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**THERMOREVERSIBLE GELATION OF
METHYLCELLULOSE AND PLURONICS IN
WATER**

**WANG QIQIANG
SCHOOL OF MECHANICAL AND AEROSPACE
ENGINEERING
2007**

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THERMOREVERSIBLE GELATION OF METHYLCELLULOSE AND PLURONICS IN WATER

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A thesis submitted to the Nanyang Technological University
in fulfilment of the requirement for the degree of
Doctor of Philosophy

2007

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Abstract

Two kinds of polymers, Methylcellulose (MC) and polyethylene oxide-polypropylene oxide-polyethylene oxide (PEO-PPO-PEO), in aqueous solutions have been studied.

Firstly, aqueous solutions of MC with different molecular weights ($M_w = 100,000$ and $310,000$, and $400,000$) have been studied. The thermoreversible gelation properties and the gel elasticity were measured as a function of polymer concentration by means of micro differential scanning calorimetry (micro DSC) and rheology, respectively. The experimental results prove that the thermoreversibility of the aqueous solutions of MC is independent of either polymer concentration or M_w . The total enthalpy required for the sol-gel transition is a linear function of polymer concentration, which is again independent of M_w . The scaling laws for the quasi equilibrium modulus G_e with concentration c were presented. At the same concentration of MC, G_e increases with increasing M_w , while the heat absorbed during the sol-gel transition remains constant.

Then the binding interactions between MC and sodium dodecyl sulphate (SDS) were studied by isothermal titration calorimetry, the temperature effect was investigated. At low temperature ($25\text{ }^{\circ}\text{C}$), the titration curve can be divided into four zones: zone 1 starts at initial injection, where only dilution of SDS micelles and non-cooperative binding of small amount of SDS to the MC backbone and/or hydrophobic groups occur. Zone 2 is an endothermic peak, where the cooperative binding of SDS to MC molecules occurs and results in formation of complex micelles. Zone 3 starts at the end of the endothermic peak and the onset of the

exothermic peak, where the aggregation complex reorganizes its structure via ion-dipole interaction. Zone 4 starts at the end of exothermic peak, where free SDS micelles start forming without the participation of MC; the reorganized aggregate complexes formed previously coexist in the system. With increasing temperature, the hydrophobicity of MC is increased. The dominant cooperative binding at low temperatures gradually changed to the dominant non-cooperative binding. The shape of the titration curve shown drastic changes; where the extent of the association between SDS and MC is strengthened with increasing temperature.

Following the work on the binding of SDS to MC, the effect of SDS on the optical transmittance, thermal, and rheological properties of MC aqueous solutions were studied. The particular interest of this work was focused on the effects of SDS on the sol-gel transition of MC. Basically, two effects of SDS have been identified, which are salt-out and salt-in effects at low (≤ 6 mM) and high (> 6 mM) concentrations of SDS, respectively. The “salt-out” effect of SDS brings the gelation of MC to lower temperatures, whereas the “salt-in” effect of SDS delays the gelation of MC to higher temperatures. In addition, SDS is also able to alter the pattern of gelation. Especially, when the concentration of SDS is greater than 8 mM, SDS not only delays the overall gelation of MC but also changes the pattern of MC gelation from a single mode to a bimodal one. Based on these results, a two-step gelation mechanism was proposed to explain the unique gelation behavior of MC under the influence of SDS.

Then, the effect of magnetic field on the sol-gel transition of methylcellulose in water was studied by means of rheology. It was found that (1) the magnetic field

caused the sol-gel transition temperature of MC to shift to lower temperature by about 3 °C, showing a salt-out like effect; (2) the magnetic field shows a weaker effect on the sol-gel transition when NaCl is present; and (3) the gel strength was not strongly affected by the magnetic field but a slight increase in the gel strength is observed. The possible mechanism for these interesting results are proposed and discussed in this thesis.

Aqueous solutions of a PEO-PPO-PEO triblock copolymer, Pluronic F108 ($\text{EO}_{133}\text{PO}_{50}\text{EO}_{133}$), with concentration ranging from 1 to 35 wt%, were studied by means of micro DSC and rheology. The thermoreversible micellization and gelation were examined through a heating and a subsequent cooling process. The critical micellization temperature, CMT, determined by the onset temperature of the endothermic peak in the heating process, was a decreasing function of F108 concentration. A small secondary endothermic peak appeared only when the polymer concentration was 22.5 wt% or higher, indicating that there was sol-gel transition but the gelation was a nearly athermic process. Upon heating, an abrupt increase was observed in both dynamic storage modulus G' and loss modulus G'' within a narrow temperature range. When $T_{G'}$ was defined as the temperature of the transition in G' , $T_{G'}$ was a linear decreasing function of polymer concentration and different from CMT. $T_{G'}$ tended to approach to CMT with increasing F108 concentration. Beyond this transition, G' reached a plateau and the plateau increased in height and broadened with polymer concentration. The value of G' at 70 °C could be approximately scaled with concentration c by $G'_{70} \propto c^{4.8}$. It was also found that the definition for a gel to obey $G' > G''$ was valid only when c was greater than 22.5 wt%, which was in agreement with the secondary endothermic peak found by DSC.

Lastly, the effects of a PPO-PEO-PPO triblock copolymer (25R4, PO₁₉EO₃₃PO₁₉) on the thermoreversible micellization and gelation properties of a PEO-PPO-PEO triblock copolymer (F108, EO₁₃₃PO₅₀EO₁₃₃) in water were studied by means of micro-DSC and rheology. A complete, mirror-image like thermoreversible behavior was observed for all the samples with various molar ratios of 25R4 to F108. At a given concentration of F108, the addition of 25R4 results in the “salt-out” like effect on the primary micellization of F108. That is, the critical micellization temperature (CMT) of F108 shifts to lower temperatures with increasing the content of 25R4. The enthalpy changes for micellization are a linear function of 25R4/F108 molar ratio at a fixed F108 concentration. Beyond the primary peak for the micellization of F108, a secondary peak or shoulder was observed in the DSC curves for the samples with the higher 25R4/F108 molar ratios, due to the formation of the hydrophobic aggregates from both the PPO blocks of F108 and those (i.e. PPO blocks) of 25R4. Furthermore, as an example, the dynamic viscoelastic properties of 18 wt% F108 solutions with various contents of 25R4 were examined. When the 25R4/F108 molar ratio ≤ 1 , 25R4 did not affect the gelation of F108 significantly. When the ratio was greater than 1, however, the formation of the 25R4-bridged micellar aggregates delayed the gelation of F108 significantly. A schematic model was proposed to explain the mechanism for the 25R4-influenced micellization and gelation of F108.

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LIST OF SYMBOLS AND ABBREVIATIONS

Mw	molecular weight
MC	Methylcellulose
LCST	lower critical solution temperature
UCST	upper critical temperature
DSC	differential scanning calorimeter
SDS	sodium dodecylsulphate
PEO	poly(ethylene oxide)
PPO	poly(propylene oxide)
HPMC	hydroxypropylmethylcellulose
DS	degree of substitution
ITC	isothermal titration calorimetry
CMC	critical micellization temperature
CAC	critical aggregation concentration
ΔH	enthalpy change
ΔS	entropy change
Cp	heat capacity
C2	saturation concentration
Cm	Second critical concentration (Cm)
DI-water	Deionized water
TEM	transmission electro microscopy
MF	magnetic field
G'	storage modulus
G''	loss modulus

G_e	quasi-equilibrium modulus
T_p	peak temperature
T_{off}	offset temperature
T_G	gelation temperature
ζ	junction length
s	multiplicity

Chapter 1

Introduction

1.1 Background

Hydrogels are now intensively being studied as potential drug delivery matrices for controlled drug release or as matrices to protect labile drug such as proteins. As more and more genetic engineering drug products are emerging, there are a great need and interest to develop novel means of delivering them. Biocompatible hydrogels are very promising candidates for these purposes. Hydrogels are also used in the industrial sectors.

A physical hydrogel is also referred to as reversible hydrogel since the cross-linking of physical gel is not permanent and can be reversed by changing of certain conditions. One common type of reversible gel is the thermoreversible gel, which appears as either a liquid state or a solid depending on the temperature of the system. Most thermoreversible hydrogels exhibit the gel state at low temperatures and become liquid when temperature is raised, while some hydrophobically modified cellulose derivatives and Pluronics behave in a reversed manner. At low temperatures, the polymer-water system from the modified cellulose or Pluronics is a solution but forms gel at elevated temperatures. This unique property makes them potentially suitable candidates of injectable matrices for drug delivery, as drug can be incorporated into the hydrogel system and injected into human body as a liquid and transits into gel in the body to gain a controlled release for traditional drug or newly developed protein drug.

CHAPTER 1

INTRODUCTION

For polymer solutions, two critical temperatures are important, which are the lower critical solution temperature (LCST) and the upper critical temperature (UCST). Most polymers either have a LCST or a UCST while some have both critical temperatures. Polymer solution with LCST behaves as an isotropic single phase below LCST and phase separates into a two phase mixture above it. While polymer solution with UCST behaves as an isotropic, single phase solution at elevated temperatures above UCST while will be phase separated below it. UCST is common to most of the polymer systems while LCST behavior is less commonly observed in polymer solutions, as evidenced by the fact that most of the naturally existing gels are “gel” at low temperatures and “melt” at elevated temperatures. In this thesis, two types of water-soluble polymers were studied, one is methylcellulose (MC), and the other is Pluronics. Both MC and Pluronics possess a LCST, which makes them more controllable as a solution at room temperature.

Although they both form gels at elevated temperatures but are soluble at low temperatures, the gelation mechanism for each of them is different. For MC, the formation of a percolation network by hydrophobic association is believed to be the main cause; while for Pluronics, the formation of free micelles and the ordering of the micelles at elevated temperatures at a sufficient concentrated solution is the direct cause of gelation.

The sol-gel transition of the cellulose derivative in water is completed in a very narrow range of temperatures. A very low concentration of MC is required to form a consistent gel with significant strength. Various conditions that may affect the sol-gel transition would be crucial for their future applications in either biomedical sector or

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industrial sector. So far, the study of these systems is still very inadequate with more theoretical hypothesis but fewer experimental supports. Besides that, the molecular weight is an important factor for the properties of polymer materials; however no study has been carried out on its effect on the solution and gelation behavior of MC in water. Salts have been reported to dramatically affect the sol-gel transition of MC, but the study on the effect of surfactant on MC's gelation is not adequate. The ordered structure of water molecules around MC is used to explain its solubility, with the breakage of the structure being one of steps leading to the gelation at higher temperatures. Will a magnetic field has any effect on the stability of the ordered water structure? In this thesis, the effects of surfactant additives and a magnetic field on the sol-gel transition of MC were investigated; several MCs of different molecular weights were used to evaluate the effect of molecular size on the gelation mechanism.

The gelation of Pluronics is as sharp as the case of MCs. However a much higher concentration is required to form the gel compared to MC gel. Compared to MC in terms of its limited solubility, Pluronics are more flexible with regard to their greater solubility at low temperatures, enabling a wider range of concentrations. The well-developed and characterized micelles of a core-corona (also referred to as core-shell) structure make the Pluronics gels promising candidates for controlled drug release. Pluronics, being a family of synthetic but environmental friendly copolymers, provides a variety of choices of different molecular weights and compositions. However, other than the commonly used light scattering techniques, thermal and rheological techniques have not been adequately utilized. The combination of the two latter techniques would provide some insight on the gelation

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behavior of Pluronics in water. Reversed Pluronics are known to lack the ability to form stable gel in water, but with the same chemical constitutional blocks as Pluronics, it will be interesting to study the mixture of two Pluronics of reversed chemical structure orderings and find out the new properties.

Rheology has been found to be a powerful tool in analyzing the sol-gel transition behavior and the mechanisms of thermoreversible gels, as it is able to measure the viscoelastic properties of a gelling system in all its phases, liquid or solid. In this thesis, two rheometers were used to reveal the evolution of the viscoelastic properties of the water-soluble polymers in water; special attention was focused on the vicinity of the sol-gel transition regime. The validity of several power laws (scaling law) was examined and compared with the existing ones.

Heat consumption or release is supposed to be involved in the sol-gel transition of methylcellulose and Pluronics aqueous solutions. A sensitive micro differential scanning calorimeter (Micro-DSC) was used to detect the heat effects. The thermodynamic mechanisms were proposed upon analyzing the results of the micro-DSC experiments in combination with the rheological results.

Thermoreversible hydrogels would be easier to manipulate and thus useful if they could respond to the external stimuli such as electromagnetic field, pH, additives et al. In this work, the effects of a magnetic field and a surfactant additive (SDS) on the sol-gel transition of the MC system are studied. New phase behaviors of Pluronics gels are discovered by adding a similar molecule with reversed architecture.

1.2 Objective and scope

The objective of this study is to provide an in depth understanding of the sol-gel transition of two types of water-soluble polymers, MC and Pluronics. For MC, the aspects such as thermoreversibility, molecular weight effect; validity of the scaling relationship, effect of surfactants, and the external magnetic effect on gelation of MC are studied. For Pluronics, a comprehensive study by various techniques such as micro differential scanning calorimetry and rheology is carried out to reveal the gelation mechanism as well as the influence of a reversed Pluronics on its gelation behavior as an additive.

1.3 Thesis organization

Literature review of all the relevant background is given in Chapter 2.

Chapter 3 describes the experimental aspects in detail as well as the information of the materials used in this thesis.

Chapter 4 describes the thermal reversible gelation of methylcellulose (MC) in water of MCs of different molecular weights to reveal the thermal, viscoelastic properties and the influence of the molecular weight on several aspects of gelation process.

Chapter 5 describes the binding behavior of MC/surfactant in water studied by ITC.

Chapter 6 describes the thermal reversible gelation behaviors of methylcellulose in the presence of a surfactant, SDS.

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Chapter 7 describes the gelation behavior of methylcellulose with and without salts under the influence of magnetic field.

In Chapter 8, F108, a member of the Pluronics family, was studied using thermal and rheological techniques, a detailed description of the gelation process is provided.

Chapter 9 describes the thermal and rheological behavior of a mixture of two Pluronics, F108 and 25R4; the two copolymers have similar molecular constitution but reversed structure of block ordering.

In Chapter 10, conclusions and recommended future work are given for the overall study.

Chapter 2

Literature Review

2.1 Hydrogel

2.1.1 Introduction

Hydrogels are hydrophilic polymer networks, which may imbibe large volume of water while maintaining the integrity as a soft solid with a certain degree of mechanical strength. A hydrogel is a system formed in water through either chemical or physical cross-linking of natural or synthetic water-soluble polymers. Distinguished by the cross-linking origin, hydrogels are often divided into chemical hydrogels and physical hydrogels. A chemical or permanent hydrogel is formed by covalently-crosslinked networks. Chemical hydrogels are prepared by a chemical reaction using one or more materials. Physical hydrogels are also called reversible hydrogels and the networks are held together by physical interactions (molecular entanglements, and/or secondary forces including ionic, H-bonding or hydrophobic forces) [Mark et al., 1981].

A particular interesting and important polymeric system is a hydrogel formed by simple phase transition of a polymer solution. This process is called a sol-gel (solution-gel) transition. The sol state is defined as a flowing fluid, whereas the gel state is non-flowing on an experimental time scale, while maintaining its integrity, which is a soft solid.

The physical gelation is usually a complex process because of the transit nature

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of the formation of the physical network junctions. A physical hydrogel may exhibit reversibility that the gel can alter its physical state from a liquid (solution) to a solid (gel), and vice versa, accordingly to the external stimuli such as temperature, pH, electric field, magnetic field, salt, surfactant, solvent composition, or light. The response is determined by the chemical structure and composition of the gelling system. Thermoreversibility refers to the reversible response to temperature. Thermoreversible hydrogels can be formed by natural, semi-natural (modified natural) polymers, or synthetic polymers.

Examples of natural or semi-natural polymers are gelatin and polysaccharides such as agarose, amylose and amylopectin, cellulose derivatives, carrageenan. Examples of synthetic polymers are N-Isopropylacrylamide copolymers, poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock polymers (PEO-PPO-PEO, or its modified forms), which form gels in water through hydrophobic association that is a function of temperature, and PEG/PLGA (poly(ethylene glycol-b-L-lactic acid-b-ethylene))block copolymers [Ostrovskii D et al., 1999] [Badiger et al., 2000].

2.1.2 Application of hydrogels

Hydrogels have long been used in many fields of industrial application such as pharmaceutical, cosmetic, textile, paint, oil drilling, detergent, adhesive, and food etc. Besides these traditional application fields, more and more efforts are being made in biomedical applications. The research on hydrogels with respect to drug delivery and biomedical devices has become extensive over the past few decades due to their biocompatible properties and easy control of transport. Natural and

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synthetic hydrophobically modified water-soluble polymers are widely used to control the rheological properties of aqueous-based formulations in numerous industrial domains, such as paints, oil recovery, cosmetics or foods. Among which, hydroxypropylmethylcellulose (HPMC) and methylcellulose (MC) are the two that have been extensively studied [Bettini et al., 2001; Ford, 1999].

One of the more recent trends in hydrogel research is the in situ hydrogel formation by phase transition or photopolymerization [Jeong et al., 2002]. In situ formation of hydrogel makes it more feasible to apply hydrogels for macromolecular deliver, tissue barriers and tissue engineering.

The design of controlled release systems using hydrogels has been well documented. The hydrophilic and hydrophobic balance of a gel carrier can be altered to provide different solvent diffusion characteristics, which in turn influence the diffusive release of drug contained within the gel matrix.

Recently, there has been an increased number of researches on the preparation and characterization of materials responsive to changing environmental conditions [Byrne et al., 2002]. The environmental conditions that can affect hydrogel swelling include pH, ionic strength, temperature, drug concentration etc. In networks containing weakly acidic or basic pendent groups, water sorption can result in ionization of these pendent groups depending on the solution pH and ionic composition. The gels then act as semi-permeable membranes to the counterions influencing the osmotic balance between the hydrogel and the external solution through ion exchange, depending on ion-ion interactions. Hydrogels have also been studied as potential carriers for controlled drug release [Hisamitsu et al., 1997].

2.2 Thermoreversible gelation of methylcellulose

2.2.1 Overview

Among hydrogels, those showing thermoreversible gelation behavior have attracted much attention. This sol-gel transformation is reversible within a certain temperature range, which does not involve the making or breaking of any covalent bonds, since the physical cross-links are based on non-covalent interactions. Compared to chemical gels, their gelation behaviors are repeatable, and no small molecules are expected to be released or trapped in the system during the sol-gel transition process, thus minimizing the risk of toxicity and other unfavorable drawbacks when being used in a biomedical application. Some of the classic examples of natural polymers exhibiting the sol-gel transition are based on hydrogen bonding, such as gelatin (protein) and carrageenan (anionic polysaccharide). These polymers form gels at lower temperature and become a solution at higher temperatures [[Grinberg et al., 2000] [Grunwald and Steel, 1995] [Nishinari et al., 1997; Nishinari et al., 2000].

In contrast to these polymers, aqueous solutions of cellulose derivatives like methylcellulose are well known to gel when increasing temperature. Questions about the gelation mechanism of methylcellulose (MC) are still not fully understood. Various gelation models have been proposed. The reports by Desbrieres et al. suggested that gelation of MC is thermoreversible and attributed to hydrophobic association [Desbrieres et al., 1998; Desbrieres et al., 2000a; Desbrieres et al., 2000b]. Dynamic rheological observation demonstrated that MC

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gels in two stages: formation of hydrophobic aggregates and connection of hydrophobic aggregate into a network. An endothermic peak is observed on heating and an exothermic peak appears on cooling.

2.2.2 Mechanism of thermoreversible gelation of MC in water

It is well known that the physical and chemical properties of macromolecules are closely related to their chemical structures and phases. Unlike the homogeneous cellulose derivatives, whose physicochemical properties may be directly predicted, the commercial cellulose derivatives are prepared under heterogeneous conditions. It's produced by a reaction in which cellulose is exposed to aqueous sodium hydroxide and methyl chloride under mechanical mixing, with the methylation occurring more rapidly in high concentration of NaOH and/or higher temperature regions. Thus, it is assumed that the distribution of methyl groups is inhomogeneous along each chain and varies chain to chain. It was reported by Ibbett et al. [Ibbett et al., 1992] that MC made under a more homogeneous manner did not undergo gelation for the same average degree of substitution (DS). The absence of a model polymer with a precise distribution of the hydrophobic substituents makes it difficult to conduct the fundamental physicochemical studies of these heterogeneous materials. The poor knowledge on relationship between the molecular structure and macroscopic behavior of these polymers prevents the improvement of their use in industrial products as well as their potential application as biomaterials. Nevertheless, a large number of experimental investigation and some theoretical studies of commercial available MC have been carried out. Different gelation mechanisms are proposed [Rubinstein and Semenov, 1998; Semenov and

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Rubinstein, 1998; Tanaka, 1996; Tanaka, 1998; Tanaka, 2002; Tanaka and Koga, 2000; Tanaka and Koga, 2001]. Some mathematics models are also proposed using both traditional polymer theories and newly developed theories, and some assumptions and theories have been experimentally confirmed [Semenov and Rubinstein, 1998; Takahashi and Shimazaki, 2001; Tanaka and Stockmayer, 1994]. The various possible mechanisms are not mutually exclusive; some are just describing the different aspects of the same mechanism.

Many experimental methods and techniques have been used to study the sol-gel transition of cellulose derivatives, such as cloud point, light scattering, X-ray diffraction, small-angle neutron scattering, rheology and micro differential scanning calorimetry (micro DSC). Among which, the rheological study and micro-DSC are mostly frequently used owing to their ability to reveal the most useful information [Winnik et al., 2000] [Bromberg, 1998] [Gilsenan et al., 2000] [Miyoshi et al., 1995].

Results of recent experimental studies prove that the associative properties of MC are primarily governed by intermolecular interactions between the hydrophobic substituents [Hirrien et al., 1998]. Owing to their unfavorable contact with water, hydrophobic groups associate, leading to cross-linking and finally forming a three-dimensional network. These gels are completely thermoreversible.

However, there exists some controversy regarding the mechanism of gelation. The major discussion concerns the nature of the junction zones involved in the gelation. Liquid crystalline and hydrophobic interactions are the two dominant assumptions supposed to be involved.

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Haque and Morris (1993) suggested crystalline zones formed during the gelation process [Haque and Morris, 1993; Haque et al., 1993]. Kato et al. (1978) concluded that the “crosslinking loci” of MC gels consist of crystalline sequence of trimethylcellulose units [Bettini et al., 2001].

Haque and Morris proposed a bundled structure where MC chains exist in solutions as aggregated “bundles”, held by packing of unsubstituted or sparingly substituted regions of cellulosic structure, and by hydrophobic clustering of methyl groups in regions of denser substitution [Haque and Morris, 1993]. As temperature is raised, the ends of the bundles come apart, exposing methyl groups to the aqueous environment and then allowing the hydrophobic association of methyl groups from different bundles to result in the formation of a gel. This model considered that a bundled structure, which is formed through intermolecular hydrogen bonding between unsubstituted or sparingly substituted regions of MC, always exists at low temperatures and even above the gelation temperature.

Takahashi et al. reported that the cross-links were formed by partial crystallization of MC polymer segments. [Takahashi and Shimazaki, 2001; Takahashi et al., 1998; Takahashi et al., 2001] The microcrystals at the junctions are supposed to be stabilized by hydrogen bonds between the hydroxyl groups and/or by the hydrophobic interaction of methyl groups.

Hirrien and Desbrieres carried out a series studies using primarily rheological and micro DSC techniques [Desbrieres et al., 1998]. Their conclusions are mainly based on the heterogeneous nature of commercial MC. Using rheological and fluorescence spectroscopic experiments, the effects of temperature and salts were

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demonstrated, confirming the hydrophobic association as the origin of the gelation process. A comparison of gelation behavior with homogeneous MC systems was made. As heterogeneous polymers can be viewed as block polymers with highly substituted and less substituted parts, the authors attributed the aggregates in the junction zone to the highly substituted part of the chain, while low substituted units do not participate. The highly substituted units are proposed to be tri-substituted part. Evenly distributed hydrophobic chains are not favorable to gelation since there are no highly substituted units. Micro DSC study was carried out to confirm if the two kinds of interactions existed, and whether they attributed to the two peaks in the cooling curve of the MC system. The two interactions are proposed to be from highly substituted units and low substituted units respectively. A paper by the above authors gave a more detailed introduction bases on rheological consideration. The result is in agreement with their previous studies [Desbrieres et al., 2000a].

Kobayashi et al. also studied the thermoreversible gelation of MC in water [Kobayashi et al., 1999]. Rheological as well as small-angle neutron scattering and dynamic light scattering technique were used to study the process. A new explanation for the double peaks on the cooling curves was proposed. Phase separation was assumed to be involved in the second stage of gelation. The authors believed that the sol-gel transition process can be expressed by two stages, the first stage of gelation corresponding to the growth of clusters or aggregates in semi-dilute solution and the second stage of gelation corresponding to liquid-liquid separation that is promoted by the association among chains. The phase separation occurring at the second stage was expressed by the turbidity change, which is not

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expected to occur if the second stage is just a continuing process of the hydrophobic association of the first stage.

Despite the recent dominance of the hydrophobic association mechanism, the study on different MC may lead to other gelation mechanisms. Yuka et al. [Sekiguchi et al., 2003] successfully prepared some O-alkylcellulose derivatives that possess a systematically controlled distribution of substituents and degree of substitution (DS); [Kondo, 1993; Kondo and Gray, 1991a; Kondo and Gray, 1991b; Kondo and Gray, 1992]. They tried to use these products to find the correlation between the physicochemical properties and the distribution of substituents in terms of hydrogen bonding formation. The distribution of substituents was found to influence the inter- and intra- molecular hydrogen bonding formation, which contributes to the solubility [Kondo, 1997], gelation [Itagaki et al., 1994; Itagaki et al., 1997], liquid crystallization [Kondo and Miyamoto, 1998], crystallization and chemical reactivity of hydroxyl groups [Kondo, 1997]. They also proposed some new mechanisms on the gelation of MC. Conclusions were made that those samples having fewer intramolecular hydrogen bonds in solution are prone to form gels on heating, which may be due to the fact that gelation is dependent on the flexibility of the cellulose molecular chains, because the intramolecular hydrogen bonds restrain the flexibility. They also suggested that for high molecular weight and high DS MCs, gelation is caused by hydrophobic interaction, whereas very low molecular weight and low DS MC forms gels at a substantially lower temperature than similar samples with higher DS. Thus, it was concluded that there may be some interactions other than hydrophobic interaction causing gelation. They also confirmed the

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existence of the hydrogen bonds between the polymer and water by FTIR spectra where the position of hydrogen bond is supposed to be C6 hydroxyl group, which has a favorable steric position, the experiment was carried out at temperature range from 30 to 90 °C [Sekiguchi et al., 2003].

2.2.3 Theoretical models of gelation for MC

Compared to the large number of experimental studies, theoretical analysis of MC gelation in water is relatively scarce due to the complex nature of the molecular structure. Two distinct theories are found in the literatures. One model was proposed by Tanaka et al. [Tanaka, 1996; Tanaka, 1998; Tanaka, 2002; Tanaka and Koga, 2000; Tanaka and Koga, 2001] and the other one is totally different, given by Semenov & Rubinstein [Rubinstein and Semenov, 1998; Semenov and Rubinstein, 1998]. The latter pointed out some flaws of the former.

The conflicting theories of the above authors come from different polymer theories in the vicinity of the sol-gel transition regime, as well as different views concerning the gelation mechanism, which led to different assumptions and models, and of cause the different results.

Tanaka used a novel modified Eldridge-Ferry method to analyze the junction structure of thermoreversible gels based on the recent molecular theory of gelation with multi-chain junctions [Tanaka et al., 2001; Tanaka, 1996; Tanaka, 1998; Tanaka, 2000; Tanaka and Ishida, 1995; Tanaka and Ishida, 1999; Tanaka and Koga, 2000; Tanaka and Koga, 2001; Tanaka and Nishinari, 1996; Tanaka and Stockmayer, 1994]. They simplified the problem to a model that binds s chains

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(junction multiplicity) via ζ sequential units (junction length) per chain. Junction multiplicity s and junction length ζ are defined by the number of chains combined into a single junction and by the number of statistical units along a single chain taking part in the junction, respectively. They showed that the new method enabled us to find ζ and s independently from the measurement of the sol-gel transition concentration and are most suitable for the description of thermoreversible gels with junctions formed by fringed-micellar crystallites. A schematic of junction and s , ζ are shown in Figure 2.1:

Figure 2.1 Schematic of multi-junction and multiplicity s and length ζ .

Takahashi and Shimazaki [Takahashi and Shimazaki, 2001; Takahashi et al., 2001] applied the above modified Eldridge-Ferry method to analyze the structure of the junctions zones formed in MC gels and concluded: (1) the junction formed by fringed-micellar crystallites in MC gels is very thin; (2) the multiplicity s decreased from 4.3 for low-temperature melting gels to 2.0 for high-temperature melting ones and (3) by increasing the molecular weight, the number of statistical units ζ along a chain increases from 27 to 54.

Semenov and Rubinstein [Semenov and Rubinstein, 1998] utilized the mean field theory of associative polymers to study the problem. A new phase diagram was developed, which is composed of a single-phase solution (sol), a single-phase reversible gel, a two-phase region with coexisting sol and gel, and a region with two

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coexisting gel phases (two-phase sol region is impossible under the Θ condition). From their result, it was concluded that the thermoreversible gelation is not a thermodynamic transition; gelation was accompanied by phase separation as shown in Figure 2.2.

Figure 2.2 Phase diagram of a θ -solution of associating polymers for $f = 20$ and $\nu = 0$, reproduced from [Semenov and Rubinstein, 1998].

2.3 Interactions between polymers and surfactants

2.3.1 Overview

Interactions between polymers and surfactants in aqueous solutions have attracted increasing attention because of their potential applications and complex behaviors. Numerous research groups have devoted their attention to advance the fundamental understanding of the physics governing these interactions. On the other hand, salts and other additives are reported to affect the sol-gel transition of polymer solutions significantly [Xu et al., 2004a; Xu et al., 2004b]. It is reasonable to relate

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the gelation properties of the mixed solution with the interactions between the polymer and surfactant. The interaction between the two solutes as well as the interactions between water and two solutes, in a complex manner, is believed to be the cause of the unusual behaviors of the system compared to the one in the absence of surfactant. The study of sol-gel transition of usually involves a wide range of temperature zones, including at least three zones: the solution zone, the transition zone and the gelation zone. The first zone and part of the second zone can be studied by isothermal titration calorimetry (ITC) due to the liquid state of the system. The interactions between the polymer and surfactant in the aqueous solution are also temperature dependent.

Many recent research activities focus on the nonionic polymer/ionic surfactant system, and the binding is the main interaction between the polymer and the surfactant in water. Recently Konop and Colby [Konop and Colby, 1999a; Konop and Colby, 1999b] reported that the electrostatic repulsion plays a minor role in the micellization and its contribution to the micellization free energy can be ignored. The main reason for ionic surfactants to possess a higher CMC is the entropy loss of a fraction of counter ions condensed on the surface of the micelles.. It has been reported that anionic surfactants exhibit a fairly strong cooperative interaction with nonionic hydrophilic polymers such as poly(ethylene-oxide) (PEO) and polyvinylpyrrolidone (PVP), while such polymers do not interact with cationic surfactants [Bloor et al., 1996; Ghoreishi et al., 1999; Rodenhiser and Kwak, 1998]. Such behavior may be related to the water structure in the aqueous medium as determined from the observation that this interaction can be controlled by the

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addition of structure breaking agents such as iodide and thiocyanate. Cationic surfactants were found to bind on polymers which are fairly hydrophobic (natural or hydrophobically modified) [Ghoreishi et al., 1999; Goddard, 1993]. Saito and coworkers have demonstrated that interaction between a polymer and a cationic surfactant can be promoted when a strongly interacting counterion is present [Goddard, 1993; Goddard and Ananthapadmanaban, 1993]. The segments of the polymer chains can be wrapped around the surfactant micelle to form a complex which relieves the stress of the polymer/surfactant pair. The features of binding between nonionic water-soluble polymers and charged surfactants can be categorized into the following [Goddard, 1993]

1. Surfactant monomers do not bind onto polymers as individually molecules but in the form of micelles.
2. The process of binding is highly co-operative.
3. The main driving force for association is a reduction in the hydrocarbon/water contact area of alkyl chains of the surfactant. Higher hydrophobicity of polymers favors the process of binding.

Another important system that is of interest to us is the hydrophobically modified polymer/surfactant system. In this system, the generally accepted ideas adopted for normal polymer/surfactant system, such as critical aggregation concentration (CAC) and the degree of binding (β) are not applicable. Modifications are needed and some features for hydrophilic polymer/ionic surfactant system summarized above cannot be observed. The hydrophobes that are distributed along the polymer backbone allow the polymer to form hydrophobic microdomains (micelles) on its

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own. The pre-existence of such hydrophobic microdomains promotes the interaction between the polymer and the surfactant molecules. These polymers have the capacity to bind individual surfactant molecules, yielding a less obvious CAC and a non-cooperative binding process [Goddard, 1993; Linse et al., 1998; Rodenhiser and Kwak, 1998].

Modeling of polymer/surfactant systems is essential to develop a good physical understanding of binding mechanism and to elucidate the precise structure of the polymer/surfactant complex. It is impossible to find a universal model for all polymer/surfactant systems because of their complexities and varieties. Different models that are suitable for describing the appropriate interactions are needed for each of the system. For linear polymers, a general model has emerged, which is often referred to as the “necklace” or “beads-on-a-string” model, where the surfactant micelles reside within the random coil of the polymer chain. The necklace model has been refined over the last 30 years and is widely accepted by many research groups as a good model to describe the complex structure of many polymer/surfactant systems. Lundahl et al. proposed a model which is called “the flexible helix” for protein/SDS system where an end-capped cylindrical SDS micelle is surrounded by a protein helix [Shirahama, 1998]. The free draining necklace model was used by Takagi to describe the structure of the micelle-polyelectrolyte complexes [Shirahama, 1998].

2.3.2 Characterization on polymer/surfactant systems using ITC

Heat effects in micellar and polymer/surfactant solutions are relatively small. However modern calorimetric methods, such as the micro-calorimetric technique is

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sensitive enough to monitor the small heat changes. Isothermal titration calorimetry can be used to extract thermodynamic parameters such as enthalpy (ΔH), entropy (ΔS), Gibbs energy (ΔG) and heat capacity (C_p), which are critical to the understanding of polymer/surfactant interactions. Micro-calorimetry also allows the characterization of polymer/surfactant systems in terms of their critical concentrations:

1. Critical aggregation concentration (CAC) corresponding to the surfactant concentration at which the binding commences;
2. Saturation concentration (C_2) referring to the surfactant concentration at which the associative junctions of polymers are fully saturated with bound surfactant [Wang et al., 1997b]
3. Second critical concentration (C_m) defined to identify the formation of free micelles in the presence of polymer.

This notations were introduced by Bloor and co-workers for systems that possess two simultaneous competing surfactant aggregation processes, namely the formation of polymer-bound mixed micelles and free micelles [Bloor et al., 1995a; Bloor et al., 1995b]. However, the identifications of CAC and C_2 from the calorimetric titration data are not consistent with each other and are still a subject of continual discussion. The shape of the titration curves is also informative, where the gradient of the binding curve is related to the cooperativity of polymer/surfactant interaction, which can be quantified by the binding constant K by fitting with a suitable mathematical model.

Shirahama and Ide estimated the enthalpy of transfer of sodium

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dodecylsulphate (SDS) from the micelle to poly(ethylene oxide) (PEO)/SDS aggregates by direct calorimetric measurement. The magnitude of the enthalpy change was small (0.6k cal/mol) and may contain considerable error [Goddard, 1993]. In 1981, titration calorimetry was first used by Kresheck and coworkers to characterize polymer/surfactant system, and to examine interactions between surfactants and biological macromolecules such as proteins and polypeptides [Olofsson and Wang, 1998]. The sensitivity and accuracy of these calorimeters are far too low compared to the current commercial microcalorimeters. Olofsson and co-workers [[Olofsson and Wang, 1994] [Wang and Olofsson, 1998]] extensively studied PEO/SDS system using the highly sensitive ITC. The critical concentrations were obtained from comparison of the titration curves done in the presence and absence of a polymer. The surfactant concentration where these two curves deviate is defined as the CAC and when they merge with each other is defined as C₂. The deviation and merging of the two titration curves suggests that the added surfactant experiences a re-organization when titrated into the polymer solution, and the aggregation behavior of surfactant is no longer influenced by the polymer when its concentration reaches C₂. For the PEO/SDS pair, a significant endothermic enthalpy and a CAC lower than CMC were detected. The enthalpy curves obtained from the titration of SDS into other nonionic polymers such as ethyl(hydroxyethyl)cellulose (EHEC) and polyoxypropylene (PPO1000) showed similar features [Olofsson and Wang, 1994; Olofsson and Wang, 1998]. Endothermic heat curves were also reported by Bloor et al. for SDS interactions with poly(propylene oxide) (PPO) and a copolymer of N-(vinylacryloyl)pyrrolidine and 4-vinylpyridine dicyanomethylide [Bloor et al., 1995a]. The values of CAC and

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C2 detected from microcalorimetry are in good agreement with the values obtained from the surfactant ion selective electrode measurements [Bloor et al., 1995b]. Similar phenomena were also observed by Wang et al. for the binding of SDS and tetradecyl trimethylammonium bromide (TTAB) on hydrophobically modified and unmodified poly(acrylamide) (HMPAM and PAM) polymers [Wang et al., 1997a]. Microcalorimetric titration curves reported by Brackham et al. based on their studies of the interactions between nonionic surfactant, n-octyl β -D-thioglucoopyranoside (OTG), and PPO1000 do not show any clear indication of CAC [Olofsson and Wang, 1998]. Similar features are also found in polyvinylpyrrolidone (PVP)/SDS system [[Olofsson and Wang, 1998]. The reasons for the absence of the threshold concentration may lie in (i) weak or non-existing interaction between polymers and surfactants, (ii) non-cooperative binding of individual surfactant molecules onto polymer and (iii) strong tendency of self-association of surfactants [Goddard, 1993; Linse et al., 1998].

Recently, interactions between hydrophobically modified water-soluble polymers and ionic surfactants have attracted much interest and are a subject of studies by several research groups. The interaction between hydrophobically modified EHEC and SDS was studied using ITC. Two steps of binding were observed. A non-cooperative binding during the early stage of interaction, followed by a cooperative binding which is similar to the one found in normal EHEC/SDS system. The early non-cooperative binding may be caused by the strong hydrophobicity introduced by the hydrophobic micro-domains along the polymer chains.

2.4 Thermal reversible gelation of Pluronics in water

2.4.1 Overview

Polymeric surfactants have been extensively studied during the past two decades. Tri-block copolymers, PEO-PPO-PEO, are one of the families of polymeric surfactants, where PEO stands for poly (ethylene oxide) and PPO does for poly (propylene oxide). Commercial available products of these copolymers are Pluronics (BASF) and Poloxamers (ICI). The ratio of the EO/PO segments as well as their sequence greatly influences their physiochemical behaviors in water. Many studies on PEO-PPO-PEO copolymers have been reported [Alexandridis et al., 1995; Kositza et al., 1999; Mao et al., 2001; Mortensen, 1992; Mortensen and Brown, 1993; Mortensen et al., 1992; Wanka et al., 1994; Wu et al., 1993]. A review for studies of PEO-PPO-PEO copolymers was given by Alexandridis et al. [Alexandridis and Hatton, 1995]. Another type of triblock copolymers with a reverse sequence is denoted as PPO-PEO-PPO. All these copolymers are non-ionic surfactants and have a wide variety of applications in the fields ranging from medicine to petroleum industries.

At low temperatures, both PEO and PPO blocks of Pluronics are soluble in water. Upon heating, the PPO blocks gradually become insoluble as they are regarded as hydrophobic at high temperatures as compared to the PEO blocks that are still hydrophilic and remain soluble. Aggregation of the PPO hydrophobic blocks leads to formation of micelles when the critical micellization concentration (CMC) or critical micellization temperature (CMT) is reached. Micelles are made

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up of a hydrophobic core surrounded by hydrophilic chains in the corona, which is described as a core-corona spherical structure.

For concentrated solutions, the micelles formed can develop into structured systems, such like micellar crystals or gels. Much work has been done to reveal the crystalline structures and gelation behaviors of Pluronics [Alexandridis et al., 1995; Kositza et al., 1999; Mao et al., 2001; Mortensen, 1992; Mortensen and Brown, 1993; Mortensen et al., 1992; Wanka et al., 1994; Wu et al., 1993].

At high concentrations, the randomly dispersed micelles can further form a close-packed crystalline lattice structure and a gel-like structure is then obtained. Depending on the chemical composition and molecular weight of a given Pluronics, temperature and concentration, several different crystalline structures have been reported, which include lamellar [Mortensen, 2001], hexagonal, [Mortensen, 2001] fcc, [Eiser et al., 2000] or bcc [Eiser et al., 2000].

The study on PEO-PPO-PEO in water, in terms of its physical states, can be separated into three parts: solution behavior, micellization and gelation.

2.4.2 Micellization of PEO-PPO-PEO in water

2.4.2.1 CMC and CMT

The critical micellization concentration (CMC) and critical micellization temperature (CMT) are two important parameters in surfactant solutions. CMC is the surfactant concentration at which micelle start forming at a given temperature while CMT is the temperature at which micelles begin forming for solution with a given concentration. Light scattering and fluorescence spectroscopy techniques are

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used to detect the CMC or CMT of the copolymer. A collective data of CMC and CMT of dilute to semidilute solutions of Pluronics polymers were given by Alexandridis [Alexandridis et al., 1994a; Alexandridis et al., 1994b].

2.4.2.2 Micellar structure

The formation of block copolymer micellar solutions is a relatively matured field. Some reviews are available which addressed block copolymer micelle formation and morphology in aqueous solutions [Alexandridis and Hatton, 1995; Alexandridis and Hatton, 1996; Webber, 1998]. In the literature, micelles are represented as hard spheres composed of a core of PPO, surrounded by a corona of hydrated PEO units [Chu et al., 1994; Goldmints et al., 1997; Linse, 1993; Liu et al., 1996; Mortensen, 1996; Mortensen and Brown, 1993; Mortensen et al., 1994; Mortensen and Pedersen, 1993]. An earlier study by Zhou and Chu revealed that that F68 ($\text{EO}_{76}\text{PO}_{30}\text{EO}_{76}$) is made up of a relatively compact liquid core of PPO blocks surrounded by a higher swollen shell of soluble PEO blocks [Zhou and Chu, 1988]. An equilibrium between the unimers and micelles in the solution can be established as:

The aggregation number (n) is a weak function of polymer concentration but changes rapidly with temperature [Goldmints et al., 1997; Liu et al., 1998b]. It's also reported that the aggregation number (n) mainly increases with increasing length of the PPO blocks. Upon raising the temperature, this number increases rapidly, but the hydrodynamic radius remains nearly constant because of the PEO

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chains getting dehydrated with increasing temperature. Conversely, the aggregation number is more or less dependent on the concentration of the Pluronic [Alexandridis and Hatton, 1995].

Micelles formed in Pluronic solutions were first detected by Rassing and Attwood using ultrasonic velocity and light scattering experiments [Rassing and Attwood, 1982]. Light scattering and small angle neutron scattering (SANS) are used to study the structures spanning the whole regime of the unimers, micelles and other high concentration phases such as rods and lamellar. Dynamic light scattering can be used to determine the association number of the micelles. SANS experiment offers information such as correlation function of the structures and the volume fraction of the micelles. Other techniques often used in the recent years are the spin probe technique, nuclear magnetic resonance spectroscopy (NMR), atomic force microscopy and cryogenic transmission electron microscopy.

Using the results of light scattering techniques, the core-shell structure of the micelle was studied in detail [Brown et al., 1991; Mortensen, 1996]. It was reported that the micelle formed in a F127 solutions had a core size (R_c) of 59 Å and the aggregation number of 145, which was independent of the polymer concentration but increased with increasing temperature. Direct image of the F127 micelles using cryogenic temperature electron microscopy (cryo-TEM) proved the micellar structure gained by scattering techniques. [Mortensen and Talmon, 1995] Temperature is the major controlling factors of the aggregation number and size. The core radius of P85 micelles increases from about 40 Å at 20 °C to 50 Å at 50 °C. [Mortensen, 1996]

2.4.2.3 Thermodynamics of micellization

The thermodynamics of the micellization of block copolymers have been reported in several papers.[Alexandridis, 1997; Alexandridis and Hatton, 1995; Alexandridis et al., 1994b; Yu et al., 1992] [Liu et al., 1997; Liu et al., 1998a] [Linse, 1993] The standard enthalpy, free energy and entropy of micellization, ΔH° , ΔG° and ΔS° are obtained [Alexandridis et al., 1994b]. The standard enthalpy change, ΔH° , is positive, indicating that the transfer of unimers from solution to the micelles is an enthalpically unfavorable endothermic process. The free energy, ΔG° , is negative, since thermodynamically stable micelles are formed spontaneously at CMT. Thus, it's clear that the negative enthalpy change, ΔH° , is the driven force for micellization of the block copolymers. Recently a thermodynamic equilibrium between unimers and micelles model was proposed by Perreux et al 2001a and 2001b to study the thermodynamic equilibrium between the unimers and micelles [Perreux et al., 2001a; Perreux et al., 2001b]. Alexandridis et al. [Alexandridis et al., 1994b] reported that the micellization process is strongly driven by entropy, and the free energy of micellization is mainly a function of the PPO block, the hydrophobic part of the copolymer, rather than PEO blocks, although the latter block's solubility also decreases at higher temperature. For the PEO-PPO-PEO copolymers with PEO blocks of constant molecular weight and PPO blocks of varying molecular weight, the CMC values for the Pluronic solutions (at a given solution temperature) decreased with increasing number of PPO segments, indicating that the polymers with a larger hydrophobic (PPO) domain form micelles at lower concentrations [Alexandridis et al., 1994b].

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For block copolymers, the micellization process in apolar solutions and aqueous solutions contrast greatly. In apolar (mostly organic solvent) solutions, micelles form upon decreasing temperature, indicating that the micellization is driven by enthalpic interactions. [Alexandridis and Andersson, 1997; Alexandridis and Hatton, 1995; Alexandridis and Hatton, 1996; Quintana et al., 1998], In other words, the process is exothermic. Cogan also reported that the micellization is an enthalpically driven process in an organic solvent, and the polymer can reduce its free energy by forming spherical aggregates to avoid the unfavorable interactions between insoluble blocks and organic solvents [Cogan et al., 1992].

An extensive thermodynamic study of aqueous solutions of some PEO-PPO-PEO was carried by Senkow et al. [Senkow et al., 2002] for dilute solutions of Pluronics L31, L35, L64, F68, P123 and 10R5, It is concluded that experimental values are sensitive to the structural state of the Pluronic in solution. Depending on either the molar mass or the PO/EO ratio of the Pluronic or the temperature, the following different structural states are present in solution: dispersed monomers, mixed individual micelles species and predominantly micelles. From the analysis of changes in these properties, thermally induced transitions are shown and related to the hydrophobic character of the Pluronic.

2.4.3 Gelation of PEO-PPO-PEO

2.4.3.1 Gelation temperature

Gelation is a description of the phenomenon in which the viscosity of a polymer solution suddenly diverges. Traditionally the term “gel” may only apply to

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those percolation type systems which possess an interconnected network in the whole span of the system, inducing a sudden change in the viscoelastic properties of the system. In the case of a Pluronics/water system, the term “gel” itself has some controversy as most literatures indicate a non-interconnected crystalline structure. Nevertheless, we still use the term gel to describe with regard to the fact that the elasticity and the physical appearance for the concentrated system beyond the transition temperature which indeed resembles the so called classic gels. The heat induced gelation in Pluronics copolymer solution was reflected in the rapid increase of the storage modulus G' by two or more orders of magnitude. The storage modulus G' approached a steady value after gel formation, which increased with increasing copolymer concentration. Some other researchers defined the gelation temperature as the temperature at which storage modulus, G' , equals the loss shear modulus, G'' [Brown et al., 1991; Brown et al., 1992].

2.4.3.2 Thermodynamics of gelation

Compared to the thermodynamics study for the micellization process, the thermodynamics of gelation is less studied. An earlier study by Vadnere et al. [Vadnere et al., 1984] provided the sol-gel transition temperature as a function of copolymer concentration for nine Pluronic PEO-PPO-PEO copolymers. The enthalpy change of gelation, ΔH_{gel} , was calculated to be positive between 5 and 10 kcal/mol of copolymer. Unlike the gelation of gelatine, where the large enthalpy change (-67 kcal/mol) favors the gelation process, the enthalpy change in the case of PEO-PPO-PEO gelation is unfavorable. The enthalpy of gel formation was not significantly altered by the added substances, suggesting that entropy plays the

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major role in the gelation process [Vadnere et al., 1984]. Yu et al. studied Pluronic F127 by differential scanning calorimetry and other techniques and concluded that both the micellization and gelation processes are endothermic (enthalpy change >0) [Yu et al., 1992]. The gelation was found to be an almost athermal process compared to micellization. Based on the presented evidence, particularly that from DSC, and considering other recent studies, it was concluded that the thermal gelation of F127 (i.e. gelation on raising the temperature) resulted essentially from the packing of spherical micelles. A small thermal event at the gelation point was ascribed to a disorder-order discontinuity.

2.4.3.3 Effects of additives on the sol-gel transition of PEO-PPO-PEO

The effects of solutes and polymers on the gelation properties of PEO-PPO-PEO were also reported. Addition of a PEO homopolymer increased the gelation temperature; the extent of this increase depended on the added PEO chain length and concentration. The effects of additives on gel formation in aqueous F127 solutions have been reported by Malmsten and Lindman [Malmsten and Lindman, 1992a; Malmsten and Lindman, 1992b; Malmsten and Lindman, 1993]. The effects of added PEO and PPO homopolymers were also investigated. It was found that PEO of intermediate molecular weight caused the gel to "melt" at a certain homopolymer amount which depended on the copolymer concentration. The efficiency of PEO in inducing melting of the gel increased with PEO molecular weight, but at very high PEO molecular weights the phase separation (rather than gel melting) occurred. Addition of PPO homopolymer, however, tended to increase the stability region of gel, although this depended on the PPO molecular weight

[Malmsten and Lindman, 1993].

The stability range of the gel phase depended strongly on the presence of salts. NaCl, which is often referred to as a typical "salting out" cosolute, displaces the whole gel region, as well as the cloud point, to lower temperatures. NaSCN, a typical "salting in" cosolute, displaces the whole gel region and the cloud point up to higher. The presence of NaCl, KCl, and NaSO₄ decreased the gel transition temperature, whereas the opposite effect was observed with urea, alcohol and sodium dodecyl sulfate (SDS) [Malmsten and Lindman, 1992a].

2.4.4 From micellization to gelation

Micellization and gelation are two processes of interest for Pluronics aqueous solutions. Because the CMC of Pluronics are relatively small, most of the solutions studied in the literature go beyond the critical concentration to form micelles, but not all the systems can form hydrogels as they required higher concentration to initiate. For a concentrated solution of PEO-PPO-PEO, the micellization and gelation normally occurred at lower and higher temperature regimes respectively, thus it is reasonable to think the micellization as a precursor of gelation. Two models are proposed to describe the relation between the micelles and the gel. Some researchers deal with the sol-gel transition as the classic gels as described by percolation using a sticky hard sphere model of Baxter. In this model, the micelles in the solution interact with each other via the adhesive force [Chen et al., 2001; Gambadauro et al., 2001; Lobry et al., 1999; Mallamace et al., 1999; Malmsten and Lindman, 1992a]. The entanglement of PEO chains extending outward from the corona part the core-corona shaped micelles between the adjacent micelles was also

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suggested [Gente et al., 2004]. In this case, a percolated micellar network would be formed involving the whole span of the system. In other words, all the micelles are associated via their PEO arms. The second model, which is suggested in most literatures, is the disorder-order transition of the micelles formed upon increasing temperature and/or concentration of the copolymer to form a liquid crystalline structure. Micelles are regarded as hard (or soft) spheres which interact with each other through hard or soft sphere potential when they are close enough to each other which are caused by the increase in size or number of the micelles by heating of a concentrated solution. The origin of the hard sphere or soft sphere potential can be understood by the analogy to van der Waals force. The consequence of this kind of ordering, on the other hand, leads to the formation of an organized phase of crystalline network made up of closed packed micelles. The micelles of such a network remain individual rather than connected as the first theory predicts.

This micellar disorder-order transition is reported to be caused by repulsive interactions [McConnell et al., 1993; McConnell et al., 1994]. Ordering in the systems by interacting through repulsive forces was first discovered in computer simulations of hard spheres forming fcc arrays by Alder et al. and was called the Kirkwood-Alder transition theory [Alder et al., 1968] [McConnell et al., 1993]. Such a system interacts via repulsions between the solvated chains forming the micellar corona. The intermicellar interaction potential can be calculated using the self-consistent mean-field model. [McConnell et al., 1994] Yu et al. studied F127 [Yu et al., 1992] and concluded that the gelation (packing of spherical micelles) was the result of the space-filling effect induced by micellization. The ordering kinetics was

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studied by Liu et al., indicating the diffusion-controlled nature of the ordering process in the micellar systems at low temperatures. The elastic modulus of the bcc phase was found to increase almost linearly with temperature; thus the assumption was made that the origin of the modulus was entropic elasticity of the corona chains in the micellar bcc lattice [Liu et al., 2004].

The ordering of the micelles in the solution is considered to occur when the density of micelles is high enough with increasing temperature or concentration, when the micelles are close enough to each other. Mortensen reported that the disorder-order transition of the micelles was a first order transition and happened when the volume fraction of the micelles in the solution exceeded 0.53 to form a cubic crystal, [Mortensen et al., 1992] while the liquid and crystalline domains coexist in the range of 0.47 to 0.53 of volumetric fraction. A kinetic study of the ordering process of body centered cubic morphology was provided by Liu et al. [Liu et al., 2004].

The second model is more convincing as it has been supported by a lot of experimental results primarily using techniques like rheology, small angle neutron scattering (SANS) and small angle X-ray scattering (SAXS), which have shown clearly that this gel-like phase is due to the micelles' crystallization for the systems studied. The crystalline phases have the property to orientate under shear, which enables them to produce characteristic diffraction patterns that can be interpreted by applying classical rules of crystallography to gain the lattice information [Perreur et al., 2002]. Depending on the nature of the polymer, temperature and concentration, several different arrangements have been reported such as lamellar [Alexandridis et

al., 1996; Hamley et al., 2000; Mortensen, 2001; Mortensen et al., 1995], hexagonal [[Alexandridis et al., 1996; Hamley et al., 2000; Mortensen, 2001], face-centered-cubic (fcc) [[Eiser et al., 2000; Mortensen, 2001] or body-centered-cubic (bcc) structures [[Alexandridis et al., 1996; Brown et al., 1991; Brown et al., 1992; Eiser et al., 2000; Hamley, 2000; Mortensen, 1997; Mortensen, 2001].

2.4.5 Association behavior of PPO-PEO-PPO in water

Compared to the large number of publications available in literature for Pluronics, PEO-PPO-PEO copolymers, much less attention has been given to Pluronics-R, PPO-PEO-PPO copolymers. D'Errico et al. studied 25R4 and 25R2 ($\text{PO}_{21}\text{-EO}_{12}\text{-PO}_{21}$) by SAXS and ^2H NMR, [D'Errico et al., 2004] and found that 25R4 and 25R2 did not form spherical micelles in dilute solutions. At low temperatures and high dilution, the copolymers exists in solution as monomers while a network is formed upon increasing temperature or concentration through the self-aggregation of PPO blocks connected by PEO. It was suggested that for Pluronics-R copolymers to form micelles, looping of the polymer chains would be required. Since the molecular looping for the Pluronics-R chains with short EO blocks will require a great reduction in entropy, however, it will not be favorable thermodynamically. However in concentrated solutions (18-40 wt %), interconnected micelles can be formed, in which the two outer PPO blocks of a chain participate in two different micelles or aggregates.[Mortensen et al., 1994] For a Pluronics-R type of copolymers, an optimal balance between the hydrophobic portion and the hydrophilic portion is necessary for such copolymers to be soluble in water and to form well-defined micellar structures upon heating. Otherwise,

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irregular aggregates will be formed or precipitation will take place.

Zhou and Chu reported that Pluronics 17R4 ($\text{PO}_{14}\text{-EO}_{24}\text{-PO}_{14}$) formed the micelles only at high copolymer concentrations within a narrow range of temperature. [Zhou and Chu, 1994] Chowdhry et al. studied Pluronics 31R1 ($\text{PO}_{27}\text{-EO}_4\text{-PO}_{27}$) by micro DSC, which has a very low EO proportion, but no conclusions were drawn on the micelle formation. [Chowdhry et al., 1999] Alexandridis et al. stated that there was no experimental evidence for Pluronics-R micellization in dilute aqueous solutions. [Alexandridis et al., 1994a] However, Mortensen reported the formation of both micelles and network-like structures in the range of semidilute concentrations for 25R8 ($\text{PO}_{15}\text{-EO}_{156}\text{-PO}_{15}$). [Mortensen et al., 1994] The author proposed that the micelles formed by the hydrophobic association of PPO blocks were connected by EO blocks, and no isolated micelles existed. [Mortensen et al., 1994] It is noted that 25R8 has a much longer EO block than 25R4 or other Pluronics R studied, which may make it more likely to form a loop structure.

Chapter 3

Materials and Experimental

3.1 Methylcellulose (MC)

Methylcellulose, also named as methyl cellulose, or cellulose, methyl ether [CAS RN: 9004-67-5] is a cellulose derivative. Commercial methylcellulose is widely used as thickener for foods and cosmetics, coating material for medicines and binder for ceramic and cement. Commercially available MC is produced from natural cellulose. Cellulose is one of the most abundant natural polysaccharides. The chemical structure of cellulose is shown as below:

Figure 3.1 Chemical structure of cellulose.

There are three hydroxyl groups in each unit of glucose of the molecule of cellulose, in which the three hydrogen atoms can be partially or wholly substituted by methyl group.

Although polysaccharides are hydrophilic in nature with many hydroxyl groups in the molecular structure, they are mostly insoluble in water because of the extensive existence of inter-molecular (within a molecule) and intro-molecular (between the different chains) hydrogen bonds. The distribution of hydrophobic

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substituents is expected to correlate with the physicochemical properties of MC in water. [Burchard, 2003] The distribution of substituents has been found to affect the formation of inter- and intra- molecular hydrogen bonding.

Figure 3.2 illustrates the chemical structure of methylcellulose. Any of the three hydroxyl groups in one cyclo-structure glucose unit could be substituted by CH_3O -group via methylation reaction. An average degree of substitution (DS) is defined and the maximum value of DS is 3, meaning that all the hydroxyl groups in each glucose unit have been substituted.

Figure 3.2 Chemical structure of methylcellulose.

Sekiguchi and Sawatari [Sekiguchi et al., 2003] studied several MC polymers using primarily near infrared spectroscopy (NIR) and small angle X-ray scattering on the effect of hydrogen bond on the thermal behavior.

From their study, the following cellulose structure (A) in Fig 3.3 may exist and the possible strong intramolecular and intermolecular hydrogen bonds may present to affect the dissolubility of cellulose. Structure (B) is one of the possible structures of MC, and the potential hydrogen bonds are shown therein. Structures A and B were proved by the authors [Sekiguchi et al., 2003].

(A) Cellulose

(B) 2,3-di-O-methylcellulose

Figure 3.3 Hydrogen bonds in MC, B and C represent two kinds of hydrogen bond.

In this study, three kinds of methylcellulose with the trade name of SM 4000, SM100 and SM8000 were used, which were manufactured by Shinetsu Chemical Co. Ltd., Japan. They were made by etherification of pulp cellulose. According to the product specification, the weight-average molecular weights of SM4000, SM100 and SM8000 are 310, 000, 100,000 and 400,000 respectively as determined by light scattering. The degree of substitution (DS) provided by the manufacturer are 1.8 for SM100, SM4000 and SM8000. The molecular polydispersity of these two products is unknown, but it is expected to be relatively broad. The materials were directly used as received. Despite the fact that the SM series of MC are commercial products, they are very pure as proved by Kobayashi et al. [Kobayashi et al., 1999] studies and our micro DSC experiments [Li et al., 2002]. To verify the

purity of the MCs, we used hot DI water (three times) and acetone (three times) to purify a MC polymer (SM100, as an example) and found that the polymer showed the same thermal properties before and after purification as verified by micro-DSC. Prior to use, these materials were vacuum dried at 50 °C for 24 hours and stored in a desiccator at room temperature. A wide range of polymer concentrations from 0.5 wt% to 4 wt% were prepared with deionized water from the Millipore water purifier. The partially dissolved samples were put into a refrigerator and kept for 24 hours before use.

3.2 Pluronics F108 and Pluronics 25R4

Water-soluble triblock copolymers of poly(ethylene oxide) and poly(propylene oxide), often denoted as PEO-PPO-PEO or $(EO)_n(PO)_m(EO)_n$, are commercially available nonionic polymer surfactant. Variation of the copolymer composition (PPO/PEO ratio) and the molecular weight (PEO and PPO length) during synthesis leads to the production of optimum properties that meet the specific requirement in many areas. As a result, PEO-PPO-PEO block copolymers are an important class of industrial surfactants and find widespread industrial applications in detergency, lubrication, and formulation of cosmetics and inks etc. They are also specially used in applications like controlled drug release. Commercial names for these surfactants are Pluronics (manufactured by BASF) and Poloxamer (manufactured by ICI).

The equations representing the two steps in the synthesis of the PEO-PPO-PEO copolymers are shown in Figure 3.4.

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Figure 3.4 Synthesis of Pluronics.

In this work, Pluronic F108 and Pluronic R 25R4 were used, which were kindly provided by BASF Corp. The molecular compositions of F108 and 25R4 are $\text{EO}_{133}\text{PO}_{50}\text{EO}_{133}$ and $\text{PO}_{19}\text{-EO}_{33}\text{-PO}_{19}$ with molecular weights of 14,600 and 3,600 respectively. F108 has a form of flakes at room temperature, and its melting point is 57°C , while 25R4 is a wax-like material at room temperature.

Some typical physical properties of F108 and 25R4 are provided by the manufacturer, as shown in Table 3.1.

Table 3.1 Physical Properties of F108 and 25R4.

	F108	25R4
Form	Cast Solid / Prill / Pastille	Liquid
Viscosity, cps at 77°C	2800	1110
Average molecular weight	14600	3600
Specific gravity	1.06 at 77°	1.048 at 25°C
Melt point	57°C	25°C (Pour point)
Cloud point (1% aqueous)	$>100^\circ\text{C}$	40°C
Solubility in water at 25°C wt%	$>10\%$	$>10\%$

3.3 Equipment

3.3.1 Micro-differential scanning calorimeter

Differential Scanning Calorimetry (DSC) measures the heat changes that occur during controlled increase (or decrease) in temperature. DSC is used to study a wide range of thermal transitions, to determine transition temperatures as well as thermodynamic parameters associated with these changes.

The VP-DSC is an ultra-sensitive differential scanning micro-calorimeter that uses a cell-feedback network (CFB) to differentially measure heat produced or absorbed between sample and reference cells.

In this work, a micro-differential scanning calorimeter (VP-DSC Microcalorimeter, Microcal Inc.) was used to determine the thermal properties of the MC solutions and F108 solutions during a thermal cycle of heating-to-cooling. The reference cell was filled with deionized water. A slow heating and cooling rate of 1 °C/min was employed to fully explore the details of the thermogelation behavior of MC or F108 in water. After each cycle was completed for the sample, the sample cell was cleaned by a continuous flow of deionized water (DI-water) for more than 1 hour. No contamination of the sample cell by the last sample was found which was confirmed by running a water-water DSC test.

3.3.2 Rheometer

Figure 3.5 ARES Rheometer (partial).

The rheometer is capable of measuring complex rheological properties such as viscoelasticity (G' , G'') as a function of frequency (time) or temperature. The changing of viscoelasticity with temperature in the solution/gel system is an indication of either a chemical or physical process in response to the temperature. This is a key result we want to obtain utilizing the rheometer.

The rheometer (ARES 100FRTN1, Rheometric Scientific), a strain controlled rheometer, was used. The rheometer was equipped with two sensitive force transducers for torque measurements ranging from 0.004 to 100 g cm. Parallel plates of 25 and 50 mm in diameter were used for relatively high and low viscosity solutions respectively. All the dynamic viscoelastic measurements (e.g. temperature sweep) were carried out at an angular frequency of 1 rad/s and low shear strains to ensure the linearity of viscoelasticity. In the experiments for obtaining G' , G'' as a

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function of angular frequency at a given gelling temperature, the sample in the liquid state was first loaded to the bottom plate of the rheometer at room temperature and then the temperature was raised to the required temperature. In Figure 3.5, a part of the ARES rheometer is show.

3.3.3 Magnetic rheometer

An advanced Magnetic Rheometer MR-Rheometer (UDS 200, Paar Physica Co.) was used to obtain the dynamic functions under a magnetic field. Figure 3.6 shows the schematic diagram of the magnetic rheometer. The system consists of four parts, i.e. the measuring drive system for testing specimen, the electronics for data acquisition and processing, the use-interface software package and the thermostat to control the working temperature.

Unlike a conventional rheometer, the MR-Rheometer is equipped with an additional MR cell which is used to generate a moderate strong magnetic field through the loading plates, as shown in Figure 3.6. The measuring gap H is fixed as 1.0 mm. With such plate-plate geometry, the torque transferred by the MR fluid from the stationary dispenser to the force transducer can be measured.

A sample of 0.4 ml is filled in the gap between the two parallel plates.

Figure 3.6 MR Cell of a Magnetic Rheometer.

3.3.3.1 Magnetic field

The magnetic field applied to a MR fluid is generated by a built-in coil of the MR cell (Figure 3.6). The copper wire coil, whose diameter is 1.0 mm, has $N = 690$ turns. The applied magnetic field is provided by the coil current (I). The magnetic field lines run perpendicular to the plate through the gap filled with a MR fluid. The magnetic flux density (BMRF) in the measuring gap depends not only on the coil current (I), but also on the materials through which the flux is flowing, in particular, the magnetic properties of the MR fluids. For a given MR fluid, a certain relationship exists between the magnetic flux density (BMRF) in the measuring gap and the driving coil current (I). However, considering the nature of our samples, which are polymer solutions, no data of the magnetic properties are available for them. However from the table 3.2, when we choose the value of current I to be around 2.0 A, the magnitude of magnetic flux density is of the range of 0.3-0.5T. For this rheometer the coil current, I , should be below 2.5 A in order to protect the coil against overheating.

After each experiment, a de-magnetising procedure is required. The remaining magnetic field after a measurement would be erased by applying either an alternating current with a decreasing amplitude or a short current pulse with reversed direction. This effect is called remanence and is a characteristic of ferromagnetic materials. Due to a remaining orientation in the material, it maintains a residual magnetic field. De-magnetising is to destroy the orientation.

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3.3.3.2 Temperature ramp test

The software of the rheometer governing the measuring system does not have the ability to conduct a temperature ramp. We had to manually choose discrete temperatures to obtain a G' & G'' -T curve, where G' and G'' were plotted against T in a semi-log coordinate.

Each measurement was conducted after a stabilization period at a given temperature and a magnetic field. The oscillatory strains of 5% to 30% were used to for the different viscosity of the sample to obtain G' and G'' . The angular frequency was 1 rad/s. The comparison experiments were conducted with or without a magnetic field implied.

3.3.3.3 Magnetic field control

For convenience, the experimental results presented in this report will be given in terms of the coil current (I) instead of the magnetic flux density (BMRF). Due to the technical limitation of the coil used, the coil current limit is 2.5 A. In the present experiment, current values of below 2.0 A were applied.

3.3.3.4 Setting up a magnetic flux

The magnetic circuit runs through the metal body of the MR cell (model: TEK 70MR), the hood and the measuring gap of the measuring system. When the different test materials are used, the field strength H is different, too. The magnetic flux is the same, so

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$$\oint Hdl = N \cdot I = \frac{B}{\mu_0 \mu_{Fe}} + \frac{B}{\mu_0 \mu_{Air}} + \frac{B}{\mu_0 \mu_{MS}} + \frac{B}{\mu_0 \mu_{Samp}} \quad (3.1)$$

μ_{Fe} , l_{Fe} : effective length and relative. permeability of the TEK 70MR

μ_{Air} l_{Air} : effective length and relative. permeability of air

μ_{MS} l_{MS} : effective length and relative. permeability of measuring geometry

μ_{MRF} l_{MRF} : effective length and relative permeability of the sample

N: coil windings

$\mu_0 = 1.2567 \times 10^{-6}$

B: Magnetic Flux

I: Current

Table 3.2 Current magnetic flux density in mT in dependence of the relative permeability of the MRF.

[A]	1	2	3	4	5	10	20	50	100
0.1	19	23	24	25	25	27	27	27	28
0.2	38	45	48	50	51	53	54	55	55
0.3	58	68	72	75	76	80	81	82	83
0.4	77	91	97	100	102	106	108	110	110
0.5	96	113	121	125	127	133	135	137	138
0.6	115	136	145	150	153	159	163	165	165
0.7	134	159	169	175	178	186	190	192	193
0.8	153	181	193	199	204	212	217	220	221
0.9	173	204	217	224	229	239	244	247	248
1	192	227	241	249	254	265	271	275	276

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1.1	211	249	265	274	280	292	298	302	303
1.2	230	272	290	299	305	318	325	329	331
1.3	249	295	314	324	331	345	352	357	359
1.4	268	317	338	349	356	371	379	384	386
1.5	288	340	362	374	382	398	406	412	414
1.6	307	363	386	399	407	424	434	439	441
1.7	326	385	410	424	432	451	461	467	469
1.8	345	408	434	449	458	477	488	494	496
1.9	364	431	458	474	483	504	515	522	524
2	384	453	483	499	509	530	542	549	552
2.1	403	476	507	524	534	557	569	577	579
2.2	422	499	531	548	560	584	596	604	607
2.3	441	521	555	573	585	610	623	632	634
2.4	460	544	579	598	611	637	650	659	662
2.5	479	567	603	623	636	663	677	686	689

Table 3.3 Flux density Current in Ampere as a function of the relative Permeability of the MRF.

[mT]	1	2	3	4	5	10	20	50	100
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
10	0.05	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04
20	0.10	0.09	0.08	0.08	0.08	0.08	0.07	0.07	0.07
30	0.16	0.13	0.12	0.12	0.12	0.11	0.11	0.11	0.11
40	0.21	0.18	0.17	0.16	0.16	0.15	0.15	0.15	0.15
50	0.26	0.22	0.21	0.20	0.20	0.19	0.18	0.18	0.18
60	0.31	0.26	0.25	0.24	0.24	0.23	0.22	0.22	0.22
70	0.36	0.31	0.29	0.28	0.28	0.26	0.26	0.25	0.25
80	0.42	0.35	0.33	0.32	0.31	0.30	0.30	0.29	0.29
90	0.47	0.40	0.37	0.36	0.35	0.34	0.33	0.33	0.33

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100	0.52	0.44	0.41	0.40	0.39	0.38	0.37	0.36	0.36
150	0.78	0.66	0.62	0.60	0.59	0.57	0.55	0.55	0.54
200	1.04	0.88	0.83	0.80	0.79	0.75	0.74	0.73	0.73
250	1.30	1.10	1.04	1.00	0.98	0.94	0.92	0.91	0.91
300	1.56	1.32	1.24	1.20	1.18	1.13	1.11	1.09	1.09
350	1.82	1.54	1.45	1.40	1.38	1.32	1.29	1.27	1.27
400	2.09	1.76	1.66	1.60	1.57	1.51	1.48	1.46	1.45
450	2.35	1.99	1.87	1.80	1.77	1.70	1.66	1.64	1.63

3.3.4 Isothermal titration calorimeter

Isothermal titration calorimeter (ITC) measures the differential enthalpy changes isothermally while one component is titrated into another. From the analysis of the ITC thermogram, various thermodynamic parameters, such as enthalpy and heat capacity could be obtained.

In this study, the ITC measurements were conducted using a Microcal isothermal titration calorimeter (Microcal Inc., MA). The details of this power compensation, differential instrument were described elsewhere [Wiseman et al., 1989]. It has a reference cell and a sample cell of 1.35 ml, both insulated by an adiabatic shield. The schematic diagram of ITC is shown in Figure 3.7. The titration was carried out by a step-by-step injection of a concentrated surfactant solution from a 250 ml injection syringe into the sample cell filled with a solvent or a polymer solution.

Figure 3.7 Schematic diagram of isothermal titration calorimetry.

The syringe was tailor-made so that the tip acts as blade-type stirrer to ensure continuous mixing efficiency at 400 rpm. Using the interactive software, an injection schedule was automatically carried out for a predefined number of

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injections, volume of each injection, and the time between each injection. The time interval between each injection is set at 4 min. The measurements were carried out at various temperatures controlled by a Polyscience water bath and temperature fluctuation was within $\pm 5\%$.

3.3.5 UV-visible spectrophotometer

To detect the clouding point of MC solutions, a HP UV-visible spectrophotometer (Agilent Technology, Germany) was used under the thermal denaturation mode at a fixed wavelength of 533 nm with path length of 1 cm. The HP-89090A temperature control system was used to control the temperature. To detect the light transmittance of the solution/gel, the same UV-visible spectrophotometer was used under the standard mode at a fixed wavelength of 533 with a path length of 1 cm.

Chapter 4

Effects of Molecular Weight on Thermoreversible Gelation and Gel Elasticity of Methylcellulose in Aqueous Solution

4.1 Introduction

Many natural polymers and their derivatives often form physical gels that are of thermoreversible nature. [Guenet, 1992; Nijenhuis, 1997]. Methylcellulose (MC), a modified product of natural cellulose is one of them.

MC is well known to gel in water upon heating and is able to turn back to the original liquid state without any changes upon cooling. In the past decades, many studies have been carried out to examine the thermal gelation properties, the mechanism of gelation, and the gel network structure of MC using various experimental techniques, which can be found in many publications. [Chevillard and Axelos, 1997; Desbrieres et al., 1998; Desbrieres et al., 2000; Haque and Morris, 1993; Haque et al., 1993; Hirrien et al., 1998; Kobayashi et al., 1999; Kundu and Kundu, 2001; Kundu et al., 2003; Li, 2002; Li et al., 2002; Matsuoka et al., 2002; Nishinari et al., 1997; Sarkar, 1995; Sarkar and Walker, 1995; Takahashi et al., 2001].

Thermodynamically, an aqueous solution of MC exhibits the lower critical solution temperature (LCST) below which the MC aqueous solution is a single-phase solution and above which a turbid gel is formed as reported by Chevillard & Axelos (1997); Desbrieres et al., 2000 and Hirrien et al., 1998. Precipitation of MC

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may take place when temperature is further increased to be higher than 80 °C [Takahashi et al., 2001]. Although the sol–gel transition of MC on heating has been confirmed physically or rheologically, as reported in the literature, [Desbrieres et al., 2000; Haque and Morris, 1993; Hirrien et al., 1998; Kobayashi et al., 1999; Sarkar, 1995; Takahashi et al., 2001], it was demonstrated by Semenov and Rubinstein that a continuous reversible gelation is not an exactly thermodynamic transition because all thermodynamic quantities are continuous at the gel point [Rubinstein and Semenov, 1998; Semenov and Rubinstein, 1998].

Rheological, calorimetric or optical methods have often been employed to study the thermoreversible gelation of MC in water. Haque and Morris (1993) reported that in the cooling process there was a bimodal exothermic peak over a broad temperature range from 55 to 25 °C. The endothermic peak was able to correlate to dynamic storage modulus G' well while the bimodal exothermic peak was linked with the two waves of reduction in G' . However, the mechanism involved in the bimodal exothermic peak was not presented by the authors. Other techniques such as NMR [Haque and Morris, 1993], static and dynamic light scattering [Kobayashi et al., 1999] and small angle neutron scattering have also been used to investigate the aggregation structures of MC in water. The formation of clusters or other molecular structures in semi-dilute solutions of MC at low temperatures is considered to be important in affecting gelation mechanisms and network structures formed by a subsequent gelation process upon heating. However, no reports have been found on the direct observation of MC gel structures. The lack of direct observation of MC gel network structures would be due to the technical

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difficulty in preparing appropriate samples of MC gels for SEM, TEM or AFM because MC does not gel at room temperature.

The rheological characteristics in the vicinity of the sol–gel transition can often be described using power laws or scaling laws. One of the most important characteristics of a gel is its elasticity evolution, which is depicted as a function of the relative distance $\varepsilon = |p - p_g|/p_g$ by the scaling law as reported by many researchers, [De Gennes, 1979; Flory, 1941; Flory, 1953; Stockmayer, 1943] which is expressed by:

$$G_e \propto \varepsilon^z \text{ for } p > p_g \quad (4.1)$$

where G_e is the quasi-equilibrium modulus, p is the gelling variable, p_g is the value of p at the sol–gel transition point, and z is the index for this scaling law, which is always positive. The theoretical and experimental values of z are typically reported to be 2.0–3.0 [De Gennes, 1979; Koike et al., 1996; Li and Aoki, 1997; Li and Aoki, 1998; Li et al., 1997; Martin et al., 1998; Winter and Mours, 1997].

Although many studies have been conducted on the thermal gelation of MC, no other reports have been found on the validity of the scaling law (Eq. 4.1). In our previous work, [Li, 2002] we initially examined the validity of the scaling law for a commercial methylcellulose with a substitution degree of 1.8 and molecular weight of 310,000. It was observed that at 70 °C the gel's elasticity G_e increased with polymer concentration and G_e could be expressed with a scaling law of $G_e \propto c^{3.03}$ ($c > 1$ wt%). We also proposed a new mechanism of degelation for explanation of the bimodal exothermic peak. [Li, 2002]

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In this chapter, as a continual work on the thermoreversible gelation of MC, two MCs, SM100 and SM8000 with different weight-average molecular weights (100,000 and 400,000, respectively) and the same degree of substitution ($DS=1.8$) were used to prepare aqueous solutions with various concentrations, and their rheological and calorimetric properties were measured as a function of temperature, polymer concentration, or dynamic frequency. This work aims at the thermoreversible gelation behavior, and the validity of the scaling law. In particular, the effects of molecular weight on the gelation and scaling were investigated and discussed.

4.2 Experimental

4.2.1 Micro-thermal analysis

A micro-differential scanning calorimeter (VP-DSC Microcalorimeter, Microcal Inc.) was used to determine the thermal properties of the MC solutions during a thermal cycle of heating-cooling. The reference cell is filled with deionized water. A slow heating and cooling rate of 1 °C/min was employed to fully explore the details of the thermogelation behavior of MC in water. Since, the major disadvantage of the micro DSC is that high viscosity samples cannot be injected to the sample cell, the highest concentration applicable in this study was below about 3 wt%.

4.2.2 Rheological measurements

The rheometer (ARES 100FRTN1, Rheometric Scientific) with parallel plates

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geometry of was used. The parallel plates of 25 and 50 mm in diameter were used for the relatively high and low viscosity solutions, respectively. The sample in the liquid state was first loaded to the bottom plate of the rheometer at room temperature and then the temperature was raised on the required temperature. Then, the sol–gel transition occurred at the desired temperature. To make sure that the gel was fully developed, each sample was allowed to equilibrium at the temperature for 30 min before testing.

Some of MC solution samples were tested through a temperature sweep mode, in which G' and G'' were measured during a thermal cycle of heating from about 20 to 75 °C and subsequently cooling from 75 to 20 °C. The heating and cooling rates were adjusted to be about 1 °C/min.

4.3 Results and discussion

Figure 4.1 Calorimetric thermograms for a 0.5 wt% aqueous solution of SM8000 during a thermal cycle. The heating and cooling rates were 1 °C/min.

4.3.1 Thermal behavior of MC solutions on heating and cooling

A typical example of calorimetric thermogram determined using micro DSC is shown in Figure 4.1 for a 0.5 wt% solution of SM8000.

Figure 4.2 Calorimetric thermograms of aqueous solutions of SM8000 with various concentrations on heating at 1 °C/min. The numerals (0.125 to 1.75) indicate the SM8000 concentrations in wt%.

The relative thermal capacity C_p is employed throughout this thesis, with regard to the nature of the DSC, which measures the relative heat between the sample and the reference. In the heating process, a sharp endothermic peak is observed at around 61 °C, while a broad exothermic peak appears at about 32 °C in the subsequent cooling process. The broad exothermic peak is also featured with a shoulder or a secondary

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peak at the higher-temperature side. Compared with our previous work [Li, 2002; Li et al., 2002; Li et al., 2001] which studied the aqueous solutions of another MC (SM4000) with a lower molecular weight of 310,000, the thermogram obtained for SM8000 is very similar to that of SM4000 although the molecular weights are different. This result indicates that SM8000 has a similar mechanism of gelation and thermoreversibility as described for SM4000 previously.

Figure 4.3 Calorimetric thermograms of aqueous solutions of SM8000 with various concentrations on cooling at 1 °C/min. The numerals (0.125 to 1.75) indicate the SM8000 concentrations in wt%.

Figure 4.2 and Figure 4.3 show the effects of polymer concentration on the heating and cooling thermograms, respectively, for SM8000. All the thermogram curves

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have been normalized by choosing an appropriate baseline in the original graph (e.g. Figure 4.1). For the ease of visualization, the thermogram curves for all the concentrations were shifted vertically by a stepwise amount to prevent the curves from overlapping.

In Figure 4.2, the endothermic peak increases in height with increasing MC concentration but the peak temperature remains almost the same at around 61 °C. In addition, the endothermic peak, although it still remains relatively narrow, becomes broader with increasing MC concentration. However, the MC solutions in the cooling process (Figure 4.3) behave completely differently from those in the heating process. A shoulder was observed above the peak temperature of around 32 °C, and the shoulder became more prominent with increasing concentration to eventually appear as a secondary peak at about 40 °C. In the cooling process, the dissociation of the associated structures of MC in water, which was formed in the heating process, appears to have to overcome two energy barriers: a primary barrier at about 32 °C and a secondary one in the broad range of temperature from 70 to 35 °C. This thermoreversible behavior is similar to SM4000, as we elucidated previously. It has also been proved that SM100 has a similar thermal behavior with SM4000 and SM8000, indicating an independence of gelation thermodynamics from molecular weight.

The enthalpies of gelation can be calculated directly by integrating the endothermic peaks in Figure 4.2 over temperature. Figure 4.4 gives a comparison of endothermic enthalpies for SM100, SM4000 and SM8000. It is found that the total enthalpy absorbed by a MC solution with the same concentration for SM100,

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SM4000 and SM8000, is approximately the same. As a result, all the data in Figure 4.4 can be fitted into one single straight line. The values of enthalpy were normalized for 1 L of MC solution.

Figure 4.4 Heat absorbed per liter of solution on heating as a function of polymer concentration for SM100 ($M_w = 100,000$), SM4000 ($M_w = 310,000$) and SM8000 ($M_w = 400,000$). The heating rate was $1\text{ }^{\circ}\text{C/min}$.

Figure 4.4 indicates that the endothermic heat is a linear function of MC concentration. And as it is concluded that SM8000, SM100 or SM4000, which have different molecular weights, exhibit the straight lines with approximately the same slope. This indicates that for the same amount (mass) of MC in solution, a MC solution needs to absorb the same amount of heat to undergo the thermal hydrophobic association, which is independent of molecular weight. It should be noted that the degree of substitution (DS) of the three MCs here are the same ($DS =$

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1.8 for SM100, SM4000 and SM8000), which enables the comparison itself since the number (or mass) of the hydrophobic group, $-\text{OCH}_3$, greatly affects the chemical properties of the polymer. It was reported that MCs with $\text{DS} < 1$ or $\text{DS} = 2$ were not soluble in water [Liu et al., 1997a; Liu et al., 1997b], thus MC solutions with different DS will not follow the above thermal property. From the similarity in the thermal properties of MC with different molecular weights, it is reasonably considered that the main mechanism of hydrophobic association, which results in the sol-gel transition of MC, is similar or independent of molecular weight. In the hydrophobic association mechanism of MC, the heat is absorbed to destroy the cagelike structures formed from the water molecules surrounding the methyl groups of MC and the hydrophobic association then takes place [Li et al., 2002]. Thus, despite the difference in molecular weight among SM100, SM4000 and SM8000, this mechanism of hydrophobic association is valid. However, the strength of a final gel formed from different molecular weights of MC at the same concentration may be different as discussed in the following session.

The thermal properties, especially the heat involved in the gelation of three MCs were found to be independent of molecular weight. Besides the mechanisms proposed above, which attributed the heat to the number of hydrophobes and their surrounding water cages, two factors else might be important. Firstly, the molecular weight difference among three of them may not be great enough for observation of their effects on gelation. Secondly, the solutions studied actually fell in the same range, which were semi-concentrated so that physical entanglements were not so substantial to reflect the effect of molecular weight difference.

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4.3.2 Viscoelastic behavior on heating and cooling

Figure 4.5 shows the dynamic viscoelastic properties of a MC (SM8000) solution of 2 wt%, at the heating and cooling rates of 1 °C/min and an angular frequency of 1 rad/s. Figure 4.6 shows the dynamic viscoelastic properties of a MC (SM100) solution of 2.8 wt%, at the same heating and cooling rate. As shown in Figure 4.5 in the heating process, there are at least four distinct regions. The first region is before the crossover of G' and G'' , where G' is below G'' , indicating a common viscoelastic behavior of a liquid. G' crosses over G'' at about 35 °C. In this region, G' increases with temperature, while G'' decreases with temperature slowly. Beyond the crossover point, G' dominates, where G' and G'' increases with temperature gradually until about 57 °C. After 57 °C, both G' and G'' curves increase sharply until about 65 °C. After that, both curves again increase slowly with temperature and tend to reach their, respective, plateaus. For SM100, as shown in Figure 4.6, a similar trend is observed.

Traditionally, two methods are used to determine the sol–gel transition point. Firstly, the crossover of G' and G'' is used as indication of the sol–gel transition point [Ferry, 1980]. Secondly, Winter et al. defined the sol–gel transition as the point where the ratio of G'/G'' is independent of frequency [Chambon and Winter, 1985; Chambon and Winter, 1987; Winter and Chambon, 1986]. As described in our previous work [Li et al., 2002], neither method was suitable for the determination of the sol–gel transition of a MC aqueous solution. It is quite obvious that the sharply increasing part of the G' curve should indicate the sol–gel transition regime, which correlates excellently with the endothermic peak observed by micro

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DSC (Figure 4.2).

The crossover point of G' and G'' occurred much earlier than the sharp increase of G' and G'' . We would consider that some weak physical entanglements would have been formed between MC chains when they became less hydrophilic at higher temperatures. However, the formation of physical entanglements seemed not to really require an endothermic heat to expel the surrounding water molecules. The similar consideration can be found from the literature [Kobayashi et al., 1999].

More recently, Yin et al. reported the formation of liquid crystal structure in MC dilute solutions using polarizing microscopic technique [Yin et al., 2006]. Biphase phase was observed in the form of birefringent dots at about 35 °C. When temperature reached 67 °C, a fingerprint texture was formed. The forming and growing of liquid crystal structure in MC solution was believed to cause the gradual increase of G' and G'' .

In the subsequent cooling process, in contrast to the sharp increase within the temperature range from 57 to 65 °C in the heating process, the decreasing rate of G' with decreasing temperature is very slow. This suggests that the thermally induced hydrophobic dissociation in the cooling process is not an exact reversal of the hydrophobic association occurred in the heating process. However, there is a sharp decrease region for the G' found in a lower temperature range near 31 °C, which is consistent with the primary exothermic peak in Figure 4.3. In the cooling process, it is noted that the crossover point of G' and G'' also shifts to a lower temperature of about 29 °C.

Figure 4.5 Storage modulus G' and loss modulus G'' as a function of temperature in a heating to cooling thermal cycle for a 2.0 wt% solution of SM8000. The heating and cooling rates were about 1 $^{\circ}\text{C}/\text{min}$.

Figure 4.6 Storage modulus G' and loss modulus G'' as a function of temperature in a heating to cooling thermal cycle for a 2.8 wt% solution of SM100. The heating and cooling rates were about 1 $^{\circ}\text{C}/\text{min}$.

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At low temperatures, MC is soluble in water. The concept of cagelike structures, which is just a hypothesis, is often used to explain the solubility and thermodynamic behavior of a solute in solution [Guenet, 1992]. When water molecules form hydrogen bonds with the hydroxyl groups along MC chains and/or the cagelike structures surround the methyl groups of MC chains, these water molecules will not be free and random, and they will have a certain degree of order. Heating of such a MC solution will cause the destruction of (a) the hydrogen bonds and/or the cage structures and (b) the exposure of the hydrophobic regions of MC, leading to the formation of hydrophobic aggregates of MC. This is the so-called hydrophobic association. Compared to the energy needed in the destruction of the cage structures, the energy for the formation of hydrophobic aggregates is much lower. As a result, the total detectable endothermic heat in the heating process is mainly attributed to the destruction of the cage structures formed from water molecules. As temperature increases, the number and the size of hydrophobic aggregates increase and a gel will be eventually formed when a percolation of the polymer chains connecting the hydrophobic aggregates is achieved across the solution volume.

The characteristic temperatures at which the endothermic or exothermic peaks occur indicate the most outstanding difference between the heating and cooling processes for the MC aqueous system. The peak temperature on heating is about 61 °C, whereas the primary peak temperature on cooling is about 32 °C. There is also a secondary peak, observed only in the cooling process. This secondary peak becomes more notable for the higher concentrations of MC. We consider that the different

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peak temperatures are due to the kinetic association and dissociation of MC in water. A delay seems to be involved in the dissociation of the gel network formed in the heating process. A detailed explanation of this delay had been given in a previous paper of our group [Li et al., 2001].

The primary exothermic peak at 32 °C corresponds to the sharp drop in G' (Figure 4.5); this step can be considered as the massive destruction of the whole gel network. Below 32 °C, all the hydrophobic junctions are disintegrated so that MC chains become free again. Simultaneously, the arrangement of water molecules for the re-formation of the cage structures takes place so that the large exothermic heat is required. As a result, the system returns to the original liquid state when the cooling temperature is below the offset temperature of the endothermic peak for each MC concentration.

4.3.3 Effects of Mw on dynamic viscoelastic properties and scaling

The dynamic viscoelastic properties of MC solutions with different concentrations were measured at a gelling temperature of 70 °C for SM100 and SM8000, respectively. As the endothermic peak temperature is about 61 °C, the temperature 70 °C was chosen to be higher than the critical gelation temperature to ensure a fully developed gel. Figure 4.7 and Figure 4.8 show G' as a function of angular frequency ω for various concentrations of MC SM8000 and SM100, respectively. For all the concentrations concerned, G' exhibits a weak dependence on ω , and the ω dependence of G' decreases with increasing concentration. When the concentration is higher than 1.0 wt% (inclusive), G' is almost independent of ω , resulting in a nice plateau. These ω -independent plateaus of G' indicate the

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formation of well-developed elastic solid-like gels. The second important feature is that G' increases with MC concentration, meaning that a denser or stronger gel can be formed from a more concentrated MC solution.

Figure 4.7 Storage modulus G' as a function of angular frequency ω for various concentrations of MC at 70 °C for SM8000.

Figure 4.8 Storage modulus G' as a function of angular frequency ω for various concentrations of MC at 70 °C for SM100.

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Now we use the results obtained in Figure 4.7 and Figure 4.8 to examine the scaling law for the elastic evolution as a function of polymer concentration. For consistency, we took the G' values at the frequency of 0.1 rad/s for all the concentrations of MC and defined them as G_e , the quasi-equilibrium modulus. In order to evaluate the dependence of G_e on polymer concentration and to examine the effect of molecular weight on scaling, the values of G_e for SM100 and SM8000 at 70 °C were plotted against MC concentration c as shown in Figure 4.9.

The best fittings to the straight lines are given with the slopes as indicated in Figure 4.9. Although they are different in slope, the important feature of this figure is that G_e of SM8000 is always greater than that of SM100 in the concentration range studied. The result in Figure 4.9 is considered to be reasonable and it is consistent well with those found from PVC physical gels, which are: (1) at the same concentration, G_e is increased by increasing PVC molecular weight and (2) the effect of molecular weight on G_e becomes weaker with increasing concentration and the G_e values of different molecular weights tend to converge with increasing polymer concentration [Li and Aoki, 1998].

This result can also be simply explained by the percolation model that deals with the three-dimensional connection for formation of a network. For a percolation, a long chain can be considered to be equivalent to a connection of several small chains, which produce the same total length as the long chain. Longer chains not only make the sol–gel transition occur more probably, but also act as some inherent junctions. The inherent junctions are stronger than the junctions formed by the hydrophobic association. But at high concentrations, as the number of

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the junctions formed by the hydrophobic association has been significantly increased to contribute to a significant increase in G_e , the inherent junctions become less important. As a result, the dependence of G_e on molecular weight tends to be weaker with increasing polymer concentration.

Figure 4.9 Quasi-equilibrium modulus G_e as a function of concentration in a log-log scale for SM8000 and SM100 at 70 °C.

4.4 Conclusions

Thermoreversible gelation and scaling of methylcellulose (MC) in aqueous solutions have been investigated using micro DSC and rheology with a specific interest in finding the effects of molecular weight. All the MC aqueous solutions exhibited the excellent thermoreversible gelation behavior. It is found that all the

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typical thermal transitions (gelation and degelation) of MC in water are independent of either polymer concentration or molecular weight. The total energy used in the sol–gel transition is a linear function of polymer concentration, but changing of molecular weight does not change the total energy at a given polymer concentration.

The effect of molecular weight on the evolution of gel elasticity was also examined. By comparing three molecular weights (from 100,000 to 400,000) of MC, the quasi-equilibrium modulus G_e was observed to increase with increasing molecular weight and the different scaling relations are found. The mechanisms for the results have been explained in detail.

Chapter 5

ITC Study of Interaction between MC and SDS

5.1 Introduction

5.1.1 Overview

Systems containing surfactants and water-soluble polymers are of great interest both for their inherently interesting and complex behaviors and widespread applications in detergency, pharmaceutical formulations, rheological control and etc. In particular, systems containing nonionic polymers and ionic surfactants have been extensively studied during the past two decades, among which Poly(ethylene oxide) and Sodium Dodecyl Sulfate (PEO/SDS) is by far the most well studied polymer-surfactant system [Wang and Olofsson, 1998; Wang et al., 1998]. Ethyl(hydroxyethyl)cellulose/Sodium Dodecyl Sulfate (EHEC/SDS) systems studied by Wang et al. exhibits similar binding and aggregation behaviors as PEO/SDS because both systems possessed similar calorimetric titration curves [Olofsson and Wang, 1994; Wang and Olofsson, 1995; Wang and Olofsson, 1998]. Dai et al. recently studied the interactions of SDS with hydrophobic ethoxylated urethane (HEUR) and PPO-PEO-PPO (25R4) using ITC. Similar binding mechanisms were proposed for the above mentioned system [Dai et al., 2001b; Dai et al., 2004].

Methylcellulose is a typical nonionic hydrophobically modified water-soluble polymer, which has been widely used in food and pharmaceutical industries.

CHAPTER 5

SDS-MC INTERACTION

However, its interactions with surfactants such as SDS have not been extensively studied. In this chapter, the interaction between SDS and MC were quantitatively studied using microcalorimetry (ITC). ITC is one of the most sensitive techniques that permit direct measurement of thermodynamic changes in the course of binding. It is hoped this study can provide a better understanding on the interaction mechanism between SDS and MC, and the effect of binding on the gelation behavior of MC/SDS system.

5.1.2 Enthalpy of SDS micelle formation in water

The ITC study on the micellization of SDS in water has been reported by Olofsson and coworkers. [Olofsson, 1985] During a titration of concentrated ($C > \text{CMC}$) SDS into water, the following situation arises: in the beginning, the injected SDS solution is diluted and demicellized. The measured enthalpy change in each injection, ΔH_{obs} , includes the enthalpy of dilution of the concentrated titrant solution, ΔH_{dil} , and the enthalpy of demicellization, $-\Delta H_{\text{mic}}$.

$$\text{Below CMC, } \Delta H_{\text{obs}} = \Delta H_{\text{demic}} + \Delta H_{\text{dil}} = -\Delta H_{\text{mic}} + \Delta H_{\text{dil}} \quad (5.1)$$

$$\text{Above CMC, } \Delta H_{\text{obs}} = \Delta H_{\text{dil}} \quad (5.2)$$

With further addition of SDS into water, the concentration of titrated SDS in water gradually increases. When it reaches CMC, the titrated SDS does not demicellize any more and the only contribution to the observed enthalpy is from the dilution heat of SDS micelles, thus and the dilution heat (ΔH_{dil}) can be evaluated. The calorimetric titration curve of SDS in water has been discussed in terms of the thermodynamic models for micelle formation by Johnson and coworkers [Olofsson,

1985].

5.1.3 Critical aggregation concentration and saturation concentration

The onset of cooperative aggregation of a surfactant in the presence of polymer is characterized by critical aggregation concentration, namely CAC. At a second critical concentration denoted as C₂, the polymer is saturated with bound surfactant molecules and free micelles start to form, marking the completion of the polymer/surfactant interaction. These critical concentrations can be obtained in a plot of incremental enthalpy changes against surfactant concentration, $[\Delta H_{\text{obs}}(k) - \Delta H_{\text{obs}}(k-1)]/\Delta m$, where $\Delta H_{\text{obs}}(k)$ is the observed enthalpy change in the k^{th} injection and Δm is the change in molality. Wang and Olofsson suggested that the easiest and most reproducible way to identify CAC with concentration for the maximum of the first peak in the difference plot which corresponds to the concentration for the inflexion point in the leading edge of the endothermic peak of the original curve [Wang and Olofsson, 1995]. For C₂, Wang et al. defined it as the concentration where the slope of the difference curve becomes zero. [Wang and Olofsson, 1995] Using ITC, the CMC of the surfactant (only for surfactant/water system) can also be obtained from the dilution curve. The CMC at 25 °C is characterized as the point that the slope of the curve changes from positive to negative.

5.2 Experiment

The microcalorimetric study was carried out using the Microcal isothermal titration calorimeter (ITC). It has a reference and a sample cell of approximately 1.35ml and the cells are both insulated by an adiabatic shield. In this study, the ITC

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measurements were conducted by titrating 0.2M SDS solution in a 250 μ l syringe into 0.1 wt% methylcellulose SM4000 solutions at 25 ± 0.02 , 30 ± 0.02 , 35 ± 0.02 and 45 ± 0.02 °C. The syringe is tailored-made such that the tip acts as a blade-type stirrer to ensure an optimum mixing efficiency at 400rpm. The sample solutions were thermostatted at the setting temperature for 1 hour before titration. The temperatures applied are all below the onset of the sol-gel transition temperatures as determined from the micro-DSC curves given in Chapter 4 to avoid inducing a large scale hydrophobic association of MC molecules. The low concentrations of the polymer solution and the moderate temperatures applied were also to provide a solution with relatively low values of viscosity at any point of titration, thus not to affect the stirring of the machine. The heat evolved or absorbed by each injection in the course of titration is directly measured by ITC unit, producing the raw heat signal, also known as cell feedback (CFB). Integration of the each CFB gives the differential enthalpy curve for the titration.

5.3 Results and discussion

Figure 5.1 Calorimetric titration curve for addition of 0.2 M SDS to 0.1 wt% MC (SM4000) solution and dilution curve in water at 25 °C.

Figure 5.2 Difference plot of Calorimetric titration curve from additions of 0.2 M SDS to 0.1 wt% MC (SM4000) solution and dilution curve in water at 25 °C.

5.3.1 Dilution behavior of SDS in water

The dilution curve of SDS into water is shown in Figure 5.1 (open circles). The concentration of SDS in syringe (titrant) is 0.2 M, which is well above CMC of SDS. When it is titrated into the sample cell filled with deionized water, the micelles of titrated SDS start dissociating to produce monomers until the concentration of SDS in the sample cell reaches its CMC. When the concentration exceeds CMC, the micelles will only be diluted. The thermodynamic properties of the demicellization can be obtained in the ITC curve.

The thermogram demonstrating the cell feedback (CFB) of the titrations at 25 °C in water is shown in Figure 5.1a. Integration of the area of CFB gives the differential enthalpy curves as shown in Figure 5.1b. The inflection point on the enthalpy curve observed at SDS concentration ~8.4 mM corresponds to the critical micelle concentration (CMC) of SDS, which is in good agreement with the reported values. At that point, ΔH_{mic} is approximately 2.0 kJ/mol. This enthalpy of micellization ΔH_{mic} is very small so that the dilution curve shown in Figure 5.1 displays only a change of slope at the CMC. These values are similar to those reported in literature [Wang et al., 1998]. ΔG_{mic} and ΔS_{mic} can be calculated using equations 5.3 and 5.4 given as below:

$$\Delta G_{mic} = (1+K) RT \ln(CMC) \quad (5.3)$$

$$\Delta G_{mic} = \Delta H_{mic} - T\Delta S_{mic} \quad (5.4)$$

Where K is the micellar change fraction and equals 0.85 for SDS. [Seng et al., 2000a; Seng et al., 2000b].

5.3.2 Binding behavior of SDS and MC in aqueous solutions

The enthalpy curve obtained from titration 200 mM SDS into 0.1 wt% aqueous solution of methylcellulose (SM4000) (filled circle) was plotted together with the dilution curve of SDS (open circle) in Figure 5.1. The difference between these two titration curves is significant, confirming that i) SDS interact strongly with methylcellulose and ii) the micellization behavior of SDS is disturbed by the presence of methylcellulose.

The binding curve (titration of SDS into SM4000) diverges from the dilution curve (titration of SDS into water) at the first injection and the enthalpy increases slightly with increase of SDS concentration. This indicates the uncooperative hydrophobic binding of individual SDS molecules to the hydrophobic backbone of methylcellulose at extremely low SDS concentration, which is similar to the phenomenon observed in the HEUR/SDS system. [Dai et al., 2001b]. Besides uncooperative binding, the deviance of the titrating curve from the dilution curve below CAC could also be caused by the change of solvent environment by the addition of SDS. This non-cooperative binding is believed to be weak and limited compared to the dominant cooperative binding observed at higher SDS concentration. To further confirm the non-cooperative binding, measuring the free SDS (those that are not bound to polymer chains or aggregate to form micelles) concentration in the solution by SDS selective electrode is needed. The SDS selective electrode was mentioned in the book “Polymer-surfactant systems” edited by Jan C. C. Kwak Marcel dekker, Inc. 1998, page 149. Unfortunately this equipment has not been commercially available.

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A non-cooperative binding is defined as the progressive binding of individual surfactant monomers to the hydrophobic site or backbone of the polymer. Non-cooperative binding is not supposed to cause the formation of polymer/surfactant complex of large size. For those polymers with stronger hydrophobicity, it is possible for them to bind surfactant molecules (monomers) in a non-cooperative manner at low surfactant concentration without exhibiting a CAC. Polymer with moderate hydrophobicity may undergo both non-cooperative and cooperative bindings, like what we observed in the MC/SDS system.

When the SDS concentration reaches $\sim 4\text{mM}$, the enthalpy increases sharply with increase of SDS concentration and reaches its endothermic maximum at SDS $\sim 6\text{mM}$, thereafter it decreases rapidly with further increase of SDS concentration. This sharp endothermic peak characterizes the cooperative binding of SDS to the methylcellulose, i.e. the formation of SDS micelles on the SM4000 chains, which solubilize the polymer backbones into the hydrophobic core of SDS micelles. The cooperative nature of the binding can be expressed by the rapid increase of enthalpy over a very narrow range of SDS concentration (from $\sim 4\text{mM}$ to $\sim 6\text{mM}$). Similar enthalpic profiles were reported by Dai et al. based on their ITC studies on the binding interactions between SDS and hydrophobically modified water soluble polymers. [Dai and Tam, 2001; Dai and Tam, 2004; Dai et al., 2001a; Dai et al., 2001b; Dai et al., 2004].

The onset of the binding, namely the critical aggregation concentration (CAC) is characterized by the commencing of the endothermic peak. The value of CAC can be accurately determined from the difference curve of the differential enthalpy

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curve as shown in Figure 5.2 and it is found to be 4.2 mM for the SM4000/SDS system at 25°C. From a thermodynamics point of view, the enthalpy change at CAC can be expressed as equation 5.5 [Meagher et al., 1998]:

$$\Delta H = \Delta H (\text{dilution of SDS micelles and monomers}) + \Delta H (\text{demicellization of SDS micelles}) + \Delta H (\text{binding of SDS monomers to polymer chains}) \quad (5.5)$$

Since the enthalpy changes of the SDS dilution and the demicellization of SDS are experimentally observed to be small at 25 °C, [Dai et al., 2001b] the measured enthalpy change (ΔH_{obs}) is mainly attributed to the enthalpy change of the formation of polymer/SDS aggregation complexes. The endothermic peak corresponding to the cooperative binding describes the formation of SDS micelles on the hydrophobic domain of the polymer backbones, yielding a mixed aggregation complex. In other words, the cooperative binding is the incorporation (solubilization) of hydrophobic polymer segments into the simultaneously formed SDS micelles at CAC. During this process, the hydrophobic polymer segments undergo a hydration process to be solubilized by SDS micelles in water phase. Formation of mix micelles and hydration are both entropy driven and enthalpy unfavorable, and a large amount of heat is needed to disrupt the ordered solvent cage around the hydrophobic moieties of the polymer and SDS, expressed by the endothermic peak on the ITC curve from SDS concentration ~3mM to ~8mM.

Similar patterns of the ITC curves have been reported in the studies on the interaction between SDS and various water-soluble polymers, indicating the similar binding mechanisms [Dai and Tam, 2001; Dai et al., 2001a; Olofsson and Wang, 1994; Wang and Olofsson, 1995]. These similarities suggested that it is reasonable

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to regard the polymer-surfactant interactions in polymer solutions as the solubilization of polymer segments and/or substituents into the surfactant aggregates to form mixed micelles. Surfactant micellization is well understood and the solubilization of small uncharged molecules in ionic micelles can be described theoretically [Jonsson and Wennerstrom, 1987].

When SDS concentration exceeds 6 mM, the enthalpy decrease rapidly and intersect with the dilution curve at $C_{\text{SDS}} \sim 8$ mM. The decrease of enthalpy signals the decrease of binding rate of SDS on SM4000. With increase of SDS concentration in the MC solution, more and more SDS micelles are bound on the polymers with ionic head groups pointing outwards. Consequently, the electrostatic repulsion between the SDS head groups accumulates, and this impedes the continuous binding of SDS to the polymer/SDS complex. Beyond a maximum ΔH , the percentage of additional SDS participating in the polymer/SDS complex decreases, leading to a steady decrease of ΔH . With further increase of SDS concentration, the enthalpy continues to decrease and exhibits an exothermic minimum at $C_{\text{SDS}} \sim 10.5$ mM, thereafter it starts to approach the dilution curve and merge with the dilution curve at $C_{\text{SDS}} \sim 14$ mM. The previous study on surfactant interactions with other water soluble polymers ascribed the exothermic minimum (relative to the dilution curve) to the changes in the composition of the aggregates [Dai et al., 2001b; Thuresson et al., 1995]. Dai et al. suggested that the exothermic minimum is caused by the structure reorganization of the complex consisting of triblock Pluronic polymer and SDS based on their ITC study [Dai and Tam, 2001]. With further increase of SDS concentration and formation of more SDS micelles on

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the polymer backbones, the outer layer of anionic SDS micelles associate with the ether bond and 1,4 glucose links of the polymer backbones via ion-dipole interaction, resulting in the structure reorganization of the polymer/SDS complex [Dai et al., 2001b; Thuresson et al., 1995]. Moreover, the structure reorganization leads to the rehydration of the polymer because the polymer backbone is freed from the hydrophobic core of SDS micelles. The exothermic ΔH is related to the ion-dipole association between SDS micelles and MC segments and the subsequent rehydration. Thermodynamically, this also minimizes the unfavorable contacts between the hydrophobic segments of the surfactant molecules and water phases. Both effects lead to the increase of SDS aggregation number as reported in the studies polymer/surfactant systems using other techniques such as fluorescence decay [Brown et al., 1992; Olofsson and Wang, 1994].

The ion-dipole association describes the interaction between the negative-charged surface of the SDS micelles and the partially positively charged carbon atoms due to molecular polarity of ether bond and 1,4 glucose links in the MC chains. A schematic was given by Dai et al. describing the ion-dipole interaction for PPO-PEO-PPO/SDS system [Dai et al., 2001b]. The mechanism would be valid for the MC/SDS system albeit the difference of polymer characters, because of the similarities in the ITC curves.

In summary, the titration curve of SDS/MC solution can be divided into four zones. The first zone starts at the initial injection and ends at CAC, where there are only the dilution of SDS micelles and the non-cooperative binding of small amount of SDS onto the MC backbone and/or hydrophobic groups. The deviance of the

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titrating curve from the dilution curve below CAC could also be caused by the change of solvent environment by the addition of SDS. The second zone starts at CAC till the end of the endothermic peak, where the cooperative binding of SDS with MC molecules continues, resulting in the complex micelles. This process is called the polymer induced micellization of SDS, which evolves the dehydration of MC followed by its solubilization in the SDS micelle cores. The third zone starts with the offset of the endothermic peak and the onset of the exothermic peak, where MC chains rehydrate from the complex aggregates into water and then bind to the surface of the SDS micelles via ion-dipole interaction. In this zone, the aggregation complex reorganizes its structure. The fourth zone starts at C₂, where free SDS micelles start to form without the participation of MC. The reorganized aggregate complexes formed previously coexist in the system. A schematic of the four zones is shown in Figure 5.3.

Figure 5.3. Schematic of SDS-MC interactions at various concentration of SDS.

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5.3.3 Temperature dependence of MC/SDS interaction

Figure 5.4 Calorimetric titration curves from additions of 0.2 M SDS to 0.1 wt% MC (SM4000) solution and dilution curve in water at 30 °C.

Figure 5.5 Difference plot of Calorimetric titration curve from additions of 0.2 M SDS to 0.1 wt% MC (SM4000) solution and dilution curve in water at 30 °C.

Figure 5.6 Calorimetric titration curve from additions of 0.2 M SDS to 0.1 wt% MC (SM4000) solution and dilution curve in water at 35 °C.

Figure 5.7 Difference plot of Calorimetric titration curve from additions of 0.2 M SDS to 0.1 wt% MC (SM4000) solution and dilution curve in water at 35 °C.

Figure 5.8 Calorimetric titration curves from additions of 0.2 M SDS to 0.1 wt% MC (SM4000) solution and dilution curve in water at 45 °C.

Figure 5.9 Difference plot of Calorimetric titration curve from additions of 0.2 M SDS to 0.1 wt% MC (SM4000) solution and dilution curve in water at 45 °C.

Figure 5.10 Calorimetric titration curve from additions of 0.2 M SDS to 0.1 wt% MC (SM4000) solution and dilution curve in water at various temperatures.

The ITC curves of titration of 200 mM SDS solution into 0.1 wt% MC (SM4000) at 30 °C are shown in Figure 5.4. Figure 5.5 gives the first derivative of the curves shown in Figure 5.4. Figure 5.6 and Figure 5.7 show the titration curve and dilution curves of the same system at 35 °C. Data at 45 °C are shown in Figure 5.8 and Figure 5.9. The temperature effect on the titration curves can be elucidated better with regard to Figure 5.10, in which all the titration curves obtained at temperatures 25 °C, 30 °C, 35 °C and 40 °C were plotted together.

It is observed that when the temperature increased as shown from Figure 5.4 to Figure 5.10, the first endothermic peak characterizing the cooperative binding decreased and almost vanished at 35 °C and 45 °C. At the same time, the exothermic hump preceding C2 disappeared. The dilution curves of SDS in water at

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different temperatures also underwent remarkable changes. The change of shape of the dilution curve is due to the change of SDS solution micellization behavior in water, which is not the objective of this work and hence is not discussed here [Dai et al., 2001b].

The titration curve in Figure 5.4 and Figure 5.5 for 30 °C still show a reduced endothermic peak compared to 25 °C and a well defined CAC can be observed from the difference plot, which implies that there are still cooperative binding at 30 °C. A reduced exothermic peak is also observed at higher SDS concentration, indicating the reorganizing of the aggregation complex due to the same mechanism as that at 25 °C. It is believed that the cooperative binding starting at CAC determines the subsequent structure reorganization and rehydration of the aggregation polymer/SDS complex and thus the emergence of the exothermic hump. The reorganization of the aggregation complex will not take place without the formation of the SDS micelles on the polymer backbone in the first place. However, the raising height of the titration curve at lower SDS concentrations and the reduced endothermic and exothermic peaks have clearly shown that the non-cooperative binding at 30 °C is much stronger than at 25 °C. We believe this phenomenon is caused by the change of hydrophobicity of MC with temperature.

Temperature is a very important factor to affect the phase behavior of water soluble polymers; some solutions may undergo a sol-gel transition either at low or elevated temperatures depending on the polymer properties. For hydrophobically modified cellulose, the increase of temperature increases its hydrophobicity leading to the exposure of the hydrophobic groups and gelation when the concentration is

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high enough (around 60 °C) [Li et al., 2002]. Thus at elevated temperatures, the SDS monomers would be more easily to bind to the MC chains. The process took place constantly and steadily, which hindered the cooperative binding of SDS to the MC molecules.

The CAC value at 30 °C is a slightly higher than the value at 25 °C, indicating a delayed cooperative binding due to the competition of non-cooperative binding. At 35 and 45 °C, the CAC cannot be defined as shown in the absence of peaks at low concentrations in Figure 5.7 and Figure 5.9.

Kameka et al. [Kamenka et al., 1994] suggested that the polymer-surfactant interaction strengthens with increasing temperature to result in a gradual changeover from a pronounced polymer-induced micellization to a more specified interaction. This theory is apparently held for the current system and the trend is clearly shown at 35 °C and 45 °C. At 35 and 45 °C, the further increase of hydrophobicity of MC makes it impossible for the cooperative binding to start, which explains the disappearance of the endothermic and exothermic peaks, as well as the CAC in the titration curves. The much higher titration curves observed at higher temperatures are caused by the increased hydrophobicity of the MC, which possess more substituents that can associate with the SDS.

It can be found that the C2 values increase with increasing titration temperature, indicating an enhanced extent of binding between SDS and MC, which can also be explained by the increased hydrophobicity of MC at higher temperatures despite the fact that the cooperative binding is gradually eliminated. This is a difference observation from the previous studies by other researchers. [Wang and

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Olofsson, 1995]. The previous studies by Wang and Olofsson for PEO/SDS and EHEC/SDS showed similar titration curves at room temperature and elevated temperatures, but for both polymers, PEO and EHEC, CAC and C2 are unchanged. [Wang and Olofsson, 1995].

Table 5.1. Critical concentrations at various temperatures.

	25 °C	30 °C	35 °C	45 °C
CAC, mM	4.2	4.8		
CMC, mM	8.4			
C2, mM	14.6	16.4	17.3	18.7

5.4 Conclusions

The binding interactions between MC (SM4000) and SDS were studied by isothermal titration calorimetry, the temperature effect was discussed. At low temperature (25 °C), the titration curve can be divided into four zones. The first zone starts at initial injection and ends at CAC, where only dilution of SDS micelles and non-cooperative binding of small amount of SDS onto the MC backbone and/or hydrophobic groups take place. The deviance of the titrating curve from the dilution curve at this region could also be caused by the change of solvent environment by the addition of SDS, even without the interaction between SDS and MC. The second zone starts at CAC till the end of the endothermic peak, where the cooperative binding of SDS to MC molecules occurs and results in complex micelles. The third zone starts at the end of the endothermic peak and the onset of the exothermic peak, where the aggregation complex reorganizes its structure via

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ion-dipole interaction. The fourth zone starts at C2, where free SDS micelles start forming without the participation of MC; the reorganized aggregate complexes formed previously coexist in the system. With increasing temperature, the hydrophobicity of MC is increased. The predominately cooperative binding at low temperatures gradually changed to the predominately non-cooperative binding. The shape of the titration curve shows the drastic changes. The extent of the association between SDS and MC is strengthened, and C2 increased with increasing temperature.

Chapter 6

Effects of SDS on the Sol-Gel Transition of Methylcellulose in Water

6.1 Introduction

Gelation of MC can be affected by many factors. While the gelation temperature of MC is not strongly affected by changing concentration of MC, many salts are found to be effective in altering the gelation properties of MC aqueous solutions [Xu et al., 2004a; Xu et al., 2004b]. Basically, two groups of salts can be classified, i.e. salt-out salts and salt-in salts. A salt-out salt can lower the gelation temperature of MC whereas a salt-in salt delays the occurrence of MC gelation. The salts such as NaCl and Na₂SO₄ show the salt-out effect. Although the gelation temperature of MC is affected linearly by the content of a salt added, the mechanism for the gelation of MC does not change with the addition of salts because the presence of a salt only affects the dehydration of MC, and the salt does not directly change the original feature of hydrophobic association of MC for gelation. [Xu et al., 2004a; Xu et al., 2004b]

We have known that a simple inorganic salt can alter the gelation behavior of MC in water [Xu et al., 2004a; Xu et al., 2004b]. As surfactants, especially ionic surfactants, can be considered to be made by chemically attaching a hydrophobic tail to an ion, it is interesting to know how a surfactant can affect the gelation behavior of MC in water. Anionic surfactants such as sodium dodecyl sulphate (SDS) are widely used in both industrial applications and fundamental studies. SDS

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is known to form micelles in water by self-assembling above its critical micellization concentration (CMC). SDS can also form the mixed micelles with polymer chains through an intermolecular binding process. After adding a surfactant, the hydrophobic association of a hydrophobically modified water-soluble polymer is expected to be affected by the interaction between the polymer and the surfactant. This kind of polymer/surfactant interactions can be conveniently studied by means of isothermic titration calorimetry (ITC) [Dai and Tam, 2001; Dai and Tam, 2004; Dai et al., 2001b; Dai et al., 2004; Olofsson and Wang, 1994; Wang and Olofsson, 1995; Wang and Olofsson, 1998].

It was reported that binding of a surfactant to a water-soluble polymer such as poly(ethylene oxide) was cooperative, which was not a case of individually binding of surfactant molecules to the polymer [Dai et al., 2001a; Dai et al., 2001b]. The higher the hydrophobicity of a polymer, the more favorable is the binding process [Dai et al., 2001a; Dai et al., 2001b]. For hydrophobically modified water-soluble polymers, on the other hand, non-cooperative binding is expected because there exist the micellar cores formed by the hydrophobic group of the polymer and the surfactant hydrophobic tails [Seng et al., 2000a; Seng et al., 2000b]. Nevertheless, the cooperative binding will still occur at higher concentrations of surfactant followed by the non-cooperative binding during the earlier stage of binding [Wang and Olofsson, 1995].

Many hydrophobically modified cellulose polymers have been investigated on the polymer-surfactant interaction [Hoff et al., 2001; Piculell et al., 2003]. For example, hydrophobically modified hydroxyethyl cellulose (HMHEC) has been

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reported to interact with many surfactants. [Piculell et al., 2003] Hydrophobically modified ethyl (hydroxyethyl) cellulose (HM-EHEC) [Hoff et al., 2001; Piculell et al., 2003] and hydroxylpropyl methyl cellulose (HPMC) [Nilsson, 1995] have also been studied. Interestingly, the interaction between surfactants and methylcellulose, the simplest form in the family of hydrophobically modified cellulose polymers, has not been reported in the literature.

In this chapter, MC (SM4000) was used to prepare aqueous solutions containing various concentrations of SDS, and the effects of SDS on the optical transmittance, thermal and rheological properties of MC solutions, especially on the sol-gel transition behaviors, have been investigated. The interesting results have been obtained and the possible mechanisms involved in these results will be proposed and discussed.

6.2 Experimental

6.2.1 Materials

Sodium n-dodecyl sulphate (SDS) was purchased from Sigma-Aldrich and used as received.

6.2.2 Sample preparation

A MC SM4000 aqueous solution with a fixed concentration of 0.03 mM (about 0.93 wt %) was first prepared by dispersing the weighed MC powder into deionized water at 70 °C and then kept in a refrigerator at about 10 °C for overnight to obtain a homogeneous and transparent solution. The weighed SDS was then added into the

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MC solution to obtain the MC-SDS solution. The concentrations of SDS were varied to be either higher or lower than 8 mM, the critical micellization concentration (CMC) of SDS in water at room temperature. All samples were prepared with deionized water from a Millipore water purifier. All of the MC-SDS solutions were stored at a low temperature (below 10 °C).

6.2.3 Turbidity measurement

An Ultraviolet-visible spectroscopy system (Agilent 8453, UV-VS, HP Co.) equipped with a temperature controller was employed for the turbidity measurements. The sample was placed in the plastic cell with dimensions of 1×1×5 cm³ for optical transmission measurements, and deionized water was used as the reference. The cell was covered by a plastic cap to prevent evaporation. The turbidity measurement was then carried out at a wavelength of 500 nm, in which the sample was first heated from 20 °C to above 80 °C, and subsequently cooled down to 20 °C at the heating and cooling rates of 1 °C/min. The absorbance due to the sample's turbidity was recorded, and then converted to transmittance according to the Beer's Law.

The experimental details about micro-DSC and rheological experiments can be found in Chapter 3.

6.3 Results and discussion

Figure 6.1 Optical transmittance at a wavelength of 500 nm for 0.03mM MC solutions containing various concentrations (in mM) of SDS during heating, at a temperature scanning rate of 1 °C/min.

Figure 6.2 Optical transmittance at a wavelength of 500 nm for 0.03mM MC solutions containing various concentrations (in mM) of SDS during cooling, at a temperature scanning rate of 1 °C/min.

6.3.1 Turbidity

Figure 6.1 and Figure 6.2 show the optical transmittance at the wavelength of 500 nm for the 0.03mM MC solutions containing various concentrations (in mM) of SDS upon heating and cooling respectively. For each solution, the heating was followed by cooling. As shown in Figure 6.1, at low temperatures (≤ 45 °C), all of the MC-SDS solutions display a high transmittance (nearly 100 %), indicating that the solutions are optically clear and the transmittance is independent of the solution composition. However, after being heated to a certain temperature, which is dependent on the solution composition, each transparent solution starts to become

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turbid, followed by the sharp decrease in transmittance. At the high temperatures, each sample becomes completely opaque within a narrow temperature range, and the transmittance drops to about zero, indicating the formation of a cloudy gel as further confirmed later by rheological measurements.

Besides the general feature on the turbidity of MC solutions, the effect of SDS on the turbidity can be observed clearly from these transmittance curves. First, the starting point for becoming turbid and the ending for becoming zero-transmitting occur differently for a different concentration of SDS but they do not follow a decreasing or increasing order with increasing the concentration of SDS. For simplicity, let's take the 50% transmittance as a critical transition point at which the corresponding temperature can be defined as the clouding point (i.e. the sol-gel transition temperature) or the clear point (i.e. the gel-sol transition temperature). This definition is reasonable because the transmittance always decreases with temperature to reach the maximum rate at approximately 50 % transmittance. The clouding and clear points obtained based on the 50 % transmittance were plotted against SDS concentration in Figure 6.10 and we will use Figure 6.10 to discuss the effect of SDS in the later text.

The decrease in optical transmission on heating is believed to be due to the formation of large clusters or aggregates and eventually a gel network structure, which leads to the strong light scattering. It should be true that the denser a gel network formed, the lower the optical transmission is. Sloodmaekers et al. [Sloodmaekers et al., 1991] in their studies on the clouding behavior of carrageenan solutions and Nossal's work [Nossal, 1985] on polyacrylamide gels proved that the

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spatial variations and dynamic concentration fluctuation of the polymers in the gelled state resulted in strong light scattering. In our study of MC gelation, the light scattering is considered to be caused by the hydrophobic aggregates of MC appearing at enhanced temperatures.

In the subsequent cooling process (Figure 6.2), the turbidity remains unchanged at high temperatures until another critical temperature, at which the opaque gel begins to dissolve, and the transmittance recovers rapidly back to the high value within a narrow temperature range. From the fact that the sample turns back to the transparent solution again after completing the thermal cycle, we may conclude that the MC gelation is thermoreversible although the cooling curve is not a mirror image of its corresponding heating one. The outstanding hysteresis between heating and cooling indicates that the thermally induced hydrophobic dissociation is not an exact reversal of the hydrophobic association occurred in the heating process. All of the MC-SDS solutions showed the complete thermoreversibility that was not changed by the addition of SDS. Thus, we may draw another conclusion that SDS does not affect the basic feature of MC gelation or in other words SDS does not alter the inherent mechanism of MC gelation, which is based on the hydrophobic association of MC chains. Similarly, we used the 50 % transmittance to define the clear point for each transmittance curve in the cooling process and then plot it in Figure 6.10.

6.3.2 Thermal behaviors

The thermal behaviors of MC-SDS solutions were studied by means of micro-DSC, and the results are shown in Figure 6.3 and Figure 6.4, which were obtained

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from the heating and subsequent cooling processes respectively. The temperature scanning rates were 1 °C/min. The relative thermal capacity C_p with a unit of Cal/L °C was used after the conversion of the sample volume of 0.516 ml to 1 liter.

Figure 6.3 Relative capacity, C_p , as a function of temperature for 0.03 mM MC solutions with various concentrations of SDS (in mM) during heating. The heating rates were 1 °C /min.

Let's look at Figure 6.3 first. All of the MC-SDS solutions show the endothermic behaviors. Before adding SDS, the MC solution shows a narrow endothermic peak with a peak temperature of about 60 °C, which corresponds to the sol-gel transition of MC. When the SDS concentration is lower than 8 mM (i.e. 2, 4, and 6 mM), the respective heating curve remains one single endothermic peak with the peak temperature slightly shifting to the lower temperature than the SDS-free MC solution. For example, the MC solution with 2 mM SDS exhibits a similar sharp peak as the pure MC solution, except that the peak slightly moves to the left side,

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indicating a weak effect of SDS on MC. This effect is a salt-out like effect because the gelation of the MC-SDS solution occurs earlier (or at a lower temperature) than the SDS-free MC solution. With further increasing SDS concentration, the peak still shifts slightly to the left until about 6 mM, and it becomes wider and more moderate, implying a stronger effect of SDS on the hydrophobic association and gelation of MC. When the SDS concentration reaches 8 mM, an obvious shoulder is observed at the higher temperature side next to the primary peak. The primary peak at 8mM SDS does not shift further to the left but begins to shift to the right with a reduced peak height. Interestingly, with increasing SDS content to exceed 8 mM, the shoulder grows to become a secondary peak whereas the primary peak shrinks in height. Eventually, the secondary peak becomes bigger than the primary peak at 15 mM SDS. The overall trend is that with increasing SDS concentration a MC-SDS solution exhibits its thermal behavior of interest over a broader range of temperature and the gelation tends to occur at higher temperatures.

Figure 6.4 Relative capacity, C_p , as a function of temperature for 0.03 mM MC solutions with various concentrations of SDS (in mM) during cooling. The heating and cooling rates were $1^\circ\text{C}/\text{min}$.

The cooling curves in Figure 6.4 also show the significant effects of varying the SDS concentration. For the MC solutions with the low concentrations ($\leq 8\text{mM}$) of SDS, the similar patterns of the exothermic curves, which are characterized with a primary valley at around 32°C and a shoulder at the elevated temperature, are observed. However, the depth of the valley decreases with increasing the SDS concentration. As SDS was further increased to 10, 12 and 15 mM, a reversed pattern of the exothermic curves was observed. That is, the primary valley at around 32°C has shrunk in depth to a shoulder, whereas the shoulder in the high temperature region has grown into a prominent valley. The valley shifts to the higher temperature with increasing the SDS concentration.

Figure 6.5 Storage modulus G' for 0.03 mM MC solutions with various SDS concentrations as a function of temperature at a heating rate of about $1^{\circ}\text{C}/\text{min}$

6.3.3 Viscoelastic properties

In Figure 6.5 and Figure 6.6, storage modulus G' and loss modulus G'' for the 0.03 mM MC solutions with various SDS contents are shown as a function of temperature in a heating process at a $1^{\circ}\text{C}/\text{min}$ respectively. The SDS-free MC solution is also shown in the figures. Four features can be observed from the figures.

Figure 6.6 Loss modulus G'' for 0.03 mM MC solutions with various SDS concentrations as a function of temperature at a heating rate of about 1 °C/min.

(1) At low temperatures, all of the samples show a liquid behavior of $G' < G''$. (2) For each MC-SDS sample, there is a relatively narrow range of temperature in which both G' and G'' show an abrupt increase. Especially, G' increases by more than 4 decades to reach a plateau at high temperatures, which is much more significantly than G'' (by 2 decades). It is believed that the sol-gel transition occurs within the temperature range for the abrupt increase in G' . (3) The samples containing 2, 4, and 6 mM of SDS show the similar transition curves, whereas the samples with the higher SDS concentrations (≥ 8 mM) shift to the high temperature side significantly, indicating a salt-in like effect. (4) Before the sol-gel transition region, the SDS-free MC solution behaves differently from the MC solutions with

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the low concentrations of SDS. That is, both G' and G'' values for the SDS-free MC solution are much larger than those of the MC solutions with the low concentrations of SDS (≤ 6 mM) in the same temperature range before the sol-gel transition. This distinctive phenomenon can be explained by a possible mechanism that the weakly entangled structure of MC chains in solution, which contributes to the high G' and G'' values as pointed out by Kobayashi et al., [Kobayashi et al., 1999] and is destroyed by SDS or unable to form in the presence of SDS. Due to the salt-out effect of SDS at the low concentrations (≤ 6 mM), the MC chains would tend to become more condensed from a looser state in the absence of SDS, so that the possibility of molecular entanglements of MC would be considerably reduced. On the other hand, if the molecular entanglements of MC are formed by the weak association of some highly hydrophobic segments of the MC chains, the binding of SDS molecules to the hydrophobic segments of MC chains would hinder the hydrophobic association between the hydrophobic groups. As a result, the molecular entanglements of MC would be reduced greatly.

To further elucidate the effect of SDS on the viscoelastic properties of the MC solutions, the G' and G'' curves of some selected samples (SDS = 0, 2, and 15 mM) are drawn in Figure 6.7. 2 and 15 mM were chosen because they were the lowest and highest concentrations of SDS used in this work. $G' > G''$ at low temperatures for the SDS-free sample, whereas $G' < G''$ for the SDS-containing samples. There is a crossover point of G' and G'' each for the samples with SDS whereas no crossover point exists for the SDS-free sample. The crossover of G' and G'' indicates the turning point from a viscous solution to an elastic solution or gel,

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and it is traditionally used as the sol-gel transition point. The crossover of G' and G'' shifts to the right with increasing the SDS concentration, showing a salt-in like effect or a delay of gelation by SDS.

Figure 6.7 G' and G'' for the 0.03 mM MC solutions with various SDS concentrations (SDS = 0, 2, and 15 mM) as a function of temperature at a heating rate of about 1 °C/min.

Where Gelation of MC Occurs?

In the previous studies on gelation of MC [Li et al., 2002], it has been found that the abrupt increase of G' in a heating process is consistent with the endothermic peak of the DSC heating curve. Thus, the consistence between the abrupt G' increasing and the endothermic peak has been used to define the gel point. When the endothermic peak is not a single and narrow peak but a bimodal and broad peak,

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however, a question raised here is which endothermic peak (i.e. primary or secondary) can be used as an indication of the gel point. To find the answer for the question, we plotted G' and C_p against temperature in one figure for the MC solutions with various SDS concentrations from 2 to 15 mM. For a better view, 6 concentrations of SDS are divided into two groups and shown in Figures 6.8 and Figure 6.9 respectively.

Figure 6.8 C_p and G' as a function of temperature for 0.03mM MC solutions with various concentrations of SDS of 2, 6 and 8 mM.

In Figure 6.8 where the concentrations of SDS are low (≤ 8 mM), all of the endothermic peaks are relatively narrow and no secondary peaks are clearly observed. It can be seen that the onset and offset of each C_p curve correspond to the onset and offset of the abrupt increase of G' respectively, beyond which a plateau

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is reached. Thus, in this case, the endothermic peak, which is within the abrupt increasing region of G' , can still be used as the gel point for each MC-SDS solution. This behavior is similar with the previous studies for the pure MC in water. [Li et al., 2002]

Figure 6.9 C_p and G' as a function of temperature for 0.03mM MC solutions with various concentrations of SDS of 10, 12, and 15 mM.

On the other hand, at the high contents of SDS (Figure 6.9), the C_p curves are featured by the broadened and bimodal peaks. The bimodal peak is an indication of a two-stepped gelation process. Taking the 10mM SDS sample in Figure 6.9 as an example, we can see that the most part of the sharp increasing curve of G' falls in the same region of the first peak of the C_p curve. Thus, it is reasonable to consider that the first peak at the lower temperature side is directly related to the starting of

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gelation. However, the gelation is not completed after the first peak because G' is still growing. Importantly, it is observed that the offset of the secondary peak is consistent with the onset of the G' plateau. If the onset temperature for the G' plateau can be considered as the ending point of gelation, the second endothermic peak is necessary for a complete gelation process. While we have known the endothermic heat, which was attributed to the first endothermic peak, is necessary to destroy the cage-like structures of water for MC molecules to aggregate hydrophobically, a new question is what did the secondary endothermic peak represent? In other words, why the MC-SDS solutions have to absorb heat by two steps?

We propose a mechanism here to explain the two-step gelation of MC in the presence of SDS. In the first step, the endothermic heat is mainly used to destroy the cage-like structures of water, which surround MC chains. Then, the hydrophobic association of MC begins and G' starts to increase. This is the same mechanism as that in a pure MC solution. However, since the binding of SDS molecules to the MC chains should be stronger than those of cage-like structures of water, a higher energy is required to remove the bound SDS molecules from the MC chains, resulting in the secondary endothermic peak. At the same time, more hydrophobic groups of MC are exposed and they then associate to form new junctions for the gel network. Eventually, all of the bound SDS molecules are removed and a complete network of MC is then formed. The two-step gelation can be also seen from the G' curves for 12 and 15 mM of SDS: there is the shoulder, followed by the continuous (but with a higher slope) growth in G' . This phenomenon becomes much clearer in

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the 15 mM SDS curve. Unfortunately, due to the limitation of the rheometer, we were unable to measure G' at temperatures higher than about 82 °C so that the completed second plateau of G' could not be fully observed.

6.3.4 The role of SDS in affecting hydrophobic association and gelation of MC

We have shown all of the optical, thermal, and rheological results in Figures 6.1-6.9 respectively for the MC-SDS aqueous solutions. Based on these results, we like to further elucidate the role of SDS in affecting the hydrophobic association of MC.

Figure 6.10 Clouding points and clear points as a function of SDS concentration.

6.3.4.1 Salt-out and salt-in effects

Two effects of SDS on the gelation of MC have been observed, which are the salt-out like effect at the low concentrations of SDS and the salt-in effect at the high

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concentrations of SDS. Regarding the two effects, the consistency among the three types of properties (i.e. optical, thermal, and rheological properties) has been verified from Figures 6.1-6.6. Let's take the optical properties as an example to discuss about the salt-out and salt-in effects of SDS. For convenience, we use the temperature at which 50% transmittance is reached to define the sol-gel transition (i.e. clouding point) on heating or the gel-sol transition (i.e. clear point) on cooling. This definition is reasonable because the decreasing rate of transmittance on heating (or the increasing rate of transmittance on cooling) reaches the maximum in the vicinity of 50% transmittance. The results are shown in Table 6.1 and Figure 6.10.

In Figure 6.10, the significant effects of SDS can be observed from the clouding-point curve, whereas the clear-point curve shows the weak effect of SDS. On heating, the salt-out and salt-in effects of SDS are shown at low (≤ 6 mM) and high (> 6 mM) concentrations of SDS respectively. The transition point is 6 mM, which is interesting to know because it is near the critical micellization concentration (CMC, 8 mM) of SDS in water. For the salt-out effect, one possible mechanism can be applied, which is the modification of water's hydrophobicity by SDS. In this mechanism, when the concentration of SDS is lower than the CMC (8mM), SDS molecules are present as free unimers and able to attract water molecules so that water molecules available for MC chains decrease and "water" becomes more "hydrophobic" for MC. When the concentration of SDS is low, the micelles of SDS are not expected to form to surround the hydrophobic blocks of MC. Thus, MC tends to undergo the hydrophobic association at an earlier stage (i.e. at a lower temperature).

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As mentioned in the introduction section, the critical association concentration (CAC) of SDS is an important parameter in a polymer-SDS solution. [Goddard and Ananthapadmanaban, 1993; Wang, 1997] The CAC of a surfactant is generally smaller than its CMC. Our results in Figure 6.10 may also suggest that 6 mM is the CAC of SDS in the presence of MC. Before 6 mM, SDS molecules are present as free unimers or some of them are bound to some MC chains. Beyond 6 mM, on the other hand, the SDS molecules begin to form the micelles to surround the hydrophobic groups or hydrophobic blocks of MC. This micellization is called “polymer-induced micellization,” which is different from the micellization of SDS in pure water. In the presence of MC, the free micelles of SDS are considered not to exist when the binding of SDS to the polymer chains has not reached the saturation.

When the SDS concentration is higher than the CAC (6 mM), the polymer-induced SDS micelles are formed and their hydrophobic cores can act as the comfortable “cages” for the hydrophobic groups of MC to reside. Since the shells of the SDS micelles are highly hydrophilic, the formation of the SDS cages is able to stabilize (or in other words, solubilize) MC chains in water so that the gelation of MC becomes more difficult. In order for MC to form a gel through the hydrophobic association, the SDS cages must be removed. A higher temperature has to be applied to destroy the SDS cages, and as a result the so-called salt-in effect is observed. The binding of SDS molecules to MC chains to form the SDS cages is schematically illustrated in Figure 6.11.

Although the thermal and rheological properties show the good consistence with the optical ones, it is noted that the critical concentrations of SDS for the

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transition from salt-out to salt-in are slightly different from that obtained from the transmittance experiments. For example, in the thermal experiments in Figure 6.3 and Figure 6.4, the lowest endothermic peak is observed at 4 mM of SDS whereas the 6 mM SDS sample has showed the slightly higher peak temperature than the 4 mM SDS one. The rheological results in Figure 6.5 and Figure 6.6 do not show the clear salt-out effect of SDS when $\text{SDS} \leq 6 \text{ mM}$. However, the notable salt-in effects of SDS are observed in all of the three cases. The unclear salt-out effect of SDS observed from the rheological results would be due to the low sensitivity of rheological measurement to the change of rheological properties caused by the small salt-out effects.

In the cooling process, as shown in Figure 6.10, there are still the similar patterns for the salt-out and salt-in effects of SDS, but the effects of SDS are weaker than those in the heating process. This difference can be explained by the different kinetics in the cooling processes from the heating process. After the heating process followed by the cooling process, all of the microstructures formed between MC and SDS are considered to have been completely broken up at the end of heating or the beginning of cooling. Thus, the recovery of the microstructures such as the SDS cages (or SDS micelles) needs to take some time, which is a kinetic process. Importantly, we should note that the re-formation of SDS micelles has to take place in the gel network of MC, which should be more difficult than that in liquid water. Thus, the effects of SDS are delayed or weakened in the cooling process.

Figure 6.11 A schematic mechanism for the two-stepped gelation of MC under the influence of SDS.

6.3.4.2 Two-step gelation

From the thermal and rheological results shown in Figures 6.3 to Figure 6.6, we

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believe that at the high concentrations of SDS (especially $\text{SDS} \geq 10 \text{ mM}$), the gelation of MC occurs by two steps, which are clearly indicated by the bimodal endothermic peaks. Our discussion here on the two-step gelation of MC can be made by referring to Figure 6.9 and Figure 6.11. From Figure 6.9, we have known that the gelation of MC begins from the onset of the first endothermic peak at each SDS concentration but ends at the offset of the second endothermic peak. The MC solutions with 12 and 15 mM of SDS show that G' grows with temperature by a two-step pattern, which is consistent with the corresponding C_p curve.

It is interesting to know the mechanism for the two-step gelation of MC under the influence of SDS. The possible mechanism that we propose here is that (1) the basic mechanism for the gelation of MC is not changed by SDS, which still occurs through the hydrophobic association of MC but the gelation of MC is delayed by SDS due to the molecular binding of SDS to MC, (2) After the water cages have been broken up by heating, MC begins to gel through the association of the hydrophobic groups or blocks of MC that have not been bound by SDS molecules or caged by SDS micelles. This is the first step of gelation. (3) For the hydrophobic groups or blocks of MC that have been caged by SDS micelles to associate with each other, the SDS cages must be removed. The removal or destruction of the SDS cages required the higher energy. This is the reason the secondary endothermic peak is observed at the higher temperature region. As the SDS cages are disrupted, more hydrophobic groups or blocks of MC are exposed and they associate to form new junctions for the gel network. As a result, the second-step of gelation is observed.

6.4 Conclusions

In this work, the optical (i.e. turbidity), micro thermal, and rheological properties of methylcellulose (MC, SM4000, $M_w = 310,000$) aqueous solutions with various concentrations of sodium dodecyl sulphate (SDS) have been measured and the effects of SDS on the sol-gel transition of MC have been systematically investigated. It is found that the effects of SDS on the turbidity of a MC solution are different, depending on the SDS concentration. The salt-out and salt-in effects are observed at the low (≤ 6 mM) and high (> 6 mM) concentrations of SDS respectively. For example, when $SDS > 6$ mM, a significant delay of gelation is observed, this is the so-called salt-in effect. A critical concentration of SDS for the transition from the salt-out to the salt-in effects is found to be about 6 mM, which is a critical association concentration (CAC) of SDS. For the salt-out and salt-in effects of SDS, the consistency among the optical, thermal and rheological results has been verified.

Addition of SDS to a MC solution changes the pattern of MC gelation and a two-step gelation of MC is observed especially at the high concentrations (> 8 mM) of SDS. A bimodal peak of endotherm is observed for the two-step gelation of MC. The two-step gelation has been explained using the mechanism based on the SDS cages. The SDS cages are formed to surround the hydrophobic units of MC and these SDS cages have to be broken up at high temperatures. The first-step gelation occurs through the association of the hydrophobic units of MC, which are not caged at low temperatures by SDS, whereas the second-step gelation does through the association of the hydrophobic units of MC that are exposed at high temperatures

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from the SDS cages.

Table 6.1 Clouding points and clear points for 0.03 mM MC solutions with various SDS concentrations.

	SDS, mM						
	0	2	4	6	8	12	15
Clouding Point (°C)	60.2	59.2	54.6	49.0	53.0	62.0	68.4
Clear Point (°C)	32.3	31.3	30.1	28.4	29.2	33.7	38.7

Chapter 7

Sol-Gel Transition of MC in Water under Magnetic Field

7.1 Introduction

Water is one of the most interesting substances because many physical properties of water are much different from other low-molecular-weight compounds. For example, unlike most low-molecular-weight compounds that are gases at room temperature, water is a liquid and has a high boiling temperature. The main reason for water to be unique is because of the strong tendency of water molecules to form hydrogen bonds with other water molecules. Each water molecule is simultaneously a hydrogen bond donor and a hydrogen bond donor acceptor. Water is also a good solvent for many biological substances due to its dipolar character. The structure of liquid water has been described as “flickering clusters” of hydrogen bonds, with remnants of the tetrahedral molecular lattice continually breaking and re-forming as the water molecules move about [Mathews et al., 2000].

Water is weakly diamagnetic and can be levitated in very high magnetic fields (10 T) [Ikezoe et al., 1998]. The effects of magnetic field on water have been studied in the literature. By simulation, it has been shown that the number of monomer water molecules is increased by low magnetic fields (0.2 T) [Zhou et al., 2000]. Experimentally, the effect of the high magnetic field (6 T) on hydrogen bonding has been observed as the melting point of H₂O and D₂O were increased [Inaba et al., 2004]. Based on the near-infrared spectral results for water and the

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glucose solutions under the magnetic fields (0 ~14 T), Iwasaka and Ueno proposed that the magnetic fields (0 ~14 T) affected the formation of hydrogen bonds of water molecules and the hydration of glucose molecules [Iwasaka and Ueno, 1998]. The magnetic effect on the degree of structuring in water may further influence many physical properties (for example, hydration, solubility, interfacial tension, etc) of solutes.

A methylcellulose (MC) aqueous solution is not a magnetic fluid. Heating a MC aqueous solution with a concentration about 1 to 3 wt% to above 60 °C (but below 80 °C) will turn the liquid solution into a solid gel. The sol-gel transition of MC in water occurs through the so-called hydrophobic association of MC chains. The breakage of the hydrogen bonds formed between water molecules and the polymer chains is a necessary precursor for the hydrophobic association of MC [Li et al., 2002].

It is simple to anticipate that any factors affecting the formation or destruction of hydrogen bonds will influence the sol-gel transition of MC in water. For the thermoreversible MC hydrogels, temperature is the key factor controlling the sol-gel transition [Li et al., 2002]. Xu et al. have recently systematically studied the effects of salts and salt mixtures on the sol-gel transition of MC in water [Xu et al., 2004a; Xu et al., 2004b]. When a salt-out salt such as NaCl is added into a MC aqueous solution, for example, the sol-gel transition temperature will shift to a lower temperature with increasing salt concentration. The reason for the phenomena is that the salt affects the structure of water [Hribar et al., 2002] through the interactions between salt ions and water molecules. Some of original hydrogen bonding network

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formed by water molecules is destroyed by the salt and this effect is similar to increasing temperature. However, a salt (no matter it is a salt-out salt or a salt-in salt) is unable to change the sol-gel transition mechanism of MC, which is still attributed to hydrophobic association.

If the dipolar moment and orientation of water molecules can be changed by a magnetic field, it is expected that the formation of hydrogen bonds between MC and water will be affected. Thus, the sol-gel transition of MC may be affected by a magnetic field. However, we have not found any reports studying the effects of magnetic field on the sol-gel transition of hydrogels from the literature. In this work, we apply a magnetic field (0.2 to 0.3 T) to the aqueous solutions of MC to study its effects on the sol-gel transition and the gel modulus. The MC solutions containing NaCl are also examined.

7.2 The sol-gel transition of MC aqueous solution under magnetic field

To verify our hypothesis that the sol-gel system will be affected by a magnetic field in the pre-gel and the sol-gel transition regimes, the dynamic rheological experiments were conducted for several MC aqueous solutions under a given magnetic field ($I = 1.9\text{A}$). The experimental details have been given in Chapter 3. The results and discussion are presented as follows.

In Figure 7.1, G' and G'' of a MC (SM4000) aqueous solution are shown in a heating process from 20 to 70°C. Two identical experiments were conducted to confirm the repeatability of the sample under the magnetic field. The “a” curve was obtained without the magnetic field, while the “B” and “C” curves are two repetitive

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curves under the magnetic field. The two experiments under the same magnetic field showed the good repeatability.

Figure 7.1 Storage modulus G' and loss modulus G'' of MC (1.53 wt% SM4000) as a function of temperature in a heating process. A strain of 10% and angular frequency of 1 rad/s were applied. The magnetic field was expressed by the current value ($I=1.9$ for B, and C and $I=0$ for A).

As shown in Figure 7.1, G'' in the vicinity of the sol-gel transition does not respond much to the magnetic field. Thus, we focus our discussion on G' of the gelling system. As already known, the sol-gel transition of the MC solution in the absence of the magnetic field occurs in a narrow temperature range around 61 °C. It is clearly observed that the G' curves (i.e. the “b” and “c” curves) with the magnetic field have a similar pattern with one without the magnetic field but shift to the lower temperature region, indicating a salt-out like effect. After the sol-gel transition

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temperature, all G' curves obtained with or without the magnetic field almost overlap, indicating the onset of a G' plateau for a well-formed gel which is almost not affected by the magnetic field. The effect of the magnetic field on the gel strength will be discussed in the next section.

This salt-out like effect can be explained through the role of hydrogen bonds or cagelike water structure surrounding the hydrophobic groups of MC, which would have been affected by a magnetic field. It is easy to understand that if the magnetic field could weaken some hydrogen bonds in the system, the hydrophobic moiety of the polymer chains could be exposed from the water cages more easily, hence causing an earlier association for gelation. This phenomenon or mechanism has not been found in the literature. The shift of the sol-gel transition is significant, but it is not as great as the salt effects by a salt-out salt. For example, NaCl, a typical salt-out salt, can lower the transition temperature of MC. The possible mechanism for this salt-out effect of NaCl is the competition between salt ions and polymer chains for water molecules. [Xu et al., 2004a; Xu et al., 2004b]. Under a magnetic field, a different mechanism should exist since there are no salt ions attracting water molecules. Thus, the most possible mechanism for the salt-out like effect of the magnetic field is that the number of hydrogen bonds formed between MC and water is reduced by the magnetic field or the hydrogen bonds have been weakened by the magnetic field. Or the both effects might be present at the same time.

It has been well accepted that when water molecules form hydrogen bonds along MC chains and/or cagelike structures surrounding the hydrophobic groups of MC, these water molecules in the solution will not be free and random and they will have

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a certain degree of order. Upon heating, the endothermic heat (i.e. $\Delta H > 0$) is mainly used to break the ordered hydrogen bonds, resulting in a disordered state of water and an increase in entropy (i.e. $\Delta S > 0$) [Li, 2002]. If a magnetic field can alter the ordered structure of the water molecules surrounding the MC chains, the effect of the magnetic field will be phenomenally similarly to the effect of heating or the effect of a salt-out salt.

Static magnetic effects have been shown to cause an increase in the ordered structure of water formed around hydrophobes and colloids [Ozeki et al., 1991]. by Higashitani et al. studied the effect of a magnetic field (0.42 T) on the fluorescent probes [Higashitani et al., 1996]. They found that the magnetic effects existed only for the fluorescent probes with an alkyl chain. They also used the concept of the ordered structure of water, which surrounded the alkyl chains and could be affected by a magnetic field, to explain the mechanism.

Our next hypothesis is that when a salt-out salt is present in a MC solution, the effect of the magnetic field will be weaker because the water molecules available for the formation of hydrogen bonds with MC chains are less than those in a MC solution without a salt. The similar rheological experiments were conducted for a 0.03mM MC solution containing NaCl (the salt concentration was varied from 0 to 0.8 mM).

7.3 The sol-gel transition of MC in salt aqueous solutions under a magnetic field

Figure 7.2 Storage modulus G' and loss modulus G'' of MC/salt aqueous system (0.03M SM4000+0.8M NaCl) as a function of temperature in a heating process. Angular frequency of 1 rad/s was applied. The magnetic field was expressed by the current value ($I=1.9$ and $I=0$ respectively).

We have conducted the rheological experiments for the MC solutions with 0.2, 0.4, and 0.8 mM of NaCl, and the similar results were obtained.

Figure 7.2 illustrates the viscoelastic behavior of the MC aqueous solution containing 0.8 M of NaCl. 0.8 M is the highest concentration of NaCl used in this work. NaCl is known as a typical salt-out salt, which is able to lower the sol-gel transition temperature of MC [Kundu and Kundu, 2001; Kundu et al., 2003; Xu et al., 2004a; Xu et al., 2004b]. For the capability of NaCl to lower the sol-gel transition

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temperature of a 0.03mM MC (SM4000) solution, Table 7.1 provides the details, which were obtained by the micro-DSC experiments. [Xu et al., 2004a; Xu et al., 2004b] As shown in Table 7.1, the salt itself has caused a shift in temperature to the left by 18 °C. As shown in Figure 7.2, the further shift of the G' curve to the left is no doubt caused by the magnetic field ($I = 1.9$ A). However, the magnetic effect in the presence of NaCl seems weaker than that in the absence of the salt as observed in Figure 7.1. This may prove our hypothesis that the effect of the magnetic field is weaker when a salt is present. The similar trend could also be seen for the MC solutions with 0.4 and 0.2 M of NaCl as shown in Figure 7.3 and Figure 7.4 respectively. However, there was no a clear tendency to show the effect of salt concentration.

Figure 7.3 Storage modulus G' and loss modulus G'' of MC/salt aqueous system (0.03M SM4000+0.4M NaCl) as a function of temperature in a heating process. Angular frequency of 1 rad/s was applied. The magnetic field was expressed by the current value ($I=1.9$ and $I=0$ respectively).

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Table 7.1 The sol-gel transition and the gel-sol transition temperatures obtained by micro-DSC for a MC aqueous system with various salt concentrations of NaCl. T_m denotes the peak temperature in the DSC curve on heating (H) and cooling (C) [Xu et al., 2004a].

Salt conc./M	0		0.2		0.4		0.8	
	H	C	H	C	H	C	H	C
$T_m/^\circ\text{C}$	61.1	31.9	55.3	28.2	50.1	24.2	43.1	18.7

Now, we believe that both a salt-out salt and a magnetic field can influence the sol-gel transition of MC aqueous solutions in the same direction but in an independent way rather than in a concerted way. Although the magnetic effect we observed is not as great as salt effects, our experimental results are the evidence that there is a magnetic effect on the sol-gel transition of MC.

As we discussed before, both the effects of a magnetic field and a salt-out salt are to decrease the hydration extent of MC in water, but with the different mechanisms that the salt compete with polymer chains for water molecules while a magnetic field reduces the hydrogen bonds to result in the exposure of hydrophobic part of the polymer more easily. Therefore, these two effects can be considered to be independent. Furthermore, in a salt solution of MC, since the water structure may have been modified or partially destroyed by the salt ions, the further effect of a magnetic field on the water structure (or hydrogen bonds) will be weaker than that in a salt-free solution of MC. [Iwasaka and Ueno, 1998].

Thus, the extent of the magnetic effect will be limited when a high concentration of NaCl is present, as the salt has provided already its salt-out effect in advance to the solution of MC and the superimposing of a magnetic field will not further

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increase this effect too much. But the superimposed effect does exist in the vicinity of the sol-gel transition regime, as verified in this work.

Figure 7.4 Storage modulus G' and loss modulus G'' of a MC/salt aqueous system (0.03M SM4000+0.2M NaCl) as a function of temperature in a heating process. Angular frequency of 1 rad/s was applied. The magnetic field was expressed by the current value ($I=1.9$ and $I=0$ respectively).

7.4 Gel strength under a magnetic field

To examine if the magnetic field will affect the gel strength of a MC hydrogel, a comparison experiment was conducted on a well developed MC hydrogel, as shown in Figure 7.5. G' and G'' were measured after a 30 min stabilizing period at 70 °C, which allowed the formation of a fully developed gel at the temperature (70 °C) without and with a magnetic field. As shown in Figure 7.1 to Figure 7.4, G' and G''

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do not change remarkably with or without the magnetic field, but it is clear that both G' and G'' do increase slightly under the magnetic field.

Figure 7.5 Storage modulus G' and loss modulus G'' of a MC (1.53 wt% SM4000) hydrogel as a function of angular frequency at 70 °C. A strain of 3% was applied.

It is reasonable that the strength of a MC hydrogel is not significantly affected by the magnetic field, because the gel network has already been well formed through the hydrophobic association. The water structure is no longer important for the gel as the breakage of the hydrogen bonds around the hydrophobes of MC has already occurred. However, the slightly increase in the gel strength under the magnetic field as observed in Figure 7.1 to Figure 7.4 may be explained by an increased resistance of the gel against the shear deformation, but this has not been experimentally proved. In other way, if the hydrophobicity of water can be modified by a magnetic field to

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result in a “more hydrophilic” environment for MC chains, the hydrophobic association of MC may be strengthened to result in a stronger gel. This hypothesis needs to be experimentally verified in future.

7.5 Conclusion

It can be concluded from the above observation and discussion that the presence of a moderately strong magnetic field (0.2 ~ 0.3 T) does affect the sol-gel transition of a methylcellulose aqueous solution and a salt-out like effect was found. The above phenomenon is probably due to the effect of a magnetic field on the hydrogen bonds and the cage-like water structure. The magnetic field weakens hydrogen bonds or promotes the destruction of the cage-like water structure to induce an earlier onset hydrophobic association in MC. The similar results have been found in the MC aqueous solutions containing various contents of NaCl. However, the effects of the magnetic field and NaCl on the sol-gel transition of MC are independent of each other.

Chapter 8

Micellization to gelation of a triblock copolymer in water: Thermoreversibility and scaling

8.1 Introduction

Temperature is a crucial factor in determining the micellar size of Pluronics in water. For example, Mortensen reported that the micellar core radius of $\text{EO}_{25}\text{PO}_{40}\text{EO}_{25}$ increased from 38 Å at 20 °C to 51 Å at 50 °C [Mortensen, 1992]. Similarly, the core radius of Pluronic F127 ($\text{EO}_{100}\text{PO}_{65}\text{EO}_{100}$) was found to increase from 50-70 Å at low temperatures to 70-80 Å at high temperatures, as determined by SANS [Mortensen and Talmon, 1995]. Therefore, it can be simply deduced from these results that the micellar aggregation number, and therefore micellar size, increases with temperature.

As introduced in chapter 2, the effect of temperature on micellization and phase separation can be described through different temperature regimes. At low temperatures, the PEO-PPO-PEO chains exist as unimers. In this regime, water plays an important role as water molecules are surrounding polymer chains to form hydrogen bonds between water and polymer chains. However, if PPO blocks cannot form strong hydrogen bonds with water, the cagelike structure may be considered, in which water molecules just surround the hydrophobic blocks, segments, or groups to make them water-soluble. It has been reported that the establishment of cage environments dominates the solvation of a solute, and when the free energy change for the establishment of the cage environments reaches equilibrium, the

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thermodynamic enthalpy-entropy compensation is produced [Grunwald and Steel, 1995]. In other words, in equilibrium, the enthalpy released (or consumed) is to compensate the entropy through the establishment (or destruction) of cage structures. At higher temperatures (above CMT), the cagelike structures are broken, and the hydrophobic PPO blocks are exposed and associate to micelles. In this regime, the unimers and micelles coexist. Because the destruction of the cagelike structures requires energy and this can occur in a relatively narrow range of temperatures, a sharp endothermic peak is generally observed. This can be considered a universal mechanism for the most nonpolar amphiphilic polymers undergoing a transition from a solution state to a micellar or gel state [Li, 2002]. At high temperatures, when the volume fraction of the spherical micelles exceeds about 0.53, the micellar liquid may freeze into a cubic crystal [Mortensen et al., 1992].

In the Pluronic family, the most extensively studied member is F127 [Alexandridis et al., 1994; Kozlov et al., 2000; Linse and Malmsten, 1992; Mortensen and Talmon, 1995; Song et al., 2000; Su et al., 2002; Wanka et al., 1994], because F127 has a relatively long chain length ($M_w = 12,600$) and an appropriate n/m ratio ($100/65 = 1.5$), which results in a 70 wt % ethylene oxide (EO) content. This molecular design of F127 ensures both good water solubility through the high content of EO and a high capacity for hydrophobic association through the relatively longer PPO block ($m = 65$). F108 ($\text{EO}_{133}\text{PO}_{50}\text{EO}_{133}$) is another Pluronic polymer with a high molecular weight of 14,600. The EO content and n/m ratio of F108 are 80 wt % and 2.8, respectively, which are much different from those of F127. Thus, the micellization, micellar structure, and phase behavior

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of F108 are expected to differ from those of F127. For example, F108 would have higher water solubility and smaller micellar core sizes than F127. A few studies have been found on F108 [Alexandridis et al., 1994; Alexandridis et al., 1995; Kozlov et al., 2000]. For example, Alexandridis and coworkers [Alexandridis et al., 1994; Alexandridis et al., 1995; Kozlov et al., 2000] used a fluorescent probe (1,6-diphenyl-1,3,5-hexatriene) to determine CMTs and CMCs for F108, which were consistent with those obtained with other techniques such as DSC, surface tension, and static light scattering. Kozlov et al. [Kozlov et al., 2000] also used fluorescent probes to investigate CMC of F108 and its partitioning of some low-molecular-weight solutes between the aqueous and micellar phases. For F108, however, we have not found any literature reporting in detail (1) the reversible thermal properties from micellization to gelation, (2) the rheological properties from micellization to gelation, and (3) the scaling laws depicting the elasticity evolution of F108 as a function of concentration.

In this chapter, we used a combination of micro-DSC and rheology to study the thermal and rheological properties of aqueous solutions of F108 as a function of the polymer concentration through a complete thermal cycle from heating to cooling at a scanning rate of 1 °C/min. The viscoelastic properties during the thermal cycle are expected to be able to link with the reversible thermal properties to provide a complete image of F108. The validity of the scaling laws is to be examined for these F108 samples.

8.2 Experimental

8.2.1 Materials and sample preparation

Pluronic F108, kindly provided by BASF Corp. The lot number was WPMU-574B. Before use, F108 was kept in a desiccator to avoid the absorption of moisture at room temperature. Aqueous solutions of F108 with various concentrations ranging from 1 to 25 wt % were prepared with deionized water from a Millipore water purifier. For high concentrations (>20 wt %) of F108, however, the solutions were prepared with cold deionized water (ca. 8 °C) because F108 had better solubility in water at lower temperatures and the CMT decreased with increasing F108 concentration (e.g., CMT of 25 wt % F108 10 °C).

8.2.2 Microthermal analysis

A differential scanning microcalorimeter (VP-DSC, Microcal, Inc.) was used. A slow heating or cooling rate of 1 °C/min was applied for all samples to explore the details of the thermally induced association behavior of F108 in water. For the microthermal analysis, the samples underwent heating from 0 to 80 °C and subsequently were immediately cooled from 80 to about 0 °C. One of the major limitations of this micro-DSC calorimeter was that a highly viscous liquid could not be injected into the sample cell. Therefore, the concentrations were restricted to be below 25 wt % F108.

8.2.3 Rheological measurements

Each solution was transferred from a glass bottle to a rheometer (ARES 100FRTN1,

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Rheometric Scientific). All the dynamic viscoelastic measurements (i.e., temperature sweep) were carried out at an angular frequency of 1 rad/s and at low shear strains (5-10%) to ensure the linearity of viscoelasticity.

8.3 Results and discussion

8.3.1 Reversible thermal behavior from heating to cooling

A typical example of calorimetric thermograms determined with micro-DSC is shown in Figure 8.1 for a 5 wt % solution of F108. During the heating process, a sharp endothermic peak can be observed at 30.4 °C, whereas an exothermic peak appears at the same temperature in the subsequent cooling process. In Figure 8.1, the endothermic and exothermic curves are exact mirror images along the baseline. Many characteristic features can be directly obtained from these calorimetric thermograms: (1) the onset temperature of the endothermic peak, which is generally defined as the CMT; (2) the peak temperature (T_p), indicating the temperature at which the micellization reaches the maximum rate; (3) the offset temperature (T_{off}), which is an indication of the end of micellization; and (4) the area under the curve, which is the total energy required for the entire micellization. Similar information can also be obtained from the cooling curve. The exothermic peak begins to emerge from a critical demicellization temperature (CDMT), as indicated in the figure. The value of this CDMT is almost the same as T_{off} . The exothermic peak appears at 29.9 °C, which is very close to that (30.4 °C) of the endothermic peak. This peak temperature is denoted TDP (the temperature at the exothermic peak), and it reflects the position at which the maximum rate of demicellization has been reached. The

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continuous cooling causes the endothermic curve to return to the baseline at the offset temperature for demicellization (T_{Doff}), which has a value similar to that of CMT. The area under the exothermic peak is the total energy released for demicellization. There are no detectable endothermic or exothermic peaks in the temperature range between T_{off} and 80 °C.

Figure 8.1 Calorimetric thermograms of a 5 wt % aqueous solution of F108 during a thermal cycle. The heating and cooling rates were 1 °C/min.

The dependence of the thermal properties on the F108 concentration is shown in Figure 8.2 and Figure 8.3 for the heating and cooling processes, respectively. The polymer concentration ranges from 1 to 25 wt %. The heating and cooling rates are 1 °C/min. In Figure 8.2, the endothermic peak temperature decreases with concentration, whereas the peak height increases with concentration. However, the

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peak does not broaden very much with concentration. Similar features can be observed for cooling [Figure 8.3]. If one plots all the endothermic and exothermic peaks in one graph as we have in Figure 8.1, mirror images can be obtained.

Figure 8.2 Calorimetric thermograms of aqueous solutions of F108 at various concentrations upon heating at 1 °C/min.

Each endothermic or exothermic peak has a certain broadness and also has a weak dependence on concentration. The broadness of the calorimetric peak may be due to two factors: (1) micellization is a kinetic process in which unimers and micelles are in equilibrium, and (2) the polydispersity of the polymer is important in reducing the CMC of these block copolymers [Armstrong et al., 1998]. However, the effect of the second factor does not help to explain the concentration dependence. As the concentration increases, the kinetic effect would become more important because more chains in a more concentrated solution may cause more possible obstructions

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for one another than in a lower concentration solution. A high concentration may also cause the formation of less perfect micelles.

Figure 8.3 Calorimetric thermograms of aqueous solutions of F108 at various concentrations upon cooling at 1 °C/min.

It can be concluded from these results that the basic thermoreversibility of an F108 solution is independent of concentration, but its temperature range and the total energy required are dependent on concentration. All characteristic values, such as the CMT, T_P , T_{off} , enthalpy of micellization (calculated by the integration of the area under the peak and converted into the unit of cal/L), TDP, and temperature difference between T_P and T_{DP} , can be obtained for all the concentrations with the method defined in Figure 8.1.

CMT and T_{off} were plotted in Figure 8.4 as a function of the F108 concentration, and this graph can simply be used as a phase diagram. At a given concentration, when the temperature is below its CMT, polymer chains in water

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exist as unimers. The micellization begins at CMT and ends at T_{off} . In the region between CMT and T_{off} , polymer chains exist as unimers, micelles, or both. Above T_{off} , all the micelles would have been formed, but this does not necessarily mean that there are no free F108 chains in the aqueous solution. However, as no significant heat is detected above T_{off} , we may consider that the remaining free polymer chains (if any) are insufficient to form micelles. Both CMT and T_{off} decrease monotonously with concentration, and T_{off} is approximately parallel to CMT. Thus, the micellization takes place within a similar window of temperature, and this window size is roughly independent of the polymer concentration. However, our results shown in Figure 8.4 do not seem consistent with those observed by Alexandridis et al., who found that CMT of F108 was approximately a linear function of the polymer concentration [Alexandridis et al., 1995]. However, the concentration range studied by Alexandridis et al. was below 10 wt %.

Figure 8.4 Phase diagram for an aqueous F108 system at a heating rate of 1 °C/min.

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8.3.2 Heat of gelation

For all F108 concentrations less than 20 wt %, we did not detect any significant heat changes in the temperature range from T_{off} to 80 °C, as shown in Figure 8.2 and Figure 8.3. For the 22.5 and 25 wt % solutions, however, we found that there was a small endothermic peak beyond the primary peak, as illustrated in Figure 8.5. An enlarged diagram is given in the inset of Figure 8.5. It is believed that this small secondary peak must be associated with some structural change in the system. No reports have been found on F108 for this phenomenon. [Alexandridis et al., 1995] Armstrong et al. [Armstrong et al., 1998] studied the effect of sodium chloride on micellization and phase separation for several PEO-PPO-PEO triblock copolymers with molecular weights ranging from 2900 to 11,400 and showed that there was a secondary transition beyond the micellization transition. The secondary transition showed negligible heat in comparison with the micellization heat, and it was explained to be due to the sphere-to-rod transition in the temperature range of 60-70 °C in the presence of salt. In the case of F108, however, we would like to attribute the secondary peak to the gelation of F108, which is induced by heating. The rheological evidence for supporting this consideration is given later in this report. Another important finding from Figure 8.5 is that the secondary peak shifts to a lower temperature with increasing F108 concentration. For 22.5 and 25 wt %, the secondary peaks appear at 35.7 and 31.1 °C, respectively, which are very consistent with those found from the rheological measurements. Although the secondary peak for the gelation of F108 in water could be nicely observed, the total heat is too small to be comparable with the heat of micellization. Therefore, the gelation can be

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approximately considered an athermic process. In terms of these results, it is concluded that the micellization is a necessary precursor for the gelation of F108 and that gelation is not possible without the formation of micelles. We explain this in detail later with a proposed schematic model for gelation from micellization.

Figure 8.5 Calorimetric thermograms for 22.5 and 25 wt % aqueous solutions of F108 on heating at a rate of 1 °C/min. The secondary endothermic peaks from 28 to 38 °C are enlarged in the inset.

8.3.3 G' on heating

G' is shown in Figure 8.6 as a function of temperature for aqueous F108 solutions ranging from 10 to 35 wt % as indicated. The angular frequency was 1

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rad/s, and the heating rate was about 1 °C/min. At room temperature (25 °C), the three highest concentrations of F108 were gel-like already, whereas the others were still liquids. Each solution showed a common liquid behavior when the temperature was below its transition temperature. $T_{G'}$ was defined as the temperature at which G' showed an abrupt increase with increasing temperature. $T_{G'}$ was easily found for the high concentrations of 20-35 wt %, but it had to be defined for the low concentrations (10-17.5 wt %) as follows. As illustrated for the 15 wt % curve, $T_{G'}$ was defined as the crossover point of the two tangent lines from the low and high portions of the G' curve, respectively.

Figure 8.6. G' as a function of temperature for aqueous F108 solutions at a heating rate of about 1 °C/min and at an angular frequency of 1 rad/s. The concentrations are indicated in the inset. The dashed lines and the arrow are used to illustrate how to define $T_{G'}$.

Below $T_{G'}$, all the solutions exhibited low values of G' , and many of them were low-

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viscosity liquids. Upon heating, a steep increase in G' was observed in the vicinity of $T_{G'}$. The degree of this steep change increased with the polymer concentration. When the concentration was 20 wt % or higher, a G' plateau nicely developed beyond $T_{G'}$, whereas the low-concentration solutions did not reach a G' plateau until the high-temperature end. Thus, it is proved for these low-concentration samples that a complete network, which is either a closed packed micellar crystal lattice or a percolation network as suggested by different mechanisms introduced in chapter 2, was never formed during the heating process.

All the values of $T_{G'}$ are plotted against concentration c (wt %) in Figure 8.4.

8.3.4 Phase diagram

From the onset and offset temperatures (CMT and T_{off} , respectively) found from the thermal measurements (Figure 8.2 and Figure 8.3) as well as $T_{G'}$, we can directly make a phase diagram. The phase diagram for the heating process is shown in Figure 8.4. This kind of phase diagram does not indicate the phase behavior in the thermodynamic equilibrium state, but it is dependent on the heating rate. At a fixed heating rate (i.e., 1 °C/min in this work), however, this phase diagram is useful in describing the kinetic phase behavior for any F108 concentration within the concentration range studied.

Through the three curves in Figure 8.4, the phase diagram can be divided into four regions: (1) the unimer region, (2) the micellization region, (3) the introductory transition region from micelles toward a gel, and (4) the gel region. For a given concentration, the micellization begins from a CMT and ends at a T_{off} . In this

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region, great endothermic heat is required for the micellization, which is a function of the polymer concentration. From the T_{off} curve to the $T_{G'}$ curve, no heat changes can be detected, and this implies an athermic process. In this temperature region from T_{off} to $T_{G'}$, however, athermic does not mean that there are no structural changes in the system. Despite the athermic heat, within this region, it has to be necessary for F108 micelles to order themselves into a crystal structure or connect with one another for the formation of a gel network. Finally, at $T_{G'}$, and a gel is formed if the polymer concentration is higher than the critical value. The DSC studies in Figure 8.5 show that the heat for the transition in the vicinity of $T_{G'}$ is very small (almost athermic if compared with that for micellization) even for high concentrations of F108.

8.3.5 Scaling in the elasticity evolution at 70 °C with the concentration

The rheological characteristics in the vicinity of the sol-gel transition can be conveniently described with scaling laws. One scaling law, which has been extensively applied to many types of polymeric gels (both chemical and physical gels), is established for the equilibrium modulus (G_e) beyond the sol-gel transition and have been introduced previously as Equation 4.1.

The relative distance of p in Equation 4.1 can be any gelling variable, such as the temperature, time, or concentration. In this work, it is convenient for us to use the concentration as p to examine the validity of Equation 4.1. To do so, we need to define the sol-gel transition concentration ($C_{G'}$). However, it is experimentally difficult to measure $C_{G'}$ because the frequency independence of loss $\tan\delta$ at $P_{G'}$ has to be confirmed first [Li, 2002]. To simplify the procedure, however, we would like

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to directly use c as we did previously for methylcellulose [Li, 2002]. From the G' curves in Figure 8.6, it is known that when the concentration is 17.5 wt % or less, the G' plateau is not well developed until the highest temperature end. This indicates the formation of an incomplete network from a low concentration, although the lowest concentration (10 wt %) has shown a dramatic increase in G' .

Figure 8.7 Dependence of G'_{70} on F108 concentration c . G'_{70} was obtained from Figure 8.6.

For us to understand how the elasticity of an F108 solution evolves at a given temperature or through a heating process, it is still quite interesting to look at the elasticity at a fixed temperature, such as 70 °C, for all the concentrations of F108. In terms of this consideration, G' at 70 °C (G'_{70}) were plotted in Figure 8.7, and the scaling was examined.

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With the solid straight line, G'_{70} can be approximately expressed as:

$$G'_{70} \sim c^{4.8} \quad (8.1)$$

Equation 8.1 is valid at least within the concentration range of 10-35 wt %. Although the fitting of the data to the straight line was not perfect, the great value of the slope indicates the high sensitivity of the elasticity evolution to the polymer concentration. In other words, a change in the polymer concentration can significantly alter the elasticity of an F108 solution at 70 °C. Even though Equation 8.1 is not the same as Equation 4.1, it is thought that the basic characteristic of the scaling does not change with not using the relative distance of gelation (C_G).

8.3.6 Unique dynamic viscoelasticity from micellization to gelation

Figure 8.8 to Figure 8.10 shows the unique dynamic viscoelastic properties of aqueous F108 solutions during a thermal cycle from heating to cooling at 1 °C/min and at an angular frequency of 1 rad/s.

Figure 8.8 (●) G' and (○) G'' as functions of temperature for aqueous F108 solutions in a thermal cycle process from heating to cooling as indicated. The angular frequency was 1 rad/s, and the heating and cooling rates were about 1 °C/min. The polymer concentrations was 20 wt %.

As shown in Figure 8.8 for 20 wt % F108, in the heating process from 10 °C to about 75 °C, there are mainly three distinct regions. The first region is before the onset of the steep increase in G' and G'' , which is about the temperature range below 33 °C. In this region, G'' is higher than G' , but both increase slightly with temperature even though micellization has already occurred below 33 °C (Figure 8.4). Thus, it is apparent that the micellization of F108 does not significantly contribute to the changes in G' and G'' when the micelles are not close enough with

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each other in a confined network. This has been confirmed from the phase diagram of Figure 8.4, in which $T_{G'}$ is always higher than T_{off} . As G' is below G'' , the solution shows a common viscoelastic behavior of a liquid [Ferry, 1980].

Figure 8.9 (●) G' and (○) G'' as functions of temperature for aqueous F108 solutions in a thermal cycle process from heating to cooling as indicated. The angular frequency was 1 rad/s, and the heating and cooling rates were about 1 °C/min. The polymer concentrations was 22.5 wt %.

In the second region from 33 to about 43 °C, both G' and G'' begin to increase from 33 °C, but they do not cross over each other. As a result, G' increases with the temperature in parallel to G'' so that loss $\tan\delta$ is always smaller than unity. Traditionally, the crossover of G' and G'' is used as an indication of $P_{G'}$ [Ferry, 1980]. This method is simple and convenient, but the gel point defined by this

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method is usually dependent on the frequency used in the measurement. Winter's group [Chambon and Winter, 1987; Chevillard and Axelos, 1997; Izuka et al., 1992; Scanlan and Winter, 1991; Winter and Chambon, 1986] defined the sol-gel transition as the point at which both G' and G'' scale with n , and the ratio of G'' to G' (i.e., $\tan\delta$) is independent of frequency. It is well known that G' should be greater than G'' beyond the sol-gel transition because a gel network is more elastic than a liquid. However, for the case of 20 wt % [Figure 8.8], there is no such point that can be found to define the sol-gel transition even though G' has shown a steep increase in the region of more than four orders of magnitude. All the F108 solutions below 20 wt % show viscoelastic behavior similar to that of the 20 wt % solution.

In the third region beyond the onset of each plateau, G' and G'' reach their own plateaus until the end temperature of heating.

In contrast, in the cooling process, the G' and G'' plateaus remain unchanged, and the system does not return to the original liquid state until the end temperature (10 °C) of cooling. However, there is a small transition at about 42 °C at which both G' and G'' drop to a lower value, and this transition temperature is in the vicinity of $T_{G'}$ found in the heating process.

The 22.5 wt % solution in Figure 8.9 exhibits the most similarities to the 20 wt % solution in Figure 8.8. However, the 22.5 wt % solution shows a great approach of G' to G'' beyond $T_{G'}$, which indicates increased elasticity with increasing concentration. This can be further confirmed by the 27.5 wt % solution in Figure 8.10, in which G' is higher than G'' beyond $T_{G'}$ and loss $\tan\delta$ reaches a low value of 0.1 at the end of cooling. There is a sudden drop in the cooling process in the

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vicinity of $T_{G'}$. Thus, it can be concluded from these results that 22.5 wt % is a critical concentration for the transition from a micellar system to a gel-like system. In other words, an elastic-dominant gel of F108 is formed only when the F108 concentration is higher than 22.5 wt %. As reported in Figure 8.5, a secondary endothermic peak was found only for the high concentrations (22.5 and 25 wt %) of aqueous F108 solutions. By comparing the values of $T_{G'}$ with the secondary peak temperatures (T_{2nd}), we find that they are quite consistent. These values are given as follows: $T_{G'} = 35.7\text{ }^{\circ}\text{C}$ and $T_{2nd} = 35.7\text{ }^{\circ}\text{C}$ for 22.5 wt % and $T_{G'} = 31.3\text{ }^{\circ}\text{C}$ and $T_{2nd} = 31.1\text{ }^{\circ}\text{C}$ for 25 wt %. This rheological evidence, together with the microthermal evidence, allows us to confidently conclude that the thermal gelation of F108 takes place only when the concentration is higher than 22.5 wt %, which is indicated by the secondary endothermic peak and the viscoelastic behavior at $G' > G''$.

Except for 10 wt % (the lowest concentration used in this work for the rheological studies), a complete recovery of G' and G'' was not observed through the cooling process down to $10\text{ }^{\circ}\text{C}$ for all concentrations of F108, as illustrated in Figure 8.8 to Figure 8.10. The G' plateau beyond $T_{G'}$ increases in height and broadens with the polymer concentration. In the cooling process, the small transition observed in the vicinity of $T_{G'}$ may be indicative of some structural changes resulting in a weaker structure from a stronger structure. On cooling, these systems are irreversible at the cooling rate used, and the irreversibility increases with concentration.

The thermal behavior of F108 is quite reversible, as shown in Figures 8.1, Figure 8.2 and Figure 8.3, but the rheological behavior shows great hysteresis

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between heating and cooling (Figure 8.8 to Figure 8.10). We believe that the hysteresis is due to the difficulty in disassociating the micelles to get either smaller or fewer micelles in order to break the network; some intermicellar molecular entanglements of the poorly hydrated PEO arms are also possible hindering factors.

Figure 8.10 (●) G' and (○) G'' as functions of temperature for aqueous F108 solutions in a thermal cycle process from heating to cooling as indicated. The angular frequency was 1 rad/s, and the heating and cooling rates were about 1 °C/min. The polymer concentrations was 27.5 wt %.

8.4 Mechanism for micellization to gelation

We propose two likely micellization-to-gelation mechanisms, each with three stages. The first mechanism: during the first stage, F108 exists as unimers distributed uniformly in water. Upon heating, the dehydration of the unimers takes place, and the micellization begins. The endothermic heat is used to remove the

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surrounding water molecules. In each micelle, PPO blocks are assumed to form the core, and PEO blocks are assumed to form the shell. The heat for micellization is detected, and this heat is a function of the polymer concentration. It is known that the heat for micellization is due to the dehydration, or destruction, of a cagelike water structure [Grunwald and Steel, 1995; Li et al., 2002]. However, at the end of micellization, there might be still some free unimers that are excluded from the micelles because there is no room in the existing micelles for them, but they should have been dehydrated already because the micellization heat is not detected beyond T_{off} of micellization. The further heating allows these free unimers to have enhanced mobility to meet together to form new micelles, but this process does not require additional energy as it is used to remove water molecules in the primary micellization process. As a result, the number of micelles will be increased from that at the end (i.e., T_{off}) of the primary micellization to that at $T_{G'}$. The increase in the number of micelles results in the increase of volume fraction of micelles in the water solution. This makes intermicellar distances shorter and results in the ordering of micelles through intermicellar interaction potential to form a crystal network and exhibits as a gel. At the same time, a closer packing of micelles will also greatly enhance the intermicellar friction, which will result in a high G'' . This would explain why G'' has the same sharp transition at $T_{G'}$ as G' does. In this mechanism, the sizes of the micelles are constant, being independent of the temperature, while the number of micelle increases with increasing temperature.

In other mechanism, we propose that the sizes of micelles can be changed by heating. During the second stage, all the polymer chains form micelles with similar

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sizes at a given temperature, but these micelles can become larger by further heating to the last stage. The increase in the micellar size for PEO-PPO-PEO triblock copolymers was reported by Mortensen. [Mortensen, 1992] As a similar effect on the increase in the number of micelles, volume fraction of micelles increased and the micellar distance will be shortened from the crystal network and friction will become possible. This mechanism is also able to explain the process from micellization to gelation. In fact, we believe that both mechanisms are possible.

8.5 Conclusions

The thermoreversible micellization and gelation of a PEO-PPO-PEO triblock copolymer (Pluronic F108) in water have been investigated as a function of the F108 concentration by means of micro-DSC measurements through a complete thermal cycle. A completely reversible thermal behavior has been observed for all the concentrations of F108 studied, ranging from 1 to 25 wt %. Each endothermic micellization curve in the heating process is a mirror image of its corresponding exothermic demicellization curve in the cooling process for a given concentration of F108. CMT decreases monotonously with increasing F108 concentration. A secondary peak has been observed beyond the primary peak for micellization only from high concentrations (22.5 and 25 wt %) of F108. This small but detectable peak indicates the sol-gel transition, and it has been further confirmed by rheological studies.

During the heating process, $T_{G'}$ is defined. Below $T_{G'}$, all the solutions are low-viscosity liquids with low values of G' . Upon heating, a steep increase in G' has

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been observed in the vicinity of $T_{G'}$. $T_{G'}$ can be approximately expressed by $T_{G'} = 72.9 - 1.65c$, where c is the F108 concentration. From CMT, T_{off} , and $T_{G'}$, a phase diagram has been obtained, which indicates that the micellization is not consistent with $T_{G'}$. However, $T_{G'}$ is not always an indication of the sol-gel transition when the polymer concentration is lower than 22.5 wt %. The scaling in the elasticity evolution with the concentration at 70 °C has been examined. When G'_{70} is used to indicate the elasticity evolved at 70 °C, the elasticity can be approximately expressed as $G'_{70} \sim c^{4.8}$. It has been found that 22.5 wt % is a critical concentration for the transition from a micellar system to a gel-like system. The elastic-dominant gel of F108 is formed only when the F108 concentration is equal to or higher than 22.5 wt %. The secondary endothermic peak found from the high concentrations (22.5 and 25 wt %) of aqueous F108 solutions are quite consistent with their $T_{G'}$'s. On the basis of these results, two mechanisms of the gelation of F108 have been proposed.

Chapter 9

Effects of a PPO-PEO-PPO Triblock Copolymer on Micellization and Gelation of a PEO-PPO-PEO Triblock Copolymer in Aqueous Solution

9.1 Introduction

9.1.1 Overview

The phase diagrams of both pure F108 ($\text{EO}_{133}\text{-PO}_{50}\text{-EO}_{133}$, Mw, 14600) [Molino et al., 1998] and 25R4 ($\text{PO}_{19}\text{-EO}_{33}\text{-PO}_{19}$) [D'Errico et al., 2004] have been available in literature. Molino et al. reported a phase diagram for F108, obtained using SANS and SAXS experiments, which showed that above 18 wt% of F108, a solid phase is formed upon heating [Molino et al., 1998], while a micellar liquid exists below 18 wt% and above the CMC. In our previous studies on F108 by means of micro-DSC and rheology, a phase diagram for the aqueous F108 system was also obtained [Lau et al., 2004]. We found that a gel was formed only at high concentrations and the gelation temperature was always higher than the offset temperature of micellization, indicating that the micellization is a precursor, followed by the gelation. [Lau et al., 2004]

No reports have been found to study a mixture of a Pluronic copolymer and a Pluronic-R copolymer in water. It will be interesting to know how the two end PPO blocks of a PPO-PEO-PPO copolymer will affect the micellization and gelation behavior of a PEO-PPO-PEO copolymer in aqueous solution. As the PPO blocks in

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both Pluronics and Pluronics-R are of the same chemical structure, it is reasonably assumed that the PPO blocks of PPO-PEO-PPO molecules will take part in the micellization of PEO-PPO-PEO molecules and vice versa. In the present work, F108 and 25R4 were used to make a mixture solution with various molar ratios of 25R4 to F108, and the interactions between F108 and 25R4 have been studied as a function of temperature and mixture composition by means of micro-DSC and rheology. The thermal and rheological results will be shown in this report and the possible mechanisms of micellization and gelation as well as the microstructures will be proposed and discussed.

9.1.2 Rheological properties of PEO-PPO-PEO

The rheological properties of PEO-PPO-PEO copolymers have been reported to be complex [Habas et al., 2004]. At high temperatures, the zero-shear viscosity of a PEO-PPO-PEO aqueous solution can diverge to result in gelation. The storage modulus G' of the gel can be as high as the corresponding loss modulus G'' , which is a very different feature from other hydrogels. For example, the hydrogels formed from aqueous solutions of methylcellulose show that the value of G' is several decades larger than that of G'' [Li, 2002]. This is due to the difference in microstructure between Pluronics and methylcellulose gels. Using SANS and SAXS, it is confirmed that the gelation of Pluronics is achieved by the micellar crystallization, which is to transform a disordered micellar liquid into an ordered micellar lattice [Perreux et al., 2002]. However, the classical, physical gelation is often induced by hydrophobic association, followed by the formation of a network across the whole span of the system [Li, 2002].

9.2 Experimental

9.2.1 Materials

Four concentrations (7.5, 10, 15 and 18 wt %) of F108 were prepared with deionized water from the Millipore water purifier. To each concentration of F108, different amounts of 25R4 were added by following the 25R4/F108 ratio from 1:2 to 4:1. For ease of recording, each ratio was denoted by a capital letter as shown in Table 9.1. The samples solutions were placed into a refrigerator and kept for 24 hours before use. Since the mixture solutions of F108 and 25R4 had better solubility at room temperature than that at the lower temperature in a refrigerator, the samples were first kept at room temperature for 30 min before testing. All the solutions were clear and homogeneous at room temperature around 25 °C.

9.2.2 Micro-thermal analysis

A micro-differential scanning calorimeter (VP-DSC Microcalorimeter, Microcal Inc.) was used to determine the thermal properties of the solutions through a thermal cycle of heating-to-cooling.

9.2.3 Rheological measurements

The rheometer (ARES 100FRTN1, Rheometric Scientific) with a geometry of parallel plates was used.

All the dynamic viscoelastic measurements (e.g. temperature ramp) were carried out at an angular frequency of 1 rad/s. The samples in the liquid state was first loaded to the bottom plate of the rheometer at room temperature and tested

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through a temperature ramp mode, in which G' and G'' were measured during a heating process from about 20 to 83 °C. The heating rate was adjusted to be about 1 °C/min, which was similar to that used in micro DSC measurements. Large strains ($> 5\%$) were applied before the vicinity of the sharp increase of G' and G'' to meet the minimum torque requirement that the transducer could detect, while from the sharp increase of G' and G'' (i.e. the sol-gel transition), the strains applied were adjusted to be below 1 % gradually to ensure the gel like sample was tested in the linear region of viscoelasticity.

9.3 Results and discussion

Figure 9.1 Relative thermal capacity C_p as a function of temperature for a 13.2 wt% solution of 25R4 during two thermal cycles A and B from heating to cooling at a scanning rate of 1 °C/min.

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9.3.1 Thermal behavior of 25R4

Before adding 25R4 into a F108 solution, we need to know the thermal behavior of 25R4. No reports have been found from literature on micro thermal properties of 25R4. To verify if 25R4 is thermally reversible, two thermal cycles A and B from heating to cooling at a scanning rate of 1 °C/min were applied by means of micro DSC to a concentrated solution (13.2 wt%) of 25R4. 13.2 wt% was the highest concentration of 25R4 in the F108/25R4 solutions used in this study. The results are given in Figure 9.1. In the first heating process (A), the solution shows a significant and relatively broad endothermic peak from 30 to about 50 °C, which is considered to be due to the hydrophobic aggregation of 25R4 upon heating. However, in the subsequent cooling process, no detectable exothermic peak(s) are obtained. We consider that the phenomenon is attributed to the precipitation of 25R4. The 25R4 precipitates could not be fully dissolved through the short period of cooling. Thus, in the subsequent second heating process (B), no significant endothermic peak(s) could be detected. The same behavior as that in the first cooling process is observed in the second cooling process. Therefore, we can conclude here that 25R4 is not thermoreversible at least at a thermal scanning rate of 1 °C/min.

Table 9.1 Symbol illustration for the molar ratio of 25R4/F108.

Symbol	P	A	B	C	D	E
Molar ratio of 25R4/F108	Pure F108	1:2	1:1	2:1	3:1	4:1

Figure 9.2 Thermoreversibility shown by the calorimetric thermogram for 10 wt% F108 aqueous solutions without and with 25R4. P curves stand for the pure 10 wt% F108 sample, while the C and E curves do for the 10 wt% F108 solutions containing 25R4 with a molar ratio of 25R4/F108 = 2:1 and 4:1 respectively. Heating and cooling rates are 1 °C/min.

9.3.2 Thermal reversibility of F108/25R4 solutions on heating and cooling

Being different from a pure 25R4 solution, the complete thermoreversibility has been verified for all the F108/25R4 solutions used in this study. An example is given in Figure 9.2 to show the thermoreversibility determined at for 10 wt% F108 aqueous solutions without and with 25R4. The relative thermal capacity C_p was employed throughout this report, with regard to the nature of the DSC, which always measures a relative heat between the sample and the reference. In Figure 9.2, the curve for the pure 10 wt% F108 sample, as well as the curves for the 10 wt%

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F108 samples containing 25R4 with the molar ratios of 25R4/F108= 1:2 and 4:1 are shown. The endothermic curves above the baseline were obtained on heating while the exothermic curves below the baseline were determined on cooling. The endothermic and exothermic peaks are attributed to the micellization and demicellization of F108 respectively [Lau et al., 2004]. As shown in the figure, the endothermic and exothermic curves are the mirror images along the baseline for each sample, indicating a complete thermoreversibility. However, the peak temperatures of the cooling curves are slightly (1.2-1.6 °C) lower than those observed in the heating process. Such a phenomenon is considered to be due to a kinetics difference between the micellization and demicellization of F108. We also note that the thermoreversibility is not affected by the addition of 25R4. The thermoreversibility means that 25R4 did not precipitate in the heating process due to the presence of F108. In other words, F108 prevents 25R4 from precipitation. Thus, it is expected that the complete thermoreversibility is attributed to the constructive interaction between F108 and 25R4. The effects of 25R4 on the micellization and demicellization of F108 will be discussed later.

Table 9.2 Peak temperatures (°C) from micro-DSC curves determined from Figure 9.3.

Concentration of F108, wt%	symbol					
	P	A	B	C	D	E
7.5	28.4	27.8	27.5	27.2	26.6	26.0
10	26.2	25.8	25.6	24.6	23.7	22.5
15	22.7	21.8	20.8	19.3	16.8	
18	20.5	19.3	18.4	15.6	13.3

Figure 9.3a Normalized heating calorimetric thermographs for the 7.5 % F108 aqueous solutions without and with 25R4. P curves stand for the pure F108 solutions, while A to E curves do for the solutions with the 25R4/F108 mole ratios from 1:2 to 4:1.

Figure 9.3b Normalized heating calorimetric thermographs for the 10 wt %F108 aqueous solutions without and with 25R4. P curves stand for the pure F108 solutions, while A to E curves do for the solutions with the 25R4/F108 mole ratios from 1:2 to 4:1.

9.3.3 Effects of 25R4 on micellization of F108

Since the endothermic and exothermic curves are symmetrical, in this report we focus our discussion on the endothermic curves that reflect the micellization of F108 affected by 25R4. Figures 9.3a, 9.3b, 9.3c and 9.3d show the calorimetric thermographs obtained on heating for 7.5, 10, 15, and 18 wt% of F108 solutions containing various molar ratios of 25R4/F108 respectively. In these figures, P denotes the pure F108 solutions, and A is used for the samples with a F108/25R4 molar ratio of 2:1, B for 1:1, C for 1:2, and D for 1:3 and E for 1:4 respectively. The

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heating rates for all the experiments are 1 °C/min. At the high concentrations (15 and 18 wt %) of F108, the samples with the molar ratio E were not used because they were too viscous to be injected into the sample cell of micro DSC. Thus, we could not measure them.

The four concentrations of F108 chosen were relatively high, as we intended to study the range of properties from micellization to gelation. All the concentrations of F108 were above its CMC as reported by Alexandridis et al. [Alexandridis et al., 1994] and the two low concentrations (i.e. 7.5 and 10 wt %) were below the gelation concentration for the fcc closed packing crystalline structure to be developed [Molino et al., 1998].

Figure 9.3c Normalized heating calorimetric thermographs for the 15 % F108 aqueous solutions without and with 25R4. P curves stand for the pure F108

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solutions, while A to D curves do for the solutions with the 25R4/F108 mole ratios from 1:2 to 3:1.

Figure 9.3d Normalized heating calorimetric thermographs for the 18 % F108 aqueous solutions without and with 25R4. P curves stand for the pure F108 solutions, while A to D curves do for the solutions with the 25R4/F108 mole ratios from 1:2 to 4:1.

The following features are observed from Figure 9.3. (1) At a given concentration of F108, the endothermic peak shifts to left, the lower temperature side, showing a “salt-out” effect. (2) At the same time, the endothermic peak becomes higher and broader with increasing 25R4 (except for the series of 15 and 18 wt% F108 in Figure 9.3c & 9.3d where the peak does not increase further with 25R4). (3) A shoulder or even a secondary peak appears beside the primary micellization peak when the content of 25R4 is high.

The first feature is the most significant effect of 25R4 on the micellization of

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F108. The so-called “salt-out” effect is well known as the effect for the increase in the hydrophobicity of water by a salt. When the salt causes the salt-out effect, it is called a “salt-out” salt. If we assume that 25R4 does not directly participate in the formation of F108 micelles and it is fully dissolved in water, the hydrophilicity of water will be modified by 25R4. Since 25R4 is more hydrophobic than water, the mixing of 25R4 into water will result in a more hydrophobic solvent than pure water. Thus, F108 will form micelles earlier at a lower temperature.

The second feature of Figure 9.3 is the evidence that 25R4 has been involved in the micellization of F108. As well known, a Pluronic polymer forms micelles in water when the hydrophobic PPO blocks lose the surrounded water, which is called dehydration. Upon heating, the PPO blocks of both F108 and 25R4 can dehydrate gradually with increasing temperature. Since the total number of PPO blocks in a F108/25R4 solution is greater than that of a F108 solution without 25R4 at the same concentration of F108, the endothermic energy used in the dehydration of PPO blocks is increased with increasing 25R4. The participation of 25R4 in the micellization of F108 can be considered in the following way. Due to the limited length of EO blocks in 25R4, it would be unlikely that both PPO blocks of each individual 25R4 molecule could be incorporated into the same core formed primarily by the PPO blocks of F108. Otherwise, a looping geometry of 25R4 is required, but it is unfavorable thermodynamically. We suppose here that only one end block (PPO) of 25R4 is associated into the core of a F108 micelle, while the other end (PPO), connected to the F108 micelle by the PEO block of 25R4, is dangling in the solution. The PPO blocks of 25R4 dangling in the solution might be

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used in two ways: either by the hydrophobic association with other dangling PPO blocks or existing as the PPO block unimers dispersed in the solution. Another scenario we need to consider is the possibility of the two hydrophobic ends of 25R4 to be incorporated into two adjacent micelles of F108. However, this would be much less possible because the middle PEO block of 25R4 would be too short to link two adjacent micelles of F108.

The third feature of Figure 9.3 is considered to be due to a direct effect of 25R4 on the F108 micellization. The strong interaction between F108 and 25R4 molecules retards some F108 molecules to aggregate to form micelles. When the concentration of 25R4 is increased, this effect is increased too. As a result, the micellization of F108 is delayed or occurs at higher temperatures.

Figure 9.4a Peak temperature as a function of molar ratio of 25R4/F108 for four F108 solutions with 25R4. The concentrations of F108 were 7.5 wt% to 18wt%.

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Figure 9.4b the normalized peak as a function of molar ratio of 25R4/F108 for four F108 solutions with 25R4 temperatures in terms of the corresponding peak temperature for the pure F108 solutions.

Table 9.3 Enthalpy changes (Cal/L solution) calculated from micro-DSC curves in Figure 9.3 for various F108/25R4 solutions.

Concentration of F108, wt%	symbol					
	P	A	B	C	D	E
7.5	284	459	596	842	1065	1338
10	372	536	660	996	1265	1558
15	559	793	1017	1386	1788	-
18	696	913	1174	1758	2192	-

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9.3.4 Effects of 25R4 on micellization peak temperature and enthalpy

The peak temperatures of F108 micellization obtained from Figure 9.3 were plotted against the molar ratio of 25R4/F108 in Figure 9.4a. The peak temperature in a DSC curve indicates the temperature at which the maximum rate of heat flow occurs. The values of all the peak temperatures are listed in Table 9.2. For each concentration of F108, all the data could be well fitted to a straight line, indicating a linear decrease of the peak temperature with the molar fraction of 25R4 in the solutions. In addition, the slopes of the straight lines increase with F108 concentration. That is, at a given molar ratio of 25R4/F108, the reduction of the peak temperature becomes more significant with increasing F108 concentration. This phenomenon proves that 25R4 has been involved in the formation of micellar core structures of F108. It seems that 25R4 can facilitate F108 to form micelles and this effect can be enhanced by increasing either the molar ratio of 25R4/F108 or F108 concentration. As the F108 concentration increases, the straight line shifts down to lower temperatures with a steeper slope. Thus, 25R4 shows a stronger effect at lower temperatures for a higher concentration of F108. From the results, it is considered that 25R4 should have the stronger interaction with F108 at lower temperatures than that at higher temperatures, which may be dominated by a phase diagram. The normalized peak temperatures are shown in Figure 9.4b just for making the feature of 25R4 effect at different loadings of F108 clearer.

Figure 9.5 Endothermic enthalpy changes for micellization, which were normalized for 1 L solutions, as a function of molar ratio of 25R4/F108 for four F108 solutions (7.5, 10, 15, and 18 wt%) containing 25R4.

Figure 9.5 shows the endothermic enthalpy changes for the same F108/25R4 solutions illustrated in Figures 9.3 and Figure 9.4. The enthalpy changes were calculated directly by integrating the endothermic peaks in Figure 9.3 over temperature. The values of enthalpy changes were then normalized for 1 L of sample volume by multiplying the original data by a factor of 1000mL/0.516mL where 0.516ml was the sample volume. The values of all the enthalpy changes are listed in Table 9.3.

As described before, two events (micellization and gelation) can occur upon heating of a F108 aqueous solution if the F108 concentration is high enough. We have found from our previous study that the heat is predominately consumed in the

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micellization while the gelation is a nearly athermic process [Lau et al., 2004]. In a heating process, the heat is used to break the cage-like ordered water structure to explore the hydrophobic blocks that will associate into micelles. However, as the gelation of F108 is achieved primarily through the arrangement of micelles in the solution into a crystalline lattice structure induced by the interaction via repulsion between the solvated chains forming the micellar corona or the formation of intermicellar entanglements, there is no considerable heat effect involved. Thus, the discussion about the heat effect can be confined to the micellization process.

It is found in Figure 9.5 that the total heat absorbed by a F108/25R4 solution with the same concentration of F108 is proportional to the molar ratio of 25R4/F108, which could be fitted to a respective straight line. Thus, the endothermic heat is a linear function of 25R4 at a given concentration of F108. It is also noted that the higher the concentration of F108 is the more heat is absorbed. Similarly to the peak temperature lines in Figure 9.4, the slope increases with increasing the concentration of F108. This indicates that with increasing the mass of F108 in solution, the interaction between 25R4 and F108 is enhanced so that more heat is required to break up the interaction between 25R4 and F108 in order for them to undergo the thermal hydrophobic association. This phenomenon can also be explained by the more hydrophobic environment (caused by both F108 and 25R4) in a more concentrated solution, which should require more “water cages” to be formed to surround the hydrophobic groups before micellization. Another hypothesis is that the extra heat is consumed by the secondary hydrophobic association of the PPO blocks from the F108 unimers affected by 25R4 and/or the

dangling PPO blocks of 25R4.

Figure 9.6 Storage modulus G' and loss modulus G'' as a function of temperature for aqueous solutions of 18 wt% F108 with various molar ratios of 25R4 at a heating rate of 1 °C/min and an angular frequency of 1 rad/s. P curve stands for the pure 18 wt% F108 sample, while A to E curve do for the solutions with 25R4/F108 molar ratios from 1:2 to 3:1.

9.3.5 Viscoelastic behavior on heating

Figure 9.6 shows the temperature-dependent dynamic viscoelastic properties (i.e. storage modulus G' and loss modulus G'') of an 18 wt% F108 solution with various contents of 25R4 at the heating and cooling rates of 1 °C/min and at an angular frequency of 1 rad/s. The rheological properties for the less concentrated solutions of 7.5 to 15 wt% are not studied here because they could not form strong gels. As shown in Figure 9.6, for the 18 wt% F108 solutions added with 25R4, there are at least three distinct regions for each molar ratio of 25R4/F108. The first region is

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before the sharp increase of both G' and G'' , where G' is below G'' , showing a common viscoelastic behavior of a liquid. In this region, G' and G'' slowly increase with temperature, indicating a continuous formation of micelles in the system. After then, the sharp increase of both G' and G'' is observed at about 31 °C for the pure F108 solution and for the solutions with the small 25R4/F108 molar ratios (= 1:2 and 1:1). The crossover of G' and G'' also occurs in this region. For the solutions of C, D and E, surprisingly, the temperatures at which G' and G'' increase sharply shift to the elevated temperatures by more than 20 °C. This region is known as the sol-gel transition region because the micelles start to form a structured network or lattice structure that will contribute to the high elasticity represented by a G' plateau. Beyond the transition region, G' becomes superior to G'' , while G' and G'' both reach their own plateaus.

The temperatures at the crossover points of G' and G'' were obtained directly from Figure 9.6 and plotted in Figure 9.7. If we define the crossover temperature as the gel point, it is interesting to note that the gel point is almost constant (or somewhat decreasing with the ratio) until the 25R4/F108 ratio of 1. The sudden increase in the gel point is shown at the 25R4/F108 ratio of 2. Beyond the ratio of 2, however, the slight decrease is shown again. We will explain this result in the later text.

We also note that the G' values of C, D and E in the plateau region, which indicate the mechanical strength of the gels, are lower than those for P, A and B. By considering both the rheological and the thermal properties, we further discuss the micellization and gelation behaviors of F108, which are influenced by 25R4.

Figure 9.7 Temperature at the crossover point of G' and G'' as a function of molar ratio of 25R4/F108 for an aqueous solution of 18 wt% F108.

Figure 9.8 C_p , G' and G'' as a function of temperature for aqueous solutions of 18 wt% F108. P curves stand for the pure F108 solution, while the D curves do for the F108 solutions containing 25R4 at a molar ratio of 25R4/F108 = 3:1.

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9.3.6 From micellization to gelation

To facilitate discussion, we have plotted C_p , G' and G'' against temperature in Figure 9.8 only for the 18 wt% F108 solutions P and D as they could represent the most important features of the F108/25R4 system studied. Let's look at the case of the pure F108 solution first. The sharp micellization peak appears at around 21 °C, and it ends at about 31 °C. On the other hand, the sharp increase in G' and G'' for gelation occurs near 31 °C. From these results, it may conclude that the micellization and gelation of F108 do not occur simultaneously. However, it should be noted that the gelation is not a process independent of the micellization. On the contrary, it is believed that the gelation should be dependent on the number and sizes of micelles as well as the possible bridges formed among the micelles. The similarity is also observed for all other samples. For example, for the sample D in Figure 9.8, although there is the broad endothermic peak with a second peak over the temperature range from 5 to 60 °C, C_p has become nearly zero at the transition temperature 55 °C for G' and G'' . There is not a detectable endothermic or exothermic peak for gelation. This result also proves that the gelation is a nearly athermic process, which is not changed by addition of 25R4. However, we should note that there is a long tail of the DSC peak for the sample D, which may be evidence that some micelles are still being formed in the vicinity of gelation, proving that the gelation is closely related to the micellization.

Before the sol-gel transition for all the samples studied, we do not consider that any network structures can be formed between F108 and 25R4 because G' is much smaller than G'' . For the pure F108 aqueous solutions, their gelation (or

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crystallization) mechanisms have been reported in the previous works. [Lau et al., 2004; Molino et al., 1998] However, the function of 25R4 in the micellization and subsequent gelation of F108 is complicate because 25R4 can cause at least three notable effects on the thermal and rheological properties of F108: namely (a) the salt-out like effect that makes the micellization occur at lower temperatures; (b) the appearance of a second peak or a shoulder in the endothermic peak; and (3) the delay of gelation.

For the effect (a), in the early part of this report we have used the change in solvent hydrophobicity, which is caused by adding 25R4 as a co-solvent, to explain the salt-out effect. The appearance of the second peak or the shoulder can be related to the delay of gelation. Here we use a schematic diagram to explain the possible mechanism involved in the micellization to gelation process.

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Figure 9.9 Schematic diagram for the mechanisms of micellization to gelation for a F108/25R4 solution. The thinner and thicker solid lines used for the molecular chains of F108 and 25R4 represent the PEO and PPO blocks respectively. The left route shows the micellization and gelation for the solutions with $25R4/F108 \leq 1$, while the right route shows the micellization and gelation for the solutions with $25R4/F108 > 1$. The solid arrows indicate the hydrophobic association of PPO blocks of 25R4, resulting in the bridged micelles.

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In Figure 9.9, the effects of 25R4 are considered to be different when the 25R4/F108 ratio is below 1 (including 1) and above 1 respectively. When the ratio ≤ 1 , 25R4 does not have the significant effect on the micellization of F108 and the 25R4/F108 solution shows the micellization and gelation behavior similar to a pure F108 solution. However, some of 25R4 molecules may be included in the micellar structures of F108, but there are no bridges of 25R4 to be formed between F108 micelles. At high temperatures, the F108 micelles will be packed into regular crystal-like network structures, which is the same as what a concentrated F108 solution can form.

On the other hand, when the molar ratio of $25R4/F108 > 1$, 25R4 has stronger interaction with F108 so that two kinds of effects may occur: (a) the enlarged micellar size due to the increased hydrophobicity of the solvent and the more PPO blocks available and (b) the formation of intermicellar bridges by the dangling 25R4 PPO blocks from the micelles. These 25R4 bridges may exist between two or a few F108 micelles, but they can retard the regular packing of F108 micelles. To be possible to pack the F108 micelles, these bridges of 25R4 have to be broken up at higher temperatures. As a combined effect, the secondary peak (or shoulder) appears and the gelation is greatly delayed. When these intermicellar bridges have been destroyed, the similar crystal-like network structure will be formed eventually.

In Figure 9.9, in both cases ($25R4/F108 > 1$ and < 1) the final microstructures are indicated by the ordered micelles structure for convenience. However, it should be noted that the real microstructure derived from each case would not be supposed to be identical as their compositions are different in terms of the content of 25R4.

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The lower G' plateaus beyond the gel point for the solutions with the high ratios of 25R4/F108 can be explained by the less perfection of crystalline structures of F108 formed under the influence of 25R4.

9.4 Conclusions

We have investigated the thermoreversible micellization and gelation for a mixture of PEO-PPO-PEO triblock copolymer (Pluronic F108) and PPO-PEO-PPO (Pluronic-R 25R4) in water as a function of mixture composition by means of micro-DSC and rheological measurements. A completely reversible thermal behavior has been observed for all the compositions. Three effects of 25R4 on micellization and gelation of F108 have been identified. The first effect is that 25R4 always shows a “salt-out” like effect on the micellization of F108, which reduces the critical micellization temperature (CMT) of F108 as a linear function of 25R4 content. The second effect of 25R4 on the micellization of F108 is the broadening of the micellization peak and the appearance of a secondary peak or shoulder. This effect is explained by the formation of the larger F108/25R4 aggregates consisting of several micelles of F108 linked with 25R4 chains. The total enthalpy required for micellization increases linearly with 25R4 content at a given concentration of F108. The third effect is the delay of gelation by 25R4 when the content of 25R4 is high. This effect is a consequence of the second effect. In other words, to form a crystal-like network from the micelles of F108, the 25R4 bridges linking F108 micelles have to be removed, leading to the difficulty in gelation or the delay of gelation. A schematic diagram has been made to explain the effects of 25R4.

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Conclusions and Recommendation for Future Work

10.1 Thermoreversible gelation of MC in water

Thermoreversible gelation and scaling of methylcellulose (MC) in aqueous solutions have been investigated using micro DSC and rheology with a specific interest in finding the effect of molecular weight. All the MC aqueous solutions exhibited excellent thermoreversible gelation behavior. It is found that all the typical thermal transitions (gelation and degelation) of MC in water are independent of either polymer concentration or molecular weight. The total energy consumed in the sol–gel transition is a linear function of polymer concentration, but changing of molecular weight does not change the total energy at a given polymer concentration.

The effect of molecular weight on the evolution of gel elasticity was also examined. By comparing three molecular weights (from 100,000 to 400,000) of MC, the quasi-equilibrium modulus G_e was observed to increase with increasing molecular weight and the different scaling relations are found. The mechanisms for the results have been explained in detail.

The binding interactions between MC (SM4000) and SDS were studied by isothermal titration calorimetry, the temperature effect was discussed. At low temperature (25 °C), the titration curve can be divided into four zones. The first zone starts at initial injection and ends at CAC, where only dilution of SDS micelles and non-cooperative binding of small amount of SDS onto the MC backbone and/or hydrophobic groups take place. The deviance of the titrating curve from the dilution

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curve at this region could also be caused by the change of solvent environment by the addition of SDS, even without the interaction between SDS and MC. The second zone starts at CAC till the end of the endothermic peak, where the cooperative binding of SDS to MC molecules occurs and results in complex micelles. The third zone starts at the end of the endothermic peak and the onset of the exothermic peak, where the aggregation complex reorganizes its structure via ion-dipole interaction. The fourth zone starts at C2, where free SDS micelles start forming without the participation of MC; the reorganized aggregate complexes formed previously coexist in the system. With increasing temperature, the hydrophobicity of MC is increased. The predominately cooperative binding at low temperatures gradually changed to the predominately non-cooperative binding. The shape of the titration curve shows the drastic changes. The extent of the association between SDS and MC is strengthened, and C2 increased with increasing temperature.

Following the study on the binding of SDS to MC, the effect of SDS on the gelation of MC was also studied.

In this work, the optical (i.e. turbidity), micro thermal, and rheological properties of methylcellulose (MC, SM4000, $M_w = 310,000$) aqueous solutions with various concentrations of SDS have been measured and the effects of SDS on the sol-gel transition of MC were investigated systematically. It was found that the effects of SDS on the turbidity of a MC solution are different, depending on the SDS concentration. The salt-out and salt-in effects are observed at the low (≤ 6 mM) and high (> 6 mM) concentrations of SDS respectively. For example, when

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SDS > 6 mM, a significant delay of gelation is observed, this is the so-called salt-in effect. A critical concentration of SDS for the transition from the salt-out to the salt-in effects is found to be about 6 mM, which is a critical association concentration (CAC) of SDS. For the salt-out and salt-in effects of SDS, the consistency among the optical, thermal and rheological results has been verified.

Addition of SDS to a MC solution changes the pattern of MC gelation and a two-step gelation of MC is observed especially at the high concentrations (> 8 mM) of SDS. A bimodal endothermic peak was observed for the two-step gelation of MC. The two-step gelation has been explained using the mechanism based on the SDS cages. The SDS cages are formed to surround the hydrophobic units of MC and these SDS cages have to be disrupted at high temperatures. The first-step gelation occurs through the association of the hydrophobic units of MC, which are not caged at low temperatures by SDS, whereas the second-step gelation does through the association of the hydrophobic units of MC that are exposed at high temperatures from the SDS cages.

Lastly, the effect of magnetic field on the sol-gel transition of MC was also studied. It is observed that the presence of a moderately strong magnetic field (0.2 ~ 0.3 T) does affect the sol-gel transition of a methylcellulose aqueous solution and a salt-out like effect is found. The above phenomenon was proposed to be due to the effect of a magnetic field on the hydrogen bonds and the cage-like water structure. The magnetic field weakens hydrogen bonds or promotes the destruction of the cage-like water structure to result in an earlier hydrophobic association of MC. The similar results were found in the MC aqueous solutions containing various contents

of NaCl. However, the effects of the magnetic field and NaCl on the sol-gel transition of MC are independent with each other.

10.2 Thermoreversible gelation of Pluronics in water

The thermoreversible micellization and gelation of a PEO-PPO-PEO triblock copolymer (Pluronic F108) in water have been investigated as a function of the F108 concentration by means of micro-DSC measurements through a complete thermal cycle. A completely reversible thermal behavior were observed for all the concentrations of F108 studied, ranging from 1 to 25 wt %. Each endothermic micellization curve in the heating process is a mirror image of its corresponding exothermic demicellization curve in the cooling process for a given concentration of F108. CMT decreases monotonously with increasing F108 concentration. A secondary peak has been observed beyond the primary peak for micellization only from high concentrations (22.5 and 25 wt %) of F108. This small but detectable peak indicates the sol-gel transition, and it has further been confirmed by rheological studies.

During the heating process, $T_{G'}$ is defined as the temperature for the transition in G' . Below $T_{G'}$, all the solutions are low-viscosity liquids with low values of G' . Upon heating, a steep increase in G' has been observed in the vicinity of $T_{G'}$. $T_{G'}$ can be approximately expressed by $T_{G'} = 72.9 - 1.65c$, where c is the F108 concentration. From CMT, T_{off} (temperature at which the micellization ends) and $T_{G'}$, a phase diagram has been obtained, which indicates that the micellization is not consistent with $T_{G'}$. However, $T_{G'}$ is not always an indication of the sol-gel transition when the

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polymer concentration is lower than 22.5 wt %. The scaling in the elasticity evolution with the concentration at 70 °C has been examined. When G'_{70} is used to indicate the elasticity evolved at 70 °C, the elasticity can be approximately expressed as $G'_{70} \sim c^{4.8}$. It has been found that 22.5 wt % is a critical concentration for the transition from a micellar system to a gel-like system. The elastic-dominant gel of F108 is formed only when the F108 concentration is equal to or higher than 22.5 wt %. The secondary endothermic peak found from the high concentrations (22.5 and 25 wt %) of aqueous F108 solutions are quite consistent with their T_G 's. On the basis of these results, mechanism of the gelation of F108 has been proposed.

Lastly the thermoreversible micellization and gelation for a mixture of PEO-PPO-PEO triblock copolymer (Pluronic F108) and PPO-PEO-PPO (Pluronic-R 25R4) in water as a function of mixture composition by means of micro-DSC and rheological measurements were studied. A completely reversible thermal behavior has been observed for all the compositions. Three effects of 25R4 on micellization and gelation of F108 have been identified. The first effect is that 25R4 always shows a “salt-out” like effect on the micellization of F108, which reduces the critical micellization temperature (CMT) of F108 as a linear function of 25R4 content. The second effect of 25R4 on the micellization of F108 is the broadening of the micellization peak and the appearance of a secondary peak or shoulder. This effect is explained by the formation of the F108/25R4 big aggregates consisting of several micelles of F108 linked with 25R4 chains. The total enthalpy required for micellization increases linearly with 25R4 content at a given concentration of F108. The third effect is the delay of gelation by 25R4 when the content of 25R4 is high.

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This effect is a consequence of the second effect. In other words, to form a crystal-like network from the micelles of F108, the 25R4 bridges linking F108 micelles have to be removed, leading to the difficulty in gelation or the delay of gelation. Recommendation on the future work

10.2.1 Non-linear viscoelastic properties of MC and Pluronics gels

Despite the large amount of work on the gelation systems of MC and Pluronics, the rheological studies on the non-linear viscoelastic properties of the polymeric gels are not adequate. The comparison of viscoelastic properties of a percolation network and a crystalline network has not been studied in detail. Rheology is especially useful to study the phase behaviors and structure of polymer gels as it is able to operate on the samples on their whole temperature range. The rheological studies on Pluronics gels are mostly carried out using static shearing method, in order to understand the aligning behavior of the crystal structure. Dynamic rheological study of the ordered phase is not adequate. As a liquid crystalline structure made up of micellar network, the viscoelastic properties such as elastic modulus are not explained well in terms of its origin. Existing literatures on the rheological aspect of Pluronics and other triblock/diblock systems discuss mostly the dynamic modulus G' and G'' as a function of oscillating frequency ω , in order to obtain the phase diagram. The shear stress relaxation technique is not fully used. Stress relaxation experiments are valuable method for the investigation of non-linear viscoelasticity in concentrated polymeric systems. Single-step and double-step shear strain relaxation tests can be used to probe the relaxation of Pluronics gels. A fast relaxation and a slow relaxation are expected to be detected.

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10.2.2 Micro-structure of MC and Pluronics gels

The microscopic study on the micro-structure of MC is difficult due to the low content of polymer in the predominately water system. Another barrier to conduct microscopic study on the gels formed by hydrophobic association is due to their unique phase behaviors in terms of the fact that the gels are formed at elevated temperature while dissolve at room temperature, which makes the conventional drying technique inapplicable. Freeze-drying is a promising technique to prepare samples containing only the polymer backbones of a MC network by evaporating the large amount of water in frozen state from the original gel. In this way, the micro-structure of the polymer network without the presence of water can be probed by scanning electron microscopy (SEM). Special attention is needed to avoid the collapse of the backbone structure during freeze-drying as well as during the other pre-treatment of the samples before SEM test. Using the SEM, the understanding to the micro-structure of the junctions in the polymeric network will be greatly improved.

The microscopic study on the Pluronics hydrogels can be done using small angle x-ray scattering (SAXS) and transmission electron microscopy (TEM) technique. Certain staining procedure is supposed to be done to make the TEM image more visible. For systems containing only PEO-PPO-PEO, the effects of polymer concentration and temperature on the structure, especially the size of the micelles can be studied. For systems containing both F108 and 25R4, the effect of the ratio of 25R4/F108 on the micellar structure, as well as the crystal structure can also be investigated.

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