₆₉-PEO₉₉)-PAA (Bromberg, 1998a). This resulted in about 30-fold growth of PAA content at comparable degrees of conversion. Although the exact ratio of reactivity of tertiary and secondary C-H groups in this system are unknown, it is reasonable to expect the tertiary groups to be 2-10 times more likely to participate in Reaction 4.3 and Reaction 4.4 than secondary ones, as the tertiary C-H group is more readily abstracted due to its higher nucleophilicity and, hence, the stability of the resultant radical (Bridger, 1963; Kopinke, 1989; Odian, 1991). This notion is further supported by the higher effectiveness of PPO as an oxidation inhibitor as compared to PEO. The antioxidant's power depends on the ability of the chain to donate H in Reaction 4.3 (Wong, 1989). Even though PVP preferred to be grafted onto PPO, there is still some possibility for the grafting to occur on PEO. Hence, different routes were used to obtain the controlled grafting products, which means the PVP grafted specially on PEO or PPO blocks of F127.

4.3.3 Disadvantage of Route 1

A systematic study of the factors affecting the free radical polymerization in solution using Route 1 was conducted. Unfortunately, since Route 1 do not offer any control in the polymerization process, the product obtained is a randomly grafted copolymer. This is PVP grafted randomly onto the PEO and PPO block chain. The solution behavior of such product is not desirable because the architecture of the molecular chain will be impossible to give the constant solution behavior. Hence, with the understanding gained

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from the study of the factors affecting the polymerization, the author goes on to another two new routes to graft PVP specially onto PEO or PPO block.

4.4 Synthesis Route 2 and Route 3

The graft copolymer synthesized using Route 1 is a randomly grafted one. In this section, two methods of control grafting using the different synthesis techniques are presented.

4.4.1 Synthesis

Route 2: F127(PPO)-g-PVP was synthesized using dispersion polymerization. The synthesis was carried out on a laboratory scale in an adiabatic mode. Pluronic (6 g) was dissolved in vinyl pyrrolidone (13 ml) under constant nitrogen purging. Lauroyl peroxide (25 mg), which has high efficiency to initiate VP, and 4,4'-azobis(cyanovaleric acid) (25 mg), which has longer half life and good solubility in system, were dissolved in 2 ml of vinyl pyrrolidone and added to the resulting solution. The resulting solution was deaerated by nitrogen bubbling for 0.5 h and added to a 250 ml three-necked flask containing 60 ml of 1 wt% solution of Ganex V-216 in dodecane. The flask was vigorously stirred by a magnetic stirrer and deaerated by constant nitrogen purge from the bottom. The flask was then heated to 70 °C in an oil bath and kept at that temperature under constant stirring and nitrogen purge. The reaction continued for 6 h. The reaction was then stopped, and the contents of the reactor were filtered using Whatman filter paper (retention size 10 µm) in heptane and cyclohexane. The products were repeatedly washed using acetone and THF and dried under vacuum.

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Route 3: F127(PEO)-g-PVP, F127 (6 g) in aqueous solution (60ml) was heated to 70 °C using an oil bath and kept at that temperature under constant stirring and nitrogen purge. At the same time, vinyl pyrrolidone (13 ml) was heated to 70 °C and transfer quickly to 250 ml three-necked flask containing F127 aqueous solution. Ammonium persulphate, which is a good water-soluble initiator, was first dissolve in the 2 ml vinyl pyrrolidone before the resulting mixture is added into F127 solution. The reaction was kept at that temperature under constant stirring and nitrogen purge for 6 h. After that, the solution containing the product was freeze-dried. The white powder was washed repeatedly using THF and acetone and dried under vacuum.

The flowchart of synthesis Route 2 and Route 3 are shown in Figure 4.11. In synthesis Route 2 and Route 3, the most important thing is to verify whether PVP has been grafted onto the different block of F127 as originally conceived. The optimal reaction time and feeding ratio investigated in synthesis Route 1 were used.

In Route 2, F127 will form PEO compact core and PPO loose corona. It will be difficult for both initiators and VP monomers to enter into the PEO compact core due to the steric hindrance and low solubility. Hence, most of PVP are grafted onto PPO block of F127. In Route 3, F127 will form PPO compact core and PEO loose corona. Most of PVP were grafted onto PEO block of F127.

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Figure 4.11 The schemes of Synthesis Route 2 and Route 3.

4.4.2 Characterization of the Products

The chemical structure of the products synthesized by Route 2 and Route 3 can be investigated using FTIR in Figure 4.12. The FTIR spectra obtained is similar to that of polymer synthesized by Route 1. All the products synthesized have -C-O-C- and -C=O chemical group and PVP is chemically bond to Pluronic F127 as shown in Figure 4.13.

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Figure 4.12 FTIR spectra of (1) Pluronic F127, (2) VP, (3) F127(PEO)-g-PVP and (4) F127(PPO)-g-PVP in KBr.

Figure 4.13 FTIR spectra of (1) F127(PEO)-g-PVP after extraction, (2) F127(PPO)-g-PVP after extraction, (3) PVP/F127 mixture after extraction and (4) PVP/F127 mixture before extraction.

^1H NMR spectrum can provide a better differentiation in the type of grafting copolymer synthesized in these 2 routes. The major features of ^1H NMR spectra obtained for the two kinds of graft copolymers are shown in Table 4.4, Table 4.5, Table 4.6. ^1H NMR spectrum was performed using 1% solutions of F127-g-PVP graft copolymers in CDCl_3 at about 295 K as shown in Figure 4.14.

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Table 4.4 Major features of ^1H NMR spectra of Poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) in CDCl_3 .

Assignment	δ , ppm
$\text{CH}_2\text{-O}$ in EO	
$\text{CH}_2\text{CH}_2\text{-O}$ in EO	3.74-3.70
	3.64-3.58
$\text{CHHCH}(\text{CH}_3)\text{-O}$ in PO	
$\text{CHHCH}(\text{CH}_3)\text{-O}$ in PO	3.43-3.36
$\text{CHHCH}(\text{CH}_3)\text{-O}$ in PO	3.58-3.50
	1.143-1.135
F127* $\text{-(CH}_2\text{-CH}_2\text{-O)}_{99}\text{-(CH}_2\text{-CH(CH}_3\text{)-O)}_{69}\text{-(CH}_2\text{-CH}_2\text{-O)}_{99}\text{-}$	

Table 4.5 Major features of ^1H NMR spectra of Poly(vinyl pyrrolidone) in CDCl_3 .

Assignment	δ , ppm
P_1^*	1.86-1.28
P_2^*	4.1-3.4
P_3^*	2.5-2.1
P_4^*	2.1-1.86
P_5^*	3.5-3.0

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Table 4.6 Major features of ^1H NMR spectra of Poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide)-g-poly(vinyl pyrrolidone) in CDCl_3 .

Assignment	δ , ppm
CH-O in EO, PO	3.5-3.3
CH ₂ -O in EO, PO	3.85-3.5
CH ₃ in PO	1.2-1.1
P ₁	1.7-1.56
P ₂	4.1-3.4
P ₃	2.5-2.1
P ₄	2.1-1.5
P ₅	3.4-3.0

The presence of well-resolved resonances in the NMR spectra allows us to conveniently monitor the chemical environment and relaxation at different sites in each block as a function of the temperature. For practical consideration of signal/noise ratio, the resonances of methyl of the propylene oxide segment in the PPO block and the methylene of the ethylene oxide segment in the PEO blocks were used as intrinsic probes. Assignments of the chemical shifts of the different resonances of F127 have been studied by others (Franco, 1996; Lele, 2002).

Figure 4.14 ^1H NMR spectrum of F127(PPO)-g-PVP (a) and F127(PEO)-g-PVP (b).

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A characteristic peak from PVP (3.1-3.3 ppm), representing P_5 , can be clearly seen in Figure 4.14(a), confirming the successful grafting polymerization of PVP on F127 in both methods. Next, which part of F127 was PVP grafted on were verified. The peak around 3.8 ppm, which only appeared in Figure 4.14(b), provides the clue to the different grafting sites of PVP on F127 using the two routes. This peak is split from the $-\text{CH}_2-$ in EO part of F127 due to the grafting of PVP on its adjacent carbon atom. The emergence of this peak indicates that in Route 2, PVP preferentially graft onto EO block of F127. The signal at 3.8 ppm is weak for the polymer synthesized using Route 3. Refer to Figure 4.14. This indicates that most of the PVP are grafted onto PO block of F127. Hence, the analysis of the NMR spectrums confirmed that the grafting site of PVP on F127 can be well controlled by selecting different solvents and initiators.

To calculate the molecular weight of the graft copolymer, the intensity ratio must first be obtained. The intensity ratio of P_5 to methyl group in PPO for the graft copolymer F127(PPO)-g-PVP can be obtained from Figure 4.14(a).

$$\frac{P_5}{CH_3} = 1.5 \times \frac{I_{\text{CH}_2\text{CO}}}{I_{\text{CH}_3}} = 5.25 : 1 \quad (4.19)$$

F127 can be taken as the internal standard because the molecular weight of F127 is known to be 12,600. Hence, the mass molecular weight of F127(PPO)-g-PVP can be estimated to be 52,400.

The intensity ratio of P_5 and methyl group in PPO for the graft copolymer F127(PEO)-g-PVP can be obtained from Figure 4.14(b).

$$\frac{P_5}{CH_3} = 1.5 \times \frac{I_{\text{CH}_2\text{CO}}}{I_{\text{CH}_3}} = 7.5 : 1 \quad (4.20)$$

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Hence, the mass molecular weight of F127(PEO)-g-PVP is about 70,000.

The calculation of number average molecular weight of products synthesized is based on the assumption. This assumption is there is no degradation of F127 during the polymerization. The molecular weight of F127(PEO)-g-PVP is higher than that of F127(PPO)-g-PVP because the repeating units of PEO is much higher than that of PPO in F127. Hence, more PVP were grafted onto PEO.

4.5 Summary

In this study, the novel graft copolymer, F127-g-PVP, was synthesized by simultaneous polymerization and chain transfer of VP monomer onto the Pluronic copolymer. The graft copolymers were successfully produced through this radical grafting polymerization. Various factors affecting the grafting were investigated to obtain the optimal grafting conditions. Once the optimal conditions were determined, a series of copolymers with varying grafting efficiency were synthesized.

It was found that with the 2.5 feeding ratio of VP to Pluronic F 127 copolymer, the highest grafting efficiency was obtained at 70 °C after 6 hours in dioxane using 2 mM lauroyl peroxide as initiator. With the increase in the feeding ratio of VP/Pluronic F127, the molecular weights of the graft copolymer increased as expected, followed by a slight decrease.

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FTIR spectra verified the chemical structure of graft copolymer and the SEC of all the graft copolymers showed only one peak, suggesting that graft copolymers were successfully synthesized.

Using ^1H NMR spectroscopy, the chemical structure of the copolymer was characterized. From the data obtained from the NMR spectra, one can confirm that the graft copolymers were synthesized by radical graft polymerization. The compositions of the copolymers were also characterized using ^1H NMR. The PVP/Pluronic F127 ratios could be obtained from the ratio of the integrated signals due to the protons PPO (CH_3) near 1.19 ppm and the protons from PVP ($-\text{CH}_2\text{CO}$) at about 3.2 ppm.

Unfortunately, the first route of synthesis does not provide much control to the site where PVP is grafted onto. Route 2 and Route 3 can control the grafting sites better than Route 1. Hence, two different F127-g-PVP graft copolymers were synthesized by using the two different reaction schemes. NMR was used to investigate the structure of these two kinds of graft copolymer. Using Route 2 and Route 3, graft copolymer of type F127(PPO)-g-PVP and F127(PEO)-g-PVP were synthesized successfully.

Chapter 5 Association Behavior of Single Surfactant Systems in Aqueous Solution

The self-assembly of some non-ionic copolymer chains in solution can be initiated either by a change in concentration or by a change in the temperature. As discussed in Chapter 2, critical micelle concentration, CMC, is defined as the polymer concentration above which the formation of micelles becomes increasingly important. Critical micelle temperature, CMT, is the transition temperature above or below which the formation of associated structures becomes appreciable, depending upon whether the self-assembly process is endothermic or exothermic. Both CMC and CMT are the fundamental parameters in characterizing the association properties of such a copolymer-solvent system. When dealing with oxyethylene polymeric surfactants in aqueous solution, one of the most distinctive properties is that the self-assembly process is strongly temperature dependent. In our study, the temperature dependent behavior was investigated. The enthalpy, entropy and free energy of micellization were also examined.

The hydrodynamic radius (R_h) is another important aspect of the physical properties. The size, shape and morphology of the micelles in the aqueous solution can be studied with the use of dynamic light scattering (DLS). Using both viscosity data and static light scattering (SLS) data, the aggregation number was calculated.

The solution behavior of graft copolymers, F127-g-PVP, F127(PPO)-g-PVP and F127(PEO)-g-PVP, synthesized using Route 1, Route 2 and Route 3, respectively, were investigated. The results are presented in the following sections.

5.1 Solution Behavior

5.1.1 Study of the Microenvironment Using Fluorescence Probing Technique

In fluorescence probing technique, pyrene was used as the probe in the polymer solution. The key feature in the properties of pyrene is a solvent-induced variation in the ratio of emission band intensities (Karpovich, 1995; Winnik, 1996). The variation of the intensities detected as a function of wavelength is shown in Figure 5.1 and can be correlated with the polarity of the probe's immediate environment. In practice, pyrene emission dependence on the solvent polarity is expressed in terms of the intensities ratio I_1/I_3 . I_1 and I_3 are the intensities of the first ($\lambda_1 \approx 373$ nm) and the third ($\lambda_3 \approx 384$ nm) vibronic bands, respectively. The intensities ratio I_1/I_3 of the two bands is a sensitive measure of the polarity of the solvating environment for pyrene. This ratio decreases with increasing hydrophobicity. Typical spectra of pyrene in Pluronic-g-PVP copolymer solution are shown in Figure 5.1. Pyrene, having low water solubility, is expected to partition preferentially to the most hydrophobic regions in a self-organized system in the solution. This provides a measure for both the presence of such regions and its hydrophobicity.

Figure 5.1 The steady state emission spectra of pyrene in solution containing various concentration of graft polymer at room temperature.

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Values for the I_1/I_3 ratio for aqueous solutions of polymer containing pyrene as a function of polymer concentration are given in Figure 5.2. The relative intensity of third band (I_3) in the fluorescence spectra and that of the excimer emission (I_1) are substantially altered when the polymer concentration is increased. As the polymer concentration increased, the I_1/I_3 ratio decreases. The values range from 1.78 in water to 1.28 in hydrocarbons. Within a particular range of concentration, the I_1/I_3 ratio for the graft copolymers solutions decreases suddenly, indicating that intermolecular interactions between pyrene and the hydrophobic core are taking place. This decrease indicates the onset of micelle formation which results in the preferential solubilization of pyrene in a hydrophobic environment. The intersection of the two extrapolations observed in the figure can be interpreted as the critical micelle or aggregation concentration. Thus, the CMC can be obtained from measuring the changes in I_1/I_3 as a function of graft copolymer concentration.

Figure 5.2 I_1/I_3 ratio of the vibronic band intensities of pyrene as a function of polymers concentration.

The critical micelle concentrations of F127-g-PVP, F127(PPO)-g-PVP and F127(PEO)-g-PVP are 7 wt%, 3wt% and 2wt% at room temperature. The value of CMC of F127 is

Chapter 5: Association Behavior of Single Surfactant Systems in Aqueous Solution shown in figure 5.2 because it cannot be obtained using pyrene as probe in fluorescence probing technique (Winnik, 1996). The possible reason is high ratio of PEO/PPO which may be beyond the sensitivity of fluorescence probe. Hence the CMC of graft copolymers cannot be compared with that of F127 here. Thus, the application of this technique is limited in this work. Another disadvantage of fluorescence methods is that the large quantity of samples has to be used. Compared to this method, surface tension measurement is quicker, easier and more suitable for obtaining the CMC of copolymers including Pluronic F127 in aqueous solution. Polymeric surfactants and air/water interfacial phenomena are discussed in the next section.

5.1.2 Reduction of Surface Tension by Polymeric Surfactants

Reduction of surface tension is one of the most commonly measured properties of surfactants in solution. Since surface tension depends directly on the replacement of molecules of solvent at the air/water interface in our systems by molecules of surfactants, it is also one of the most fundamental of interfacial phenomena. Why and how do the changes of surface tension define the critical micelle concentration and provide information on the interactions of the molecules in the solution systems? The following discussion will address this question in part. The next two chapters discuss the interactions of the molecules in the solution system with respect to surface tension.

The results of surface tension measurements for F127 copolymer are given in the Figure 5.3 where the surface tension values are plotted as a function of concentration of the copolymers. In general, the surface tension decreases linearly with the increase in concentration of surface active molecules. Beyond a particular concentration, when the surfactant concentration increased, the surface tension stayed constant. That means the

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extra surfactant molecules in the solution form micelles instead of migrating to the air/water interface. Hence the higher concentration break in the surface tension curve corresponds to the formation of micelles. The plateau observed in the surface tension curve can also verify that the higher concentration break is CMC. A further increase in the concentration of copolymer solution will result in the formation of more micelle in the bulk solution. The activity of the copolymer remains constant, and the surface tension does not change. Other studies also verified the break in surface tension curve at higher concentration corresponds to CMC of Pluronic triblock copolymers by showing the good agreement with the values obtained from dye solubilization (Alexandridis, 1994) and this break is shown to have a strong dependence on the temperature (Mortensen, 1993).

Looking at the surface tension data as shown in Figure 5.3, more than one break in the surface tension following the increase in the concentration of F127 aqueous solutions were found. Similar observation was also reported by other researchers (Hecht, 1994). When the concentration increased, the surface tension dropped sharply at first, and then decreased slowly. The reason is because F127 molecules tend to go to the interface of solution and air first. The polymers at the interface help to reduce the surface tension. With increasing concentration, the amount of F127 molecules at the interface increased correspondingly. Hence the surface tension decreases at the beginning.

As discussed above, there seems to be two breaks in the surface tension data. There are two possible explanations for the observations. Hecht and coworkers (1994) attributed this break to the broad molecular distribution of the copolymers. They divided the copolymer into more surface active material and less surface active material. At the beginning, the more surface active material aggregate at the air/interface while the less surface active material remain in bulk solution. That is the reason why there is a break in

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the surface tension curve at lower concentration of solution. This break does not change with change in temperature whereas the break corresponding to the CMC is temperature dependent. Crook and coworkers (1963) also studied the effect of molecular weight distribution on the surface tension of nonionic surfactants. They measured the surface tension of normal distribution of single species and mixtures of single species and normal distribution of [(octylphenoxy)ethoxy]ethanols, and found that there is preferential adsorption of molecules with shorter PEO chain length at the air/water interface.

However, Alexandridis and coworkers (1994a) believed that the break in surface tension at lower concentration was not related to the molecular weight distribution and impurities in the copolymer. They suggested the formation of “monomolecular micelles” in the bulk aqueous phase and a “phase separation” of the copolymer at low concentration are the possible reasons to explain this low concentration break. At low concentration, the polymer molecules exist as an extended configuration when they are adsorbed on the interface between air and water. The surface tension decreases with increasing the concentration. In the range of 10^{-6} to 10^{-3} % concentrations, constant surface tension attained is due to the proposed orientations of PEO chains located at the air/water interface. When the concentration increases to higher than 10^{-3} %, this configuration is changed to be more compact and expelled water around it. The surface tension decreases with an increase of bulk concentration but at a slower rate. Subsequently further increase in the concentration resulted in micellization and the surface tension remains as a constant. This hypothesis is more reasonable, because polymeric surfactants have long chains which are different from small molecule surfactants. These long chains of polymeric surfactants first arrange in a loose order at the air/water interface. They will rearrange to form a more compact order at the air/water interface following the increase in concentration of surfactant in the bulk solution. This behaviour will result in the

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reduction of the surface tension at a slow rate to create the first break at lower concentration of polymeric surfactant solution.

The CMC in weight concentration of three kinds of graft copolymers synthesized are higher than that of F127 as shown in Figure 5.4, Figure 5.5 and Figure 5.6. Comparing the surface tension curves of F127, F127(PEO)-g-PVP and F127(PPO)-g-PVP, lower concentration break show the narrower changes. One possible reason to explain the changes is that the effective volume of the polymer became very large after grafting PVP, which is five-ring structure. The larger steric hindrance of the copolymers attributed by PVP grafted onto F127 make a bigger inverted “U” at the air/water interface. With a further increase in the concentration of copolymer molecules, the surface tension attains a steady value that does not change with increasing the concentration. This corresponds to the micellization concentration. Beyond this concentration, the surface tension does not change with increasing copolymer concentration. The CMC of F127(PEO)-g-PVP and F127(PPO)-g-PVP is larger than that of F127 in weight percent concentration. This is because the molecular weights of the graft copolymers are much larger than that of F127. The molecules needed to form micelle became relatively fewer. The CMC of F127-g-PVP, F127(PPO)-g-PVP and F127(PEO)-g-PVP in molar concentration are 2.3 mM, 0.8mM and 0.43 mM respectively shown in Table 5.1. In mole concentration, the CMC of F127(PEO)-g-PVP is slightly lower than that of F127. The CMC of F127(PPO)-g-PVP is similar to that of F127 because the effect of grafting hydrophobic PVP than PEO counteract by the effect of larger steric hindrance in PPO core of micelle due to grafting PVP onto PPO.

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Figure 5.3 Surface Tension behavior of Pluronic F127 in water as a function of concentration at room temperature.

Figure 5.4 Surface Tension behavior of Pluronic F127-g-PVP in water as a function of concentration at room temperature.

Figure 5.5 Surface Tension behavior F127(PPO)-g-PVP in water as a function of concentration at room temperature.

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Figure 5.6 Surface Tension behavior F127(PEO)-g-PVP in water as a function of concentration at room temperature.

Table 5.1 The CMC of F127.

Copolymers	CMC (wt%)	CMC (mole fraction)
F127	0.8	0.64mM
F127-g-PVP	6	2.3mM
F127(PPO)-g-PVP	4	0.80 mM
F127(PEO)-g-PVP	3	0.43 mM

5.1.3 Summary

CMC of our graft copolymer in aqueous solution can be obtained using both fluorescence probing techniques and surface tension measurements. Surface tension measurement was found to be more suitable since it needed only a small amount of the sample and fewer steps.

5.2 Thermodynamics of Micellization

As mentioned in the literature review, micellization is generally observed to be an endothermic process. The observed increase in the enthalpy is related to the

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transformation of one mole of copolymers from the ideal solution (unimer state) to that of a solvated micellar state.

The association behaviour of Pluronic copolymers in aqueous medium is strongly temperature dependent. To be specific, the CMC decreases with increasing temperature and the CMT decreases with increasing copolymer concentration. Micellization is predominantly driven by an increase in the entropy of the system when the molecules associate into micelles. This is because unassociated molecules lead to an ordering of the surrounding water. In this section, the study on thermal-reversible property of the copolymers will be discussed. The changes in CMT, enthalpy, entropy and free energy during micellization due to grafting were investigated in detail and will be presented here.

5.2.1 Thermal Reversible Property

Differential Scanning Calorimetry is a thermal analysis technique which has been used for more than two decades to measure the temperatures and heat flows associated with transitions in materials behavior as a function of time and temperature. Such measurements provide quantitative and qualitative information about physical and chemical changes that involve endothermic or exothermic processes, or changes in heat capacity. Hence, in this work, DSC is used extensively for the measurement of micellization in solution.

When dealing with the PEO-PPO-PEO copolymer (Pluronic) micellization in aqueous solution, one of the most distinctive properties is the strong temperature dependence of self-assembly process. Pluronic copolymer is a thermal-reversible polymer. PVP does not show thermal responsive behavior. When Pluronic F127 is modified by PVP, the

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excellent thermal responsive property can be observed in all the graft copolymers. A typical DSC thermograph is shown in Figure 5.7. The heating and cooling rate is 5 °C/min. In the heating cycle, an endothermic peak was observed. In the cooling circle, the exothermic peak appeared broader at a lower temperature. A possible reason is that the kinetics of the association and dissociation are different. Association behaviour of Pluronic obeys closed association model. There are CMC existing in the system and an equilibrium between unimers and molecular micelles after micellization. When micelles dissociate, there is a shoulder peak due to step by step release of the polymer chain from micelle.

Figure 5.7 Thermal-reversible micellization processing of graft polymer, F127-g-PVP (15wt%).

The micellization transition is clearly observed using differential scanning calorimetry. The observed endothermic peak in DSC scan is an indication of a phase transition. In this case, this phase transition is the micelle formation that involves the processes of dehydration and association, and perhaps a change in the conformation of the hydrophobe. All graft copolymer solutions show a broad endothermic peak because it is associated with a rather broad molecular weight distribution.

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5.2.2 Enthalpy of Micellization and Entropy-driven Nature of the Self Assembly Process

The critical micelle temperatures of the graft copolymer are higher than that of F127 as shown in Figure 5.8. The CMT of F127 is similar to what other groups have found (Hecht, 1995). Figure 5.8 shows that the CMT of the graft copolymer increases with decreasing the concentration in aqueous solutions. It is generally believed that the dehydration of the PPO chain with increasing temperature is responsible for the micelle formation.

Figure 5.8 Effect of the concentrations of polymer in aqueous solution on CMT.

Copolymers form micelles in selective solvents which are thermodynamically good solvents for one block and precipitants for the other block. Thermodynamics of micelle formation is well established. In general, the micellization of copolymers, as in the case of conventional detergents, obeys the closed association model, which assumes an equilibrium between molecularly dispersed copolymer (unimer) and multimolecular aggregates (micelles). As mentioned in the earlier chapters, there are two main approaches to the thermodynamic analysis of the micellization process: the phase

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separation model, in which the micelles are considered to form a separate phase at the CMC, and the mass-action model that considers micelles and single polymer chains (unimers) in association-dissociation equilibrium. In both approaches, the standard free-energy change for the transfer of 1 mol of amphiphile from solution to the micellar phase (free energy of micellization), ΔG° , in the absence of electrostatic interactions (non-ionic surfactants) is given by

$$\Delta G^\circ = RT \ln(X_{\text{CMC}}) \quad (5.1)$$

where R is the gas law constant, T is the absolute temperature and X_{CMC} is the critical micelle concentration in mole fraction units. It is assumed that the concentration of the free surfactant in the presence of micelles is constant and equal to the CMC value, in the case when the micelle aggregation number is large for the mass-action model.

Applying the Gibbs-Helmholtz equation and assuming the aggregation number to be independent of temperature in the case of the mass-action model, the standard enthalpy of micellization, ΔH° , can be expressed as

$$\Delta H^\circ = R[\partial \ln(X) / \partial (1/T)]_p \quad (5.2)$$

Finally, the standard entropy of micellization per mole of surfactant, ΔS° , can be obtained from

$$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ) / T \quad (5.3)$$

It has been shown for copolymer micellization that, within experimental error,

$$[\partial \ln(X_{\text{CMC}}) / \partial (1/T)] = \partial \ln(X) / \partial (1/T_{\text{CMT}}) \quad (5.4)$$

X is the concentration expressed as mole fraction and T_{CMT} is the critical micelle temperature; thus, Equation 5.6 becomes

$$\Delta H^\circ = R[\partial \ln(X) / \partial (1/T_{\text{CMT}})]_p \quad (5.5)$$

$$1/T = (R/\Delta H)\ln(X) + \text{constant} \quad (5.6)$$

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Figure 5.9 Reciprocal T_{CMT} versus molar concentrations of F127, F127-g-PVP, F127(PPO)-g-PVP and F127(PEO)-g-PVP, used for the determination of the micellization enthalpy.

Hence, plot of $1/T_{CMT}$ vs $\ln(X)$ will indicate the mode of copolymer association. The inverse CMT values were plotted as a function of the logarithm of copolymer concentration (mole-fraction units) for both Pluronic F127 and the graft copolymers, as shown in Figure 5.9. The CMT data, plotted in this manner, are generally fitted well by a straight line. The plot for F127 may have slight deviation. This fit may not be perfect because of the limited number of data points. The slope appears to increase at high concentrations. The hydrated PEO chains of the micelle coronas will overlap and entangle with increasing polymer concentration, up to the formation of a gel-like structure.

Using both Equation 5.3 and Equation 5.6, the standard free energies, the enthalpies and the entropies of Pluronic F127 and graft products can be calculated. The values are shown in Table 5.2.

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Table 5.2 The free energies (ΔG°), enthalpies (ΔH°), and entropies (ΔS°) of micellization of F127 and F127-g-PVP copolymers at their CMT for 1 wt% solutions.

Polymer	PVP/F127	ΔH°	ΔG°	ΔS°
		kJ/mol	kJ/mol	kJ/(mol K)
F127	0	277.13	-10.33	0.91
F127-g-PVP	0.52	83.14	-12.84	0.23
F127(PPO)-g-PVP	0.76	207.85	-13.93	0.65
F127(PEO)-g-PVP	0.82	166.28	-14.65	0.51

The copolymers dissolved in water as unimers up to high surfactant concentrations. The low hydrophobicity is a result of hydration of the PO groups. With increasing temperatures, the PO groups become dehydrated. Malmsten et al. (1992) also found increasing hydrophobicity of both PPO and PEO with increasing temperatures in the ternary phase diagrams. Hence, micellization occurs due to the increase in hydrophobicity of the chains.

During micellization, the increase in enthalpy of F127 is much higher than that of the graft copolymer shown in the Table 5.2. A possible reason is that there are more conformational changes in Pluronic as a result of its hydrophobic behaviour. In the graft copolymer case, there is steric hindrance for some of the conformational changes. Hence there is a reduction in the gain in enthalpy due to conformational changes. The change in entropy of F127 is greater than that of graft polymer, because the water molecules arrangement is more ordered around Pluronic F127 due to its hydrophobicity. As PVP is more hydrophilic than PPO, the ordering of the molecules for the graft copolymer is less prior to micellization. Hence when micellization occurs, the increase in entropy is less for the graft polymers compared to F127.

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Free energies of micellization per mole of polymer in solution, ΔG° are calculated at the critical micelle temperatures for the aqueous solution of the various copolymers. The data indicate that the graft copolymer has greater propensity to form micelles at CMT because the free energies is more negative compared to the original copolymer (ungrafted). PVP is more hydrophobic than PEO block, after PVP is grafted onto F127, the graft copolymer becomes more hydrophobic. An increase in hydrophobic part of a polymer will increase its ability to form micelles in aqueous solution. Another possible reason may be the higher molecular weight of graft copolymer during micellization. However, after PVP grafted onto whether PEO or PPO block of F127, the steric hindrance became larger. This will decrease the ability of micellization for graft copolymers. These two main factors compete with each other. F127-g-PVP and F127(PPO)-g-PVP have higher CMT than that of F127.

DSC is a simple and efficient method to get the information on the micellization behavior. It verified that the unique thermal reversible property was attached to the graft copolymers after modification. Using the data obtained from the DSC, the change of the enthalpies, the entropies and the free energies of the graft products could be calculated and compared with Pluronic copolymer. Lower changes in the enthalpy and the entropy of the graft copolymer have been found. A more negative free energy was also obtained.

5.3 Aggregation Characteristics

The dynamic light scattering can provide information on the micelle size in terms of hydrodynamic radius, R_h . The static light scattering technique is most often used to determine the molecular weight of the micelle formed in solution. Knowing the molar mass of a single copolymer molecule, we can determine the micellar association number

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which is also known as the aggregation number. The aggregation number increasing with temperature, as observed in F127 (Karlstrom, 1985; Attwood, 1985), indicating that micellization is a stepwise association process. In addition, knowing the micellar size and intrinsic viscosity, the association number of F127 can be calculated. In this section, the hydrodynamic radius of F127, F127-g-PVP, F127(PPO)-g-PVP and F127(PEO)-g-PVP and their polydispersity were studied. The relationship between temperature, viscosity and aggregation number of the copolymers was also investigated.

5.3.1 Micelle size

Hydrodynamic diameter (the micelle diameter plus the double layer thickness, which is induced by dissociation of ionogenic groups in the particle surface and the differential adsorption of solution ions into the surface region.) of a micelle can be determined using photon correlation spectroscopy (PCS). Hydrodynamic diameter is the diameter that a sphere would have in order to diffuse at the same rate as the micelle being measured. It is also known as the equivalent sphere diameter.

When a distribution of sizes is present, the effective diameter measured is an average diameter which is weighted by the intensity of light scattered by each micelle. This intensity weighting, which will be presented, is not the same as the population or number weighting used in a single micelle counter such as in electron microscopy.

5.3.1.1 The effect of grafting efficiency on micelle size and its polydispersity

Many of the difficulties associated with dynamic light scattering can be attributed to the presence of dust particles in the solution, especially when using a polar solvent such as

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water. On top of that, the equilibration between the unimers and micelles take some time. All the samples were prepared at least 24 hours before carrying out the DLS experiments.

For water-soluble Pluronic copolymers, the core of the micelle consists of PO groups. The hydrated PEO chain constitutes the outer shell with a relatively low density of polymer segments. Many researchers (Desai, 2001; Chou, 1996) studied the hydrodynamic radius of F127 using different methods and the results are different due to differences in conditions. In general, the average hydrodynamic radius of F127 is in the range of 11.5 nm. After modification of Pluronic F127 using PVP, the hydrodynamic radius of the graft copolymer is larger than that of Pluronic F127. When the percentage of grafting is higher, there is an increase in the micellar size as shown in Table 5.3.

Table 5.3 Influence of percentage of grafting on micelle size of F127-g-PVP.

Sample	Percentage of grafting (%)	R_h (nm)	Polydispersity
0	0	11	0.02
1	30	140	0.005
2	45	237	0.005
3	57	341	0.005

The reason for this increase is due to the increase in steric repulsion of PVP branches. Such steric repulsion makes both the compact inner core of PPO and the soluble corona of PEO larger. PVP may also form another layer in the micelle or may form smaller micelles existing in both the core and corona of F127.

From Table 5.3, the polydispersity of all graft copolymers with the different percentage of grafting are lower than that of Pluronic F127. This shows that the modification of

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Pluronic F127 using PVP improved the size distribution of the aggregates in aqueous solution. It is known that for pharmacological applications, especially in the drug release system, a copolymer with a narrow polydispersity is preferred.

Figure 5.10 shows the dynamic light scattering (DLS) results for 5 wt% F127 in water at 25°C. While the DLS results for 5 gdl⁻¹ F127 in water showed a micellar peak (diameter of about 22±1 nm) along with unimer peak (diameter ~5 nm), the 10 gdl⁻¹ solution showed only one single micellar peak (diameter of ~29 nm). The hydrodynamic micelles diameter for 5wt% F127 solution was found to be 30 nm at 5wt% by Desai and coworkers (2001) which agree well with present results. Chu and Zhou (1996) observed that the hydrodynamic diameter of F127 was 22-24 nm and also showed that the unimer peak disappears with increase in concentration or increase in temperature.

Figure 5.10 Dynamic light scattering data for F127 in aqueous solutions at 25 ° C.

5.3.1.2 Micelle Size of Graft Copolymer Obtained Using Three Routes

The sizes of the micelles formed by F127, F127-g-PVP, F127(PEO)-g-PVP and F127(PPO)-g-PVP at different angles are shown in Table 5.4 and Table 5.5. The micelle sizes of copolymers measured at 45° usually seem to be larger than those measured at

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higher angles such as 90° and 135°. A possible reason is due to the nature of the technique. The measurements at lower angles are more sensitive to larger particles present in the system. In DLS experiment, sample preparation consists of three parts: solvent purification, cell cleaning, and solution preparation. Hence, the major problems are stray light and dust. The goniometer in DLS instrument was designed to minimize stray light. The properly aligned laser and scratch-free sample cells minimized stray light problem. Dust is a general name given to any undesirable large scatterer that contributes to the signal. Most often dusty samples limit the reproducibility of the results. On the other hand, dust is much more of a problem in highly polar liquids, especially in water. It is often visible through the detector eyepiece as a short burst of light. Since dust is usually a large particle, the light scattered from it is more visible at lower angles.

Table 5.4 Micelle size of F127, F127-g-PVP, F127(PPO)-g-PVP and F127(PEO)-g-PVP in 1 wt% concentration at different temperature without filtering.

Average Eff. Dia. (nm)	25 °C			39 °C		
	45°	90°	135°	45°	90°	135°
F127	13	14	14	18	19	19
F127-g-PVP	889	845	729	717	607	405
F127(PPO)-g-PVP	426	273	278	277	178	88
F127(PEO)-g-PVP	49	40	41	44	39	41

Table 5.5 Micelle size of F127, F127-g-PVP, F127(PPO)-g-PVP and F127(PEO)-g-PVP in 1 wt% concentration at different temperature after using 200nm filter.

Average Eff. Dia. (nm)	25 °C			39 °C		
	45°	90°	135°	45°	90°	135°
F127	12	11.5	11.5	19	18	18
F127-g-PVP	754	457	497	106	106	81
F127(PPO)-g-PVP	113	102	92	55.6	51	50
F127(PEO)-g-PVP	40	39	39	40	37	37

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From Table 5.4 and Table 5.5, the data for F127-g-PVP, F127(PEO)-g-PVP and F127(PPO)-g-PVP without filtering have low repeatability due to the existence of dust in the solution and larger size of the micelles. F127-g-PVP, which PVP grafted onto F127 randomly, has much larger micelle size independent of testing temperature and angle. The micelle sizes are different at different measurement angle. PVP grafted onto PEO block of F127 has smaller micelle size in aqueous solution than F127(PPO)-g-PVP. The micelle sizes of three graft copolymers are all larger than that of F127. The reason may be that PVP either on PEO or PPO part of the chain will provide a steric hindrance to the formation of the compact corona or core.

5.3.2 Flow Behavior Study Using Viscosity Measurement

Micelles are sometimes used as a micro-container to transport hydrophobic drugs or other similar molecules in an incompatible medium, such as water. The flow behavior of the micelles is thus very important. This section discusses the study on the flow behavior of micellar solution using viscosity measurements. All the viscosity measurements were repeated four times. Since the repeat flow time measured showed no significant deviation from the original flow time, it would seem that the flow of the solution through the narrow capillary does not affect the shape of the micelles to an extent that it will alter the flow behavior of the solution.

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Figure 5.11 Reduced viscosity versus F127 concentration at different temperatures.

Figure 5.12 Reduced viscosity versus F127-g-PVP concentration at different temperatures.

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Figure 5.13 Reduced viscosity versus F127(PPO)-g-PVP concentration at different temperatures.

Figure 5.14 Reduced viscosity versus F127(PEO)-g-PVP concentration at different temperature.

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The flow behaviour of the micellar solutions is shown in Figure 5.11, Figure 5.12, Figure 5.13, and Figure 5.14. The reduced viscosities of polymer solutions obtained using intrinsic viscosity [refer to Tables 5.6 to 5.8] measurement increased linearly in certain range of the copolymer concentrations. The solution behaves like normal polymer solution and it follows the Huggin's equation for dilute suspension or polymer solution closely. Refer to Equation 3.14. A micellar solution can be considered as a nano-size particle 'suspension'. The reduced viscosities of polymer solution decreased following an increase in the temperature.

5.3.3 Association number

Static light scattering techniques is most often used to determine the molecular weight of the micelle formed in solution (Alexandridis, 1994b). Knowing the molar mass of a single copolymer molecule enables the micellar association number or the aggregation number to be determined. The term association number appears to be more appropriate because micelles are a thermodynamically stable and equilibrium system, while aggregation usually refers to a non-equilibrium growth of lyophobic colloidal particles into cluster. Another method to determine the association number is to couple the intrinsic viscosity $[\eta]$ and hydrodynamic radius R_h together to obtain association number (N_{agg}) using the following relationship (Pandya, 1993):

$$R_h^3 = \frac{3[\eta]M_w}{10\pi N} \quad (5.7)$$

where M_w is the micellar molecular weight and N is Avogadro constant.

Figure 5.11 shows the reduced viscosity plotted against the different concentrations of F127 in water at different temperatures ($T = 25, 30, 40, 50^\circ\text{C}$). In all cases, the plots are

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found to be linear, behavior typical of an uncharged polymer and which yields intrinsic viscosity $[\eta]$ at zero concentration. The intrinsic viscosities of F127 obtained under different solution conditions are shown in Table 5.6 and the viscosities of F127 in water are in agreement with the earlier reports (Rassing, 1983).

The calculated association numbers are also shown in Table 5.6, Table 5.7 and Table 5.8. The increasing trend of aggregation number with increasing temperature may be due to the dehydration of PEO corona. From Table 5.6, Table 5.7 and Table 5.8, the tendency for the aggregation number to increase following an increase in temperature becomes slower for both graft copolymers, F127(PPO)-g-PVP and F127(PEO)-g-PVP, as compared to F127. The most likely reason for the different speed of these increases in aggregation number is that the steric hindrance existing in graft copolymers becomes more and more important following an increase in temperature. This means that the graft copolymer solution systems tend to form more micelles instead of having more unimers added into one micelle at higher temperature. Hence, the sensitivity of aggregation number of F127(PPO)-g-PVP and F127(PEO)-g-PVP to temperature is lower than that of F127.

This method of calculating the association number using Equation 5.7 is not suitable for the F127-g-PVP graft copolymer since micelle size is too large. From Table 5.6, Table 5.7 and Table 5.8, the aggregation number of F127(PPO)-g-PVP and F127(PEO)-g-PVP is smaller than that of the F127. A possible reason is that the steric hindrance of PVP side chain influenced the compactness of the aggregates.

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Table 5.6 $[\eta]$ and N_{agg} of copolymer of F127 in water at different temperatures.

Temperature, °C	$[\eta]$, dl/g	N_{agg}
25	0.188	63
30	0.160	74
40	0.144	82
50	0.132	90

Table 5.7 $[\eta]$ and N_{agg} of copolymer of F127(PPO)-g-PVP in water at different temperatures.

Temperature, °C	$[\eta]$, dl/g	N_{agg}
25	0.305	62
30	0.294	65
40	0.281	68
50	0.275	69

Table 5.8 $[\eta]$ and N_{agg} of copolymer of F127(PEO)-g-PVP in water at different temperatures.

Temperature, °C	$[\eta]$, dl/g	N_{agg}
25	0.273	26
30	0.249	29
40	0.241	30
50	0.220	33

Static light scattering measurement was also used to measure the aggregation numbers of F127, F127-g-PVP, F127(PPO)-g-PVP and F127(PEO)-g-PVP. The results are shown in Figure 5.15, Figure 5.16, Figure 5.17 and Figure 5.18. The aggregation numbers found are presented in Table 5.9. Comparing the aggregation numbers obtained by SLS to those calculated using the intrinsic viscosity, the aggregation number measured using SLS is

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lower than that calculated using the intrinsic viscosity. A possible reason is that the two techniques were based on different principle. Static light scattering technique is more accurate because intrinsic viscosity measurement and the measurement of hydrodynamic radius includes the associated solvent molecules. This hydrodynamic radius consists of water association corona of micelle and core. Owing to this factor, the value of the aggregation number calculated from intrinsic viscosity and hydrodynamic radius is relatively less accurate than that calculated from SLS. Hence, SLS is more suitable for this measurement.

Table 5.9 The aggregation numbers of F127, F127(PPO)-g-PVP and F127(PEO)-g-PVP at 30 ° C obtained by the method of SLS.

Copolymer	M_w of the aggregates	N_{agg}
F127	6.62×10^5	53
F127-g-PVP	1.27×10^6	49
F127(PPO)-g-PVP	1.97×10^6	38
F127(PEO)-g-PVP	8.12×10^5	12

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Figure 5.15 Zimm plot of light scattering data (shown as point) taken at different angles θ and different concentration of F127.

Figure 5.16 Zimm plot of light scattering data (shown as point) taken at different angles θ and different concentration of F127-g-PVP.

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Figure 5.17 Zimm plot of light scattering data (shown as point) taken at different angles θ and different concentration of F127(PPO)-g-PVP.

Figure 5.18 Zimm plot of light scattering data (shown as point) taken at different angles θ and different concentration of F127(PEO)-g-PVP.

5.4 Summary

The CMC of graft copolymers was investigated using surface tension measurement which is considered to be the most suitable method for this study since it needed a small amount of the sample and fewer steps compared with fluorescence method. The thermodynamics of copolymer micelle formation showed that the micellization of the graft copolymers form micelles in aqueous solution and the micellization process obeys the closed association model and is thermo-reversible. The critical micellization temperature of the graft copolymers decreased with an increase in polymer concentration. The aggregation sizes increased with increasing the percentage of grafting. The association number of three graft copolymers and F127 were obtained in different temperature using intrinsic viscosity and SLS. The association numbers of the graft copolymers are found to be smaller than that of F127.

Chapter 6 Mixed Surfactant Systems

Mixed surfactant systems are encountered in nearly all practical applications of surfactants. There are several sources for these mixtures. One is the natural polydispersity of commercial surfactants which results from the impurities in starting material and variability in reaction. The other is the deliberate formulation of mixtures of different surfactant types to exploit synergistic behavior in mixed systems or to provide qualitatively different types of performance in a single formulation. Another source is the addition of surfactant additives required by practical formulations to help control the physical properties of the product or improve its stability. Hence, the synergism of surfactant and polymers in aqueous solution has been a focus of intense fundamental and applied research.

This chapter discusses the properties and behavior of mixed surfactant systems which were measured experimentally. The investigation of normal surfactant and polymeric surfactant binary systems was carried out for two concentration regions. The two regions are low and moderate concentrations. At the low concentration region, the polymeric surfactants exist in unimeric state. At the moderate concentration region, polymeric surfactants exist in micellar state. The modeling for mixed micelle solutions is discussed in Chapter 7. In Chapter 6 and Chapter 7, mixed surfactant systems using the randomly grafted F127-g-PVP which was synthesized using Synthesis Route 1 as mentioned in Chapter 4 will not be investigated. The study of the solution behavior of this F127-g-PVP presented in Chapter 5 shows that it is not suitable for further investigation. In this chapter, a general description of mixed surfactant solutions is presented, followed by a

more detailed examination of mixed micelles and surfactant mixtures at air/water interfaces of mixed systems.

6.1 Introduction to Mixed Surfactant Systems

Aqueous solutions of surfactants, whether mixtures or single surfactants, exhibit a variety of interesting and useful phenomena. Even at low concentrations of surfactant in water, significant effects can be observed at solution/air interface. The most pronounced effect is a lowering of interfacial tension due to preferential adsorption of surfactant molecules at solution interfaces. With increasing surfactant concentration, the experimentally measured decrease in surface tension depends logarithmically on the surfactant concentration and surfactant monolayers are formed at solution interfaces. Finally, a concentration is reached where this logarithmic decrease in surface tension suddenly stops. Striking changes in the solution can be observed using light scattering in solution. This concentration is known as the critical micelle concentration (CMC). In this process, both ideal and non-ideal mixing contributions may occur. Since the hydrophobic effect which drives the overall process is not specific to surfactant hydrophilic group, in a mixed surfactant system, the formation of randomly mixed surfactant aggregates tend to be favored (Tanford, 1973).

Mixtures of different surfactant types often exhibit strong interaction in their effects on the properties of the system (Rosen, 1984; Zhu, 1984; Rosen, 1991). The observed synergism can be attributed to non-ideal mixing effects in the aggregate, and results in substantially lower CMCs and interfacial tensions than would be expected based on the

properties of the unmixed surfactants alone. This situation has led to both theoretical and practical interest in developing a quantitative understanding of the behavior of mixed surfactant systems. The author would like to begin the discussion with the topic of mixed micelles since unimer-micelle equilibrium exerts a key controlling influence on the behavior of the overall mixed surfactant system.

6.2 Mixed Micellar Solution

A mixed micellar solution of binary system includes a mixed micelle, mixed monolayer at air/solution interface and so on. Rapid equilibrium between unimers and micelles establishes the concentration of each of the surfactant species in solution and, thereby, controls their chemical potential. The chemical potentials, in turn, represent the thermodynamic driving force for processes such as interfacial tension lowering or contact angle changes, and at equilibrium, establish a thermodynamic link between surfactant molecules at interfaces and the mixed micellar solution.

Mixed micellar systems involve a wide range of surfactant types. These types include all combinations of typical non-ionic, anionic, and cationic surfactants, as well as binary mixtures of each of these with zwitterionic surfactants. Different surfactant types often exhibit different properties. When such surfactants are mixed with each other, there is synergism in some of the system (Rosen, 1984; Zhu, 1984). Due to the interactions in a mixed micelles system, CMCs and interface tensions of the mixed system in certain ratio of normal surfactant to polymeric surfactant are usually lower than that in a single surfactants system.

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The most widely used technique for the study of mixed micellar systems employs surface tension measurements. The surface tension of a solution is measured at different surfactant concentrations and the result is plotted against the logarithm of surfactant concentration. In this work, three kinds of binary systems were investigated. They are polymeric surfactant/anionic surfactant, polymeric surfactant/cationic surfactant and polymeric surfactant/non-ionic surfactant.

The concentrations of polymeric surfactants were fixed and those of normal surfactants were varied. When the normal surfactant is added into the polymeric surfactant solution, it moves to the air/water interface or stays in the bulk solution. When the normal surfactant reaches to the air/water interface, it decreases the surface tension. And when the normal surfactant binds with polymeric surfactant existing at air/water interface, this behavior increases the surface tension because the binding of the normal surfactant to polymeric surfactant results in a less surface active complex and this complex leaves the air/water interface.

Other researchers have used micro-DSC to identify the synergistic interaction between F127 and SDS which result in the lowering of the CMT of F127 (Hecht, 1995). Li, Y. (2001a) made use of light scattering with a spectrofluorophotometer to monitor successively the onset and growth of F127 micelles. Other groups of researchers used Electromotive force measurement (EMF) to determine ionic surfactant unimers concentration in the solution and isothermal titration calorimetry (ITC) to monitor enthalpy changes associated with the various processes occurring in the solution (Thurn, 2002).

6.3 Systems Studied

Studies on 3 groups of binary surfactant systems were carried out. They were the binary systems of polymeric surfactant with anionic surfactant, cationic surfactant and non-ionic surfactant. In each group, two concentration regions of polymeric surfactant solution were investigated. One region (low concentration), the polymeric surfactants, exists in unimer state, the other region (moderate concentration) polymeric surfactants, exists in micellar state.

6.3.1 The Interaction between Anionic Surfactant and Non-ionic Polymeric Surfactants

Recently, there have been many researches on anionic surfactant, sodium dodecyl sulfate, SDS. The structural formula of sodium dodecyl sulfate (SDS), is shown in Figure 6.1.

Figure 6.1 The structural formula of SDS.

Many different experiments such as differential scanning calorimetry (DSC), small angle neutron scattering (SANS) and surface tension measurement (ST) have been conducted to study the physical properties. Unfortunately, most research groups were limited by the range of techniques available to them. The comparison of data is difficult because the studies were performed under different experimental conditions. In this work, the conditions of all the experiments are similar. Hence, the results of the experiments can be compared.

6.3.1.1 Interaction of SDS with Unimer Solutions

The interaction between the normal surfactant, SDS, with unimers of polymeric surfactant in aqueous solution was investigated and the results are presented in this section.

Previous DSC studies as described in Chapter 5 have shown that the CMTs of 0.01 wt% F127, F127(PEO)-g-PVP and F127(PPO)-g-PVP are all above 30 °C. This means, at room temperature (about 23 °C in our laboratory environment), which is well below the CMT, it is reasonable to believe that no micelles are present in a 0.01 wt% solution of F127, F127(PPO)-g-PVP and F127(PEO)-g-PVP. At 23 °C, the solution of F127, F127(PPO)-g-PVP and F127(PEO)-g-PVP is expected to behave like a solution of any conventional water-soluble non-ionic polymer. The chains exist in unassociated single unimer units. The CMC of SDS in water is 0.25wt% (8mM) as shown in Figure 6.2. This value is very similar to what has been reported (Technical resource, 2004). The surface tension measurements at varying concentration SDS in water, in 0.01 wt% F127, in 0.01 wt% F127(PEO)-g-PVP and in 0.01 wt% F127(PPO)-g-PVP are shown in Figure 6.3, 6.4 and 6.5, respectively.

Determining the accurate value of C_{onset} and C_{sat} is crucial to study the interactions between the surfactant pairs. The way to determine these critical points is to find the intersection of the tangent to the slope.

Figure 6.2 The CMC of anionic surfactant, SDS.

Figure 6.3 Surface Tension behavior of SDS in 0.01 wt% F127 as a function of concentration at room temperature.

Figure 6.4 Surface Tension behavior of SDS in 0.01 wt% F127(PPO)-g-PVP as a function of concentration at room temperature.

Figure 6.5 Surface Tension behavior of SDS in 0.01 wt% F127(PEO)-g-PVP as a function of concentration at room temperature.

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The curves obtained when varying concentration of ionic surfactants were added to fixed concentration of the copolymers (Figure 6.3, Figure 6.4 and Figure 6.5). At low copolymer concentration, the distinct behavior at different SDS concentration regions was identified. At very low SDS concentration, the surface tension decreased with increase in concentration (Region I). In this region, the anionic surfactants, SDS, remained in their unimer state. They might have competed with the polymer for adsorption at the air/water interface. Region II started at C_{onset} . That means that SDS starts to bind to polymeric surfactants at air/water interface as well as in the bulk to form the complexes. These complexes were less surface active and desorbed from the interface. As a result, the surface tension increased in this region. Finally all F127 copolymer molecules were saturated with SDS molecules at C_{sat} . With further increasing concentration, the excess surfactant molecules adsorbed to the air/water interface, which lowered the surface tension (Region III). Once the air/water interface was saturated with SDS molecules, and when the free surfactant concentration increased further, SDS micelles were formed. The surface tension remained nearly constant in region IV.

One might ask: Does SDS have any preferential binding to either the PEO or PPO part of the copolymer? Using NMR, Algren (1991) reported that most of SDS will prefer to bind to the most hydrophobic groups which are the PO groups. Since the binding of surfactant changes the environment of the methyl groups, the binding is reflected in the shift of the NMR signals of the CH_3 groups. But when the repeating units of PPO are higher than 20, PPO chain cannot be soluble in the water. The binding of SDS on PPO would become very difficult. The addition of hydrophilic PEO into both sides of PPO block in Pluronic F127 increases the solubility of PPO in water. SDS prefers to interact with PPO part in this system.

With reference to Figure 6.4 and 6.5, the surface tension curves of the graft copolymers also showed the four regions when interacting with anionic surfactant, SDS. C_{sat} for F127(PEO)-g-PVP and F127(PPO)-g-PVP with SDS were different from that of F127. To explain this difference, one has to look at the orientations of the copolymers at air/water interface. The hydrophobic PPO chains are oriented near to the air phase and hydrophilic PEO chains are oriented towards the water phase. This orientation makes the copolymer form 'U' shape at the air/water interface. The number of molecules of graft copolymer at the air/water interface is much less than that of F127 due to bigger "U" shape form by graft copolymers due to the steric hindrance of branching structure. At the same time, the PVP added can also interact with SDS and bind to SDS. It needs more SDS to saturate the graft copolymer.

6.3.1.2 Interaction of SDS with Micellar Solutions

This section presents the results of the interaction between the normal surfactant, SDS, with micelles of polymeric surfactant in aqueous solution.

The micellar state of polymeric surfactant, those are F127, F127(PEO)-g-PVP and F127(PPO)-g-PVP, were verified. Previous DSC studies have shown that the CMT of 5 wt% F127, F127(PEO)-g-PVP and F127(PPO)-g-PVP are 17, 18 and 20 °C, respectively. Therefore, at experimental environment, 5 wt% F127, F127(PEO)-g-PVP and F127(PPO)-g-PVP solution. All samples were equilibrated overnight at room temperature.

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Since micelles are already formed at 23 °C for all three solutions, the solutions should contain both unimers and micelles. The micelles are in dynamic equilibrium with a small amount of unimers as discussed in Chapter 5. Therefore, normal surfactants, such as anionic surfactant, SDS, may bind to either the copolymer molecules in the solution (unimers) or/and the micelles to form the mixed aggregates. How does one determine which is preferred?

Figure 6.6 Surface Tension behavior of SDS in 5 wt% F127 as a function of concentration at room temperature.

Figure 6.7 Surface Tension behavior of SDS in 5 wt% F127(PPO)-g-PVP as a function of concentration at room temperature.

Figure 6.8 Surface Tension behavior of SDS in 5 wt% F127(PEO)-g-PVP as a function of concentration at room temperature.

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Most researchers agree that there are two simultaneous binding processes taking place in SDS/F127 solution (Li, 2002). They are:

- (1) SDS binds to micellar F127 followed by the breakdown of these mixed micelles to smaller aggregates.
- (2) SDS micelles bind to unimers of F127.

Figure 6.6, 6.7 and 6.8 shows that surface tension variation in “polymeric” surfactant micelles and “normal surfactant” binary system. The surface tension variation with an increase in anionic surfactant, SDS, concentration at a fixed concentration of “polymeric” surfactants was measured. In Region I, the surface tension of the binary systems tends to decreased before increasing due to the equilibrium between an increase in the concentration of SDS which decreased the surface tension and the release of complexes of polymeric surfactant with SDS from air/water interface increased the surface tension. In Region II, the decrease in surface tension was probably due to the increased surface activity resulting from polymeric surfactant unimers being released into solution and, hence, the air/water interface. The polymeric surfactant unimers were the results of the breakdown of the mixed micelles. Region III showed the increase in surface tension due to unimers leaving air/water interface. This is due to the binding of SDS aggregates which are less surface active complex. With an further increase in SDS concentration, the behavior was similar to last parts of the curves in “polymeric” surfactant unimer and “normal” surfactant system. The behavior of the graft copolymer F127(PPO)-g-PVP and F127(PEO)-g-PVP also obeyed the interaction model of SDS and F127 system.

6.3.1.3 Analysis of the Mechanism of the Interaction

Interaction between surfactant and polymer does not mean that surfactant binds covalently to the polymer. Generally, the solution properties of water-soluble, neutral polymers are easier to study than that of charged polymer because neutral polymer has less complex solution properties. However, the interaction between neutral polymers and surfactants is more difficult to understand than that between polyelectrolytes and surfactants. This is because electrostatic interactions strongly dominate and determine whether an interaction occurs in the latter systems and such interaction is weaker in the neutral polymer and surfactant systems. There are many researchers who investigated SDS and F127 binary system using many different methods such as light scattering, small angle neutron scattering, electromotive force measurements, and isothermal titration calorimeter (Hecht, 1994; Hecht, 1995; Li, 2000; Almgren, 1991; Cardoso, 2002). Most of them concluded there is strong interaction between F127 and SDS since the critical aggregation concentration of surfactant in polymer solution is usually lower than the critical micelle concentration of the surfactant in water by a factor of 1 to 10 (Goddard, 1993; Kwak, 1998; Zana, 2003).

Homopolymer, PEO, and the surfactant, SDS, has been the most often used in the study of neutral polymer and ionic surfactant interactions. Silva and coworkers (2004) proposed that PEO/SDS complex is stabilized by hydrophobic interactions between PEO methylene groups and SDS alkyl chain, or by interactions between PEO ether groups and sulfate groups in SDS, or by effects related to the nature of the micelle-water interface. The hydrophobic interaction is from the exclusion of the solvent, water. Water molecules expel the hydrophobic part of the polymer to make them form a more stable structure.

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This results in aggregation. None of the foregoing proposals has been clearly substantiated and the driving force for the binding of SDS to PEO is open to debate.

Compared to the research on PEO with SDS, the studies on interaction between PPO and SDS have been limited. Since the PPO polymer is more hydrophobic than PEO polymer, it should interact with SDS more strongly. But this strong interaction is limited by PPO's lower aqueous solubility. The methyl group on the ethoxyl chain of PPO, especially the high molecular weight of PPO, largely influences its solubility in water. An increase in the molecular weight of PPO will lead to a strong interaction of it with SDS, which is verified by lower critical aggregation concentration of surfactant and the micelle being more ionized than normal micelles (Rodenas, 1996; Bloor, 1995). Ballerat and his coworker (2001) studied the interactions between poly(propylene) glycols and SDS in aqueous solutions using thermodynamic analysis. From his analysis of the variations in densities and heat capacities as a function of the surfactant concentration, he concluded that strong hydrophobic interactions are involved in the interaction between PPO and SDS. Roscigno and coworkers (2001) proposed using the "exclude volume effect" to explain the interaction between PVP and sodium alkyl sulfate.

The ratios of SDS to PEO, PPO and PVP in unimer state in polymeric surfactant solution at saturated point in Figure 6.3, Figure 6.4 and Figure 6.5 were calculated and listed in Table 6.1. The ratios of SDS to PEO, PPO and PVP in micellar state in polymeric surfactant solution was not calculated since the binary surfactant system for polymeric surfactant in micellar state is very complicated and one cannot be sure every polymeric surfactant molecules are bond with SDS. In order to simplify the calculation, SDS was assumed to only interact with PVP and PPO well. This assumption was based on the

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studies of Rodrigo (2002) and Almgren (1991). Rodrigo investigated the interaction of copolymer L121, P123 and F127 with SDS. L121, P123 and F127 were used in order of increasing PEO block size and the PPO block size is constant. He found the interaction of SDS with unimers of L121, P123 and F127 in the solution is similar. That means the increase in the length of PEO will not influence the interaction between SDS and Pluronic copolymers. Almgren studied the interaction of SDS with L64 and F68. He concluded the hydrophobic PPO block of copolymer strengthens the interaction with SDS far beyond that in PEO.

Table 6.1 Binding ratios of SDS to polymeric surfactants and their repeating units.

	C_{onset}	C_{sat}	C_{binding}	C_{polymer}	SDS/polymer	SDS/PO	SDS/VP
F127	0.4300	0.8800	0.4500	0.0079	56	0.8116	
F127(PEO)- g-PVP	0.3200	0.7300	0.4100	0.0014	292	0.8116	0.4565
F127(PPO)- g-PVP	0.4300	0.8200	0.3900	0.0019	205	0.5960	0.4565

Table 6.1 shows the binding ratios of SDS to polymeric surfactants and their repeating units. The actual amount of SDS surfactant that involved in binding with polymeric surfactants (C_{binding}) was calculated by deducting those SDS that sit at water/air interface (C_{onset}) from the total amount of SDS when saturation of the binding occurred (C_{sat}). The surfactant/polymer ratio is estimated by $C_{\text{binding}}/C_{\text{polymer}}$.

It is quite obvious that the binding ratios of SDS to both graft copolymers were much higher than that of SDS/F127. This must be due to the presence of the relatively large amount of PVP segments along the F127 main chain. As discussed above, we assumed that most of the SDS bound to PPO segments. Thus, we can expect that the presence of PVP should reduce the binding between SDS with PPO segments in F127(PPO)-g-PVP

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since PVP segments which had grafted mainly on PPO segments would further hinder the SDS from approaching to the PPO main chain by providing spatial obstacles. On the other hand, the effect of PVP on the binding of SDS and PPO in F127(PEO)-g-PVP should be less obvious. If we made a further assumption that the grafting site of PVP (whether on PPO or PEO) had little affect on the interaction between PVP and SDS, combining with the analysis stated above, a rough estimate of the binding ratios of SDS to segments of PPO and PVP is obtained as is listed in table 6.1.

It is found that the binding ratio of SDS/PO was reduced from 0.8 to 0.6 when the grafting sites of PVP on F127 moved from PEO (F127(PEO)-g-PVP) to PPO (F127(PPO)-g-PVP), which corresponds well to our analysis above, indicating that our assumptions are reasonable. (On the other hand, it has been also assumed that most of the SDS bound with PEO instead of PPO, and SDS/VP is indifferent of the grafting sites. The calculated results showed that when the grafting sites of PVP moved from PEO (F127(PEO)-g-PVP) to PPO (F127(PPO)-g-PVP), SDS/PEO that should increase due to the increase in binding sites and absence of spatial hindrance, was found to be reduced. Thus, we excluded this situation.)

The calculated results also shows that the binding ratio of SDS/PO was higher than that of SDS/VP, suggesting that the tendency of SDS binding with PPO is stronger than that with PVP. This conclusion is supported by the fact that PVP is more water soluble than PPO is, and one can deduce that the hydrophobic interactions between SDS and PPO might be stronger than that between SDS and PVP. Therefore, although the numerical number obtained from the calculation might not be very accurate due to the approximations resulted from the simple assumptions, the general conclusions drawn from the calculations is still reasonable.

6.3.2 The interaction between Cationic Surfactant, TTAB, and Non-ionic Polymeric Surfactants

The chemical structure of cationic surfactant: tetradecyltrimethyl – ammonium bromide (TTAB) is shown in Figure 6.9.

Figure 6.9 The structural formula of cationic surfactant, TTAB.

Figure 6.10 The CMC of TTAB at room temperature.

The critical micellization Concentration (CMC) of tetradecyltrimethyl ammonium bromide (TTAB) is shown in Figure 6.10. CMC of TTAB in water is similar to that reported in literature (Yoon, 2002). As discussed in the previous section, there are many studies on the synergistic nature of the interaction between F127 and SDS, in a binary mixture of the anionic surfactant and F127. However, the investigation for the interaction of F127 with TTAB is rare (Li, Y., 2001b). The reason for this may be that most cationic surfactants generally do not interact with “polymeric” surfactants. In the following

sections, the results on the interaction of cationic surfactant and polymeric surfactant are presented.

6.3.2.1 Interaction of TTAB with Unimer Solutions

As mentioned before, 0.01 wt% F127(PPO)-g-PVP and F127(PEO)-g-PVP will form micelles at above 30 °C. At a temperature of 23 °C, the solution of F127, F127(PPO)-g-PVP and F127(PEO)-g-PVP is expected to behave like a solution of any conventional water-soluble non-ionic polymer. The chains will exist as unassociated single unimer units.

Figure 6.11 Surface Tension behavior of TTAB in 0.01 wt% F127 as a function of concentration at room temperature.

Figure 6.12 Surface Tension behavior of TTAB in 0.01 wt% F127(PPO)-g-PVP as a function of concentration at room temperature.

Figure 6.13 Surface Tension behavior of TTAB in 0.01 wt% F127(PEO)-g-PVP as a function of concentration at room temperature.

Figure 6.11, 6.12 and 6.13 show surface tension variation in “polymeric” surfactant unimers and “normal surfactant” binary system following an increase in TTAB concentration at a fixed concentration of “polymeric” surfactants. The curves exhibit reduction in surface tension at very low TTAB concentration increased. This is due to the weak influence of TTAB on the surface tension. The value of surface tension in the mixture systems was lower than that of water due to the strong influence of “polymeric” surfactants. The surface tension decreased with increasing TTAB concentration. This corresponds to the increase in surface activity due to the addition of unimeric TTAB at the air/water interface. This decrease stopped when the TTAB concentration reached C_{onset} which is 0.18, 0.15 and 0.15 for F127, F127(PPO)-g-PVP and F127(PEO)-g-PVP, respectively. The surface tension increased due to the binding of TTAB aggregates to “polymeric” surfactants unimers. The reason for this is that loss in the surface activity of polymeric surfactant unimers bound by TTAB decreased substantially and the polymeric surfactant unimers left the air/water interface. Finally, the surface tension decreased again after F127 was saturated with TTAB.

6.3.2.2 Interaction of TTAB with Micellar Solutions

Previous DSC studies have shown that the CMT of 5 wt% F127, F127(PEO)-g-PVP and F127(PPO)-g-PVP are all above 17, 18 and 20 °C, respectively. Therefore, 5 wt% F127, F127(PEO)-g-PVP and F127(PPO)-g-PVP are all micellar solutions. All the samples were equilibrated overnight at room temperature.

Figure 6.14 Surface Tension behavior of TTAB in 5 wt% F127 as a function of concentration at room temperature.

Figure 6.15 Surface Tension behavior of TTAB in 5 wt% F127(PPO)-g-PVP as a function of concentration at room temperature.

Figure 6.16 Surface Tension behavior of TTAB in 5 wt% F127(PEO)-g-PVP as a function of concentration at room temperature.

Figure 6.14, 6.15 and 6.16 show the surface tension variation in “polymeric” surfactant micelles and “normal surfactant” binary system following an increase in TTAB concentration at a fixed concentration of “polymeric” surfactants. From a to b, the surface tension decreased and then increased slightly. This is because the equilibrium between an increase in the concentration of TTAB resulting in a decrease in the surface tension and the leaving of the TTAB/ polymeric surfactant complexes from the air/water interface resulting in an increase in the surface tension. After b, the decrease in surface tension is probably due to the increased surface activity resulting from polymeric surfactant unimers, which were bond to the micelle previously, is being released into solution and hence the air/water interface. From c to d, the increase in surface tension is due to the polymeric surfactants being saturated with TTAB and left the air/water

interface. The behavior is similar to last parts of the curves in “polymeric” surfactant unimer and “normal” surfactant system.

6.3.2.3 Analysis of the Mechanism of the Interaction

The interaction between a series of n-alkyl trimethyl ammonium bromides and polyvinyl pyrrolidone was studied by Gharibi and coworkers (1998) using a surfactant-selective electrode. They used three dominant forces to explain polymer-surfactant interactions: electrical, hydrophobic interaction and Van der waals force. The first is the charge-charge interactions between surfactant and polyelectrolyte and dipoles of a non-ionic polymer. The hydrophobic interaction is from the exclusion of the solvent, water. Water molecules expel the hydrophobic part of the polymer to make them form a more stable structure. This results in aggregation. Van der waals force is from the nearest neighbor molecules and is small in comparison with electrical and hydrophobic interactions. Gharibi et al. concluded that the process of micellization of ionic surfactant is the result of a balance between several forces favoring and resisting aggregation. One of the main forces resisting aggregation is the crowding together of the ionic head groups at the surface of the micelles. The high charge density in this zone favors the tight binding of counterions which reduces the electrical potential and headgroup repulsion. Therefore, the reduction of this unfavorable situation will promote micellization.

Similar strategy that was used to study SDS/polymeric-surfactant systems in section 6.3.1.3 has been adopted to study the binding of TTAB to PO, EO and VP segments. TTAB was assumed to only interact with PPO and PVP, which is supported by the studies of Goddard (1993), Li, Y. (2001b) and Ghoreishi (1999). Li, Y. (2001b) found

TTAB bond to both unimeric and micellar F127 and TTAB formed a polymeric/micellar TTAB complex with unimeric F127. This means there is the interaction between F127 and TTAB. Ghoreishi and coworkers (1999) did much work on the interaction of TTAB with F127 using electron moving force (EMF) measurements and isothermal titration calorimetry (ITC) and concluded that if the separate EO and PO blocks of F127, TTAB only interacted with more hydrophobic block, PPO.

Table 6.2 Binding ratios of TTAB to polymeric surfactants and their repeating units.

	C_{onset}	C_{sat}	C_{binding}	C_{polymer}	TTAB/ polymer	TTAB/ PPO	TTAB/ PVP
F127	0.2100	0.2500	0.0400	0.0079	5	0.0725	
F127(PEO)- g-PVP	0.1800	0.3000	0.1200	0.0014	85	0.0725	0.1547
F127(PPO)- g-PVP	0.1500	0.1900	0.0400	0.0019	21	0	0.0585

Table 6.2 summarizes the calculated results of binding ratios between TTAB and those polymeric surfactants as well as their repeat unions. It is noticed that the binding ratios of TTAB to those graft copolymers were higher than that of TTAB/F127, and the binding ratio of TTAB/ F127(PEO)-g-PVP was much higher than that of F127(PPO)-g-PVP. Following the assumption that the interaction between TTAB and PEO was negligible, the binding ratios of TTAB/PPO in F127 and TTAB/PVP in F127(PEO)-g-PVP were obtained, with the latter much higher than the former. This could be the indication that TTAB interacts stronger to PVP than to PPO, in contrast to SDS, which interacts stronger with PPO due to their stronger hydrophobic force. This contradiction can be resolved by an explanation that hydrophobic force was not the dominant force governing the binding between TTAB and those polymeric surfactants studied here. Van der waals force, which is much weaker than the hydrophobic force, might have played a major role in this

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process. If it is true, it also helps to explain why the interaction of TTAB to F127 was much weaker than that of SDS to F127 although they both have long hydrophobic tails. Another finding inconsistent with the assumption in table 6.2 is that the binding ratio of TTAB/VP reduced substantially when the grafting site of PVP shifted from PEO segments to PPO segments. Therefore, the assumption that PVP is indifferent to the grafting site when binding with other surfactants fails to stand here. To explain this, the graft ratios of VP/EO and VP/PO are calculated, which are 2.61 (517/198) and 5.20 (359/69), respectively. It is quite obvious that when PVP was grafted on PPO segments, the core become overcrowded. This denser packing of PVP has prevented substantial amount of TTAB from approaching to the inner part of the graft copolymer, that is, the weak Van der waals force is not enough for TTAB to overcome the spatial hindrance caused by denser packing. Thus, it is not surprising that no binding was find between PPO and TTAB on F127(PPO)-g-PVP. On the other hand, although SDS was facing the same hindrance, the much stronger hydrophobic force might have helped them to penetrate further.

From the analysis above, we concluded that although the ST measurements showed similar trend of transition for both ionic and cationic surfactants when they are interacting with polymeric surfactants, their interacting behavior are far from similar.

6.3.3 The Interaction between Non-ionic Surfactant, C₁₂EO₆, and Non-ionic Polymeric Surfactants

The chemical structure of non-ionic surfactant, hexaethylene glycol monododecyl ether, C₁₂EO₆, is shown in Figure 6.17.

Figure 6.17 The structural formula of cationic surfactant, $C_{12}EO_6$.

In Figure 6.18, the CMC of $C_{12}EO_6$ in water is 0.08 mM which is similar to that reported by Yoon (2002).

Figure 6.18 The CMC of $C_{12}EO_6$ at room temperature.

Very few studies on the interaction between F127 and $C_{12}EO_6$ has been conducted. In general, the synergistic effect between non-ionic surfactant and F127 in binary mixture is not obvious. In 2001, Couderc and coworkers (2001) reported that the interaction of F127 with $C_{12}EO_6$ was synergistic. The interaction of the polymeric surfactants, F127, F127(PEO)-g-PVP and F127(PPO)-g-PVP with $C_{12}EO_6$ was investigated and the findings are presented in the following section.

6.3.3.1 Interaction of $C_{12}EO_6$ with Unimer Solutions

The surface tension behaviors of $C_{12}EO_6$ with unassociated “polymeric” non-ionic surfactants are shown in Figure 6.19, 6.20 and 6.21.

Figure 6.19 Surface Tension behavior of $C_{12}EO_6$ in 0.01 wt% F127 as a function of concentration at room temperature.

Figure 6.20 Surface Tension behavior of $C_{12}EO_6$ in 0.01wt% F127(PPO)-g-PVP as a function of concentration at room temperature.

Figure 6.21 Surface Tension behavior of $C_{12}EO_6$ in 0.01 wt% F127(PEO)-g-PVP as a function of concentration at room temperature.

At first, a small amount of $C_{12}EO_6$ was added into the system, and the surface tension decreased due to more $C_{12}EO_6$ going to the air/water interface. As $C_{12}EO_6$ concentration reached C_{onset} which is near the critical micelle concentration of $C_{12}EO_6$, $C_{12}EO_6$ began to bind to polymeric surfactant resulting in an increase in surface tension. The polymeric surfactants left the air/water interface in a form of complex with $C_{12}EO_6$ and this behavior increased the surface tension. As more $C_{12}EO_6$ was added, the surface tension increased due to more “polymeric” non-ionic surfactants leaving the surface as a result of the binding process. When $C_{12}EO_6$ concentration reached about 10 mM, which is denoted as C_{sat} , the surface tension did not increase more because the “polymeric” surfactants were saturated with normal surfactant $C_{12}EO_6$.

6.3.3.2 Interaction of $C_{12}EO_6$ with Micellar Solutions

The surface tension behaviors of $C_{12}EO_6$ with micellar “polymeric” non-ionic surfactant are shown in Figure 6.22, 6.23 and 6.24. When $C_{12}EO_6$ was first added to micellar “polymeric” surfactants, the surface tension decreased due to an increase in $C_{12}EO_6$ concentration. After that, the surface tension increased from a to b because of the formation of complexes of polymeric surfactant with $C_{12}EO_6$. After b, the decrease in surface tension was probably because of the increased surface activity resulting from polymeric surfactant unimers being released into solution and, hence, the air/water interface. The replacement of polymeric surfactants is caused by the breakdown of the mixed micelles. From c to d, the increase in surface tension was due to unimers leaving air/water interface resulting from the binding $C_{12}EO_6$ aggregates. When the $C_{12}EO_6$ concentration was beyond d, the surface tension decreased. The $C_{12}EO_6$ saturated the polymeric surfactant in the solution. The surface tension decreased is due to more and more $C_{12}EO_6$ aggregated to the air/water interface. At high $C_{12}EO_6$ concentration, the surface tension remains constant due to the formation of $C_{12}EO_6$ micelles in the solution.

Figure 6.22 Surface Tension behavior of $C_{12}EO_6$ in 5 wt% F127 as a function of concentration at room temperature.

Figure 6.23 Surface Tension behavior of $C_{12}EO_6$ in 5 wt% F127(PPO)-g-PVP as a function of concentration at room temperature.

Figure 6.24 Surface Tension behavior of $C_{12}EO_6$ in 5 wt% F127(PEO)-g-PVP as a function of concentration at room temperature.

6.3.3.3 Analysis of the Mechanism of the Interaction

The ratios of $C_{12}EO_6$ to PEO and PVP in unimer state in polymeric surfactant solution at saturated point (Figure 6.19, Figure 6. 20 and Figure 6.21) were calculated and tabulated

in Table 6.3. Among the data, the binding ratios of $C_{12}EO_6$ /PEO and $C_{12}EO_6$ /PVP were obtained based on the assumption that $C_{12}EO_6$ interacts with PEO and PVP segments only.

Table 6.3 Binding ratios of $C_{12}EO_6$ to polymeric surfactants and their repeating units.

	C_{onset}	C_{sat}	$C_{binding}$	$C_{polymer}$	$C_{12}EO_6$ / polymer	$C_{12}EO_6$ / EO	$C_{12}EO_6$ / VP
F127	0.2200	1.9400	1.7200	0.0079	217	1.0960	
F127(PEO)-g-PVP	0.2900	0.5800	0.2900	0.0014	207	0.0636	0.3760
F127(PPO)-g-PVP	0.2200	0.8900	0.6700	0.0019	352	1.0960	0.3760

$C_{12}EO_6$ contains a hydrophilic head consisting of ether oxide groups that are identical to the repeat unions of PEO segments and a hydrophobic tail. Generally, for non-ionic surfactants, their aggregation behavior was induced by their hydrophobic interactions. Thus, it is expected that the interaction between the hydrophobic tail of $C_{12}EO_6$ and hydrophobic PPO segments in F127 should dominate the binding between them. However, the calculation results show that after grafting PVP onto the hydrophilic segments of PEO, the binding ratio of $C_{12}EO_6$ /polymeric surfactant has reduced a little bit (from 217 to 207), while when PVP was grafted on more hydrophobic segments of PPO, the binding ratio of $C_{12}EO_6$ /polymeric surfactant increased substantially (from 217 to 352). These results indicate that when the more hydrophilic segments were covered by less hydrophilic segments, their binding with $C_{12}EO_6$ was reduced; while the more hydrophobic segments were covered by less hydrophobic segments, their binding with $C_{12}EO_6$ was increased. This trend contradicted with the expectation that hydrophobic interaction is dominant. On the other hand, calculations based on the assumption that hydrophobic interaction is dominant, that is, $C_{12}EO_6$ /PPO is dominant and $C_{12}EO_6$ /PEO is

negligible, have been conducted. The results obtained, showing an increase in the binding ratio of $C_{12}EO_6$ /PPO after PVP grafting site moved from PEO to PPO. Therefore, the results does not support the assumption. Combining these evidences, the assumption that hydrophobic interaction dominated the binding process was excluded.

It is thus natural to assume the opposite: $C_{12}EO_6$ was mainly bonded to PEO segments of F127. Based on this assumption, reasonable values of $C_{12}EO_6$ /EO and $C_{12}EO_6$ /VP were obtained and listed in table 6.3. The binding ratio of $C_{12}EO_6$ /EO for F127(PEO)-g-PVP was much lower than that of the other two polymers. This can be attributed to that the grafting of PVP on the PEO segments has changed the PEO structure chemically, and depriving its resemblance to the hydrophilic head of $C_{12}EO_6$, thus substantially reduced the binding between them. Another finding that the binding ratio of $C_{12}EO_6$ /VP is lower than that of $C_{12}EO_6$ /EO, is also consistent with the fact that PVP is less hydrophilic than PEO. Thus, all the calculated data supports the assumption made earlier. Although more evidences are still needed to support this assumption and to describe such interactions, the analysis above is believed to have shed some light on the directions to explore.

6.4 Summary

The binary surfactant systems of polymeric surfactant with normal surfactant were investigated. The concentration of polymeric surfactants was fixed at 0.01wt% and 5wt% and the concentration of normal surfactants was changed. It was found that the hydrophobicity of PPO is higher than that of PVP and PEO and the hydrophobicity of PVP is higher than that of PEO. Also, SDS and TTAB interact with more hydrophobic

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chains, PPO and PVP. $C_{12}EO_6$, on the other hand, interacts with more hydrophilic PEO, and PVP mostly. Based on the calculation, it is clear that although the same trend of transitions were found for all the normal surfactant and polymeric surfactant pairs, their interaction behaviors are definitely different. The surface tension measurement can clearly and directly describe the process of the interaction between “polymeric” non-ionic surfactants and “normal” surfactant by fixing the concentration of one component and changing the concentration of the other component.

Chapter 7 Modeling Mixed Micellar Systems

In most practical applications, mixtures of surfactants, rather than individual surfactants, are used. In commercial surfactants, it is rare to find pure surfactant. Most commercial surfactants are made up of mixed surfactants. In some cases, different types of surfactants are deliberately used in the formulation to improve the properties of the final products. They are found in fluids for enhanced oil recovery, food preparations, cosmetics formulations and pharmaceutical compositions. In most cases, synergism is desired when different types of surfactants are mixed deliberately. Synergism is the condition when properties of the mixture are better than those attainable with the individual components by themselves.

Although the existence of synergistic relationships between certain types of surfactants has been known and utilized for many years now, the investigation of synergism in quantitative terms is a very recent development based upon a simple, convenient method for measuring molecular interactions between surfactants. From the relevant properties of the individual surfactants and the values of the molecular interaction parameters, it is possible to predict whether synergism exists in a mixture of surfactant and, if so, the ratio of the materials at which synergism is optimal.

In this chapter, general information about binary aqueous solutions is presented. Typical models for treating mixed micellization which are based on an equilibrium thermodynamic approach are discussed. The theory relating to these models and the

evaluation of molecular interaction parameters through experimental, ideal theory and non-ideal regular solution theory are also presented. .

7.1 Ideal and Non-ideal Mixing micellar model

The micelles formed in the binary solutions have been found to be composed of both surfactants and they are in equilibrium with the monomeric species in aqueous phase. The description of the physical behavior of binary surfactant mixtures above the mixed critical micelle concentration depends upon both the value of the CMC and the distribution of surfactant components between micellar and aqueous phase. Phenomena where such a description is mandatory are adsorption and solubilization. Hence, interaction behavior in the mixed surfactant system is related to monomer concentration and mixed micelle composition.

Typical models for treating mixed micellization are based on an equilibrium thermodynamic approach. They differ in how the micellar aggregate is modeled, that is, whether counterions are taken into account and the way non-ideality is treated. Generally, the approach that is selected depends on the complexity of the system to be modeled, the properties to be described and the desired level of details.

7.1.1 Ideal Mixing Models

The earliest approach for modeling mixed micellization was developed in the 1950s for binary surfactant system by Shinoda (1954). This was based on the pseudophase

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separation approach with the assumption of ideal mixing in the micelles. This widely used approach assumes that the mixed micelle or other surfactant aggregate can be treated much like a separate phase (Shinoda, 1962). While it is clear that micelles do not constitute a thermodynamic phase, they do mimic phase-like behavior in the sense that they can act as both a source and a sink for surfactant species in solution. This approach represents a limiting case where the aggregation number of the micelle is formally assumed to approach infinity. Using this approach greatly simplifies the modeling of complex mixed surfactant systems. Generally, ideal mixing models have been successful in describing the CMC behavior of binary ionic surfactant systems (Barry, 1970; Shedlovsky, 1963).

Ideal mixing models have also been generalized for treating multicomponent surfactant mixtures with an arbitrary number of components (Holland, 1984; Warr, 1983). Treatment of multicomponent ideal mixtures has also been extended to two phase systems which contain an oil phase in addition to the surfactant solution (Harusawa, 1981).

There is limitation in the ideal mixing models for treating mixed micellization in binary surfactant systems. The ideal mixing model treats micellization as a phase separation process with the micelle aggregation number taken to approach infinity. The critical micelle concentration in mixed surfactant system is lower than the value expected based on ideal mixing theory. This deviation in results from experiments can be attributed to non-ideal mixing effects between the different surfactant components in the micelle. This has led to the development of non-ideal mixed micelle models such as those based on the regular solution approximation.

7.1.2 Non-ideal mixing Models

The regular solution approximation for treating non-ideal mixing has been one of the most widely used methods to model mixed surfactant systems. This approach was first applied by Rubingh (1979) to a broad range of different binary mixed surfactant systems. Although this model was formally designed for treating non-ionic surfactants, the approach was also found to be successful at describing the behavior of mixtures with ionic surfactants. Over the years, this binary non-ideal mixed micelle model has been used to model a wide variety of micellar solutions (Rosen, 1982; Holland, 1983; Rosen, 1984). The model has also been used as the basis for developing treatments of synergism in binary mixed systems (Rosen, 1991; Zhu, 1984).

The regular solution approach for non-ideal mixed micelles has been extended to multicomponent mixtures by using a generalized pair-wise expression for activity coefficients based on the regular solution approximation and interaction parameters determined from binary mixtures (Holland, 1986; Graciaa, 1989; Holland, 1992). This allows non-ideal behavior in multicomponent non-ideal systems to be described without adjustable parameters (Holland, 1992). A regular solution model which provides explicit treatment of counterion effects for binary ionic mixed micelles has been developed by Kamrath and Franses (Kamrath, 1983) and also extended to explicitly treat counterions in binary ionic-non-ionic mixtures (Kamrath, 1986).

The regular solution approximation itself formally assumes that the entropy of mixing is zero and, therefore, the excess heat of mixing dominates the mixing process. Calorimetric measurements of micellar mixing have shown that this assumption does not hold in many

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systems (Holland, 1983; Rathman, 1988). Nonetheless, the functional form of the regular solution approach has been demonstrated to provide a robust and tractable basis for describing non-ideal behavior in many mixed surfactant systems. This has led to a suggestion that the mixing parameter that arises in the regular solution approach be interpreted more generally as an excess free energy of mixing parameter which reduces to excess enthalpy only when the excess entropy is zero (Holland, 1983; Holland, 1992). Hall and coworkers (1992) have completed a detailed thermodynamic analysis of a non-ideal cationic-sulfobetaine mixture which they find to conform well to regular solution theory.

Alternatives to the much-used regular solution approach for treating non-ideality in mixed micelles have also been developed. These include pseudophase separation models based on the Gibbs-Duhem equation which use slopes of the CMC as a function of monomer concentrations (Nguyen, 1986). This approach offers the advantage that it does not assume a particular form for the free energy of mixing and can be used as input data to calculate other properties. However, it cannot be used to predict CMCs. Among the more interesting developments is a pseudophase model developed by Rathman and Scamehorn (Rathman, 1984; Rathman, 1987) which is based on electrostatic interactions only. This provides a reasonable description of non-ideal binary mixed CMCs in ionic/non-ionic systems without a non-ideal interaction parameter using only single surfactant CMCs and fractional counterion binding on the pure ionic micelles. These results provide strong evidence of the importance of electrostatic interactions but have limited application in non-ideal mixing in ionic/non-ionic systems. The regular solution theory, RST, deviated from pseudo-phase separation approach is chosen for use in this

work because it can predict the critical micelle concentration and it is more suitable for use in a wide range of mixed surfactant system.

7.2 Regular solution Theory

Regular solution theory is based on pseudo-phase separation approach. An important motivation for understanding the behavior of mixed micellar solutions in this approach is that the micelles establish the chemical potential of the different species in bulk solution. From this perspective, the micellar problem represents the first step toward a more generalized model for the behavior of non-ideal mixed surfactant systems.

7.2.1 Pseudo-phase Separation Approach

In this approach, the micellar aggregates are taken like a separated phase and the aggregation number is assumed to be infinity. Based on these assumptions, a generalized theory for this micellization process can be developed by considering the chemical potentials of the individual surfactant components. Clint (1975) derived the following expressions.

The chemical potential of monomeric component 1, μ_1 , in the binary surfactant solution can be written as:

$$\mu_1 = \mu_1^0 + RT \ln C_1^M \quad (7.1)$$

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where μ_1^0 is the standard chemical potential of monomeric surfactant 1, C_1^M is the concentration of monomeric surfactant 1. The chemical potential of component 1 in the mixed micelle μ_1^M is given by

$$\mu_1^M = \mu_1^{M_0} + RT \ln f_1 X_1 \quad (7.2)$$

where $\mu_1^{M_0}$ is the chemical potential of surfactant 1 in pure micelle, f_1 is activity coefficients of surfactants 1 in the mixed micelle, X_1 is mole fraction of surfactant 1 in the mixed micelle.

Using a phase separation model of micellization, Equation 7.2 can be written for component 1 in the pure micelle

$$\mu_1^{M_0} = \mu_1^0 + RT \ln CMC_1 \quad (7.3)$$

where CMC_1 is the CMC of pure surfactants 1.

At equilibrium $\mu_1 = \mu_1^M$, hence

$$C_1^M = X_1 f_1 CMC_1 \quad (7.4)$$

Similar relationship can be derived for surfactant 2,

$$C_2^M = (1 - X_1) f_2 CMC_2 \quad (7.5)$$

Below the concentration of mixed micelle formation, the concentration of component 1 is simply given by

$$C_1^M = \alpha CMC_{mixed} \quad (7.6)$$

where α is mole fraction of surfactant 1 in total mixed solute. The concentration of component 2 is given by

$$C_2^M = (1 - \alpha) CMC_{mixed} \quad (7.7)$$

Hence,

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$$\alpha CMC_{mixed} = X_1 f_1 CMC_1 \quad (7.8)$$

and

$$(1 - \alpha) CMC_{mixed} = (1 - X_1) f_2 CMC_2 \quad (7.9)$$

X_1 can be eliminated to give

$$\frac{1}{CMC_{mixed}} = \frac{\alpha}{f_1 CMC_1} + \frac{1 - \alpha}{f_2 CMC_2} \quad (7.10)$$

If $f_1 = f_2 = 1$ for the ideal approximation, then

$$\frac{1}{CMC_{mixed}} = \frac{\alpha}{CMC_1} + \frac{1 - \alpha}{CMC_2} \quad (7.11)$$

Then the mole fraction of component 1 in the mixed micelle at the CMC

$$X_1 = \frac{\alpha f_2 CMC_2}{\alpha f_2 CMC_2 + (1 - \alpha) f_1 CMC_1} \quad (7.12)$$

Above CMC, mole fraction of surfactant 1 in mixed micelle can be expressed as

$$X_1 = \frac{\alpha C - C_1^M}{C - C_1^M - C_2^M} \quad (7.13)$$

where C is the total concentration of surfactant 1 and 2. By substituting for C_1^M and C_2^M from Equations 7.4 and Equations 7.5, the resulting quadratic expression in X_1 can be solved to yield

$$X_1 = \frac{-(C - \Delta) + \sqrt{(C - \Delta)^2 + 4\alpha C \Delta}}{2\Delta} \quad (7.14)$$

where $\Delta = f_2 CMC_2 - f_1 CMC_1$.

Finally, using Equation 7.4 again, the monomeric concentration of component 1 can be written explicitly as

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$$C_1^M = \frac{-(C - \Delta) + \sqrt{(C - \Delta)^2 + 4\alpha C \Delta}}{\left(\frac{f_2 CMC_2}{f_1 CMC_1} - 1\right)} \quad (7.15)$$

while

$$C_2^M = \left(1 - \frac{C_1^M}{f_1 CMC_1}\right) f_2 CMC_2 \quad (7.16)$$

Although Equations 7.15 and 7.16 are correct expressions for micelle composition and monomer concentrations, they are not helpful without some relationship between activity coefficients in the micelle and micelle composition. It is here that the activity coefficient is introduced in the mixed micelle

$$f_1 = \exp \beta (1 - X_1)^2 \quad (7.17)$$

$$f_2 = \exp \beta X_1^2 \quad (7.18)$$

the parameter β is related to molecular interactions in the mixed micelle

$$\beta = N(W_{11} + W_{22} - 2W_{12}) / RT \quad (7.19)$$

where W_{11} , W_{22} are the energies of interaction between molecules in the pure micelle and W_{12} is in the interaction between the two species in the mixed micelle. N is Avogadro's number. It can be demonstrated within the regular solution context that the excess enthalpy is given by

$$H_e = \beta RT X_1 (1 - X_1) \quad (7.20)$$

Since this is not zero if β is not zero this model considers both enthalpy and entropy (ideal mixing) in mixed micelle formation. When regular solution approximation is introduced

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to treat the nonideality of mixing by assuming that the excess entropy of mixing is zero, H_e could be substitute by the excess free energy of mixing (Holland, 1986). If β is negative, H_e is negative. The more negative free energy implies the more synergistic and spontaneous interaction in the system.

7.2.2 Non-ideal Mixed Micellar System

The use of regular solution theory (RST) results in a set of relations between mixed micelle CMC, micelle composition, monomer concentration and the interaction parameter. To use these relations to find the monomer concentrations, Equation 7.14 may be solved iteratively for X_1 with a chosen β value followed by solution of Equations 7.4, 7.5, or 7.15 and 7.16.

Alternatively, it may be of interest to find β as an experimental parameter from CMC measurements and apply this β to interpretation of subsequent experiments. This would be appropriate for the calculation of monomer concentrations in the interpretation of adsorption experiments from mixed systems. In this case, the following relationships which permit solution for β in terms of C_1 , C_2 and C^* , are useful.

$$\frac{X_1^2 \ln\left(\frac{CMC_{mixed}\alpha}{CMC_1 X_1}\right)}{(1-X_1)^2 \ln\left(\frac{CMC_{mixed}(1-\alpha)}{(1-X_1)CMC_2}\right)} = 1 \quad (7.21)$$

$$\beta = \frac{\ln\left(\frac{\alpha CMC_{mixed}}{CMC_1 X_1}\right)}{(1-X_1)^2} \quad (7.22)$$

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In some mixtures, when one of the surfactants is ionic, its free monomer concentration m_1 can be measured directly using a surfactant-selective electrode. In the simplest case, where mixed micelles show negative deviation from Raoult's law, the free monomer concentration for ionic component 1 (m_1) at the CMC of the mixed micelle is given by (Rubingh, 1979; Holland, 1986)

$$m_1 = \alpha CMC_{mixed} = CMC_1 X_1 \exp[\beta(1 - X_1)^2] \quad (7.23)$$

7.3 Evaluation of Molecular Interaction Parameters

As mentioned, the interaction parameter β is largely empirical. However, it can still provide a useful way to verify synergistic interaction when its value is negative, and antagonistic interaction when it is positive in two surfactants solution system. At the same time, the values calculated using ideal mixing theory and regular solution theory can be compared with the experimental values to see whether the interaction between the specific surfactants fits this approach. The comparison in three kinds of binary surfactant systems has been done. They are anionic surfactant, SDS, and polymeric surfactant system, cationic surfactant, TTAB, and polymeric surfactant system, and non-ionic surfactant, C₁₂EO₆, and polymeric surfactant system.

7.3.1 Interaction Parameters of Polymeric Non-ionic Surfactants with Anionic Surfactant, Sodium Dodecyl Sulfate, SDS

The critical micellar concentrations of various mixtures of F127, F127(PPO)-g-PVP, F127(PEO)-g-PVP with SDS at different mole fractions, ranging from pure SDS to pure

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polymeric surfactants have been determined. The CMC can be measured by surface tension (ST) plotted against different concentrations of the mixtures. All measurements were carried out at room temperature. Although mixed F127/SDS aggregates has been confirmed and explained in detail by many researchers using many methods (Jones, 1967; Li, 2000), investigation on the interaction between F127 and ionic surfactant with the fixed molar ratio is limited.

The critical micellar concentrations of various mixtures of SDS and F127 at different mole fractions ranging from pure SDS to pure F127 have been determined using surface tension measurements. In Figure 7.1, typical surface tension results showing CMC_{mix} are shown. The CMC_{mix} of different molar ratio of F127 to SDS are listed in Table 7.1 together with the value of interaction parameter, β , the molar ratio of SDS in the mixed micelle, X_{SDS} , the free monomer concentration for ionic surfactant of SDS, m_{SDS} , and two activity coefficients of the surfactants, f_{SDS} and f_{F127} . This study verified the synergistic interaction between F127 and ionic surfactant SDS. Using regular solution theory and an average interaction parameter, β , of about -2.79 , the calculated CMC curve for the mixed micelle fits the experimental data (Refer to Figure 7.2). The interaction of two graft copolymers, F127(PPO)-g-PVP and F127(PEO)-g-PVP, with normal anionic surfactant, SDS were also investigated. The mean values of β for F127(PPO)-g-PVP/SDS and F127(PEO)-g-PVP/SDS systems are -3.64 and -3.81 respectively.

Figure 7.1 Surface tension measurements for different SDS and F127 concentration, the SDS molar ratio being constant and equal to 0.4 at room temperature.

Table 7.1 Critical Micelle concentrations of aqueous mixtures of F127/SDS at room temperature deduced from ST measurement.

% SDS	CMC _{mix} (mM)	m_{SDS} (mM)	X_{SDS}	β	f_{SDS}	f_{F127}
100	8.00	8.00				
95	2.75	2.61	0.550	-2.57	0.594	0.459
90	1.96	1.76	0.470	-2.69	0.469	0.551
80	1.40	1.12	0.378	-2.57	0.370	0.693
60	0.957	0.574	0.280	-2.63	0.256	0.814
40	0.700	0.280	0.220	-3.02	0.159	0.864
20	0.620	0.124	0.158	-3.27	0.0981	0.921
0	0.640	0				

Table 7.2 Critical Micelle concentrations of aqueous mixtures of F127(PPO)-g-PVP/SDS at room temperature deduced from ST measurement.

% SDS	CMC _{mix} (mM)	m_{SDS} (mM)	X_{SDS}	β	f_{SDS}	$f_{\text{F127(PPO)-g-PVP}}$
100	8.00	8.00				
95	2.79	2.65	0.568	-2.89	0.583	0.394
90	1.74	1.57	0.490	-3.53	0.399	0.429
80	1.28	1.02	0.420	-3.53	0.305	0.536
60	0.94	0.56	0.327	-3.39	0.216	0.696
40	0.72	0.29	0.275	-3.87	0.131	0.746
20	0.70	0.14	0.195	-3.72	0.090	0.868
0	0.80	0.00				

Table 7.3 Critical Micelle concentrations of aqueous mixtures of F127(PEO)-g-PVP/SDS at room temperature Deduced from ST measurement.

% SDS	CMC _{mix} (mM)	m_{SDS} (mM)	X_{SDS}	β	f_{SDS}	$f_{\text{F127(PEO)-g-PVP}}$
100	8.00	8.00				
95	2.18	2.07	0.504	-2.71	0.514	0.503
90	1.33	1.20	0.431	-3.27	0.347	0.545
80	0.74	0.59	0.379	-4.24	0.195	0.544
60	0.63	0.38	0.269	-3.25	0.176	0.790
40	0.55	0.22	0.170	-2.64	0.162	0.926
20	0.43	0.10	0.145	-3.57	0.074	0.928
0	0.43	0.00				

The CMC_{mix} of different molar ratio of graft copolymers F127(PEO)-g-PVP and F127(PPO)-g-PVP to SDS are listed in Table 7.2 and Table 7.3, respectively. The value of interaction parameter, β , the molar ratio of SDS in the mixed micelle X_{SDS} and the free monomer concentration for ionic surfactant of SDS, m_{SDS} , (see Equation 7.23) are also

listed in Table 7.2 and 7.3. The experimental values of CMC_{mix} of graft copolymer/SDS systems shown in the tables fit the curves calculated by using the Regular Solution Theory shown graphically in Figure 7.3 and Figure 7.4.

These results show that there is synergy between F127-g-PVP and SDS at room temperature. The β values for both F127-g-PVP/SDS systems are lower than that of F127/SDS systems. As discussed in Section 7.2, the lower β value means stronger interaction between a “normal” ionic surfactant and a “polymeric” non-ionic surfactant system. A detailed explanation on the interaction between polymeric surfactant and SDS has been presented in Chapter 6. The results show that regular solution theory can be extended to binary surfactant system, which involves polymeric surfactants such as F127 and its graft copolymer F127-g-PVP with anionic surfactant, SDS.

Figure 7.2 Critical micelle concentration data as a function of SDS mole fraction from surface tension (◆) measurements for F127 and SDS mixtures at constant molar ratios at room temperature. The solid lines correspond to the calculated CMC's according to regular solution theory with an average β equal to -2.79 (purple line) and the calculated CMC's according to ideal mixing theory (blue line).

Figure 7.3 Critical micelle concentration data as a function of SDS mole fraction from surface tension (◆) measurements for F127(PPO)-g-PVP and SDS mixtures at constant molar ratios at room temperature. The solid lines correspond to the calculated CMC's according to regular solution theory with an average β equal to -3.49 (purple line) and the calculated CMC's according to ideal mixing theory (blue line).

Figure 7.4 Critical micelle concentration data as a function of SDS mole fraction from surface tension (◆) measurements for F127(PEO)-g-PVP and SDS mixtures at constant molar ratios at room temperature. The solid lines correspond to the calculated CMC's according to regular solution theory with an average β equal to -3.28 (purple line) and the calculated CMC's according to ideal mixing theory (blue line).

7.3.2 Interaction Parameters of Polymeric Non-ionic Surfactants with Cationic Surfactant, Tetradecyltrimethylammonium Bromide (TTAB)

Some researchers studied the interaction between cationic surfactant, TTAB and non-ionic “polymeric” surfactant, F127 (Yoon, 2002; Li, Y., 2001b). They have suggested there is no obvious interaction between F127 and TTAB although the mechanism of interaction of F127 with TTAB is similar to that of F127 with SDS. Others confirmed the existence of interaction in binary surfactant system of F127 and TTAB and the model of interaction is similar to that of F127 and SDS. To date, no one has used the regular solution theory to evaluate the interaction between F127 and TTAB. In this section, we presents the results of our evaluation using this theory.

The critical micellar concentrations of various mixtures of TTAB and “polymeric” surfactant, F127, F127(PPO)-g-PVP and F127(PEO)-g-PVP, at different molar fractions ranging from pure TTAB to pure polymeric surfactants were measured. These measurements were also taken using surface tension (ST) measurement by continuously diluting the solution with the highest concentration. The CMC_{mix} were determined from the turning point in the plot of surface tension against concentrations similar to the curve shown in Figure 7.1.

Table 7.4, 7.5 and 7.6 show the CMC_{mix} of different molar ratios. The values of interaction parameter, β , the molar ratios of TTAB in the mixed micelle X_{TTAB} , the free monomer concentrations for ionic surfactant of TTAB, m_{TTAB} , and two activity coefficients of the surfactants, f_{TTAB} and f_{F127} are also presented in these tables.

Table 7.4 Critical Micelle concentrations of aqueous mixtures of F127/TTAB at room temperature Deduced from ST measurement.

% TTAB	CMC _{mix} (mM)	m_{TTAB} (mM)	X_{TTAB}	β	f_{TTAB}	f_{F127}
100	4.00	4.00				
90	1.65	1.49	0.550	-1.94	0.675	0.556
80	1.20	0.960	0.440	-1.93	0.545	0.688
60	0.900	0.540	0.324	-1.92	0.417	0.818
40	0.740	0.320	0.234	-1.83	0.342	0.905
20	0.680	0.140	0.130	-1.73	0.269	0.971
0	0.640	0				

Table 7.5 Critical Micelle concentrations of aqueous mixtures of F127(PPO)-g-PVP/TTAB at room temperature Deduced from ST measurement.

% TTAB	CMC _{mix} (mM)	m_{TTAB} (mM)	X_{TTAB}	β	f_{TTAB}	$f_{\text{F127(PPO)-g-PVP}}$
100	4.00	4.00				
90	1.80	1.62	0.578	-2.00	0.701	0.513
80	1.40	1.12	0.476	-1.93	0.588	0.645
60	1.00	0.600	0.357	-2.10	0.420	0.765
40	0.880	0.352	0.254	-1.90	0.346	0.884
20	0.760	0.152	0.170	-2.17	0.223	0.939
0	0.800	0				

Table 7.6 Critical Micelle concentrations of aqueous mixtures of F127(PEO)-g-PVP/TTAB at room temperature Deduced from ST measurement.

% TTAB	CMC _{mix} (mM)	m_{TTAB} (mM)	X_{TTAB}	β	f_{TTAB}	$f_{\text{F127(PEO)-g-PVP}}$
100	4.00	4.00				
90	1.20	1.08	0.500	-2.46	0.540	0.540
80	0.870	0.696	0.408	-2.43	0.426	0.667
60	0.600	0.360	0.306	-2.54	0.294	0.788
40	0.500	0.200	0.220	-2.44	0.227	0.889
20	0.425	0.0880	0.135	-2.42	0.163	0.957
0	0.430	0

Figure 7.5 Critical micelle concentration data as a function of TTAB mole fraction from surface tension (◆) measurements for F127 and TTAB mixtures at constant molar ratios at room temperature. The solid lines correspond to the calculated CMC's according to regular solution theory with an average β equal to -1.87 (purple line) and the calculated CMC's according to ideal mixing theory (blue line).

Figure 7.6 Critical micelle concentration data as a function of TTAB mole fraction from surface tension (◆) measurements for F127(PPO)-g-PVP and TTAB mixtures at constant molar ratios at room temperature. The solid lines correspond to the calculated CMC's according to regular solution theory with an average β equal to -2.02 (purple line) and the calculated CMC's according to ideal mixing theory (blue line).

Figure 7.7 Critical micelle concentration data as a function of TTAB mole fraction from surface tension (◆) measurements for F127(PEO)-g-PVP and TTAB mixtures at constant molar ratios at room temperature. The solid lines correspond to the calculated CMC's according to regular solution theory with an average β equal to -2.46 (purple line) and the calculated CMC's according to ideal mixing theory (blue line).

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The experimental values of CMC_{mix} of F127/TTAB and graft copolymer/TTAB systems shown in Tables 7.4, 7.5, and 7.6 fit the curves well as calculated by using the regular solution theory as shown in Figures 7.5, 7.6 and 7.7. The results show synergistic interactions of polymeric surfactants, F127, F127(PPO)-g-PVP and F127(PPO)-g-PVP with cationic surfactant, TTAB.

Gharibi and coworkers (1998) studied the interaction between a series of n-alkyl trimethyl ammonium bromides and polyvinyl pyrrolidone and proved that the process of micellization of ionic surfactant represents a balance in several forces. TTAB bound to both monomeric and micellar F127 and formed a polymeric/micellar TTAB complex with monomeric F127 that was reported by Li, Y. (2001b). Ghoreishi and coworkers (1999) suggested TTAB only interacted with more hydrophobic block, PPO, if EO and PO blocks of F127 were separate. In Chapter 6, the ratios of TTAB to PEO, PPO and PVP in polymeric surfactant solution have been calculated and it was concluded that PVP interacted with TTAB stronger than PEO block. This can also be verified by the lower β values of TTAB with graft copolymer than with F127.

This the first time, the regular solution theory is used to study the interaction between TTAB and polymeric surfactants systems. The results show that regular solution theory can be applied to polymeric surfactant and cationic surfactant binary system as well.

7.3.3 Interaction Parameters of Polymeric Non-ionic Surfactants with Non-ionic Surfactant, Hexaethylene Glycol Mono-n-dodecyl Ether ($C_{12}EO_6$)

Although, in general, non-ionic surfactant interacts with F127, which is non-ionic polymeric surfactant, more poorly than ionic surfactants, Couderc and coworkers (2001) discovered that the non-ionic surfactant hexaethylene glycol mono-n-dodecyl ether ($C_{12}EO_6$) interacts strongly with the triblock copolymer F127. They applied the regular solution theory to non-ionic surfactant, $C_{12}EO_6$, and F127 system. The regular solution theory has also been applied to non-ionic surfactant and graft copolymer systems in our work.

The critical micellar concentrations of various mixtures of $C_{12}EO_6$ and “polymeric” surfactant, F127, F127(PPO)-g-PVP and F127(PEO)-g-PVP, at different molar fractions ranging from pure $C_{12}EO_6$ to pure polymeric surfactants. These measurements were also taken using surface tension measurement by continuously diluting the solution with the highest concentration. The CMC_{mix} were determined from the turning point in the plot of surface tension against concentrations, similar to Figure 7.1.

The CMC_{mix} for the different molar ratios are tabulated in Tables 7.7, 7.8 and 7.9, together with the value of interaction parameter, β , the molar ratio of $C_{12}EO_6$ in the mixed micelle $X_{C_{12}EO_6}$, the free monomer concentration for ionic surfactant of $C_{12}EO_6$, $m_{C_{12}EO_6}$, and the activity coefficients of two surfactants, $f_{C_{12}EO_6}$ and f_{F127} .

Table 7.7 Critical Micelle concentrations of aqueous mixtures of F127/ C₁₂EO₆ at room temperature Deduced from ST measurement.

% C ₁₂ EO ₆	CMC _{mix} (mM)	<i>m</i> _{C₁₂EO₆} (mM)	X _{C₁₂EO₆}	β	f _{C₁₂EO₆}	f _{F127}
100	0.0800	0.0800				
90	0.0780	0.0702	0.896	-2.19	0.977	0.172
80	0.0800	0.0640	0.850	-2.69	0.941	0.143
60	0.0900	0.0540	0.770	-2.49	0.877	0.229
40	0.110	0.0440	0.690	-2.36	0.797	0.325
20	0.160	0.0320	0.580	-2.11	0.690	0.492
0	0.640	0				

Table 7.8 Critical Micelle concentrations of aqueous mixtures of F127(PPO)-g-PVP/ C₁₂EO₆ at room temperature Deduced from ST measurement.

% C ₁₂ EO ₆	CMC _{mix} (mM)	<i>m</i> _{C₁₂EO₆} (mM)	X _{C₁₂EO₆}	β	f _{C₁₂EO₆}	f _{F127(PPO)-g-PVP}
100	0.0800	0.0800				
90	0.078	0.0702	0.900	-2.53	0.975	0.129
80	0.079	0.0632	0.847	-2.98	0.933	0.118
60	0.088	0.0528	0.770	-2.91	0.857	0.178
40	0.110	0.0440	0.703	-2.78	0.782	0.253
20	0.160	0.0320	0.600	-2.53	0.667	0.402
0	0.800	0				

**Table 7.9 Critical Micelle concentrations of aqueous mixtures of F127(PEO)-g-PVP/
C₁₂EO₆ at room temperature Deduced from ST measurement.**

% C ₁₂ EO ₆	CMC _{mix} (mM)	m _{C12EO6} (mM)	X _{C12EO6}	β	f _{C12EO6}	f _{F127(PEO)-g-PVP}
100	0.0800	0.0800				
90	0.0700	0.0630	0.850	-3.30	0.928	0.0928
80	0.0720	0.0578	0.800	-2.63	0.900	0.185
60	0.0750	0.0450	0.715	-2.95	0.787	0.221
40	0.0850	0.0340	0.630	-2.88	0.675	0.319
20	0.120	0.0240	0.536	-2.70	0.560	0.461
0	0.430	0

Figure 7.8 Critical micelle concentration data as a function of C₁₂EO₆ mole fraction from surface tension (◆) measurements for F127 and C₁₂EO₆ mixtures at constant molar ratios at room temperature. The solid lines correspond to the calculated CMC's according to regular solution theory with an average β equal to -2.37 (purple line) and the calculated CMC's according to ideal mixing theory (blue line).

Figure 7.9 Critical micelle concentration data as a function of C₁₂EO₆ mole fraction from surface tension (◆) measurements for F127(PPO)-g-PVP and C₁₂EO₆ mixtures at constant molar ratios at room temperature. The solid lines correspond to the calculated CMC's according to regular solution theory with an average β equal to -2.75 (purple line) and the calculated CMC's according to ideal mixing theory (blue line).

Figure 7.10 Critical micelle concentration data as a function of C₁₂EO₆ mole fraction from surface tension (◆) measurements for F127(PEO)-g-PVP and C₁₂EO₆ mixtures at constant molar ratios at room temperature. The solid lines correspond to the calculated CMC's according to regular solution theory with an average β equal to -2.89 (purple line) and the calculated CMC's according to ideal mixing theory (blue line).

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The experimental values of CMC_{mix} of graft copolymer/SDS systems shown in the tables fit the curves calculated by using the Regular Solution Theory (Figure 7.8, Figure 7.9 and Figure 7.10). The curves calculated according to RST depend on the average β values (Table 7.7, Table 7.8, and Table 7.9).

Couderc (2001) confirmed there is synergistic interaction between F127 and C_{12}EO_6 . Nikas and coworkers (1992) reported their results of theoretical and experimental studies of the adsorption of surfactants at the solution-air interface from two aqueous binary nonionic surfactant mixtures: C_{12}E_6 - C_{12}E_8 and C_{12}E_6 - C_{10}E_4 . The hydrophobic interaction of C_{12}EO_6 with PVP is better than with PPO since the solubility of PVP in water is better than hydrophobic chain, PPO. The interaction parameter, β , of graft copolymer mixed surfactant system is lower than that of F127 system. Applying the regular solution theory in C_{12}EO_6 and polymeric surfactant systems show that regular solution theory has broader extent of application not only on F127/ C_{12}EO_6 binary surfactant system, but also on F127-g-PVP/ C_{12}EO_6 binary surfactant systems.

7.4 Summary

The interaction of SDS with the graft copolymers is strong enough to influence the behavior of the copolymer and SDS in the aqueous solution. A single CMC relating to the mixed micelles formation in the binary surfactant systems indicates that the two surfactants could form mixed micelle in aqueous solution. The interaction behavior of graft copolymers with SDS is more synergistic than that of F127 with SDS because the latter system has a more negative interaction parameter, β .

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TTAB interacts with the graft copolymers strongly enough to influence the behavior of the copolymers and TTAB in the aqueous solution. The CMC of the mixed micelles in the binary surfactant systems at a particular ratio is smaller than both CMC of pure surfactants. The more negative interaction parameter, β , calculated based on regular solution theory verifies a more synergistic interaction of TTAB with graft copolymers than with F127.

The synergistic interaction of $C_{12}EO_6$ with the graft copolymers was verified by negative interaction parameter, β . The CMC of the mixed micelles in the binary surfactant systems confirmed that two surfactants could form mixed micelles. The more negative β shows that the interactions between graft copolymers and $C_{12}EO_6$ are stronger than that between F127 with $C_{12}EO_6$.

F127(PPO)-g-PVP and F127(PEO)-g-PVP interacted more synergistically with all three normal surfactants than F127. F127(PEO)-g-PVP had a lower average interaction parameters, β , than those of F127(PPO)-g-PVP shown in Figure 3, 4, 6, 7, 9, 10. This means there are the stronger interactions of normal surfactants with F127(PEO)-g-PVP than those with F127(PPO)-g-PVP because more PVP, which can interact with all surfactant better than PEO, were added on F127 in F127(PEO)-g-PVP.

Chapter 8 Conclusions

In this study, the novel graft copolymers, F127-g-PVP, F127(PPO)-g-PVP, F127(PEO)-g-PVP were synthesized by free radical initiated polymerization and chain transfer of VP monomer onto the Pluronic copolymer. The copolymer, F127-g-PVP produced through radical grafting solution polymerization, was randomly grafted by PVP. Varying conditions were investigated thoroughly to obtain the optimal grafting conditions. Once the optimal conditions were determined, a series of copolymers with varying grafting efficiency were synthesized.

It was found that, with the 2.5 feeding ratio of VP to Pluronic F 127 copolymer, the highest grafting efficiency was obtained at 70 °C after 6 hours in dioxane using 2 mM lauroyl peroxide as initiator. With the increase in the feeding ratio of VP/Pluronic F127, the molecular weights of the graft copolymer increased as expected, followed by a slight decrease. That reason is the long the reaction time, the more chance the oxidation and degradation reactions happen.

FTIR spectra verified the chemical structure of graft copolymer and the GPC chromatograms of all the graft copolymers show only one peak, suggesting that graft copolymers were successfully synthesized.

Using ^1H NMR spectroscopy, the chemical structure of the copolymer was characterized. From the data obtained from the NMR spectra, one can confirm that the graft copolymers were synthesized by radical graft polymerization. The compositions of the copolymers were also characterized using ^1H NMR. The PVP/Pluronic F127 ratios could be obtained

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from the ratio of the integrated signals due to the protons PPO (CH_3) near 1.19 ppm and the protons from PVP ($-\text{CH}_2\text{CO}$) at about 3.2 ppm.

Unfortunately, the first route of synthesis does not provide much control to the site where PVP is grafted on. Two other synthesis routes - Route 2 and Route 3, were used to control the grafting sites better. Two different kinds of F127-g-PVP graft copolymers were synthesized by using the two different reaction schemes. NMR results provide information about the structure of these two kinds of graft copolymer. Through Route 2 and Route 3, graft copolymer F127(PPO)-g-PVP and F127(PEO)-g-PVP were synthesized successfully.

The aqueous solutions of three graft copolymer were prepared by dissolving in water and then equilibrating for 24 hours at room temperature. The effect of the concentration of the copolymer on CMT and the value of CMC at room temperature were investigated and compared with that of Pluronic F127.

CMC of graft copolymers was obtained using fluorescence probing techniques and surface tension measurement. Surface tension measurement is more suitable, since it needs small amount of sample and fewer steps.

Thermodynamics of copolymer micelle formation were investigated using the DSC. It is found that the micellization of the graft copolymers form micelles in aqueous solution and the micellization process obeys the closed association model and it is thermo-reversible.

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The concentration of the copolymer in aqueous solution also affects the critical micellization temperature of the graft copolymers. Investigation was carried out with different concentrations. It was found that if the concentration is increased, the temperature at which the copolymer becomes micelles in the solution will decrease.

The effect of the different percentage of grafting on the aggregation sizes was also investigated. It can be concluded that the aggregates formed from the graft copolymers have the narrower polydispersities in water at room temperature. The aggregation size increases with increasing the graft efficiency.

The aggregation number of three graft copolymers and F127 were investigated in different temperature. The aggregation number of F127(PEO)-PVP and F127(PPO)-g-PVP obtained using intrinsic viscosity increased following with increasing the temperature. The aggregation numbers of three graft copolymers are smaller than that of F127 resulting from static light scattering measurement, because M_w calculated using the Equation 5.7 included the weight of water associated with micelles.

The binary surfactant systems of polymeric surfactant with normal surfactant were investigated by surface tension measurement. The process of the interaction between “polymeric” non-ionic surfactants and “normal” surfactant can be clearly and directly described. It is found that SDS and TTAB prefer to interact with more hydrophobic chain segments, PPO and PVP; while $C_{12}EO_6$ tends to interact with more hydrophilic ones, PEO and PVP. Hydrophobic forces are believed to dominate the interaction process between SDS and polymeric surfactants, while much weaker Van der Waals forces govern the TTAB and polymeric surfactants. The interaction of $C_{12}EO_6$ with the hydrophilic

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segments is surprising and further study is needed to explain it. These findings have shed some light on the direction to explain the interactions in molecular scales.

In spite of their different binding behaviors, all of the binary surfactant systems of normal surfactants with graft copolymers have shown synergetic effect by showing a negative interaction parameter, according to the regular solution theory. Such synergistic effect is found to become stronger for the grafted copolymers than that for F127, benefiting from grafting of PVP onto F127 main chains.

Over all, novel polymeric surfactants, Pluronic-g-PVP, have been synthesized using free radical polymerization and they are found to have integrated the benign nature of F127 and PVP successfully.

Chapter 9 Future Work

This study has demonstrated that the improved properties were obtained by chemical bonding of PVP with F127. In particular, it has led to some insight in thermal-sensitive property and strong interaction with many additives. Nevertheless, further study is warranted in several areas to corroborate and extend this study. In this chapter, recommendation for future work will be presented.

1. The mechanism of the interaction in two surfactant system can be fully understood by using computer simulation. The mesoscale simulation of binary surfactants system can be used to study the kinetics of the interaction. Mesoscale simulation can be implemented using MesoDyn, in Materials studio by Accelrys, which is based on dynamic mean field density functional theory. There are two parameters which need to be determined. One is the interaction energies of the various components. The interaction energy between each two components should be studied. The other is coarsened chain architecture which is already defined by Lam et al. (Y.M. Lam, 2003).

2. The type of micelles formed in the aqueous solution of two kinds of graft copolymer surfactant can be estimated by considering the ratio of R_g/R_h . R_g is the radius of gyration from the angular distribution of time-averaged scattered intensity extrapolated to infinite dilution. R_g can be measured by using Static light scattering (SLS).

3. The solution behavior of two kinds of graft copolymers, F127(PEO)-g-PVP and F127(PPO)-g-PVP in single surfactant system and binary surfactant system should be compared to the other regular Pluronic® polymer surfactants. There is a variety of Pluronic® available with varying chain length, block length ratio, and chain architecture.

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They have the different abilities to self-assemble in aqueous solutions and even to form the different shapes, such as micelle, cylinder and lamellar. Depending on the type of Pluroinc®, the spherical micelles have different hydrodynamic radius and aggregation number.

4. The copolymers are potential hydrophobic or hydrophilic matter carriers that can be used to improve the entrapment efficiency. The micelles are fairly stable, which are expected to improve its recovery.

The amount of non-entrapped hydrophobe in aqueous medium will be determined and the amount of entrapped within micelles will be calculated by the difference between the total amount and the amount of the hydrophobe present in the aqueous phase.

Loading (%)

$$= \text{Mass of matter in formulation} * 100 / \text{mass of copolymer used in formulation} \quad (9.1)$$

5. Surface chemistry can be exploited to control a wide range of phenomena such as hydrophobicity. PEO is unique material since it is one of a few materials that have lower critical solution temperature, LCST. LCST is the temperature above which the isotropic single phase polymer solution will phase separate into a two phase mixture. That means a transition happens from hydrophilic behavior at certain temperature to hydrophobic behaviour above its LCST. The polymer that has LCST was used as smart surface successfully reported by Graham (1982), Andrade (1996) and Wang (2002). The schematic description of the device coating with graft copolymer works as smart surface shown in Figure 9.2. (a) Thin film with coating of graft copolymer. (b) Device consists of micro-heaters under thin film. (c) Active heater turns the surface hydrophobic and

fouling. Selective solvent absorption occurs exclusively on heated areas. (d) Different solvent absorption occurs. (e) Different solvent absorbed on the same surface of the device.

Figure 9.1 Schematic description of graft copolymer coating devices.

6. In many practical applications, two or more surfactants are employed to obtain the synergism or other properties which each pure surfactant does not have. More binary systems of anionic, cationic and nonionic normal surfactant with polymeric surfactants can be studied to determine the interactions between the surfactants.

7. Synthesis series of graft copolymer F127(PEO)-g-PVP and F127(PPO)-g-PVP which have different graft percentage by investigating mode chemistry synthesis method such as ATRP to fulfill the better control of the reaction. The solution behavior of these graft copolymers in aqueous solution can be studied, especially their CMT and CMC. These graft copolymers can be use in many different applications with different requirements.

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APPENDIX

Publications and Conferences

1. Y. Zhang, Y.M. Lam, (2005) Poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide)-*g*-poly(vinyl pyrrolidone): synthesis and characterization, *Journal of Colloid and Interface Science*, 285(1):80-85.
2. Y. Zhang, Y.M. Lam, W. S. Tan, (2005) Poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide)-*g*-poly(vinyl pyrrolidone): Association behaviour in aqueous solution and interaction with anionic surfactants, *Journal of Colloid and Interface Science*, 285(1):74-79.
3. Y. Zhang, Y. M. Lam, Controlled synthesis, association and interaction behavior of graft Pluronic in aqueous solutions, *Journal of Physical Chemistry B*, is submitted.
4. Y. Zhang, Y. M. Lam, Study of Mixed Micelles and Interaction Parameters for “Polymeric” Nonionic and “Normal” Surfactants, *Journal of Nanoscience and Nanotechnology*, is submitted.
5. Y. Zhang, Y.M. Lam, Poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide)-modified-poly(vinyl pyrrolidone): synthesis and characterization, ICMAT 2003.
6. Y. Zhang, Y. M. Lam, The investigation of binary surfactant system, ICMAT 2005.