Interactions between amphiphilic polymers and cyclodextrins

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2007

Liao, D. S. (2007). Interactions between amphiphilic polymers and cyclodextrins. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/35990>

<https://doi.org/10.32657/10356/35990>

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Interactions Between Amphiphilic Polymers and Cyclodextrins

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School of Mechanical and Aerospace Engineering

A Thesis Submitted to the Nanyang Technological University

in Fulfillment of the Requirement for the

Degree of Doctor of Philosophy

2007

ABSTRACT

The solution properties of various types of telechelic hydrophobically modified ethylene oxide urethane polymer (HEUR) in the presence of cyclodextrins were examined.

Methylated β -cyclodextrin (m- β CD) could effectively reduce the steady shear viscosity and the dynamic moduli of HEUR aqueous solutions. It was found that m- β CD interacts with HEUR in three progressive steps. At very low m- β CD concentrations, m- β CD encapsulates the hydrophobes of looping HEUR chains, which destabilizes the transient network, while maintaining the number of mechanically active chains. However, the m- β CD/HEUR complex solutions become more sensitive to shear stress. At moderate m- β CD concentrations, m- β CD begins to deactivate the bridging chains resulting in a reduction in the number of mechanically active chains and this further weakens the transient network. Finally, when m- β CD is in excess, the network Methylated β -Cyclodextrin could effectively reduce the steady shear viscosity and dynamic moduli of HEUR aqueous solutions.

α -Cyclodextrin was found to reduce the steady shear viscosity and dynamic moduli of HEUR aqueous solutions. However, rheological studies revealed some subtle differences between α -CD/HEUR and m- β CD/HEUR system. For the m- β CD/HEUR system, the temperature dependence of low shear viscosity can be described by Arrhenius equation. On the other hand in α -CD/HEUR system, the low shear viscosity $\sim$ temperature relationship does not follow the Arrhenius relationship, where the viscosity increases with increasing temperature within a defined temperature range, Exhibiting a unique viscosity recovery at elevated temperature. The transient hydrophobic network, which is suppressed by the addition of α -CD is partially restored with increasing temperature, which is evident by dynamic mechanical measurements.

Cyclodextrin is capable of completely suppressing the hydrophobic association in HEUR solution, resulting in a viscosity identical to PEO solution of similar concentration. However, the addition of surfactant restores the viscosity and viscoelasticity. The magnitude of viscosity recovery depends on the types of cyclodextrins. With m- β CD, the viscosity only recovers partially, while for α -CD, the viscosity recovers almost completely. The difference between these two systems is attributed to the different binding interaction between CD and SDS molecules.

The interaction between methylated β -cyclodextrins and perfluorocarbon derivatives (F-HEUR) (C_6F_{13} and C_8F_{17}) of poly(ethylene glycol)s (PEGs) of molecular weights 20K and 35K g/mol was studied. The viscosity of F-HEUR solution is greatly reduced in the presence of methylated β -cyclodextrins, because of the disruption of intermolecular hydrophobic association. A multi-sites adsorption model was proposed for the first time to describe the relationship between G_N^0 and cyclodextrin concentrations. It is observed from ITC thermograms that the complex formation of methylated β -cyclodextrin and fluorocarbon group revealed a stoichiometry of 1 and 2 for C_6F_{13} and C_8F_{17} respectively. DLS results showed a different mechanism for C_6F_{13} and C_8F_{17} fluorocarbon hydrophobes, which are in agreement with the results determined from activation energies and ^{19}F -NMR spectra.

HEUR solutions became turbid when α -CD concentration is extremely high. Saturated α -CD solution was added into the polymer solution and the precipitates were recovered, and examined by DSC, TGA and XRD techniques. From TGA curve, it is evident that the heat stability of cyclodextrin is significantly enhanced in the presence of PEG. From DSC scan, the PEG crystalline is disrupted by the presence of CD, while XRD spectra indicate that α -cyclodextrin can pass through the carboxyl group and reside on PEO segment. Solid complex with channel structure was produced at high CD concentration. We observed that α -CD is not able to squeeze through the bulky IPDI segment on the backbone of PEG copolymer. Therefore no channel structure is observed for the mixture containing HM-PEG-IPDI and α -CD.

Acknowledgments

I would like to express my sincere gratitude to Professor Tam Kam Chiu for his continuous guidance, support and encouragement throughout the duration of this project. In addition, I wish to thank Drs. Dai Sheng, Yao Jia, P. Ravi and Wang Chang for their assistance and support. I also wish to extend my sincere thanks to all technical staffs and friends in Materials Laboratory, especially for their kind support. Lastly, I wish to acknowledge NTU for providing me the opportunity to pursue my PhD study and the financial supports from Dow Chemicals and Singapore-MIT Alliance (SMA), Singapore.

List of Publications

- (1) Liao, D. S.; Dai, S.; Tam, K. C., Rheological Properties of Hydrophobic Ethoxylated Urethane (HEUR) in the Presence of Methylated β -cyclodextrin, *Polymer*, 2004, 45, 8339-8438
- (2) Liao, D. S.; Dai, S.; Tam, K. C. Effect of Temperature on Interaction of Cyclodextrin and Telechelic Associative Polymers, *Polymer Preprint*, 2005, 46(1), 634-635.
- (3) Liao, D. S.; Dai, S.; Tam, K. C., Rheological Properties of Telechelic Associative Polymer in the Presence of α - and β -Cyclodextrins, *J. Phys. Chem. B*, 2006, 111(2), 371-378
- (4) Liao, D. S.; Dai, S.; Tam, K. C., Interaction between Fluorocarbon HEUR and Cyclodextrins, *Macromolecules*, 2007, 40, 2936-2945
- (5) Liao, D. S.; Dai, S.; Tam, K. C., Anomalous Rheological Properties of Telechelic Associative Polymer (HEUR) in the Presence of α -Cyclodextrin, *Langmuir* (submitted)
- (6) Liao, D. S.; Dai, S.; Tam, K. C., Surfactant Influences on the Cyclodextrin-HEUR Complex, (in preparation)

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List of Symbols and Abbreviations

A	A is the Arrhenius constant
A_2	Second virial coefficient
AP	Associative polymer
AT	Associative thickener
C	Concentration
C^*	Overlap concentration
C_2	Saturation concentration for polymer-surfactant systems
CAC	Critical aggregation concentration
C_m	Critical micellization concentration of surfactant in polymer solution
CD	Cyclodextrin
CMC	Critical micellization concentration
C_p	Heat capacity
CP	Control Polymer
D	Diffusion coefficient
D_0	Diffusion coefficient at infinite dilute solution
DLS	Dynamic light scattering
DIMEB	Dimethyl- β -cyclodextrin
DLS	Dynamic light scattering
dn/dc	Refractive index increment
E_a	Activation energy
E_m	Activation energy for disengagement
FT-IR	Fourier transform infrared spectrum
F-HEUR	Fluorocarbon HEUR
FITC	Fluorescein-4-isothiocyanate
GPC	Gel permeation chromatography
G_N^0	plateau modulus
G'	Elastic component of the complex shear modulus (i.e., storage modulus), [dyne/cm ²]
G''	Viscous component of the complex shear modulus (i.e., loss modulus), [dyne/cm ²]
HASE	Hydrophobically modified alkali soluble emulsion

HEC	Hydroxyethyl celluloses
HEUR	Hydrophobic ethoxylated urethane
HEURASE	Hydrophobically modified ethylene oxide urethane alkali-soluble/swellable emulsions
HMHEC	Hydrophobically modified hydroxyethyl celluloses
HMN	Hydrophobically modified nonionic non-urethanes
HM-PEO	Hydrophobically modified PEO
I	Light intensity
IPDI	Isophorone diisocyanate
ITC	Isothermal titration calorimetry
K	Equilibrium constant
k_B	Boltzmann constant (1.38×10^{-23} J/K)
k_D	Diffusion second virial coefficient
LLS	Laser light scattering
M_n	Number-averaged molecular weight
m- β CD	Methylated β -cyclodextrin
M_w	Weight-averaged molecular weight
MWD	Molecular weight distribution
n	Refractive index
N_0	Mean number of bridging chains per micelle
N_A	Avogadro constant (6.02×10^{23} /mol)
NaPSS	Poly(4-sodium styrenesulfonate)
N_{agg}	Aggregation number
NMR	Nuclear magnetic resonance
PA	Nylon-6
PCS	Photon correlation spectroscopy
PDI	Polydispersity index
PEG	Polyethylene glycol
PEO	Poly(ethylene oxide)
PG-NMR	Pulse gradient NMR
PMMA	Poly(methyl methacrylate)
PPG	Polypropylene glycol
PS	Polystyrene

PVC	Polyvinyl chloride
q	Scattering wave vector
R	Gas constant (8.31 J/molK)
REPES	Regularized positive exponential sum
R_g	Radius of gyration
R_h	Hydrodynamic radius
R_θ	Excess Rayleigh ratio at scattering angle θ
$S(q)$	Static structure factor
SDS	Sodium dodecyl sulfate
SLS	Static light scattering
T	Temperature
TGA	Thermogravimetric Analyzer
THF	Tetrahydrofuran
TRIMEB	Trimethyl- β -cyclodextrin.
UV	Ultraviolet
V	Volume
W	Well depth
ΔG	Gibbs free energy
ΔH	Enthalpy
ΔS	Entropy
θ	Scattering angle
ϕ	Volume fraction
$[\eta]$	Intrinsic viscosity
Γ	Decay rate
ν_{eff}	Number density of mechanically effective chains
ϵ	Dielectric constant
η	Viscosity
η_0	Low shear viscosity
$\dot{\gamma}$	Shear rate
σ	Shear stress
λ	Relaxation time
ω	Angular frequency

μ	Chemical potential
τ	Relaxation time
Θ	Fraction of hydrophobic polymeric segments that are capped with CD

Chapter 1. Introduction

1.1 Background

Associative polymers are hydrophobically modified water-soluble polymers. The polymer usually consists of a hydrophilic backbone with hydrophobic groups either located at the ends of the polymer chain or distributed along the polymer backbone. In aqueous solution, the hydrophobic groups of associative polymers tend to aggregate to reduce their interfacial area with water molecules. The hydrophobes on the polymer chain aggregate to a significant degree at a more or less well-defined concentration to yield a polymer network. This network provides viscosity far in excess of the polymer solution with similar backbone without hydrophobes.

Associative polymers are widely used as rheology modifiers in latex paints and many other applications. HEUR (hydrophobic ethoxylated urethane) offers the best balance of application rheology and dry film performance and are generally considered to be the premium products among the various commercial associative thickeners [Schaller and Sperry, 1992]. In addition to their commercial potential as rheology modifiers for waterborne surface coatings, such end-capped linear polymers are ideal systems for fundamental study. These thickeners are in essence amphipathic ABA block copolymers comprising short hydrophobic A chains blocked onto both ends of a long hydrophilic B chain. Recently, the transient network theory was developed to statistically model the dynamics and rheological behaviors of this type of reversible cross-linked polymer network typically found in HEUR associative polymer solutions [Annable et al., 1993]. In dilute solution, the association structures contain well-defined micelles formed by the aggregation of hydrophobic groups at the ends of looped chains, with dangling ends from chains with hydrophobic substitution

at one end. With increasing thickener concentration, a network consisting of connecting micelles linked to one another by bridging chains is formed, producing a larger network of polymeric chains, which is physical cross-linked by hydrophobic junctions. The rheological properties change significantly with the formation of three dimensional transient network.

Cyclodextrins (CDs) are well-known in supramolecular chemistry as molecular hosts capable of selective inclusion of a range of guest molecules in their hydrophobic cavities via noncovalent interactions. Cyclodextrin is a cyclic oligomer consisting of glucose units joined by α -1, 4-glycosidic linkages. The glucose units can be six, seven or eight, corresponding to α -, β - and γ -cyclodextrins respectively [Rusa et al., 2001]. It possesses the shape of a truncated cone with a hydrophilic exterior and a hydrophobic cavity, thus CD molecules tend to form inclusion complexes in aqueous solutions with systems containing lipophilic groups. Addition of cyclodextrins to aqueous solutions of associative polymer can suppress the viscosity of aqueous HEUR solution. In addition the viscosity suppressing function of the cyclodextrin compounds can be readily reversed, and restored by the addition of a surfactant. The hydrophobic association also makes it difficult to extract information, when characterizing the character of single chain, such as gel permeation chromatography (GPC). The removal of hydrophobic interaction would make it simpler and facilitate a better understanding on the physical property of these polymers.

The structural difference among α -, β - and γ -cyclodextrins imparts different physical properties and characteristics to the molecules and also their corresponding interaction with polymers. Adding α -cyclodextrin into PEG solution produces crystalline complex at stoichiometric proportion [Harada and Kamachi, 1990].

However, β -CD does not form complexes with PEG of all molecular weights. Harada found that β -CD and γ -CD formed complexes with poly(propylene glycol)(PPG) [Harada and Okada, 1999; Harada et al. 1993b] to produce crystalline complexes at high yields. But α -CD did not form complexes with PPG of different molecular weights. The complexes were characterized by IR, ^1H -NMR, ^{13}C -CP/MAS-MNR, and ^{13}C -PST/MAS-MNR spectra, X-ray (powder) diffraction, thermal and elemental analysis. In recent years, modern experimental and theoretical methodologies have provided new insights into the amphiphilic polymer/cyclodextrin systems. However, there are very few reported studies on the amphiphilic polymer and cyclodextrin interactions. In order to further elucidate the nature of amphiphilic polymer/cyclodextrin systems, a detailed study on the interaction between various amphiphilic polymers, such as hydrocarbon and fluorocarbon modified PEO and cyclodextrins using more precise and sensitive research tools are needed.

1.2 Objectives and Scope of Project

The main objective of this study is to obtain a molecular-level understanding on the interaction between amphiphilic polymer and cyclodextrins in solution. A considerable amount of work has been carried out using rheometry, isothermal titration calorimeter (ITC), and laser light scattering (LLS) techniques to elucidate the binding behaviors of these polymer/cyclodextrin systems. The solid complex was also characterized using XRD, DSC, TGA, and some other physical techniques.

The second objective is to achieve a better understanding on the association mechanism and associative structure of HEUR associative polymers in aqueous solution. By combining the results of different physical techniques, the binding mechanisms between various types of cyclodextrins and associative polymers will be

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elucidated. The characterization of single HEUR chain was achieved with the aid of cyclodextrin complexation, which is essential for exploring the association mechanism and structure of HEUR polymers.

The scope of the project involves examining the rheological properties of different molecular weights HEUR systems at various temperature regimes. Comparison between the interaction of cyclodextrins and partially or fully capped polyethylene-oxide systems will be investigated. The temperature dependence of viscosity for different cyclodextrin/polymer systems was also investigated. These interactions in aqueous solution were further investigated utilizing ITC and laser light scattering. Different hydrophobes (hydrocarbon or fluorocarbon) were introduced to the PEO chains. Their rheological properties were examined and their interactions with cyclodextrin were compared. The effect of surfactant on the interaction between HEUR and cyclodextrin were examined by conducting detailed rheological measurements. It is hoped that such studies could provide a molecular-level understanding on the interaction in a three-component system. Finally, the polymers were added to saturated α -CD solution and the solutions (or precipitate) were characterized by means of XRD, DSC and TGA to determine the influence of cyclodextrins on the crystalline and heat stabilities of hydrophobic modified PEO systems.

1.3 Overview of the Thesis

This thesis contains nine chapters. A brief introduction to this research work is given in Chapter 1. In Chapter 2, the basic theories and previous work of HEUR solution and cyclodextrin inclusion compound are discussed in the literature review. The experimental details, such as the basic operating principles and the measurement

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conditions of the equipment are described. The synthesis and characterization of well-defined hydrophobically-modified PEO polymer, sample preparations, materials and the optimization of the experimental condition are provided in Chapter 3. Chapter 4 presents a detailed study on the steady shear flow, viscoelastic properties of HEUR solution in the presence of methylated β -cyclodextrins. The relationship between rheological properties and the binding mechanism is discussed. The details of the interactions/microstructure of dilute and concentrated polymer solutions and cyclodextrins derived from light scattering data are proposed. Chapter 5 examines the steady shear flow, viscoelastic properties of HEUR solution in the presence of α -cyclodextrins. The different interaction mechanisms between α - and β - cyclodextrin are compared. The stimuli-responsive properties of α -cyclodextrin/HEUR system is observed and explored extensively. In comparison, a model polymer comprising of a hydrophobically end capped PEO with narrow molecular weight distribution and functionality of 2 (HM-PEO) was synthesized and the effect of α -CD on the rheological properties of HM-PEO was studied. Chapter 6 presents the effect of surfactant on the interaction of cyclodextrin and HEUR. Prior to the tri-component system, the dual systems of SDS/HEUR, SDS/cyclodextrin were investigated and finally the possible mechanism of the tri-component interaction is proposed. The mechanism is further proved from ITC and DLS measurements. In Chapter 7, rheological studies on the fluorocarbon modified PEO (F-HEUR) were carried out. A new adsorption model is introduced to interpret the experimental results. The modeling results are consistent with experimental data. Chapter 8 presents the characterization of solid complex using XRD, DSC, TGA and other complementary techniques. Some new phenomenon is analyzed. Chapter 9 concludes the thesis and recommends experiments for future study.

Chapter 2. Literature Review

The literature review is divided into four separate parts. The first part summarizes the self-assembly behavior of hydrophobically modified ethylene oxide (HEUR) in solution. The second part outlines the basic properties of cyclodextrins and their complexes with low molecular organic compounds. The third section reviews the recent development on the interaction between polymers and cyclodextrins. The fourth part introduces some major techniques used in the investigation of polymer and cyclodextrin interaction.

2.1 Amphiphilic polymer

2.1.1 Basic theory of associative thickener

Water-soluble, hydrophobically modified polymers are increasingly being used in a wide range of industrial application, including paint formulation and paper coatings. In paint formulation, these polymers are used as thickener to increase the low shear viscosity, to prevent pigment settling during storage, and to instill a suitable pseudoplastic and thixotropic behavior for proper application at high shear rates.

Before the commercial introduction of associative thickeners, the cellulose derivatives, especially the cellulose ethers are predominantly used in the paints industry [Tothill and Seal, 1993; Croll and Kleinlein, 1986]. Although the cellulose ethers have been the standard thickeners in the latex paint industry for about four decades, they have been unable to provide latex paints with the application and appearance properties of solvent-based alkyd paints. Leveling of brush marks is impeded by high viscosity at low shear rates, while film build, important for both hiding and protection of the substrate, is limited by low viscosity at high shear rates.

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Gloss development is hindered by the tendency of the conventional cellulosic thickeners to flocculate latex formulations [Sperry, 1984; Thibeault et al., 1984]. High molecular weight cellulose ether thickeners also cause paints to spatter excessively when applied by roller because of the chain entanglement [Blake, 1983; Glass, 1978a-1978c]. Like other naturally derived thickeners, they are also prone to enzymatic degradation and therefore result in the loss of viscosity during storage [Graffith et al., 1987]. Associative polymers were developed to replace cellulosic thickeners and to eliminate these undesirable application characteristics [Glass et al., 1990].

Associative thickeners are defined as thickeners that build a network structure in solution by interacting with themselves and with other formulation components within a latex paint. These products range from those that thicken by linking together to form a microstructure, (clay platelets, for example), to those with “relative surfaces”, (silica spheres, for example), which form networks through hydrogen bonding [Goncharov et al., 1986; Hall, 1987; Boxall, 1990]. Associative polymers are hydrophobically modified water-soluble block copolymers composed of both water-soluble and insoluble components; the water insoluble components interact in solution and adsorb onto latex particles to form a microstructure that improves the rheological properties of a latex paint [Schulz, 1991; Glass, 1996; Alenandridis, 1996]. In principle any water-soluble polymer can be modified to produce an associative polymer. However, only five classes have so far been offered for commercial applications as thickeners for coatings [Schaller and Sperry, 1992]. These are the nonionic hydrophobically modified ethylene oxide urethane (HEUR), block copolymers, hydrophobically modified alkali-soluble/ swellable emulsions (HASE), hydrophobically modified hydroxyethyl celluloses (HMHEC), hydrophobically modified nonionic non-urethanes (HMN), and hydrophobically modified ethylene

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oxide urethane alkali-soluble/swellable emulsions (HEURASE). A summary of the comparisons on the performance of three different types of associative thickeners is listed in Table 2-1. [Schaller and Sperry, 1992]

Table 2-1: Advantages of HEUR associative Thickeners

Property	HEUR	HASE	NMHEC
Cost	Highest	Depend on grade	Slight >HEC
Spatter resistance	Excellent	Very good	Good
Leveling	Excellent	Fair to excellent	Good
High shear viscosity	Very good	Fair to very good	Fair
High gloss potential	Very good	Fair to very good	Fair
Scrub resistance	Very good	Fair to good	Good
Alkali resistance	Very good	Poor to good	Very good
Corrosion resistance	Very good	Poor	Unknown
Microbial degradation	None	None	Possible
Sensitivity to pH	Insensitive	Sensitive	Insensitive
Sensitivity to formulation	Very sensitive	Moderately to very sensitive	Moderately sensitive

An alkali-swellable associative polymer is a hydrophobically modified carboxylic acid containing copolymer, with a molecular weight of usually several hundred thousands that swells in aqueous media upon neutralization. These polymers thicken through association, and from the expansion of the polymer backbone at high pH due to Coulombic repulsions between neutralized carboxylic acids. The hydrophobically modified urethane based associative polymers most commonly have

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a linear poly(oxyethylene) backbone, and hydrophobes distributed along the backbone, and at the backbone termini [Hoy, 1984].

In aqueous solutions, the hydrophobic groups of associative thickeners tend to aggregate to reduce their interfacial area with water molecules. The hydrophobes of this type of thickener aggregate to a significant degree, at more or less well-defined concentration to yield a polymer network. This network provides viscosity far in excess that of polymer solutions with similar backbone without hydrophobes. Generally, the HEUR polymer depends almost entirely on association to build viscosity, whereas in the HASE type there is a major contribution from the negatively charged high molecular weight backbone and in turn is less dependent on association. HMHEC has a molecular weight within the range of conventional HEC thickeners used in coatings and is probably less dependent on association mechanism for its efficiency.

Associative polymers alter the rheological properties of latex paints by interacting with themselves and with other solutes in the aqueous dispersion medium to build a shear-sensitive associative network. Surfactants and co-solvents can disrupt this association process, which permits the formulator to independently manipulate a paint's high shear and low shear viscosities to achieve a satisfactory combination of film build and leveling properties [Thibeault et al., 1986]. Because the low shear viscosity depends on the degree of association by the associative polymer, the formulator can add sufficient associative polymer to achieve the desired high shear viscosity, and then add surfactant or co-solvent to reduce the low shear viscosity to an acceptable level. The result is a more Newtonian and desirable viscosity profile than can be achieved with cellulosic thickeners, which imparts improved flow and leveling,

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improved film build in pad, brush, or roller application, spray pattern and bubble release, and reduced roller spatter in the latex paint.

The rheological differences observed for associative thickeners and conventional non-associative thickeners are keys to the basic features of the former: (1) ability to self-associate, (2) ability to adsorb on particle surfaces, and in most cases, (3) lower molecular weight. As non-associative thickeners rely on high molecular weight for thickening efficiency, they can produce significant viscoelastic effects and tend to result in spatter and tracking. Associative thickeners can achieve high thickening efficiency at relatively low molecular weight to provide excellent resistance to spatter.

Associative thickeners also suffer from some limitations, which pose problems for the formulator. The principle one is cost. Even though associative polymers are more expensive than cellulose, their use in formulation of latex paints may actually result in a raw material cost savings for the entire latex paint, because the thicker and smoother films produced by associative polymers permit the paint to contain a lower concentration of titanium dioxide pigment without sacrificing hiding power. Another difficulty is that associative polymers can interact with other formulation ingredients in an unpredictable way, and slight deviations in the formulation recipe can have a dramatic effect on the physical properties of the paint. Associative ability, and hence thickening efficiency, depends on the nature and concentration of surfactants, dispersants, dispersed particles, and solvents in the formulation. Understanding the association mechanism and how it relates to the molecular structure of the thickener molecule would aid in the prediction of the properties of paints containing associative polymer.

2.1.2 Studies on HEUR associative Thickeners

Telechelic associating polymers have received substantial attention over the past several years. The first reported study on HEUR polymers appeared in the mid-1980's in publications by Glass and coworkers [Glass et al., 1984; Fernando and Glass, 1984; Karunasena et al., 1989] and Schaller and Sperry [Schaller and Sperry, 1992; Thibeault et al., 1986]. The early study of model and better defined HEUR polymers was conducted by Jenkins and coworkers [Jenkins et al., 1989; Jenkin, 1991]. This was followed by a very important paper by Annable et al. [Annable et al., 1993], who examined similar polymeric system. Both groups examined a series of hydrophobic ethoxylated urethane (HEUR) polymers prepared by condensing PEG of molecular weight of about 8000 with isophorone diisocyanate in the presence of linear alcohol that serves to end-cap the polymer. These studies were reviewed by Howard et al. [Howard et al., 1992], who also provided a guide to the use of these polymers as rheology modifiers in paint formulations.

Many of the earlier studies on associative thickeners utilized commercial products of unknown composition, which make a detailed interpretation of the results difficult. Even the model polymers used by Jenkins and Annable have a broad molecular weight distribution (MWD) and incomplete end-group functionalization, due to the preparation method. Winnik and co-workers provided the spectroscopic evidence that the end groups in these polymers associate to form micelle-like aggregates [Wang and Winnik, 1990]. However, during recent years, more fundamental work has been carried out on HEUR model thickeners with very narrow MWD, and qualitative models have been proposed [Fonnum et al., 1993; Lundberg et al., 1990 and 1991; Jenkins, 1991; Richey et al., 1991]. The striking feature of all these polymers is that the steady-shear rheological behavior is complex whereas the

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oscillatory shear behavior is simple. Solutions of these polymers with concentration greater than 1 wt% exhibit Newtonian behavior (shear-rate independent viscosity) for shear rates up to 10 s^{-1} , followed by a sharp, orders of magnitude reduction in viscosity at shear rate of 100 s^{-1} . Over the concentration range of 1 to 2 wt%, these solutions often exhibit an increase in viscosity (shear thickening) prior to the onset of shear thinning. When subjected to oscillatory shear, these solutions exhibit a simple rheological response that can be characterized in terms of a single relaxation time and a plateau modulus.

It is generally agreed that the hydrophobic modifications of the thickeners aggregate in an aqueous medium, leads to the formation of larger polymer network of polymeric chains, which is physical cross-linked by hydrophobic junctions. A qualitative model describing such networks was first proposed by Bieleman et al., [Bieleman et al., 1986]. Further, it is assumed that the surfactants interact with the hydrophobic aggregates formed by associative thickeners, resulting in some form of mixed surfactant-thickener aggregates that alter the network.

It is widely accepted that the primary hydrophobicity of most commercial and model HEUR associative thickeners comes from their alkanol end-groups. The viscosity and viscoelasticity of HEUR associative thickener solutions depend strongly on the size of the terminal hydrophobes of the thickeners [Lundberg et al., 1990]. In addition, Glass et al. showed that the viscosity profile of HEUR associative thickener solutions was significantly influenced by the number of hydrophobes, their geometrical placement [Karunasena et al., 1989], the hydrophobicity of the internal urethane coupling units, and the oxyethylene chain length between the primary hydrophobes. Rheological studies of HEUR associative thickener solutions suggested

that a network forms in the aqueous phase through self-association of hydrophobic end-groups in the micelle-like junctions, as shown in Figure 2.1.

Figure. 2.1 Schematic diagram depicting the microgel model for the HEUR structure in aqueous solution [Tam et al., 1998]

The Newtonian flow behavior in the regime of low shear rates suggests that the hydrophobic junctions, which make up the network are constantly breaking and forming caused by Brownian motion of the polymer chains. In these polymers, the hydrophobic groups self-assemble to form micelle-like junctions, and the chains bearing the hydrophobes act as bridges between these junctions. The stress relaxation occurs when hydrophobes are detached from a micelle [Annable et al., 1996]. Once this occurs, one end of the chain become free and it can rapidly dissipate its stress through its Rouse relaxation modes. The exit of this hydrophobe is an activated process, and applied forces, which are induced either by shear or extensional flow, enhance the exit rate and cause the bridging chains to stretch. The single relaxation

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time found in the oscillation shear experiments can be explained if the exit rate of the hydrophobe from a junction is the slowest step in the system and all hydrophobes are identical. The most common explanation for shear thinning in networks of telechelic polymers involves network fragmentation as a consequence of chain-end pullout. Because E_m (where E_m is the activation energy for disengagement which will be taken as equal to the binding energy of one chain in a micelle.) is large, the free chain end rapidly enters a new micelle, often the same micelle in which the other end resides, that is, a stress-induced bridge-to-loop transition.

There are currently two different views regarding the origin of the rheological behavior of HEUR associative thickener solutions. One opinion deems that in aqueous solution, these polymers associate into three dimensional network by successive aggregation of terminal hydrophobes into hydrophobic junctions [Maechling et al., 1992; Tanaka and Edwards, 1992a and 1992b]. Because this theory only considers the bridging chains, it is often referred as the “transient cross-linked model” or “open” association model. In contrast, the “closed” association model [Yekta et al., 1993; Annable et al., 1993 and 1994] proposes that in dilute solution the association structures contain well-defined micelles formed by the aggregation of hydrophobic groups at the ends of looped chains, with dangling ends from chains with only hydrophobic substitution on the PEO backbone. With increasing thickener concentration, a network consisting of connecting micelles linking one another via bridging chains. This “closed” association model is known as the “transient micellar network”. In the “open association” model, the dynamics and rheological properties of the network systems are described by two similar statistical transient-network theories developed by Jenkins, Tanaka and Edwards. It was shown that the predictions of this statistical theory are consistent with many rheological properties of HEUR

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associative thickener solutions. On the other hand, in the “closed association” model, the rheological properties of HEUR associative thickener solutions can be modeled by assuming that, with increasing thickener concentration, the proportion of bridging to looping chains gradually increases, resulting in the network formation. In all networks, looped chains are mechanically inactive, and only the bridging chains contribute to the plateau modulus. Plateau modulus increases strongly with polymer concentration, in terms of the functionality of the network and the fraction of bridging chains. In the simple theory of rubber elasticity, the plateau modulus $G_N^0 = \nu_{\text{eff}} RT$, is proportional to the number density of mechanically effective chains ν_{eff} . where R is the gas constant, and T the temperature. In these telechelic systems, it is widely believed that entanglements play a small role, so that ν_{eff} measures the number of chains per unit volume attributed to bridging micelles involved in the extended networks. Taking the micelle as the fundamental building block of the network, the functionality f_n of the network can be calculated using this expression;

$$f_n = 2N_0 = 2\nu_{\text{eff}}/[\text{micelle}] \quad (2.1)$$

where N_0 is the mean number of bridging chains per micelle. Yekta et al. observed that the functionality and the fraction of bridging chains increased linearly with polymer concentration, and about 18% of the chains were involved in bridges at 3 wt% polymer concentration [Xu et al., 1996; Yekta et al., 1996a].

Most of the research effort has also focused on determining the aggregation number of the micelle. Yekta et al. [Yekta et al., 1995 and 1996b] detected flower micelles in a HEUR polymer of composition, C_{16} -IPDU- EO_{800} -IPDU- C_{16} using both dynamic light scattering (DLS) and PG-NMR measurements. The micelle had a hydrodynamic radius, R_h of 20 nm. This radius includes the contribution of free

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dangling chain ends as 15% of the polymer chains contain only one hydrophobe. Several groups had studied telechelic associative polymers using DLS and PG-NMR techniques, focusing on the complex relaxation behavior at concentrations where the association is more pronounced. Many of these publications reported that in the low concentration region ($c < 1$ wt%), the autocorrelation decay is a single exponential function which is consistent with a single diffusing species of individual micelle.

Some interesting features of the HEUR networks formed by telechelic polymers are that the rheological relaxation time is concentration-dependent. Annable et al. [Annable et al., 1993] had attributed this behavior to the existence of super-bridges in the system. Super-bridges are a string of bridged micelles through which stress is transmitted. Breaking the string at any junction allows the stress of the entire string to relax. This degeneracy leads to enhanced fragmentation rates for long strings. At higher polymer concentration, the super-bridges are shorter on average, leading to an increase in the relaxation time. This view on the role of super-bridges is confirmed in the recent simulations of associative polymer behavior by Groot and Agterof [Groot and Agterof, 1995].

In many water-borne coating formulations, polymer and surfactants are frequently employed together, particularly to achieve colloidal stability, structuring and rheological control. The addition of surfactant to solution of AP has a profound effect on their properties [Piculell et al., 1995]. Addition of small amounts of surfactant to solutions of HEUR and other PEG-based associative polymers leads to a large increase in viscosity, followed by a breakdown in viscosity at high surfactant level [Effing et al., 1994]. Nonionic surfactants at low concentration maintain the simple Maxwell viscoelastic response of the system, leading to an increase in both the plateau modulus and the relaxation time of the system. The rheological response in

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the presence of sodium dodecyl sulfate (SDS) is more complex, presumably because this surfactant can interact with the PEG backbone as well as the micelles. A simple model for describing the increase in viscosity involves the formation of mixed micellar aggregates, where each surfactant molecule replaces a chain end in a micellar junction, freeing polymer chain ends to form new bridging micelles. At high surfactant concentration, the mixed aggregates are comprised primarily of surfactant molecules, with very few bridges between them. At a high ratio of surfactant to polymer molecules, the N_R values of the mixed aggregates approach that of pure surfactant micelles themselves. Tam and co-workers [Dai et al., 2001a and 2004] studied binding characteristic of HEUR and SDS and found that at low SDS concentration, SDS monomers bind to the PEO segments and hydrophobic core of the micelles. With increasing SDS concentration, the aggregation number increases and the PEO segments are re-hydrated to form ion-dipole association with SDS head groups. PEO wraps on the surface of SDS micelles to form a necklace-like structure, which is confirmed by light scattering and titration calorimetric studies.

2.1.3 Studies on HEUR with fluorocarbon hydrophobes

Fluorocarbon associative polymers are interesting because of their low surface energy, biocompatibility, oleo-and hydrophobic properties, and also because of the considerably better viscosifying properties compared to the hydrocarbon counterparts. New applications with fluorocarbon hydrophobes include wastewater treatment, oil recovery, control of surface erosion and antibacterial activity [Amis et al., 1996; Sawada et al., 1999; Tae et al., 2001, 2002a and 2002b, Cathebras et al., 1998]. The prototypical polymer from the fluorocarbon telechelics is made from water-soluble poly(ethylene oxide) (PEO) chain and end-caps that are partially or fully fluorinated

and of the form $C_nF_{2n+1}(CH_2)_m$. Depending on the synthesis, polymers with n equals to 6, 8 or 10 and $m=1-11$ have been produced. As in hydrophobically ethoxylated urethane (HEUR) telechelics, the spacer between the water-soluble PEO chain and the hydrophobe carries a urethane function. By extension, associative polymers with a structure analogous to that of HEUR and terminated by a fluorinated group are designated as F-HEUR.

During the last decade, F-HEURs have been investigated thoroughly using spectroscopy, scattering and rheological experiments. From this large body of work, a consistent picture for the self-assembly and flow behaviors has emerged. In many respects, the phenomenology that we describe for fluorocarbon telechelics is similar to that of the hydrocarbon analogues. At very low concentrations, above the critical aggregation concentration, F-HEUR self-assemble in water into mono-disperse flower-like micelles. They are composed of a dense core made of the insoluble $C_nF_{2n+1}(CH_2)_m$ -segments surrounded by a swollen corona of neutral PEO chains (Figure 2.2). The aggregation number N_{agg} ranges from 30 to 50, and in general it is independent of polymer concentration [Serero et al., 1998 and 2000]. Semenov et al. [Semenov et al., 1995] have studied theoretically the phase behavior of telechelic polymer system with large aggregation numbers, and, they predicted that neighboring aggregates are able to form bridges and give rise to an effective attraction potential between flower micelles. If the attraction energy is larger than the thermal energy, phase separation is predicted. This transition is of first-order and analogous to a liquid-gas transition, which was later confirmed by Russel and coworkers for systems with hydrocarbon alkyl chain ends [Pham et al., 1999a and 1999b]. Kornfield and coworkers have shown that in addition to F-HEUR containing $C_8F_{17}(CH_2)_2$ chain ends, the phase separation depends on the molecular weight of the PEO backbone [Tae et

al., 2002b]. It has been found that the phase behavior of telechelic systems depends on the proportion of extremities that were actually end-capped by the hydrophobic groups during the synthesis process [Zhang et al., 1998b; Calvet et al., 2003].

Figure 2.2 Schematic representation of the flower-like micelles produced from fluorocarbon telechelic polymers [Grest et al., 1996].

In fluorocarbon telechelic systems, the onset of viscoelasticity coincides with the formation of an associative network of flower micelles. The relationship between the elastic moduli $G'(\omega)$ and $G''(\omega)$ and the frequency was carefully determined [Tae et al., 2001]. It was found that the associating gels are true viscoelastic liquids with mechanical characteristics close to that of a Maxwellian fluid, which is characterized

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by a single relaxation time. In telechelic systems, the micellar cores serve as the temporary junction points, which are connected by bridging chains to form a polymer network. One crucial difference between the hydrocarbon and fluorocarbon telechelic systems is the range of relaxation times that characterize the viscoelastic solutions within the polymer network regime. Due to the strong hydrophobicity of the fluorinated end-caps, the network relaxation time can be of the order of minutes, whereas for the hydrocarbon analogues it seldom exceeds 1 second. For the partially fluorinated end-capped $C_nF_{2n+1}(CH_2)_m$ - segments, we assume that rheological properties of telechelics with one CF_2 is equivalent of those with 1.5 CH_2 groups [Sadler et al., 1998]. The longer relaxation time facilitates the study of stress relaxation in telechelic transient networks, which provides new insights in the dynamic of exchange the block copolymers in selective solvent [Willner et al., 2001]. There exist strong similarities in the non-linear rheology of hydrocarbon and fluorocarbon associative polymers. With increasing shear rates, the steady shear viscosity exhibits three flow regimes, which are, Newtonian, shear-thickening and shear-thinning. The shear-thickening has been attributed either to the non-linear stretching of polymeric chains between the nodes or the increase in the number density of mechanically active chains. For the shear-thinning effect, Berret et al. have demonstrated that this excessive shear-thinning is actually a true discontinuity of the flow curve between the shear-thickening and shear-thinning regimes [Berret et al., 2003]. Using flow visualization technique it was shown that above the discontinuity, shear induces a fluid fracture similar to that reported for brittle solids. The fluid fracture, described as a localization of the shear in a narrow region of the gel is at the origin of shear banding. Due to the finite relaxation time of the polymer network, and contrary to ordinary gels, the fracture can be created and restored.

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Research on HEUR polymers is actively being pursued and new insights are being added to the scientific community. Most of the important advances have involved model water-soluble polymers with hydrophobic end groups, and much has been gained through our understanding on the characteristics of hydrophobic interaction and the resultant associative structure. There is also a growing interest in the interaction of amphiphilic polymer with surfactant and other ingredients, e.g., cyclodextrin to control the rheological properties. Through these studies, one could anticipate interesting and new properties to be developed for these systems.

2.2 Cyclodextrins**2.2.1 Cyclodextrins and their structures**

Cyclodextrins are well-known in supramolecular chemistry as molecular hosts capable of selective inclusion of a range of guest molecules via noncovalent interactions in their hydrophobic cavities. Cyclodextrins are used to obtain certain benefits that result from complexation to enhance the solubility of guest molecules, stabilization against the effects of light, heat and oxidation, masking of unwanted physiological effects, reduction of volatility, and others. The first reference to a substance which later proves to be a cyclodextrin, was published by Villiers in 1891 [Villiers, 1891]. However, the structure, physical and chemical properties, as well as their inclusion complex forming properties were discovered by the end of 1960s, when the methods for laboratory-scale preparation of cyclodextrins was established [Thoma and Stewart, 1965; Caesar, 1968].

Cyclodextrins comprise a family of three well-known industrially produced major, and several rare, minor cyclic oligosaccharides. The three major cyclodextrins

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are crystalline, homogeneous, non-hygroscopic substances, which are torus-like macro-rings build-up from glucopyranose units. The α -cyclodextrin comprises six glucopyranose units, β -cyclodextrin comprises seven such units, and γ -cyclodextrin comprises eight glucopyranose units.

As a consequence of the 4C_1 conformation of the glucopyranose units, all secondary hydroxyl groups are situated on one of the two edges of the ring, whereas all the primary ones are placed on the other edge. The ring, in reality, is a cylinder, or better said a conical cylinder, which is frequently characterized as a doughnut or wreath-shaped truncated cone. The cavity is lined by hydrogen atoms and the glycosidic oxygen bridges, respectively. The non-bonding electron pairs of the glycosidic oxygen bridges are directed toward the inside of the cavity, producing a high electron density and lending to it some Lewis base characteristics. The chemical structure and approximate dimensions of cyclodextrins are shown schematically in Figure 2.3.

The C-2-OH group of one glucopyranoside unit can form a hydrogen bond with the C-3-OH group of the adjacent glucopyranose unit. In the cyclodextrin molecule, a complete secondary belt is formed by these H bonds, therefore the β -cyclodextrin is a rather rigid structure. This intramolecular hydrogen bond formation is probably the explanation for the observation that it has the lowest water solubility among all the cyclodextrins. The hydrogen-bond belt is incomplete in the α -cyclodextrin molecule, because one glucopyranose unit is in a distorted position. Consequently, instead of the six H-bonds, only four can be established fully. The γ -cyclodextrin is a non-coplanar, and more flexible structure, therefore it is the most soluble of the three cyclodextrins. The structure of cyclodextrin is shown below.

Figure 2.3 Chemical structure of β -cyclodextrin (a) and molecular dimensions of (left to right) α -, β - and γ - cyclodextrins (b) [Rusa et al., 2001]

In an aqueous solution, the slightly apolar cyclodextrin cavity is occupied by water molecules which are not energetically favored (polar-apolar interaction), and therefore can be readily substituted by appropriate “guest molecules” which are less polar than water. The dissolved cyclodextrin is the “host” molecule, and the “driving force” for the complex formation is the substitution of the high-enthalpy water molecules by an appropriate “guest” molecule.

A large number of modified cyclodextrins have been synthesized in an attempt to alter or improve their inclusion properties and also to induce biomimetic function

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[Jicsinszky and Fenyvesi, 1996]. Methylation is the simplest modification, because of the differences in reactivity between O-2H, O-3H, and O-6H hydroxyl groups, two types of Methylated cyclodextrins have been prepared, dimethyl- β -cyclodextrin(DIMEB), and trimethyl- β -cyclodextrin (TRIMEB). The round macrocyclic conformation of dimethyl- β - cyclodextrin is maintained by intramolecular O-3H...O-2 [Harata, 1998] hydrogen bonds, the three O-6CH₃ methyl groups are directed toward the molecular axis such that the cavity is closed at the O-6 end. No water molecules have been identified in the cavity; instead, the remaining volume of the bowl-shaped cavity is occupied by an O-6 methoxyl group from an adjacent molecule, which is related to the first by a 2-fold screw symmetry. The complete methylation of β -cyclodextrin markedly affects not only its macrocyclic ring but also the conformation of its glucose units. When the trimethyl - β -cyclodextrin is complexed, one of its trimethylglucose units is converted from a ⁴C₁ chair conformation into a ¹C₄ conformation with axial C-2-O-2, C-3-O-3, and C-5-C-6 bonds. This unusual conformation of the trimethylglucose unit distorts the macrocyclic ring and reduces the vacant space in the molecular cavity. It has been suggested that intramolecular C-6H...O-O-5 hydrogen bonds, which form between adjacent methylglucose units stabilize the macrocylic structure. When they are complexed, the trimethyl -- β -cyclodextrin molecules rearranged to form a head –to-tail channel type structure.

2.2.2 Inclusion Complexes

Cyclodextrins are able to interact with a variety of ionic and molecular species. The resulting inclusion compounds belong to the type of “host-guest” complexes.

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guest” complexes. Several requirements must be met for the host-guest relationship to form, one being that the binding sites of the host and guest molecules should be stereoelectronically complement. The characteristic feature of the host molecule is that the binding sites are oriented to the same spatial direction, whereas in the guest molecule the binding sites are diverging in the complex. It is the association of converging and diverging binding sites by which a complex of the host-guest type is formed [Szejtli, 1988]. Cyclodextrins are always the hosts in the inclusion complexes, while the guest material can be of many different types.

Most frequently, the host/guest molar ratio is 1/1, which is the essence of “molecular encapsulation”. However, 2:1, 1:2, 2:2 or even more complicated associations, and higher order equilibrium exist [Stezowski et al., 1978], and β -cyclodextrin always forms a 1:2 complex with hydrogen iodide. One I⁻ ion is included in the cavity but the other is located outside the cavity [Lindner and Saenger, 1982]. In the 1:1 complex of β -cyclodextrin with methanol, the guest molecule (methanol) is too small to fill the cavity and water molecules are co-included. Channel type packing is formed in complexes of cyclodextrin with a variety of guest molecules, like I₂•I₂•I₃⁻, benzil, carmofur, etc [Hamilton et al., 1981; Harding et al., 1978]. Among all the complexes, only head to head arrangement has been observed with the dimmer units of β -cyclodextrin stacked nearly linearly along the channel, but in crystals, the β -cyclodextrin is arranged along a zigzag line. When the length of the guest molecules does not match the length of the repetition unit in the host channel, layer-type packing structure is formed. As a result, both ends of the cavity are open to the intermolecular space of the adjacent layer. The guest molecule is too large to be fully included in a single cavity but does fit in the expanded space.

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2.2.3 The mechanism and energetics of inclusion in cyclodextrin complex

The inclusion of a guest in a cyclodextrin cavity is essentially a substitution of the included water molecules by a less polar guest. This process is an energetically favoured interaction of the relatively non-polar guest molecule with an imperfectly solvated hydrophobic cavity. In this process both entropy and enthalpy changes have a role.

The driving force for complexation is the result of various effects. The contribution of the various effects depends on the guest and on the cyclodextrins. These effects are:

- (1) Electrostatic interaction: the electrostatic interaction energy is the energy of interaction between the undistorted charge distributions of two molecules interacting with each other. It includes all electrostatic forces between permanent charges, dipoles and higher multi-poles present in the system. Usually, three types of electrostatic interactions are the most important, i.e., ion-ion interaction, ion-dipole interaction, and dipole-dipole interaction. [Grayeski and Woolf, 1984]
- (2) Cyclodextrin-ring strain release on complexation [Hingerty and Saenger, 1976]
- (3) Van der Waals interactions, and in case of some guests, hydrogen bonding between host and guest. [Bergeron, 1984]

The role of substitution of water by a guest of appropriate size, shape and polarity, seems to be universal. Cyclodextrins may be regarded as hydrophobic in the sense that their solubility improve slightly when a small amount of a relatively apolar solvent, such as ethanol, is added to water. This shows that the cyclodextrin cavity is

hydrophobic in comparison with water. The solvation of this hydrophobic region is far from being ideal.

Water molecules in the cyclodextrin cavity cannot satiate their tetrahedral hydrogen bonding capacity as can those in the bulk of the solvent. They may therefore be regarded as molecules of enhanced energy or enthalpy. A decrease in the energy of the system is caused by the increase of the solvent/solvent interaction, since the contacting surfaces between the solvent and guest molecule, as well as between the solvent and cyclodextrin cavity are reduced [Komiya and Bender, 1978]. The cavity for γ -cyclodextrin is wide, and it may accommodate many water molecules that their properties resemble water molecules in the bulk of the solvent, consequently the driving force of complex formation tends to decrease.

The release of ring strain, i.e. the transition of the cyclodextrin ring from strained to relaxed state on penetration of the guest, is apparently significant only in the case of α -cyclodextrin. The structure of α -cyclodextrin hydrate is distorted; the structures of β - or γ - cyclodextrins are not. Even with α -cyclodextrin, this is not the most important effect. Increase of ring strain as a consequence of complexation has been reported [Tabushi et al., 1978].

The enthalpy and entropy of complexation, ΔH^0 and ΔS^0 , respectively, of more than 2000 natural cyclodextrin complexes and more than 100 modified cyclodextrin complexes have been determined [Easton and Lincoln, 1999]. In the overwhelming majority of cases, ΔH^0 is negative and ΔS^0 is usually negative. As a consequence, cyclodextrin complexation is said to be “enthalpy driven”. In the “classical” hydrophobic interaction between nonpolar molecules the structure of the neighbouring water is a critical factor, both ΔH^0 and ΔS^0 are positive, and the

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interaction between nonpolar molecules is said to be “entropy driven”. An extensive range of cyclodextrin complexations show an enthalpy-entropy compensation where, for a given cyclodextrin, a plot of ΔH^0 against ΔS^0 is linear for all guests and has a positive slope [Rekharsky and Inoue, 2002].

$$T\Delta S = \chi\Delta H^0 + T\Delta S_0^0 \quad (2.2)$$

$$T\delta\Delta S_0 = \chi\delta\Delta H^0 \quad (2.3)$$

The linear relationships indicate that the dominant stabilizing factors within each set of cyclodextrin complexes are similar, and that a change in $T\Delta S^0$ is compensated by a change in ΔH^0 as the guest changes, as indicated by Equations. (2.2). and (2.3) which show that the overall entropy change is made up of one term, $T\Delta S^0$, which is proportional to the enthalpy change and independent of it $T\Delta S_0^0$. When $\Delta H^0=0$ the complex is still attainable provided that $T\Delta S_0^0$ is positive. Since,

$$\delta\Delta G^0 = \delta\Delta H^0 - T\delta\Delta S^0 \quad (2.4)$$

$$\delta\Delta G^0 = (1-\chi) \delta\Delta H^0 \quad (2.5)$$

Equation (2.5) can be derived, shows that χ represents the entropic contribution which decreases the enthalpic stabilization of the cyclodextrin complex such that only a $(1-\chi)$ portion of $\delta\Delta H^0$ contributes to increased stability of the complex. It has been deduced that χ arises from conformational changes and that $T\Delta S_0^0$ arises from the extent of dehydration occurring during the complex formation, and that these are the dominant effects determining the stability of cyclodextrin complexes. For α - cyclodextrin, β - cyclodextrin and γ - cyclodextrin, χ increases in the sequence: 0.79, 0.80 and 0.97, respectively, and $T\Delta S_0^0$ increases in the sequence 8,

11 and 15 kJ mol⁻¹, respectively. These increases in χ and $T\Delta S_0^0$ are thought to be consistent with increases in conformational change and dehydration occurring as a result of complexation. This is in accordance with the expected increase in the flexibility and the number of water molecules in and around the annulus as cyclodextrin size increases. Complex formation comprises the following elementary steps [Easton and Lincoln, 1999; Abou-Hamdan et al., 2000]:

- 1) The water molecules escape from the cyclodextrin cavity and move to an energy level corresponding to that in the gaseous state. As a consequence, van der Waals interactions and the number of hydrogen bonds are decreasing, whilst the translational and three-dimensional rotational degrees of freedom of the free water molecules are increased.
- 2) The conformation energy of the cyclodextrin ring decreases on relaxing in the case of α - or capped β -cyclodextrins. [Harada et al., 1977; Szejtli, 1988]
- 3) The apolar guest molecule sheds its hydrated shell and also assumes the state of an ideal gas. This empty hydrated shell collapses and rearranges.
- 4) The guest molecule, regarded as being in the ideal gaseous state, enters the empty cyclodextrin cavity and the complex is stabilized by van der Waals interactions, and sometimes by hydrogen bonding. The guest molecule retains a one-dimensional rotational freedom.
- 5) The displaced water molecules condense from the gaseous state to the liquid state. Changes in enthalpy and entropy can be regarded as identical with those of the well-know water condensation.
- 6) The structure of water is restored around the exposed part of the guest molecule, and integrated with the cyclodextrin ring hydrate-shell.

2.3 Cyclodextrin-Polymer inclusion complexes

In most cases, the guest molecules are small molecules. Even the interaction between cyclodextrin and some polymers e.g. polyvinyl chloride (PVC), Nylon-6 (PA), polystyrene (PS) etc., had been observed in 70's [Ogata et al., 1976; Maciejewski, 1979a; Maciejewski et al., 1979b, Maciejewski and Durski, 1981]. It is until early 90's when Harada and co-workers reported preparation of polyrotaxane from cyclodextrin and polymers [Harada and Kamachi, 1990], much attention was given to these supramolecular complexes of cycloamyloses due to their significance for understanding noncovalent binding forces, the selectivity and molecular recognition of the guest molecules, and for their industrial importance, particularly with respect to drug encapsulation and targeting. Up to now, three types of cyclodextrin-polymer inclusion complexes have been found:

- a) Main chain inclusion compound.
- b) Side-chain inclusion compound and
- c) tandem inclusion compound.

Figure 2.5 Complexation modes of polymer inclusion compound [Lu et al., 2000]

2.3.1 Main chain inclusion compound:

Most of cyclodextrin-polymer inclusion compound studied fall into this category, for example, PEO, PMMA, polyolefin, polyamide, polyester, polyimide etc. According to the definition, cyclodextrins are threaded onto the polymer backbone to form inclusion complex. Harada and coworkers [Harada and Kamachi, 1990; Harada et al., 1993a] added PEG solution into saturated aqueous solutions of α -cyclodextrin at room temperature, and the solution became turbid and the complexes were formed as crystalline precipitates. In these complexes, polymer chains were threaded into cyclodextrins and recognized by the host. But β -cyclodextrin did not form complexes with PEG of all molecular weights. However, Harada and coworkers found that β -cyclodextrin and γ -cyclodextrin formed complexes with poly(propylene glycol) (PPG) [Okada et al., 1999; Harada and Okada, 1999] to produce crystalline complexes at high yields. They were isolated and found to be 2:1 (monomer unit:CD).

Figure 2.6 Proposed structure of the complex between β -cyclodextrin and PPG [Harada et al., 1995]

But α -cyclodextrin did not form complexes with PPG of any molecular weight. The complexes were characterized by FT-IR, ^1H NMR, ^{13}C CP/MAS MNR, and ^{13}C PST/MAS MNR spectra and X-ray (powder), thermal, and elemental analysis were

also conducted to explore the structure and properties of the complexes. All the results showed that the complex exhibits packing that is different from free cyclodextrin and has channel structures. The inclusion complex formation of polymers with cyclodextrins is entropically unfavorable. However, formations of the complexes are thought to be promoted by hydrogen bond formation between cyclodextrins. This character was used to prepare thermoreversible hydrogel network with a supramolecular structure that consisted of biodegradable and biocompatible components [Huh et al., 2001]. Therefore, the head to head and tail to tail arrangement, which result in a more effective formation of hydrogen bonds between cyclodextrins, is the most probable structure. The cross-sectional area of a polymer correlates with the size of the cyclodextrin with which it forms a complex [Harada et al. 1995]. Weickenmeier and coworkers [Weickenmeier and Wenz, 1997] prepared polyester of octanedicarboxylic acid and polyethylene glycol and found that it forms water-soluble inclusion compound with α - and β -cyclodextrin. The ^1H NMR shows that the solubility of the host/guest complex in water is due to a partial coverage of the polymer chain by the host. The cyclodextrin rings occupy the alkyl segments rather than the poly(oxyethylene) segments. The driving force for the inclusion of the polyesters is a strong exothermic interaction between host and polymeric guest. On the other hand, the inclusion complex of PEG appears to be mainly driven by the precipitation of the inclusion compound.

All the systems mentioned above belong to main-chain inclusion compound. Compared with the polymer before complexation, the properties were significantly changed.

2.3.2 Side chain inclusion compound

Side chain inclusion compound is much more complicated than that of main chain. Born and Yamaguchi [Born and Ritter, 1995 and 1996; Yamaguchi et al., 1997; Harada et al., 1997] reported preparation of this material in 1995 and 1997; Leclercq [Leclercq et al., 1998] reported the interactions between β -cyclodextrin and a water-soluble polymer: poly(4-sodium styrenesulfonate) which proved that the aromatic residues of NaPSS were included in the cavity of β -cyclodextrin and a network of hydrogen bonding between sulfonic acid residues and the hydroxyl groups of β -cyclodextrin occurred. Islam and co-workers [Islam et al., 2000] used cyclodextrin in the characterization of hydrophobically modified alkali-soluble emulsions (HASE) and successfully measured the single chain molecular weight and hydrodynamic radius. Weickenmeier and coworkers [Weickenmeier et al., 1997] also reported a host-guest system: host polymer with pending β -cyclodextrin side-groups and a guest polymer with pending hydrophobic 4-tert-butylanilide side groups were synthesized by polymer-analogous reactions starting from poly[(maleic anhydride)-alt-(isobutene)] ($M_w = 60000$) The inclusions of both polymers with complementary monomeric guests and hosts were proven by microcalorimetry, where the interaction of the host polymer and the guest polymer in aqueous solution is accompanied by a tremendous increase in viscosity.

2.3.3 Tandem polymer inclusion

Report on tandem polymer inclusion compound is rare. Born [Born and Ritter, 1995] prepared this compound with β -cyclodextrin in 1995. The cyclodextrins have some optically active substituents on the β - cyclodextrin thus can interact with chiral

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groups of guest molecular, which can be used to prepare material with optically active molecules. It can be removed under certain condition, which shows potential application in medical and synthesis of new material. The solubility and heat stability of drug can be increased by formation of inclusion complex, which can be critical in the preparation of some drugs and new material. Afterward the cyclodextrins can be removed, so the structure and properties do not change.

Stimuli-responsive polymers have been extensively investigated as smart materials. These polymers exhibit unique phase transition behavior in response to external stimuli, such as temperature [Huh et al., 2004; Jeong et al., 2002], pH [Moine et al., 1998; Choi et al., 2004], and light [Hu et al., 2004; Tomatsu et al., 2005]. Hu et al. prepared a novel azobenzene-functionalized hydroxypropyl methylcellulose polymer, which shows interesting sol-gel transition behavior in aqueous solutions. In the absence of α -cyclodextrin, the gelation temperature after UV irradiation, while in the presence of α -cyclodextrin, the gelation temperature decreases after UV irradiation.

Figure 2.7 Effect of photoirradiation on the sol-gel transition behavior of AZO-HPMC and its α -CD complex [Hu et al., 2004]

Fujita and co-workers [Fujita et al., 1999a-c] prepared a series of polyrotaxane, in which many β -cyclodextrins are threaded onto a triblock copolymer of poly(ethylene glycol) (PEG) and poly(propylene glycol) (PPG) capped with fluorescein-4-isothiocyanate (FITC). The interaction of the β -cyclodextrins with terminal FITC moieties in the polyrotaxane was observed at low temperature. However, the interaction of the β -cyclodextrins with the PPG segment was observed with increasing temperatures. On the basis of these results, it is concluded that the majority of the β -cyclodextrins move toward the PPG segment with increasing

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temperature although some β -cyclodextrins may reside on the PEG segments. Thermally responsive properties can be used for controlled release of drugs.

Cyclodextrins have been used together with amphiphilic polymers with the purpose of reducing the viscosity of an aqueous solution. This was described for the first time in early 1990's [Eishenhart et al., 1992; Lau and Shah, 1994]. Firstly the purpose was to reduce viscosity of a highly concentrated aqueous solution of an associative thickener to facilitate incorporation of a thickener into technical formulations, e.g., paint. More recently the concept of controlling the self-association of hydrophobically modified PEO by addition of cyclodextrin has been more thoroughly studied in two papers by Zhang et al. and Akiyoshi et al [Akiyoshi et al., 1998; Zhang et al., 1998a]. A conclusion from these investigations was that cyclodextrin molecules form complexes with the hydrophobic end groups of the hydrophobically modified PEO polymer chains, which means that polymer hydrophobic tails are hidden within the cyclodextrin cavities and only the hydrophilic outer shell of the cyclodextrin molecules is exposed to the aqueous environment. In polymer solutions, the viscosity then decreases since the three dimensional polymer network is disrupted when the possibility to form inter-polymeric hydrophobic associations is reduced. The concept of encapsulating the hydrophobic tails of HM-PEO with cyclodextrin has also been used to remove hydrophobic interactions when properties of individual polymer molecules were in focus and investigated with techniques such as gel-permeation chromatography and static light scattering [Islam et al., 2000]. Karlson and co-workers [Karlson et al., 2002 and 2003] investigated how the viscosity in an aqueous solution of HM-PEO decreased in the transition region where the concentration of cyclodextrin was lower than the total concentration of hydrophobic group. There was reasonable agreement with a simple association model

from which the effective binding constant could be extracted together with the concentration of binding sites (Figure 2.8). They suggested that the addition of the first molecules of cyclodextrin mainly reduces the probability for hydrophobic associations inter-connecting different clusters of polymer micelles whereas at high cyclodextrin concentrations a disengagement of the individual clusters into separate HM-PEO molecules becomes important.

Figure 2.8 Relative viscosity of HM-EHEC solution (1% w/w) as a function of the cyclodextrin concentration, c_{CD} . The full lines represent a fit of simple adsorption model to the data. [Karlson et al., 2002]

In the study of cyclodextrin and amphiphilic polymer interaction, it is also interesting that the reduction in polymer viscoelasticity in the presence of cyclodextrin is reversibly recovered upon subsequent addition of different nonionic surfactants that have a higher propensity to complex with the cyclodextrin than the hydrophobic segments of the amphiphilic polymer [Abdala et al., 2003].

There are however relatively few reported studies on the interaction between F-HEUR and cyclodextrin. Zhang and co-workers [Zhang et al., 1998a] studied the complex formation β -cyclodextrin/perfluorocarbon modified water-soluble polymer by ^{19}F NMR, and found that the viscosity is greatly reduced by β -cyclodextrin as a result of intermolecular hydrophobic association disruption. Addition of stoichiometric β -cyclodextrin completely suppressed hydrophobic association in this solution. The possible complex mechanism is proposed (Figure 2.9). In order to further elucidate the nature of the interaction, a detailed study on the interaction between various amphiphilic polymer like hydrocarbon and fluorocarbon modified PEO and cyclodextrins using more precise and sensitive research tools is needed.

Figure 2.9 Complex formation of β -CD and Perfluorocarbon modified water-soluble polymers [Zhang et al., 1998a]

2.4 Main techniques used in study of cyclodextrins-polymer inclusion complexes

Cyclodextrin-polymer complexes can be soluble or insoluble in aqueous solution. Harada [Harada et al., 1993a] prepared PEG- α -cyclodextrin complex in the form of crystalline. X-ray crystallography has been the major source of information about the three-dimensional structure of the host-guest interactions. When the complexes are soluble in water, the solution can be studied by a variety of methods, such as rheometry, fluorescence spectroscopy, ultraviolet (UV), nuclear magnetic resonance (NMR) and calorimetry (ITC) and dynamic light scattering (DLS).

2.4.1 Rheological properties of cyclodextrins-polymer solutions

Rheology, the study of the flow and viscoelastic properties of polymers, provides very important information on the structure and behavior of solutions. Rheological measurements are the source of information on how solutions respond to stresses imposed on them in various ways.

2.4.1.1 Viscous flow

The viscosity of a material expresses its resistance to flow under a mechanical stress. It is defined quantitatively in terms of two basic parameters, the shear stress σ and the shear rate (more correctly, the rate of shear straining) $\dot{\gamma}$, i.e., the ratio of shear stress to shear rate:

$$\eta \equiv \frac{\sigma}{\dot{\gamma}} \quad (2.6)$$

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Newton's "law" of viscosity states that the shear stress is linearly proportional to the shear rate, the proportionality constant being the viscosity, η . This type of flow behavior would be expected for small molecules, where the structure, and therefore the resistance to flow, does not change with the intensity of shearing. But rheological properties of polymer solutions are usually both shear and time-dependent. When sheared at a constant rate or stress, the viscosity of a thixotropic fluid decreases over a period of time, implying a progressive breakdown of structure. If the shear is stopped for a while, the structure reforms, and the experiment may be duplicated.

2.4.1.2. Linear Viscoelasticity

The word "viscoelastic" means the simultaneous existence of viscous and elastic properties in a material. A linear viscoelastic response can be simply defined as one in which ratio of overall stress to overall strain, (e.g., the overall modulus), is a function of time only, and not the magnitudes of stress or strain. As an aid in visualizing viscoelastic response, the Maxwell model (the simplest linear viscoelastic mechanical model) as shown in Figure 2.10 can be used to represent a special case of the mechanical response. The Maxwell elements in Figure 2.10 are a simple series combination of a linear viscous element (dashpot) and a linear elastic element (spring). The constitutive equation for a Maxwell element is;

$$\sigma = \eta \dot{\gamma} - \frac{\eta}{G} \dot{\sigma} = \eta \dot{\gamma} - \lambda \dot{\sigma} \quad (2.7)$$

where G is the elastic modulus. The quantity $\lambda = \eta/G$ has the dimensions of time and is known as a relaxation time.

Figure 2.10 Two linear viscoelastic models: Single Maxwell model (left) and Generalized Maxwell Model (right)

The most frequently used experimental techniques for studying the mechanical behavior of viscoelastic materials are oscillatory shear (dynamic mechanical test). It is based on the fundamentally different response of viscous and elastic element to a sinusoidally varying stress and strain. A “complex shear modulus” G^* is defined through the equation

$$\sigma(t) = G^*(\omega)\varepsilon(t) \quad (2.8)$$

It is customary to write

$$G^* = G' + iG'' \quad (2.9)$$

Where the in-phase component G' and the out-of-phase G'' are referred as the “storage modulus” and “loss modulus”, respectively and ω is the frequency. For the special case of the Maxwell model, it can be shown that;

$$G^* = \frac{i\omega\eta}{1+i\omega\lambda}, \text{ or alternatively } G^* = \frac{i\omega\lambda G_N^0}{1+i\omega\lambda} \quad (2.10)$$

and

$$G' = \frac{\eta\lambda\omega^2}{1+\omega^2\lambda^2} \text{ or alternatively } G' = \frac{G_N^0\omega^2\lambda^2}{1+\omega^2\lambda^2} \quad (2.11)$$

$$G'' = \frac{\eta\omega}{1+\omega^2\lambda^2} \text{ or alternatively } G'' = \frac{G_N^0\omega\lambda}{1+\omega^2\lambda^2} \quad (2.12)$$

HEUR plays important roles as thickeners and viscosity modifiers in a variety of water-borne technologies including paints, inks and cosmetics. Much of our recent understanding of the behavior of these associative polymers in aqueous solution comes from rheological studies. It has been shown the interaction between HEUR and other materials significantly affects the rheological properties. Addition of small amount of surfactant to solutions of HEUR leads to a large increase in viscosity, followed by a breakdown in the viscosity at high surfactant level. Nonionic surfactants at low concentration maintain the simple Maxwell viscoelastic response of the system, leading to an increase in both the plateau modulus and the relaxation time of the system [Hulden, 1994; Annable et al., 1994]. The results were interpreted as follows; the increase in viscosity involves the formation of mixed micellar aggregates. Each surfactant molecule replaces a chain end in a micellar junction, freeing polymer chain ends to form new bridged micelles. At high surfactant concentration, the mixed aggregates are comprised primarily of surfactant molecules, with very few bridges between them.

2.4.2 Static and dynamic properties of dilute polymer solution

Light scattering has been widely used to study the polymer chain properties in solution [Brown, 1993 and 1996; Chu, 1991; Pecora, 1985; Schmitz, 1990; Joosten, 1991]. Not only weight averaged molecular weight M_w , radius of gyration R_g and second virial coefficient A_2 but also the hydrodynamic radius and the conformation of polymer chains in solutions could be determined from light scattering experiments. As an incident light beam I_i passes the polymer solution, the scattered light intensity I_s is recorded at different scattering angles, θ . If the time-averaged scattered intensities are measured and analyzed, only information on time-averaged properties are obtained where this technique is commonly referred to as static light scattering (SLS). If the intensity fluctuations with time are recorded and analyzed based on the photon correlation spectroscopy (PCS), the temporal variations of the scattered radiation yield the familiar Doppler shift, and the broadening of the central Rayleigh line can be used to determine the dynamic properties of the system, and thus this technique is called as dynamic light scattering (DLS). Light scattering is a phenomenon of absorption and re-emission of electromagnetic radiation. In a typical experiment, a dispersion of particles is illuminated by an incident beam. The direction of propagation of this beam is defined by an incident wave vector $\mathbf{k}$, with magnitude $k = 2\pi n/\lambda = n\omega_0/c$, where n is the medium refractive index and ω_0 is the circular frequency in vacuum. The radiation scattered under an angle θ with respect to the incident beam is characterized by a scattering wave vector: $\mathbf{q} = \mathbf{k}_i - \mathbf{k}_s$. By taking into account $|\mathbf{k}_i| = |\mathbf{k}_s|$, the magnitude of $\mathbf{q}$ can be represented by the expression:

$$q = \frac{4\pi n}{\lambda} \sin\left(\frac{\theta}{2}\right) \quad (2.13)$$

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(a) Static properties

For Rayleigh scattering, the intensity of scattered light for a small particle can be described by,

$$\frac{I_s}{I_i} = \frac{\pi^2 \alpha^2 \sin^2 \theta}{\lambda^4 \epsilon_0^2 r^2} \quad (2.14)$$

where α the polarizability of the particle, ϵ_0 the electric permittivity of vacuum. However, when the particle size is greater than $\lambda/20$, (e.g. high molecular weight polymer chain), the Rayleigh scattering no longer applies. In this condition, the light scattered from different points of the particles will reach the detector with different phases. The beams scattered from different points if coherent will lead to the phenomenon called intra-particle interference. Then the scattering intensity could be described by,

$$\frac{I_s}{I_i} = \frac{\pi^2 \alpha^2 \sin^2 \theta}{\lambda^4 \epsilon_0^2 r^2} \sum_{i,j=1}^N \exp[iq \cdot (r_i - r_j)] \quad (2.15)$$

For condition when the scattering volume contains several polymer chains, the inter-particle interference also contributes to the scattered intensity. However at low concentration, polymer chains are sufficiently far apart from each other, and the scattering intensity for the dilute polymer solution can be described by,

$$\frac{I_s}{I_i} = \frac{\pi^2 \alpha^2 \sin^2 \theta}{\lambda^4 \epsilon_0^2 r^2} n_p \sum_{i,j=1}^N \langle \exp[iq \cdot (r_i - r_j)] \rangle \quad (2.16)$$

where n_p is the number of polymer chains in the scattering volume and the static structure factor $S(q)$ is defined as the summation factor divided by N , the monomer number of the polymer chain.

$$S(q) = \frac{1}{N} \sum_{i,j=1}^N \langle \exp[iq \cdot (r_i - r_j)] \rangle \quad (2.17)$$

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The local segment density, which corresponds to the number of monomers per unit volume, is defined as

$$\begin{aligned}\rho(\vec{r}) &= \sum_{m,i} \delta(\vec{r} - \vec{r}_{mi}) \\ \rho &= \langle \rho(\vec{r}) \rangle = n_p N / V\end{aligned}\quad (2.18)$$

where the pair distribution function $\langle \rho(\mathbf{r})\rho(0) \rangle$ is called the autocorrelation function of the segment density. The static structure factor is related to the density autocorrelation function by,

$$S(q) = \frac{4\pi}{\rho} \int_0^\infty \langle \rho(\vec{r})\rho(0) \rangle \frac{\sin qr}{qr} r^2 dr = \frac{N_A N}{CM} \int_V \langle C(\vec{r})C(0) \rangle \exp(i\vec{q} \cdot \vec{r}) d\vec{r} \quad (2.19)$$

For a polymer chain with any conformation at low angle where $qR_g < 1$, the static structure can be approximated as,

$$S(q) = \frac{N}{1 + q^2 R_g^2 / 3} \quad (2.20)$$

In addition, the $S(q)$ for a Gaussian chain at any scattering angles can be determined from the Debye function $f_D(x)$ as defined by,

$$f_D(x) = 2x^{-2} [1 - x^{-2} (1 - \exp(-x^2))] \quad (2.21)$$

$$S(q) = N f_D(qR_g) \quad (2.22)$$

It is obvious that a plot of $S(q)$ as a function of q^2 at small q gives the radius of gyration for any conformation, but beyond that range, $S(q)$ depends on the conformation. The form factor or the internal structure factor $P(q)$ is defined as the ratio of $S(q)$ to $S(0)$. For Gaussian chain $R_g^2 = Nb^2/6$ and

$$P(q) = \frac{S(q)}{S(0)} = \frac{S(q)}{N} = f_D(qR_g) \quad (2.23)$$

For a hard sphere with the radius of R_s , $R_g^2 = 0.6R_s^2$,

$$P(q) = [3(qR_s)^{-3} (\sin(qR_s) - (qR_s) \cos(qR_s))]^2 \quad (2.24)$$

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While for a rod with rod length of L , $R_g^2 = L^2/12$,

$$P(q) = \frac{2}{qL} \int_0^{qL} \frac{\sin z}{z} dz - \left(\frac{2 \sin(qL/2)}{qL} \right)^2 \quad (2.25)$$

For static light scattering on the polymer solutions, the molecular parameters can be determined from the well-known Zimm Plot as described by equation (2.26),

$$\frac{KC}{R_\theta} = \frac{1}{M_w} \left(1 + \frac{1}{3} q^2 R_g^2 \right) + 2A_2 C \quad (2.26)$$

where $K (=4\pi^2 n^2 (dn/dC)^2 / N_A \lambda^4)$ is an optical constant with N_A , n , and λ being the Avogadro's number, the solvent refractive index, and the wavelength of the light in vacuum, respectively. C is the polymer concentration in gram per milliliter and R_θ is the excess Rayleigh ratio at scattering angle θ . The refractive index increment of the polymer solutions, (dn/dC) , can be measured using a differential refractometer. The z -averaged radius of gyration R_g , the second virial coefficient A_2 and the weight average molecular weight M_w can be determined from the above equation by extrapolating to zero concentration and zero angle. Most of this information can be derived by constructing the Zimm plot.

(b) *Dynamic properties*

The center-of-mass diffusion and the viscosity are the main dynamic properties of a polymer solution. A small change in the thermodynamics, for instance A_2 , causes a large shift in the solution dynamic properties.

Dynamic light scattering takes into account the frequency broadening of the scattered light due to the transfer of a small amount of kinetic energy from the incident light. Hence, DLS examines the intensity fluctuations with time and correlates these fluctuations to the properties of the scattering objects. These

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fluctuations can be caused by either translational diffusion arising from the motion of particles themselves as they move in and out of the scattering volume, or by rotation of non-spherical particles while present in the scattering volume. In general, the term of correlation functions of dynamic variables are commonly used to describe the response of the scattering molecules to the incident light. At time t and a delay time τ , the intensity-intensity autocorrelation function is the average $\langle I(t)I(t+\tau) \rangle$, which is a function of τ . Under the ergodicity assumption of the intensity, the autocorrelation function can be expressed by,

$$\langle I(t)I(t+\tau) \rangle = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T I(t)I(t+\tau)dt \quad (2.27)$$

When τ is 0, $\langle I(t)I(t+\tau) \rangle$ becomes $\langle I^2 \rangle$. When τ is close to ∞ , $\langle I(t)I(t+\tau) \rangle$ becomes $\langle I \rangle^2$ where $I(t)$ and $I(t+\tau)$ are irrelevant. The normalized intensity-intensity autocorrelation function $g_2(t)$ is related to the electric field autocorrelation function $g_1(t)$ by the Siegert relations with β the coherence factor,

$$g_2(t) = 1 + \beta (g_1(t))^2$$

$$g_2(t) \equiv \frac{\langle \Delta I(t) \Delta I(t+\tau) \rangle}{\langle \Delta I^2 \rangle} \quad (2.28)$$

In DLS, the dynamic structure factor $S(q, t)$ is defined as,

$$S(q, t) = \left\langle \frac{1}{n_p} \sum_{m, n=1}^{n_p} \exp[i\vec{q} \cdot (\vec{r}_m(0) - \vec{r}_n(t)) \right\rangle \quad (2.29a)$$

Hence,

$$g_1(t) = \frac{S(q, t)}{S(q, 0)} \quad (2.29b)$$

For the dynamic structure factor, when the t is 0, it is the same as the static structure factor. Thus, $S(q, t) = g_1(t)$. The dynamic structure factor or the field correlation function for single particle is related to the decay rate Γ by,

$$S(q, t) = \exp(-\Gamma t) \quad (2.30)$$

The decay rate Γ is the inverse of the relaxation time t . However, for multiple decay processes, the summation in Equation (2.30) can be replaced by an integral, leading to the following expression:

$$g_1(t) = \int w(\Gamma) \exp(-\Gamma t) d\Gamma \quad (2.31)$$

where $w(\Gamma)$ is a continuous distribution function of decay rate Γ . For translational diffusion decay, the decay rate

$$\Gamma = Dq^2 \quad (2.32)$$

where D is the diffusion coefficient. Through the Stokes-Einstein equation, the hydrodynamic radius can be determined from the diffusion coefficient,

$$D = \frac{kT}{6\pi\eta R_h} \quad (2.33)$$

where k is the Boltzmann constant, T the absolute temperature, η the solvent viscosity and R_h the polymer hydrodynamic radius [Noggle, 1996]

For polydispersed systems, more than one decay processes may exist. The relaxation behavior observed from light scattering are more complex, since light scattering is sensitive to both diffusive and non-diffusive processes. Several decay rates and decay times, Γ_i , τ_i , respectively are present in the system under investigation, thus the field correlation function $g_1(t)$ is the weighed sum of the individual contributions,

$$g_1(t) = \sum w_i \exp(-\Gamma_i t) \quad (2.34)$$

where w_i is the amplitude corresponding to the decay rate, Γ_i . for multiple decay processes, the summation in equation (2.34) can be replaced by in intergral, leading to the following expression [Chu, 1991; Brown, 1993]:

$$g_1(t) = \int w(\Gamma) \exp(-\Gamma t) d\Gamma \quad (2.35)$$

where $w(\Gamma)$ is a continuous distribution function of decay rate Γ . if the relationship between $w(\Gamma)$ and Γ is desired, the mathematical transformation needed to obtain such a relationship is rather complex and will not be discussed here. Significant research has been devoted to this field and much success has been achieved and it is now possible to obtain such relationship without much difficulty [Stepanek, 1993].

Isothermal titration calorimetry (ITC)

In the chemical industry, many manufacturers have shifted away from producing commodity chemicals to high value added specialty chemicals. In order to maximize the product performance and quality and to minimize the production cost, colorimetric methods are used to characterize these sophisticated products with detailed information in a relatively short time.

Calorimetry is the measurement of heat. It is interpreted as the amount of energy exchanged in the form of heat flow between two systems within a period of time. From calorimetry, useful thermodynamic parameters such as enthalpy (ΔH), entropy (ΔS), Gibbs free energy (ΔG) and heat capacity (C_p) are obtained in order to understand the principles behind polymer-surfactant interactions. A detailed classification of calorimetric methods can be found in monograph by Hemminger [Hemminger 1994]. The “micro”-prefix in microcalorimetry refers to a calorimetric measurement that is able to measure heat changes as low as $1\mu W$. There are many types of microcalorimeters used for thermodynamics studies. Depending on their

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applications and the method of study, these include flow, titration, and dilution calorimeters.

Titration calorimetry is the technique that combines thermochemical and analytical application, where the enthalpy change of a chemical reaction as a function of the amount of titrant is quantified. The measuring principle of the Microcal ITC is the detection of heat flow based on the power compensation technique. In a power compensated calorimeter, the effect of the heat to be measured (in this case the change in temperature) is suppressed by means of an input source. The advantage of this kind of calorimeter lies in its quasi-isothermal condition during the measurement where heat loss does not contribute to large errors and therefore more precise measurement of the heat is possible.

Other techniques such as FT-IR and NMR are widely employed in the characterization of HEUR polymers and also for exploring the complexation reactions of cyclodextrins and interaction between HEUR and surfactant.

So far, most of the researches on cyclodextrin inclusion compounds were focused on cyclodextrins and small molecules, where the inclusion mechanism is well established. However, there are few reported studies on cyclodextrin-polymer inclusion complex, and most of the studies focused on simple water-soluble polymers such as PEO, PEO-PPO block copolymer. In addition, the focus of these researches is predominantly on the characterization of solid complex, and to determine the relationship between properties and evolving structures. Research on the solution behavior of cyclodextrin and amphiphilic polymer is scarce. The mechanism of complexation and stoichiometry is not fully understood. Thus, the purpose of this thesis is to examine the interaction between various types of amphiphilic polymers and cyclodextrins using various physical characterization techniques, such as

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rheometry, light scattering, ITC, NMR etc. We seek to elucidate the complexation process and its implication on the flow properties of the solution mixtures. Physical and mathematical models were developed to describe the observed behavior.

Chapter 3 Materials and Experimental Techniques

3.1 Polymers and Cyclodextrins used in this study

Two groups of associative polymers were examined in this study. The first group consists of model HEUR associative thickeners, which were synthesized by Dow Chemicals [Jenkins, 1991]. The second group was synthesized in our laboratory, and possesses a better control of molecular weight distribution and functionality.

3.1.1 Model HEUR associative thickeners synthesized by Dow Chemicals

Model HEUR associative thickeners examined in this study are termed as HEUR-C0, HEUR-C12 and HEUR-C16 (The number corresponds to different length of hydrophobic end-group respectively), which were kindly donated by Dow Chemicals. The associative thickeners have nominal molecular weights of 17,500, 34,200, 51,000, 67,600, 100,400 Da. The chemical structure of HEUR associative thickeners comprises of a linear water-soluble polyoxyethylene backbone, end-capped with linear alkyl chains. These thickeners were originally prepared by melt condensation of a mixture of dried poly(ethylene glycol) of $M_w = 8,200$ Da, isophorone diisocyanate, and n-hexadecyl alcohol of a well-defined stoichiometric ratio to give the desired product. Therefore, the thickeners have the following chemical structure:

The three series of polymers differ from each other only in the length of hydrophobes, with all other compositional parameters kept constant. The hydrophobes in HEUR-C0, HEUR-C12 and HEUR-C16 are hydroxyl (-OH), dodecyl ($C_{12}H_{25}$) and n-hexadecyl ($C_{16}H_{33}$) respectively.

The molecular weight of HEUR was measured by size exclusion chromatography using DI water as elution solvent. The characterization of HEUR polymer has been conducted by other research group [Tam et al, 1998; Jenkins, 1991]. Typically the PDI fall in the range from 1.7 to 2.0. The associative thickeners were used as received without further purification. The details of associative polymer samples are summarized in Table 3.1.

3.1.2 Synthesis of polymers

a. Synthesis of Hydrophobically Modified Telechelic PEO

Two types of hydrophobically modified PEO were synthesized. The first one contains a bulky segment of IPDI on the backbone (Scheme 1) [Lundberg et al., 1994] and the second consists of a linear aliphatic structure on the backbone (Scheme 2) [Vorobyova et al., 1998].

Scheme 1

Isophorone diisocyanate (IPDI) was purchased from Sigma-Aldrich and distilled under vacuum prior to use. Poly(ethylene glycols) (PEGs) with M_n of 35,000, 20,000, and 5,000 Da were purchased from Fluka. GPC traces reveal the narrow molecular weight distribution with M_w/M_n less than 1.20. Toluene, tetrahydrofuran (THF) and petroleum ether were stirred for 24 hours over 40 mesh calcium hydride and distilled under argon. Water used in the viscometric analysis was passed through

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a Milli-Q (Millipore) ion exchange filtration system. Dibutyl tin diacetate and dibutyltin dilaurate were obtained from Alpha.

Table 3.1. Details of the HEUR Associative Thickeners from Dow Chemicals

Sample number	Structure R	n	Nominal Molecular weight
HEUR-C16-17K	C ₁₆ H ₃₃	2	17,500
HEUR-C16-34K	C ₁₆ H ₃₃	4	34,200
HEUR-C16-51K	C ₁₆ H ₃₃	6	51,000
HEUR-C16-67K	C ₁₆ H ₃₃	8	67,600
HEUR-C16-85K	C ₁₆ H ₃₃	10	85,000
HEUR-C16-100K	C ₁₆ H ₃₃	12	100,400
HEUR-C12-17K	C ₁₂ H ₂₅	2	17,500
HEUR-C12-34K	C ₁₂ H ₂₅	4	34,500
HEUR-C12-51K	C ₁₂ H ₂₅	6	50,700
HEUR-C12-67K	C ₁₂ H ₂₅	8	67,600
HEUR-C12-100K	C ₁₂ H ₂₅	12	100,400
HEUR-C0-17K	H	2	17,500
HEUR-C0-34K	H	4	34,200
HEUR-C0-51K	H	6	50,200
HEUR-C0-67K	H	8	67,500
HEUR-C0-100K	H	12	100,400

Scheme 1. Synthesis of hydrophobically modified telechelic PEO with IPDI

The pre-polymer of PEO was prepared on a large scale by the stoichiometric reaction of PEO, with excess of IPDI (1:200 equivalent ratio) and subsequently dividing the product into smaller portions for reaction with alcohol containing different hydrophobes (Scheme 1). The pre-polymer was prepared by adding 20 g of PEO ($M_w = 35K$) to a 250-mL, three-necked, break-away reaction flask, equipped with a Dean Stark water trap and condenser, argon inlet tube, and mechanical stirrer. The PEO was dried by azeotropic distillation in toluene. About 30 mL of the toluene was removed through the Dean Stark trap, and 40 g of dry, distilled tetrahydrofuran and 20 g of IPDI were then added. A small portion of the solution was withdrawn from the mixture after 36 h at 45 °C and placed in methanol for size exclusion chromatographic analyses. The remainder of the solution was precipitated into petroleum ether, filtered and dried under vacuum. The isocyanate content was determined by di-n-butylamine titration[Lundberg et al, 1994], which was determined

by reacting an aliquot with an excess of a standard solution of di-n-butylamine and back-titrating the residue di-n-butylamine with a standard hydrochloric acid solution. The isocyanate content was 0.23% and the pre-polymer was stored under argon at dry ice temperature until it was ready for reaction with alcohols containing variable hydrophobe sizes.

The following description of the hydrophobic modification of telechelic pre-polymer with hexadecanol is a representative of all end-capping reactions with hydrophobic, active-hydrogen containing compounds. In a 100 mL three-necked, round-bottom flask equipped with a magnetic stirrer, argon inlet tube, and thermometer, 5 g of the telechelic pre-polymer (-N=C=O , 0.29 mmol) was dissolved in 15 mL of dry, distilled THF. Dry hexadecanol (1.9 g, 8.5 mmol -OH ; 25 mol excess of -OH to -N=C=O) was dissolved in a small amount of THF and added to the flask and the content were heated to 40 °C. A drop of dibutyltin diacetate was added to catalyze the addition reaction and the mixture stirred for 12 h. Fourier transform infrared (FT-IR) is used to monitor the disappearance of the isocyanates peak in the spectra. After the reaction was completed, the solution was concentrated and precipitated in n-hexane, filtered and dried under vacuum. The procedure was repeated twice to ensure the complete purification of polymer. Finally the crude polymer was dissolved in water at pH of 7-8 and extracted from methylene chloride. After drying over magnesium chloride for 12 hours, the solvent was removed under vacuum and dried to obtain the purified polymer.

Scheme 2:

For a typical experiment, in a three-neck round-bottom flask, required amounts of PEO were dissolved in 200 mL of dry toluene. The trace amount of water

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in PEO was removed from toluene using azeotropic distillation. After removing 40-50 mL of toluene from the reaction mixture by distillation, the reaction mixture was cooled to 0 °C. To the reaction mixture, triethylamine (1.5 molar equivalent to PEO) was added under continuous stirring, and palmitoyl chloride (1.5 molar equivalent to -OH) was added drop-wise over a one-hour period using pressure equalizer funnel. Then the reaction mixture was stirred for 24 h at room temperature. After the disappearance of hydroxyl group which is monitored by IR, the solution was filtered to remove triethylamine hydrobromide. The solution was concentrated and precipitated in n-hexane, filtered and dried under vacuum. The procedure was repeated twice to ensure the complete coupling of the end groups, which is monitored by IR. Finally the crude polymer was dissolved in water at pH of 7-8 and extracted from methylene chloride. After drying over magnesium chloride for 12 hours, the solvent was removed under vacuum and dried to obtain the purified polymer.

Scheme 2. Synthesis of hydrophobically modified telechelic PEO with linear hydrocarbon

b. Synthesis of F-HEUR

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This procedure for synthesis of fluorocarbon end-capped HEUR and hydrocarbon end-capped HEUR is identical. Scheme 1 was also used for the preparation of fluorocarbon HEUR. But heptadecafluoro-1-decanol and tridcafluoro-1-octanol were used to prepare F-HEUR containing different length of fluoro-hydrophobes.

c. Synthesis of mono-capped hydrophobically modified PEO

Scheme 2 was also used to prepare mono-substituted hydrophobically modified PEO, but the PEO used in this experiment is methylated PEO with the structure of $\text{CH}_3\text{-O-(CH}_2\text{CH}_2\text{-O)}_n\text{-H}$ and molecular weight of 5000 Da. The procedure is identical to Scheme 2 described previously.

3.1.3 Cyclodextrins

The cyclodextrins used (Fluka) are listed in Table 3.2. All cyclodextrins were used as received without further purification.

Table 3.2 Characteristics of Cyclodextrins

	α -CD	β -CD	γ -CD
Number of glucose unit	6	7	8
Molecular Weight	972	1135	1297
Solubility in water g/100ml at ambient temp.	14.5	1.85	23.2
Cavity Diameter(Å)	4.7-5.3	6.0-6.5	7.5-8.3
Height of Torus (Å)	7.9	7.9	7.9
Dia. Of periphery (Å)	14.6	15.4	17.5

Sample preparation and measurements

Dry samples of model HEUR associative thickeners were stored in the refrigerator. Stock solutions were prepared by slowly dissolving solid polymers in distilled deionized water. The dissolution process usually took a week, which includes 5-6 days of swelling in sealed bottles kept in the refrigerator, followed by 24 hours dissolution by rotating in a tumbler at room temperature. The stock solution prepared has a concentration of 2.0 wt% unless otherwise stated. Sample solutions were prepared by dilution from stock solutions and stored in the dark at room temperature to promote their long term stability.

3.2 Equipments

3.2.1 Rheometer: Contraves Low Shear Rheometer (LS40)

One of the rheometer used in this project is the Contraves Low Shear 40 rheometer (LS40), which is a controlled rate rotational rheometer equipped with Couette geometries. The aim of the measurements is to obtain information on the steady and dynamic flow behaviour of viscoelastic solutions. The LS 40 is controlled by a computer through a user-friendly software package named SWR 40. This software allows the computer to control the instrument to perform measurements and to evaluate and store experimental raw data. The basic equipment of LS 40 measuring system includes a measuring instrument, control unit, thermostat and a computer with printer. Rheological experiments of less viscous samples were conducted using a controlled rate Contraves LS40 rheometer. The LS40 was fitted with a concentric cylinder of geometry: bob and cup radii at 5.5 and 6 mm respectively. The shear rate range of the steady measurements is from 0.001 to 100 s⁻¹ for LS40. Other measurements that involved more viscous solutions were performed on a controlled stress Carri-Med CSL 500 rheometer.

3.2.2 Rheometer: Controlled Stress Rheometer CSL500

CSL500 rheometer is a controlled stress Rheometer that can perform steady shear, dynamic and creep experiments over a wide range of frequencies and temperatures. Controlled stress rheometers employ a torque motor to apply a deforming stress to the sample and an optical encoder to measure the resultant strain developed within the sample. The CSL500 enable users to measure the viscosities over a wide range of shear rates and/or temperatures, enabling differences in flow properties to be quantified. The cone-and-plate measuring system was used on the CLS500 that has a diameter of 40 mm and a cone angle of 2 degree. All the rheological measurements were carried out at a temperature of 25 °C unless otherwise stated. The shear stress ranges from 0.2 to 1000 Pa on CSL500. The frequency dependent moduli were measured over an angular frequency range of 0.03 to 200 rad/s. preliminary experiment was conducted to establish that the viscosity data was repeatable. It can be seen from the Appendix that this was indeed so.

3.2.3 Isothermal Titration Calorimeter

Isothermal titration calorimeter (ITC) measures the differential enthalpy changes, while titrating one component to another. From the analysis of the ITC thermogram, various thermodynamic parameters, such as enthalpy and heat capacity could be obtained. In this study, all calorimetric measurements were performed 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 3.1. The titration

was carried out by a step-by-step injection of concentrated surfactant solutions from a 250 ml injection syringe into the sample cell filled with solvents or polymer solutions. The syringe is tailor-made so that the tip acts as a blade-type stirrer to ensure continuous mixing efficiency at 400 rpm. Using interactive software, an injection schedule was automatically carried out for a predefined number of 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 different temperatures controlled by a PolyScience water bath and the temperature fluctuation was within ± 0.02 °C. The reproducibility of the titration data was checked by repeating similar ITC experiments and it suggests that the thermodynamic parameters derived from ITC experiments are reliable and reproducible to within ± 5 % [Dai and Tam, 2003].

Figure 3.1 The schematic diagram of isothermal titration calorimeter.

3.2.4 Laser Light Scattering

Both static and dynamic light scattering were carried out using a Brookhaven laser light scattering system (Brookhaven Instruments Corp., NY). The system consists of a BI200SM goniometer, BI-9000AT digital correlator and other supporting data acquisition and analysis software and accessories. A 488 nm power adjustable Argon-ion laser was used as the light source. A BI-SFS sample filtration system was used to remove dust. An Atago 3T Abbe refractometer was used to measure the refractive index and a BI-DNDC differential refractometer was used to determine the refractive index increment. The measurement temperature was controlled by a PolyScience water bath. The schematic representation of the light scattering system is shown in Figure 3.2.

Figure 3.2 Schematic representation of BIC laser light scattering system.

For static light scattering (SLS), Zimm plot was used to analyze the experimental data. Toluene (Sigma, HPLC grade) was used as the reference in SLS. For dynamic light scattering (DLS), the inverse Laplace transform of regularized positive exponential sum (REPES) was used to analyze the intensity-intensity autocorrelation functions

(TCF) [Brown, 1993]. The grid was set to 10 and the probability of reject was set to 0.5.

3.2.5 Capillary Viscometer

The intrinsic viscosity related both the inherent viscosity and reduced viscosity of the associative polymers were measured with the PolyVISC automatic Viscometer (CANNON Instrument Co.). The intrinsic viscosity was calculated by the extrapolation of viscosity versus concentration for several solution concentrations. Measuring temperature was set to 25 °C for all the samples.

3.2.6 DSC and TGA

Differential Scanning Calorimeter (DSC) measurements were performed using a TA Instruments 2920 differential scanning calorimeter equipped with an auto-cool accessory and calibrated using indium. The following protocol was used for each sample: heating from 20 to 200 °C at 10 °C/min, and cooling to 20 °C at 10 °C/min. It then goes through the same cycle one more time, and data were collected during the heating run. Transition temperatures were taken as peak maxima. Thermogravimetric Analyzer (TGA) was made using a TA TGA 7 Thermogravimetric Analyzer. Samples were heated at 20 °C/min from room temperature to 600 °C in a dynamic nitrogen atmosphere (flow rate = 70 ml/min).

3.2.7 NMR

The ^1H NMR spectra were recorded on a Bruker DRX-400 NMR spectrometer at 400 MHz at room temperature. The ^1H NMR measurements were carried out with an acquisition time of 3.2 s, a pulse repetition time of 2.0 s, a 30°C pulse width, 5208-Hz spectral width, and 32K data points. Chemical shifts were referred to the solvent peaks ($\delta = 7.30$ and 2.50 ppm for CDCl_3 and DMSO-d_6 , respectively). The ^{19}F NMR

spectra were recorded on a Bruker AM-360FT-NMR spectrometer operating at 339 MHz using a 5 mm quadrinuclear probe. The chemical shifts of the ^{19}F signals were referenced to aqueous solutions of $\text{NaSO}_3\text{-CF}_3$ at -78.25 ppm.

3.2.8. GPC

Gel Penetration Chrommatography measurements were carried out An Agilent 1100 series GPC system equipped with an LC pump, a PLgel 5 mm MIXED-C column, and an RI detector was used. The system was calibrated with the provided narrow molecular weight polystyrene standards at ambient temperature. HPLC-grade THF was used as the mobile phase with a flow rate of 1.0 mL/min. The polymer were dissolved as 0.5 weight percent in THF. Frshely prepared solutions were tested within a week after dissolution. The sample were diluted with THF to the required concentration and then filtered with 0.5 micrometer pore size cellulose acetate syringe.

4. Polymer Characterization

Three types of block copolymers consisting of an alkyl chain hydrophobic segment and PEG were prepared by a synthetic procedure as illustrated in Scheme 1 and 2. HM-PEG-IPDI was prepared as described in Scheme 1, which contains a bulky IPDI segment on the backbone. HM-PEG was prepared using Scheme 2, with both linear aliphatic alkyl hydrophobe capped at both ends of the PEG chain. HM-PEG-Mono was also prepared through Scheme 2, but mono-substituted PEG $[\text{CH}_3\text{-O-CH}_2\text{CH}_2\text{O}]_n\text{-OH}$ was used in the reaction, therefore the final products have the following structure:

HM-PEG-IPDI:

HM-PEG:

HM-PEG-Mono:

The details of the ^1H -NMR spectra and GPC trace are shown in Figure 3.3.

^1H -NMR of the HM-PEG-IPDI revealed two peaks at 4.18 ppm (c) and at 4.36 ppm (a), which corresponds to the ester $-\text{CH}_2$ of cetyl group and ester $-\text{CH}_2$ PEG respectively. The integration of these two peaks (1:1) confirmed more than 95% substitution of IPDI to PEG at both the ends as well as the complete esterification of the cetyl alcohol to IPDI. For the other two polymers, similar method was used to identify and determined the degree of substitution. The results are described in Table 3.3.

Figure 3.3a ^1H NMR of as-synthesized hydrophobically modified PEG

Figure 3.3 b Gel Penetration Chromatogram traces of HM-PEG with different end groups

CHAPTER 3

EXPERIMENTS

Table 3.3 Molecular Characteristics of Copolymer

Copolymers	M _n	M _w	PDI	Conversion* (%)
HM-PEG-IPDI	3.06x10 ⁴	3.3 x10 ⁴	1.07	97
HM-PEG	1.72x10 ⁴	2.1 x10 ⁴	1.23	99
HM-PEG-Mono	6.9x10 ³	7.4x10 ³	1.07	99

Degree of substitution was determined by ¹H NMR spectroscopy.

Chapter 4 Interactions Between Methylated β -Cyclodextrin and Hydrophobic Ethoxylated Urethane in Aqueous Solution

4.1 Introduction

Hydrophobic ethoxylated urethane (HEUR) is one common associative polymer used in many water-borne coating formulations [Schaller and Sperry, 1992; Winnik and Yekta, 1997]. In the mid-1980s, Glass and co-workers [Glass et al., 1984; Karunasena et al., 1989] and Thibeault [Thibeault et al., 1986] were among the first to report on such telechelic associating polymers. Since then, research on telechelic associative polymers has been actively pursued, and many publications have appeared in the literature.

Cyclodextrins have been used together with amphiphilic polymers for reducing the viscosity of the amphiphilic polymer solution. It was proposed that cyclodextrins reduce the viscosity of associative thickener by deactivating the hydrophobic association [Zhang et al., 1998a]. In present study, we examined the rheological behavior of HEUR polymer solution in the presence of methylated β -cyclodextrin (m- β CD) and to elucidate the mechanism of cyclodextrins polymer complexation. The scope includes investigating the effects of m- β CD concentrations on the steady shear and viscoelastic properties of 2 wt % model HEUR polymer containing hydrophobic $C_{16}H_{33}$ alkyl chain. The strength of the associative junctions was quantified by examining the Arrhenius dependence of the viscosity on temperature. Superposition of oscillation experiments on steady shear flows was utilized to investigate the change of transient network structure of HEUR in the presence of m- β CD. At the same time, the effect of m- β CD on the dilute solution

properties was investigated by ITC and DLS, which further verifies the mechanism from rheological properties of semidilute solution.

4.2 Rheology of HEUR Solutions

4.2.1. Steady shear flow

The rheology of HEUR solution has been extensively studied and several association models have been proposed to explain the viscoelastic behavior. There are however still unresolved issues that need to be clarified even though the models predicted that the high viscosity depends on the degree of hydrophobic association. Issues, such as the mechanism to explain the formation of transient network (open or close model) and the cause of shear-thickening (chain extension or looping to bridging chain conversion) are still being debated. Therefore, it is necessary to investigate the rheological behavior of HEUR solution to enhance our understanding on such polymer solutions.

a. Effect of HEUR concentrations

Figure 4.1 shows the dependence of steady shear viscosity on the shear rate of various concentrations of HEUR-C16-51K. The viscosity profile of HEUR (shear rate dependent viscosity) is clearly a function of polymer concentration. At low HEUR concentration (< 0.7 wt%), HEUR solutions possess a low viscosity, which is Newtonian over the entire shear rates. As the concentration is increased to greater than 1.0 wt%, the low shear viscosity increases significantly and the solution exhibits shear-thickening behavior at moderate deformation, followed by a shear-thinning region at high shear rates. It is apparent that the changes in the flow properties (from

Newtonian to shear-thickening, and then to shear-thinning) shift to lower shear rates as the solution concentration is increased.

For all HEUR solutions from dilute, semi-dilute to concentrated solution, Newtonian viscosity is observed at the low shear rate regime, no shear-thinning was detected even when the time-temperature superposition principle was used to extend the data to extremely low shear rates [Li, 1995]. Thus, the low shear viscosity approaches the zero shear viscosity at low shear rates.

Figure 4.1 Dependence of shear viscosity on shear rate for 0.2 to 2 wt% HEUR-C16-51K aqueous solution.

It has been proven by extensive series of spectroscopy and scattering measurements, that HEUR polymer chains associate through their end-groups to form micelle-like junctions in aqueous solution []. At low polymer concentrations, when the chain ends are sufficiently hydrophobic, the polymer chains associate to form flower micelles consisting of looped chains where both end groups occupy the same

micelle. In these flower-like micelles, the PEG segments in the corona are stretched relative to the normal coil dimensions of a PEG chain in water. Since HEUR polymers normally have a substantial fraction of chains with only one hydrophobic substitution, the free ends lacking a hydrophobe do not participate in the association. In the flower micelles, these chains are free to dangle in the bulk solution, extending beyond the corona consisting of looped chains. At higher polymer concentrations, a secondary association process occurs, accompanied by the formation of bridges between adjacent micelles. As the polymer concentration is increased further (> 1.0 wt%), percolation structures are formed that span the rheological cell and lead to a large increase in solution viscosity.

Shear-thickening occurs when percolation structures are formed. Since the associations are dynamic in nature, and the process is rapid, the shear deformation has an effect in increasing the density of mechanically effective chains. Application of shear causes an increase in the ratio of bridging to looping chains. A likely source of this increase is the incorporation of aggregates of finite size into the percolation structures of the network, leading to the formation of shorter super-bridges, which should lead to longer relaxation times, whereas only a small increase in relaxation time is observed in this regime.

The viscosity of most polymeric systems generally obeys the Arrhenius relationship given by Equation (4.1),

$$\eta_o = Ae^{E_a/RT} \quad (4.1)$$

where η_o is the low shear viscosity; A is the Arrhenius constant; E_a is the activation energy (J/mol); R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$); and T is the absolute temperature (K).

Our experimental results indicated that the low shear viscosity of HEUR solutions exhibit an exponential dependence on temperature. The activation energy of each polymer solution is approximately related to the overall network strength of the mechanically active junctions. Activation energies were calculated from the slope of Arrhenius plot and summarized in Table 4.1. The activation energy increases with increasing of polymer concentration, which is evident that increases in concentration strengthens the overall network strength.

Table 4.1 Temperature dependence of η_0 for HEUR- C_{16} -51K aqueous solution of different concentrations

Concentration	Viscosity (Pa.s)				E_a
(wt%)	15 °C	25 °C	35 °C	40 °C	(kJ/mol)
0.4%	0.00387	0.00322	0.00263	0.00218	28.0
0.7%	0.0567	0.0335	0.0206	0.0138	68.7
2.0%	14.0	3.07	1.64	1.0	75.5

b. Effects of Molecular Weight

HEURs with similar hydrophobic moiety (C_{16}), but different molecular weight were investigated. With an increase in molecular weights, the low shear viscosity, η_0 decreases. The change in the flow behavior from Newtonian to shear-thickening, or from shear-thickening to shear-thinning, shifts to a higher shear rate as the HEUR molecular weight is increased. The results are shown in Figure 4.2.

Li [Li, 1995] reported that the molecular weight has a smaller effect on the viscosity than the concentration of hydrophobe. The concentration of terminal hydrophobes determined the total number of elastically active chains, or the density of

cross-linking junctions and the functionality of the junctions of the polymer network. Therefore, the effect of HEUR molecular weight on the viscosity of the solution mainly comes from the associative thickener's (AT's) ability to modify the topology of the association structure, such as the functionality of the cross-linking junction and the association energy of the terminal hydrophobe in the junction. According to the chemical structure of HEUR, it is obvious that with an increase in molecular weight, the hydrophobe concentration decreases. The result from Figure 4.2 shows that the viscosity is about 2 orders in magnitude lower when molecular weight of HEUR is increased from 17,000 to 100,000 g/mol. In contrast, the viscosity of PEO increases with increasing molecular weight, and this will be discussed later.

Figure 4.2 Shear viscosity of 2 wt% HEUR aqueous solutions with C₁₆H₃₃ hydrophobe but different molecular weights.

Figure 4.3 The influence of terminal end groups on viscosity of 2 wt% HEUR aqueous solution

Figure 4.4 Storage modulus G' (●), loss modulus G'' (■) and dynamic viscosity (▲) as function of angular frequency for a 2.0 wt% HEUR- C_{16} -51K solution.

c. Length of hydrophobic end group

Figure 4.3 illustrates how the length of HEUR hydrophobic end group affects the viscosity and shear-thickening behavior. These three polymers have similar molecular weight (M_w : about 50,000 g/mol), and concentration (2 wt%) but different hydrophobic modification, where HEUR-C₁₆-51K possesses C₁₆H₃₃, HEUR-C₁₂-50K with C₁₂H₂₅ and HEUR-C₀-50K with CH₃ alkyl chain. The comparison of low shear viscosities between associative polymer solution and control polymer solutions shows the effect of hydrophobic end group on the viscosity profiles. The low shear viscosity of HEUR solution is four orders of magnitude higher than their corresponding counterparts without hydrophobic modification. The result confirms that the length of hydrophobe is critical in controlling the shear viscosity and shear-thickening behavior. The viscosity enhancement arising from the formation of the network, also produces shear-thickening behavior as revealed by the solution of hexadecyl terminated HEUR. Shear-thickening is not observed for the C₁₂H₂₅ hydrophobic moiety, which exhibits a characteristic Newtonian behavior. This implies that the association energy of terminal C₁₂ hydrophobe in HEUR is too weak to produce a robust transient network at 2 wt%. The evidence that viscosity enhancement results from a network can only be derived from the viscoelastic measurements or other direct measurement of network structures; a large viscosity by itself does not necessarily imply the existence of a network. From the result it is evident that hydrophobic chain length of hexadecyl is critical to the formation of transient network.

4.2.2 Viscoelastic properties

Oscillatory measurement provides additional information on the characteristics of the network. When the concentration of HEUR solution is lower

than 1.0 wt%, the solution does not exhibit viscoelastic property. However, at concentrations exceeding 1.0 wt%, polymer networks are formed by hydrophobic associations, and the dynamic mechanical properties of HEUR associative network can be characterized in terms of a single relaxation time and a plateau modulus. Figure 4.4 shows the storage G' and loss G'' moduli of 2 wt% hexadecyl terminated HEUR. All HEUR solutions were tested in the linear viscoelasticity regime, where the measured properties do not depend on the amplitude of the oscillating shear strain. Thus, the measurements did not significantly perturb the network from its equilibrium state, and did not change the number of effective physical cross-links of the association network. In the figure, G' and G'' has a slope of 2 and 1 respectively at low frequencies on a logarithmic plot. This indicates that the response is viscous at low frequencies since the complex viscosity tends toward the limiting zero shear viscosity. At higher frequencies, G' increases and crosses G'' and then reaches an entanglement plateau, where G'' passes through a maximum. Other samples with different end groups (HEUR- C_{12} -50K and HEUR- C_0 -50K) do not exhibit viscoelastic properties at similar concentration. Therefore, it is evident that the length of hydrophobe is the main factor controlling the viscoelasticity of polymer solution.

The viscoelastic properties of 1.0, 1.5 and 2 wt% HEUR- C_{16} -51K solution is shown in Table 4.2. With increasing concentration, the relaxation time and plateau modulus increase sharply. Since the plateau modulus is proportional to the number of mechanically active chains and relaxation time is the average residence time that hydrophobe stay inside the micellar junction. It is obvious that increasing HEUR concentration strengthens the transient network. For 2 wt% HEUR solution, angular frequency dependence of G' and G'' can be described by a single Maxwell model, which indicate the formation of a well-defined polymer network.

Table 4.2 relaxation time and plateau modulus of HEUR-C₁₆-51K solution

Concentration (wt%)	1.0	1.5	2.0
Relaxation time λ (s ⁻¹)	0.008	0.05	0.07
Plateau modulus G_N^0 (Pa)	18	37	80

4.3 Effects of m-βCD concentration on solution viscosity

The shear rate dependence of the solution viscosity for a 2.0 wt% HEUR aqueous solution with different amounts of m-βCD is shown in Figure 4.5. The HEUR solution without m-βCD exhibits a Newtonian viscosity at low shear rates, a shear-thickening behavior at moderate shear rates, and a shear-thinning region at high shear rates. With the addition of m-βCD, the low shear viscosities decrease significantly. The characteristic shear-thickening and shear-thinning becomes less significant with increasing m-βCD concentration. It is evident that both transitions in the flow characteristics (from Newtonian to shear-thickening and from shear-thickening to shear-thinning) shift toward higher shear rates when m-βCD concentration is increased. When the m-βCD/hydrophobe molar ratio exceeds 1.0, shear-thickening characteristic disappears and only shear-thinning is observed at high shear rates. At even higher m-βCD concentrations, the solutions are essentially Newtonian over the entire shear rate range. When m-βCD concentration exceeds 5.0 mol of m-βCD per hydrophobe, no further reduction of viscosity is evident.

Figure 4.5. Effect of m-βCD on the shear viscosity of 2.0 wt% HEUR-C₁₆-51K aqueous solution. The number corresponds to the molar ratios of m-βCD to hydrophobe.

Figure 4.6 shows the low shear viscosity η_0 of the solution of m-βCD/HEUR complex as a function of m-βCD concentration. The control polymer (CP), which is the HEUR parent polymer with same molecular weight but no hydrophobic modification, was also studied for comparison. The m-βCD concentration dependence of the low shear viscosity of m-βCD/CP mixed solution as denoted by open circles reveals that the flow behavior is not affected by the addition of m-βCD due to the fact that no hydrophobic association presents in CP aqueous solutions. On the other hand, the low shear viscosity of HEUR changes significantly with the addition of m-βCD, where the final low shear viscosity is three orders in magnitude lower at m-βCD/hydrophobe (CD/Hy) molar ratio of 5.0. The final viscosity of m-βCD/HEUR complex solution approaches that of the CP polymer without hydrophobes. Thus, it is evident that the hydrophobe associative network is

completely destroyed when m- β CD concentration exceeds 5.0 mol of m- β CD per hydrophobe.

Figure 4.6 M- β CD /hydrophobe molar ratio dependence of the low shear viscosity of 2 wt% HEUR- C_{16} -51K and different concentrations of m- β CD in aqueous solution. The open circle is the m- β CD/CP system at the same measurement condition, where CP is the control polymer with same molecular weight but no hydrophobic modification.

As shown in Figure 4.6, we can separate the viscosity profile into three distinct regions;

- (i) Region 1. When the CD/Hy molar ratio is lower than 0.1, the low shear viscosity decreases marginally with increasing CD concentrations.
- (ii) Region 2. As the CD/Hy molar ratio ranges from 0.1 to 5.0, the viscosity decreases significantly with increasing CD concentrations.

- (iii) Region 3. When the CD/Hy molar ratio exceeds 5.0, the further reduction in the low shear viscosity is negligible.

The interactions between m- β CD and HEUR polymers of different molecular weights were examined. The viscosity of control polymer (CP) increases with increasing molecular weights. On the other hand, HEUR polymers exhibit an opposite trend; i.e. the solution with HEUR higher molecular weights displays a lower viscosity because the low shear viscosity is affected by the end-group concentration. Figure 4.7 indicates that the addition of m- β CD significantly reduces the low shear viscosity of HEUR solution, where the influence of m- β CD on the viscosity of lower molecular weight HEUR is more significant than that of higher molecular weight. When m- β CD/hydrophobe molar ratio exceeds 5, no further reduction in viscosity was observed. It is interesting to note that at m- β CD/hydrophobe molar ratio greater than 5, the solution of higher HEUR molecular weight possesses a higher viscosity. This phenomenon is in contrast to original HEUR solution, but it follows the same trend as unmodified control polymer and the viscosity is also identical to unmodified control polymer. which reinforces the hypothesis that the hydrophobic association has been completely suppressed by formation of hydrophobe/CD inclusion complex when m- β CD/hydrophobe molar ratio exceeds 5. Since the viscosity of HEUR solution is derived almost completely from the hydrophobic association, the contribution of polymer backbone (PEO) is usually very small. Only when the hydrophobic association has been completely removed, then the polymer solution shows the conventional characteristic behavior of PEO solution, and the viscosity is attributed to the polymer backbone as depicted by the higher viscosity observed for PEOs with higher molecular weight.

Figure 4.7 Effect of HEUR molecular weight on the low shear viscosity of m- β CD/HEUR complex solutions. The number corresponds to the m- β CD/hydrophobe molar ratio. CP is the control polymer with same backbone but no hydrophobe.

4.4 Temperature dependence of viscosity.

The activation energy E_a can be used to provide information on the strength of overall network junctions at various CD concentrations. In m- β CD/HEUR system, it is observed that the activation energy decreases with increasing m- β CD concentration as shown in Figure 4.8. When the m- β CD/hydrophobe molar ratio is less than 0.1, E_a decreases marginally with increasing m- β CD concentration, which suggests that m- β CD does not affect the network junctions significantly. At m- β CD/hydrophobe molar ratio ranging from 0.1 to 5.0, a sharp reduction in E_a is observed, and this is attributed to the disruption of the associative network junction by m- β CD. When the molar ratio exceeds 5.0, E_a approaches an equilibrium value of ~ 25 kJ/mol, which is

identical to the activation energy of unmodified control polymer. This confirms that the transient network is completely destroyed beyond this limit, which is further reinforced from dynamic measurements.

Figure 4.8 Effect of m- β CD/hydrophobe molar ratio on the activation energies of HEUR-C₁₆-51K/m- β CD complex.

4.5 Dynamic rheological properties of HEUR/CD solution

Figure 4.9 shows the storage $G'(\omega)$ and loss $G''(\omega)$ moduli of 2 wt% solutions of hexadecyl terminated HEUR polymers in the present of m- β CD. The viscoelastic properties of m- β CD/HEUR complex solution can be fitted using simple single Maxwell model: At low frequencies, $G'(\omega)$ and $G''(\omega)$ possesses a slope of 2 and 1 respectively. At higher frequencies, $G'(\omega)$ increases and reaches an entanglement plateau region.

Figure 4.9 Shear moduli of 2 wt% HEUR- C_{16} -51K aqueous solution with different amount m- β CD. The number corresponds to the molar ratio of m- β CD/hydrophobe. Open symbols are G' and filled symbols are G'' .

Addition of m- β CD into HEUR solution reduces both storage and loss moduli, and when the m- β CD/hydrophobe molar ratio exceeds 2, $G'(\omega)$ has decreased to the point where it is not accurately detectable by the cone-plate rheometer. The higher dependence of the moduli on angular frequency at intermediate m- β CD concentrations is an indication of weaker polymer network structures. In order to verify whether Maxwell model is valid for the m- β CD/HEUR complex solution, a Cole-Cole plot was constructed. The advantage of Cole-Cole plot is that plateau modulus can be accurately determined from the intersection of the semicircle with the horizontal x-axis. If the fitting to the experimental data with the model is perfect, G'' versus G' plot should form a semicircle as described by Equation (4.2),

$$G''(\omega) = [G'(\omega)G_N^0 - G'(\omega)^2]^m \quad (4.2)$$

where $m = 0.5$. Data that fitted the Maxwell model yielded a perfect semicircle when G'' was plotted against G' . Several sample solutions were studied using this method to examine the effect of m- β CD on the rheological properties of HEUR and the result is shown in Figure 4.10. For 2 wt% HEUR solution without m- β CD, the fitting yielded $m \sim 0.497$, which corresponds to an ideal fit to Maxwell model. When m- β CD/hydrophobe molar ratio equals 1.0, the fitting results of m is 0.465 and the viscoelasticity of m- β CD/HEUR may still be approximately described by Maxwell model.

Figure 4.10 Cole-Cole plot of the dynamic properties of 2.0 wt% HEUR- C_{16} -51K solution and different concentrations of m- β CD with the accompany fitting of the Maxwell model. The number corresponds to the molar ratio of m- β CD/hydrophobe. molar ratio 0 to 0.2, data fit to line 1 (outer line); molar ratio 0.3 to 0.5, data fit to line 2 (mid line); molar ratio above 0.8, data fit into line 3 (intra line).

Since the viscoelasticity of the solution can be describe by a single Maxwell model, $G'(\omega)$ and $G''(\omega)$ can be expressed by Equations. (4.3) and (4.4) respectively:

$$G'(\omega) = \frac{G_N^0 \omega^2 \lambda^2}{1 + \omega^2 \lambda^2} \quad (4.3)$$

$$G''(\omega) = \frac{G_N^0 \omega \lambda}{1 + \omega^2 \lambda^2} \quad (4.4)$$

where the relaxation time λ and the plateau modulus G_N^0 are given by Equation (4.5),

$$\lambda = \frac{1}{\omega_c} \quad \text{and} \quad G_N^0 = \frac{\eta_0}{\lambda} \quad (4.5)$$

The relaxation time λ and plateau modulus G_N^0 of methylated β- CD/HEUR solution were extracted from the dynamic oscillatory experiments and plotted in Figure 4.11.

Comparing HEUR polymer and unmodified control polymer, the latter shows Newtonian behavior at this concentration (2 wt%) with a much lower viscosity value and the viscosity is independent of the m-βCD concentration, which is evident from Figure 4.6. Thus, it can be concluded that the contribution of polymer backbone entanglement to the plateau modulus is negligible. The relatively high value of G_N^0 even at m-βCD/hydrophobe ratios of 1.0 is mainly attributed to the fact that the polymer network structure formed through hydrophobic association has not been completely destroyed. According to the simple theory of rubber elasticity based on the transient network theory proposed by Green and Tobolsky [Green and Tobolsky, 1946], G_N^0 is proportion to the number density of mechanically active chains,

$$G_N^0 = \nu RT \quad (4.6)$$

where ν is number density of mechanically active chain in the network, R is the gas constant, and T is the temperature in Kelvin.

By combining Equations (4.5) and (4.6), the zero shear viscosity is given by Equation (4.7):

$$\eta_0 = \nu \lambda RT \quad (4.7)$$

According to Equation (4.7), the low shear viscosity is a function of the number density of mechanically active chain ν in the transient network and the relaxation time λ at a fixed temperature. The temperature dependence of the relaxation time is more representative to the strength of the junction for the polymer network structure. Based on the Arrhenius relationship, the activation energy could be determined from the slope. The activation energies from relaxation time measurements show similar trends as those from previous steady flow experiments.

Figure 4.11 Effect of m- β CD/hydrophobe molar ratio on the plateau moduli and the relaxation times of 2 wt % HEUR-C₁₆-51K solution with different concentrations of m- β CD. G_0 : open symbol; λ : filled symbol.

It is generally agreed that cyclodextrins interact with hydrophobically modified associative polymer by threading the hydrophobe in the hydrophobic cavity of cyclodextrin therefore deactivating the mechanically active chains, which disrupts the associative network, thereby reducing the viscosity. However, a systematic study

on this has not been reported. It is interesting to note from Figure 4.11 that the plateau modulus does not show any significant decrease when m- β CD/hydrophobe molar ratio is lower than 0.2. According to Equation (4.7), the low shear viscosity is proportional to relaxation time if the plateau modulus remains constant. This condition corresponds to stage 1 (Figure 4.12), where the reduction in the low shear viscosity is caused predominantly by the reduction in the relaxation time, which weakens the associate network. The solution relaxation time indicates the strength of the hydrophobic association, which is a strong function of temperature and a weak function of solution concentration [Li, 1995]. There is no significant reduction in the number of mechanical active chain, which is proportional to plateau modulus. But relaxation time, which is the strength of hydrophobic association, reduces significantly. This implies that at these concentrations, m- β CD/HEUR interaction does not deactivate the mechanically active chains, but it only weakens the strength of each hydrophobic domain due to the capping of the hydrophobes of the looping chains. Since the relaxation time corresponds to the lifetime of the association junction, the reduction in life time weakens the network junction thereby producing a lower viscosity. In stage 2, where the m- β CD/hydrophobe molar ratio is greater than 0.2, both the plateau modulus and relaxation time start to decrease rapidly, confirming the disruption of the polymer network into smaller isolated clusters. We observed that G_0 decreases more rapidly than the relaxation time.

Figure 4.12 Schematic representation of the interaction mechanism between m- β CD and HEUR. The thick line represent uncapped PEO. Thin line represent capped PEO.

4.6 Superposition of Oscillation on Shear Flow

Our instrument allows us to examine samples where the oscillatory shear can be superimposed on the solution subjected to a continuous shear deformation. In these experiments, a stress or a shear gradient was applied on the sample and once equilibrium was attained, an oscillatory shear was superimposed onto the sheared sample, and the linear viscoelastic properties were measured over a wide frequency range of between 0.1 to 200 rad/s. Using this approach, we are able to probe the structural behavior of the polymer network under different shear conditions [Seng et al., 2000; Tirtaatmadja et al., 1997], and this will permit us to examine the impact of methylated β -cyclodextrin on the HEUR network structure at different shear deformations.

The shear-stress dependence of the plateau modulus, relaxation time and dynamic viscosity of 2 wt% HEUR were plotted in Figure 4.13. It is observed that the dynamic viscosity profile follows the same trend as the steady shear viscosity profile. Using this technique, we hope to be able to probe the structure behavior of the polymer network under different shear conditions. Shear-thickening occurs at applied stress ranging from 10 to 100 Pa, which is attributed to shear induced polymer association or aggregation including temporary network formation during shear [Tam et al 1998]. When the applied stress was increased further, the dynamic viscosity began to decrease. The plateau modulus continues to increase even though the viscosity of solution has started to decrease when the applied stress exceeds 100-120 Pa. Tam and co-workers [Tam et al., 1998] observed that only when shear stress was increased beyond 300 Pa, the plateau modulus started to decrease significantly. In contrast, the relaxation time follows the same trend as the viscosity. Initially the relaxation time increases, but the onset for the decrease occurs at a somewhat lower stresses than the maximum of the dynamic viscosity in the shear-thickening region. Thus, the results indicated that the shear-thinning is a consequence of a shear enhanced exit rate of the hydrophobic end groups from the micellar junctions of the network, which also were observed for other systems, such as gelatin solution [Andrews and Reed, 1978; Groot and Agterof, 1996].

Addition of m- β CD has different effects on the plateau modulus and relaxation time of HEUR solution. The results are shown in Figures 4.14 and 4.15, the proposed interaction mechanism has depicted in Figure 4.12.

Figure 4.13 Relationship of relaxation time (O), dynamic viscosity (□) and the plateau modulus (Δ) and applied stress for 2.0 wt % HEUR-C16-51K solution.

Plateau Modulus. According to transient network theory [Tanaka and Edwards, 1992a-c], loop chains are mechanically inactive. Only bridging chains contribute to the plateau modulus, which is mechanical active. The magnitude of plateau modulus is proportional to the number density of mechanically active chains in the network according to Equation (4.6). Thus, an increase in the plateau modulus within the shear-thickening regime is evidence that shear-thickening occurs because of a shear-induced rearrangement of the network resulting in a larger proportion of active junctions which comes about through an increase in the ration of bridging to looping chain [Tam, 1998]. The applied stress facilitates loop-to-bridge transitions, which lead to the increase in the number of junctions.

In region 1, where m- β CD concentration is relatively low, there is no significant change in G_N^0 at low to moderate shear stresses, but some differences are

observed at higher applied stresses. At applied stress of 250 Pa, a slight decrease in G_N^0 is evident for m- β CD/hydrophobe molar ratio of 0.005, compared with HEUR solution. At 0.05 mol m- β CD per hydrophobe, the plateau modulus decreases sharply when the applied stress exceeds 250 Pa. These results indicate that in region 1, G_N^0 remains constant at low applied stresses, but the number of mechanically active chains created within the shear-thickening regime decreases with increasing m- β CD concentrations. Thus, it is evident that addition of m- β CD does not deactivate the mechanically active chains, instead it interacts with loop chains within the rosette micelles thereby reducing the probability of loop to bridge transition. In region 2, the plateau modulus decreases significantly even at very low stresses, indicating that m- β CDs have deactivated the mechanically active chains. Finally, beyond 1 mol m- β CD per hydrophobe, the transient network is disrupted into smaller isolated clusters, thereby removing the viscoelastic characteristics of the solution.

Figure 4.14 Relationship of plateau moduli of 2 wt % HEUR-C16-51K and different concentrations of m- β CD and applied stress. The number corresponds to the molar ratio of m- β CD/hydrophobe.

Relaxation time. A system that obeys the simple Maxwell model is characterized by a dominant single relaxation process. This relaxation process is governed by the exit rate of a hydrophobic group from the junction point in these end-capped systems [Annable et al, 1993; Tanaka and Edwards, 1992]. Karlson [Karlson et al., 2002a, 2002b] also observed such a phenomenon when about 0.1 mole fraction of β CD was added to hydrophobically modified poly(ethylene glycol) polymer. Li [Li, 1995] pointed out that relaxation time increased with increasing HEUR concentration up to 4 wt%. In our experiments, we observed that the relaxation process is more sensitive to changes in the system than the plateau modulus. A slight increase in m- β CD concentration or applied stress causes a significant reduction in the relaxation time. At m- β CD/hydrophobe molar ratio of 0.005 and applied stress of 250 Pa, the plateau modulus of complex is similar to pure HEUR at different applied stresses, however the relaxation time is significantly lower. When the m- β CD/hydrophobe molar ratio is increased to 0.05, the relaxation time of m- β CD/HEUR complex solution is lower than that of pure HEUR solution at all applied stresses. However, when the ratio is greater than 1.0, the relaxation time is only one-tenth that of the original HEUR solution.

Figure 4.15 Relationship of relaxation time of 2 wt % HEUR- C_{16} -51K and different concentrations of m- β CD and applied stress. The number corresponds to the molar ratio of m- β CD/hydrophobe.

Because the associative junctions are dynamic, the micro-Brownian movement of network chain segments and junction breakage and restructuring processes are at equilibrium. When m- β CDs are added into HEUR solution, it interacts with the micelles and the encapsulation of hydrophobes by m- β CD will reduce the aggregation number in the hydrophobic domain or junction, which destabilizes the micelles, resulting in a corresponding reduction in the relaxation time. It is proved later by DLS that the micelles are destroyed by cyclodextrin and finally single polymer chain is obtained. In the mean time, bridging chains are not affected as suggested by the constant G_N^0 up to m- β CD/hydrophobe molar ratio of 0.1. However, the magnitude of shear-thickening becomes lower at high stress as evident from

Figure 4.15. Since total number of chains and bridging chains do not change with addition of cyclodextrin at low cyclodextrin concentration, so hydrophobic chain/cyclodextrin interaction happens between looping chain and cyclodextrin. Total number of looping chains is reduced since the hydrophobes have been deactivated when they are encapsulated by m- β CDs, thus, the transition from loop to bridge chain is minimized. Therefore, the origin for the large decrease in the viscosity with the addition of cyclodextrins is related to the shear-induced increase in chain-end exit rate, which is attributed to the reduction in the aggregation number of the micellar junctions.

4.7 Effect of m- β CD on the properties of dilute HEUR solutions

4.7.1 Intrinsic Viscosity and Huggins constant

Figure 4.16 shows the dependence of reduced and inherent viscosities on the concentration for hydroxyl and hexadecyl hydrophobic end-groups. As evident from Figure 4.16a, the reduced viscosity of a hydroxyl terminated model associative polymer is linearly proportional to the concentration over the measured concentration range, with the Huggins constant K' determined to be about 0.35, which is the typical value for most conventional polymer-solution systems. In contrast, the model associative polymer with the alkyl end groups interact at extremely low concentrations to produce a rapid increase in the reduced viscosity, which then deviates from the linear behavior predicted by the Huggins Equation. Figure 4.16b shows the reduced and inherent viscosities of hexadecyl hydrophobic end-groups terminated model associative polymer, and they increase as both the concentration and alkyl chain lengths are increased. The viscosity enhancement becomes more dramatic at concentrations exceeding 0.7 g/dl, which heralds the formation of

CHAPTER 4**m- β CD/HEUR SYSTEM**

associative clusters in solution, and the incorporation of the associative polymer chains to the clusters is enhanced as the length of the hydrophobic end-group relative to the polymer backbone increases. The shape of the curves in Figure 4.16b suggests that the network build up over a range of concentrations, rather than at a particular critical micellar concentration as in the case of ordinary surfactants or hydrophobically modified hydroxyethylcellulose. The Huggins parameter K' for the polymer with hexadecyl possesses an extremely high value of 6.0. Jenkins [Jenkins, 1991] used the absorbance measurement on model star shaped associative polymers, and they observed that the large values of K' for associative polymer solutions corresponded to the formation of a hydrophobic domain in solution. Hence, the large value of K' and the rapid increase in specific viscosity with increasing polymer concentration indicate association of the model polymer chains containing the hexadecyl end-groups.

Addition of m- β CD into dilute solution of model associative polymers produces different characteristics with different hydrophobic end-groups. The results are summarized in Table 4.3

Table 4.3 The effect of m- β CD on the intrinsic viscosity and Huggins parameter of associative polymer solution

	m- β CD/HEUR-C ₁₆ -51K		m- β CD/ HEUR-C ₀ -51K	
CD/hy	$[\eta]$ (dl/g)	K	$[\eta]$ (dl/g)	K
0	1.13	5.98	0.64	0.35
1	0.96	3.4	0.64	0.35
2	0.95	1.95	0.64	0.35
4	1.00	1.00	0.64	0.37
8	1.00	0.48	0.64	0.36
14	1.00	0.35	0.64	0.36

Figure 4.16 Concentration dependence of the reduced and inherent viscosities of polymers: (a) HEUR-C₀-51K and (b) HEUR-C₁₆-51K

As shown in Table 4.3, the intrinsic viscosity values for the two systems are different with the addition of m- β CD. For the HEUR-C₀-51K, there is no hydrophobic association, hence the addition of cyclodextrins does not alter the intrinsic viscosity and Huggins parameter K'. However for HEUR-C₁₆-51K, which possesses a hexadecyl moiety at both ends of the PEO chains, a significant reduction in the Huggins parameter was observed with increasing cyclodextrin concentrations. The effect of m- β CD on K' is consistent with the dependence of the chemical potential of the associative polymer's hydrophobes on these interaction parameters given by Equation (4.8). The chemical potential of a hydrophobe $\Delta\mu$ can be estimated from Scott-Hildebrand theory [Hoy, 1984]

$$\Delta\mu = 2RT - \frac{V_s + V_p}{2} (\delta_s - \delta_p)^2 x^2 \quad (4.8)$$

where R is the gas constant, T is the absolute temperature, V_s and V_p are the molar volume of the solvent and hydrophobe respectively, δ_s and δ_p are the solubility parameters of the solvent and hydrophobe respectively, and x is the volume fraction of the hydrophobe in solution. As discussed by Hoy and co-workers [Hoy, 1984], the driving force for forming and sustaining intermolecular associations increases as the chemical potential of the hydrophobic groups become more negative. Thus, the Huggins parameter is an indicator for the degree of intermolecular association. Adding cyclodextrin to HEUR solution increases the solubility of hydrophobe by threading the hydrophobe into the hydrophobic cavity of cyclodextrin. The solubility of a hydrophobe can be changed upon complexation with cyclodextrin. When a hydrophobe is complexed by a cyclodextrin, the hydrophobe in the cavity of the cyclodextrin is essentially surrounded by the molecule of cyclodextrin. The hydrophobic groups that would be in contact with the solvent in the free state interact

with the atoms of the cavity of the cyclodextrin instead. The outer surface of the cyclodextrin contribute to the solubility of the complex and not the portion of the hydrophobic group interacting with the cavity of the cyclodextrin [Hedges, 1998]. For example, the solubility of Paclitaxel can be enhanced from 4×10^{-4} mM to 39.6 mM in the presence of m- β CD, with the enhancement factor of 99 [Loftsson and Brewster, 1996]. Thus the difference between δ_S and δ_P becomes smaller, hence the chemical potential becomes more positive according to Equation (4.8). Therefore the driving force for producing and sustaining intermolecular associations is reduced.

4.7.2 Isothermal titration calorimetry (ITC) Studies

Figure 4.17 shows the isothermal titration curve of 8.8 mM methylated β -CD solution into 0.1 wt% HEUR- C_{16} -51K solution together with the dilution curve of 8.8 mM methylated β -CD in water. There is no significant enthalpy change for the dilution of m- β CD, which indicates weak dissolution of m- β CD in water. The m- β CD /HEUR titration curve is a standard “S” curve, which usually corresponds to one site binding mechanism. The HEUR polymer used in this experiment has a functionality of 1.7 [Tam et al, 1998] , therefore there are still 30 % HEUR polymer chains with only one end capped by a hydrophobe, while the other end do not possess a hydrophobe. The un-capped PEO chains are hydrophilic, so they do not participate in hydrophobic association, and it extends into the aqueous solvent as dangling chains. Therefore, there are theoretically two possible binding sites for cyclodextrin; uncapped PEO hydroxyl end and the alkyl chain ends. The ITC thermogram suggests that the reaction is a one-site binding, which implies that m- β CD does not interact with un-capped PEO chain, which is supported by the findings of Harada for the interaction of PEO homopolymer with different cyclodextrins [Harada and Kamachi,

1990]. Because of the hydrophobic interaction between the hydrophobe of HEUR polymer and the hydrophobic cavity of the m- β CD, a negative enthalpy is observed, which suggests that the interaction is exothermic. The enthalpy gradually decreases with increasing m- β CD concentration. Fitting of the data with a one site binding model allows us to determine the binding enthalpy ΔH , entropy ΔS , Gibbs free energy ΔG and the stoichiometric ratio. It is interesting that the stoichiometry was found to be 1, which is consistent with the previous published results [Weickenmeier and Wenz, 1997].

Figure 4.17 Calorimetric titration curves of 8.8mM m- β CD into water (filled circles) and 0.1 wt% HEUR-C₁₆-51K solution (opened circles) at 25°C

4.7.3 Laser Light Scattering

Laser Light scattering has been widely used to study the microstructure of the polymer chain conformation in solution. By monitoring the dynamics of solutions, we can better understand the associative mechanism of polymers and the interaction

between cyclodextrins and HEUR. Not only the weight averaged molecular weight M_w , radius of gyration R_g and second virial coefficient A_2 but also the hydrodynamic radius and the conformation of polymer chains in solution could be determined. Parameters such as HEUR and CD concentrations, detection angles, etc were carried out to analyze the possible microstructure of complexes.

4.7.4 Static light scattering

For static light scattering, the weight-averaged molecular weight (M_w), the second virial coefficient (A_2) and the z-averaged radius of gyration (R_g) of polymers can be obtained from Equation 4.9 [Flory, 1953].

$$\frac{KC}{R_\theta} = \frac{1}{M_w} \left(1 + \frac{1}{3} q^2 R_g^2 \right) + 2A_2 C \quad (4.9)$$

where $K (= 4\pi^2 n^2 (dn/dC)^2 / N_A \lambda^4)$ is an optical constant with N_A , n , and λ being the Avogadro's number, the solvent refractive index, and the wavelength of the light, respectively. C is the polymer concentration, R_θ is the excess Rayleigh ratio at scattering angle θ , and $q (= 4\pi n \sin(\theta/2) / \lambda)$ is the scattering vector. The refractive index increment of HEUR polymer solution at 25°C, (dn/dC) , was determined from a BI-DNDC differential refractometer and found to be 0.160 ml/g for HEUR- C_{16} -51K.

Figure 4.18 shows the Zimm-plot of dilute HEUR- C_{16} -51K solution at 25°C. The apparent weight-averaged molecular weight and the radius of gyration of HEUR- C_{16} -51K were found to be 930,000 g/mol and 51 nm respectively. Winnik and co-workers had previously reported that the CMC for this polymer is about 0.01 wt% [Zhang et al. 1996]. The molecular weight obtained is much higher than that of HEUR unimers, reinforcing that the polymer chains are in the form of self-associated micelles. The number of HEUR unimer chains per micelles can be calculated from the expression:

Figure 4.18 Zimm plot of dilute HEUR-C₁₆-51K in aqueous solutions at 25 °C. (Concentrations: 2 mg/ml to 10 mg/ml; measurement angles: 45 to 135 °) [Dai et al., 2001a]

$$N_w = \frac{M_w(\text{micelles})}{M_w(\text{unimers})} \quad (4.10)$$

The calculated N_w is approximately 11. Since the averaged capping rate of the HEUR is 1.7 and there is only one association core in the micelle, the aggregation number of each micelle was determined from $N_{\text{agg}} = 1.7 \times N_w = \sim 19$. This value is identical to the aggregation number of 20 as reported by Winnik and co-workers using fluorescence spectroscopy [Xu et al., 1996; Yekta et al., 1996].

4.7.5 Dynamic light scattering of HEUR dilute solution

The relaxation time distribution functions of HEUR-C₁₆-51K at different polymer concentrations are shown in Figure 4.19.

Figure 4.19 The relaxation time distributions of different concentrations of HEUR-C₁₆-51K in aqueous solutions at 25 °C. (Measurement angle of 90°).

Only one peak is evident from the distribution functions. The distribution and location of the peak does not change with increasing HEUR concentrations. When the concentration was further increased to 0.4 wt%, the second relaxation peaks appear as slow relaxation modes at longer relaxation time, which suggests the onset of interaction between individual micelle. The linear dependence of the decay rates on q^2 suggests that the relaxation mode is a translational diffusion mode and the slope corresponds to the translational diffusion coefficient of HEUR micelles. The concentration dependence of the diffusion coefficients is shown in Figure 4.20.

Figure 4.20 The relationship between diffusion coefficients and concentrations of HEURC_{1651K} at 25°C. [Dai et al., 2001a]

The diffusion coefficients decrease with increasing polymer concentrations. The diffusion coefficients determined at finite concentration are characterized by the diffusion second virial coefficient, k_D , described by the equation below [Brown, 1993];

$$D = D_0 (1 + k_D C + \dots \dots) \quad (4.11)$$

where D_0 is the translational diffusion coefficient at infinitely dilute solution. It possesses a value of $7.1 \times 10^{-12} \text{ m}^2/\text{s}$, which is identical to the self-diffusion coefficient for HEURC_{1651K} micelles as determined from pulse-gradient NMR experiments [Zhang et al., 1996]. From the Stokes-Einstein expression, the hydrodynamic radius, R_h , can be determined from,

$$R_h = \frac{kT}{6\pi\eta_0 D_0} \quad (4.12)$$

where k is the Boltzmann constant, T the absolute temperature in Kelvin, η_0 the solvent viscosity. The hydrodynamic radius of HEUR-C₁₆-51K micelle was determined to be ~ 34.5 nm.

Li [Li, 1995] reported that the critical network formation concentration c^* , is the concentration where solution viscosity starts to significantly increase and the concentration at which shear thickening flow behavior begins to occur at a moderate shear region. It can be consequently assumed that the shear-thickening phenomenon of HEUR solution is a characteristic flow behavior of an associative network structure. The critical network formation concentration for HEUR is about 0.7 wt%, which is consistent with the results of Persson et al. [Persson et al., 1992] This shows that the flower-like micelle starts to interact with each other to form larger clusters and eventually they produce a transient network. Only one slow decay mode was observed when the concentration is greater than 2 wt%, suggesting that a well-defined polymer network has been produced.

4.7.6 DLS of Different Cyclodextrins

Dynamic light-scattering measurements were initially conducted on several pure cyclodextrins at different CD concentrations, and the results are shown in Figure 4.21. All three types of CDs show similar distribution functions. Two decay modes are observed in all the samples. The fast mode is attributed to the translational diffusion of single CD molecule in solution (size of ~ 0.8 nm) and it does not change with CD concentrations. The slow mode is attributed to CD aggregates, which are formed through intermolecular hydrogen bonding in water. The relaxation time of slow mode is concentration dependent, which increases with increasing CD concentration. In order to verify the formation of β -CD aggregation in water, the

sample was first subjected to ultrasonic treatment. After 10 minute of ultrasonic treatment, dynamic light scattering was performed and negligible change was observed. The β -CD solution was also passed through a 0.2 micron filter and then measured under similar condition. This filter is used to remove impurity and large aggregation that may affect the measurement of DLS. The slow mode disappeared when measurements were performed immediately, however, when the filtered CD solution was left for one day at room temperature, the slow decay mode reappeared. This confirmed that the slow decay mode in the decay time distribution function is dynamic and is attributed to the CD aggregations. Coleman [Coleman et al., 1992] had examined the aggregation behavior of cyclodextrins and they concluded that the solubility is related to the interaction of aggregate structure with that of water. Although the amounts of CD aggregates are small, their contribution to the scattered light intensity is significant due their relatively larger size. Owing to the large size of the clusters, their contribution to the overall scattered intensity is high compared to the contribution from unimeric CDs. Since the scattered intensity scales with the number of particles (C) and is also proportional to r^6 , where C and r is the concentration and radius of the particle respectively, the scattering is thus dominated by the slower mode [Gaitano and Brown, 1997]. The presence of large aggregates complicates the binding interaction study between cyclodextrin and HEUR using the light scattering technique.

Figure 4.21 (a) Decay time distribution of β – cyclodextrins at different concentrations

Figure 4.21 (b) Decay time distribution of different concentrations of methylated β -cyclodextrin

4.7.6.1. 0.1wt% HEUR solution in the presence of m-βCD

The relaxation time distribution functions of 0.1 wt% HEUR-C₁₆-51K aqueous solution in the presence of m-βCD are shown in Figure 4.22. When m-βCD concentration is low, only one peak is observed, which corresponds to the HEUR micelle. The relaxation time of this peak does not change with CD concentration. However, the relaxation distribution broadens when m-βCD concentration was increased. When concentration of m-βCD exceeds 10 mol CD per hydrophobe, two relaxation modes are apparent; the slow mode corresponding to the aggregation of β-CD complex and the fast mode corresponds to HEUR unimers, which are encapsulated by m-βCD. The minimum size of HEUR/cyclodextrin complex is about 10 nm, which agrees with the size of PEO chain in solution. The relaxation time of the fast mode decreases with increasing m-βCD concentration and when m-βCD increases beyond 20 mol per hydrophobe, it becomes constant. However, the relaxation time of the slow mode increases with m-βCD concentration, which is identical to that observed for m-βCD in water.

Since the fast mode corresponds to the HEUR unimers encapsulated by cyclodextrin molecules, the angle dependence of the correlation function was also measured to verify whether it bears the signature of a translational diffusion object. The light scattering vector, q , is defined as the intensity difference. i.e. $q = \mathbf{k}_i - \mathbf{k}_s$ where the magnitude of q is given in the equation below:

$$q = \frac{4\pi n}{\lambda} \sin\left(\frac{\theta}{2}\right) \quad (4.13)$$

where n is the refractive index of the solvent, λ the wavelength of the incident beam and θ , the scattering angle. The decay rate is linked to the translational diffusion coefficient D by:

$$\Gamma = Dq^2 = \frac{D(4\pi m)^2}{\lambda_0^2} \sin^2\left(\frac{\theta}{2}\right) \quad (4.14)$$

The relationship between the decay rate Γ and q^2 should be linear and the slope corresponds to the translational diffusion coefficient D . Time-dependent phenomena other than translational diffusion can contribute to the measured correlation function, and these include rotational diffusion and intramolecular relaxation modes. A flexible Gaussian coil can possess a number of internal modes due to flexing of the chain segments, which are not q^2 dependent. The CD/HEUR complex was examined and observed results confirm that the scattering is attributed to translational diffusion. Therefore Equation 4.12 is valid to calculate the hydrodynamic radius of HEUR/cyclodextrin complex in aqueous solution. The minimum size of HEUR/cyclodextrin complex is about 10 nm, which agrees with the size of PEO chain in solution.

Figure 4.22(a) The relation distribution functions of β -CD /0.1wt% HEUR- C_{16} -51K complex at measurement angle of 90° . Numbers correspond to the CD/hy molar ratio.

Figure 4.22(b) Angle dependence of the fast decay mode of the complex of HEUR-C16-51K/m- β CD complex at molar ratio of 20

It is evident that methylated β -cyclodextrin interacts with HEUR chain in aqueous solution and alters the characteristic micellar structure of HEUR polymer chains. Even though there are two kinds of possible binding sites in the solution, ITC results suggest that only one-site binding is observed, which implies that m- β CD selectively bind to hydrophobes of HEUR polymer chain. There is no threading m- β CD on PEO chains, and this agrees with the work of Harada [Harada, 1997]. m- β CDs can only be threaded on the hydrophobic alkyl chain ends, and it then releases the looped chains from the micellar aggregates. When m- β CD concentration is low, β -CD encapsulates a single HEUR chain and co-exists with HEUR micelle in aqueous solution, which produces a broader distribution of decay times. When β -CD concentration was further increased, the size of micelle decreased continuously, which indicates that the micellar structure has become less stable. When the concentration of β -CD was increased to 20 mol per hydrophobe, the micelles are completely destroyed

to yield individual HEUR chains that are encapsulated by m- β CDs.

4.8 Summary

Methylated β -Cyclodextrin could effectively reduce the steady shear viscosity and dynamic moduli of HEUR aqueous solutions. From the rheological study, it was found that m- β CD interacts with HEUR in three progressive steps. At very low m- β CD concentrations, m- β CD encapsulates the hydrophobes of the looping HEUR chains, which destabilizes the transient network, but maintaining the number of mechanically active chains. However, the m- β CD/HEUR complex solutions become more sensitive to shear stress. At moderate m- β CD concentrations, m- β CD begins to decouple the bridging chains resulting in a decrease in the number of mechanically active chains and this further weakens the transient network. The decrease in the plateau modulus and relaxation time results in a corresponding reduction in solution viscosity. Finally, when the amount of m- β CD is in excess, the network structure is completely destroyed, which produces individual polymer chains in solution. The dilute solution properties of HEUR were also studied in the presence of m- β CDs. It is confirmed that m- β CD only interact with the hydrophobe of HEUR polymer chain and there is no interaction between m- β CD and PEO segment. The interaction between m- β CD and hydrophobe of HEUR causes the micelle of HEUR to dissociate to produce HEUR unimer encapsulated with m- β CDs.

Chapter 5 Interaction Between α -Cyclodextrin and Hydrophobic Ethoxylated Urethane Polymer in Aqueous Solution

5.1. Introduction

Cyclodextrins (CDs) are well-known in supramolecular chemistry as molecular hosts capable of selective inclusion of a range of guest molecules via non-covalent interactions in their hydrophobic cavities. Cyclodextrins are used to achieve certain benefits resulting from complexation, such as enhancing the solubility of guest compounds, stabilization against effects of light, heat and oxidation, masking of unwanted physiological effects, reduction of volatility, and others. Cyclodextrins comprise of a family of three well-known industrially produced materials: α -cyclodextrin containing six glucopyranose units, β -cyclodextrin with seven such units, and γ -cyclodextrin with eight such units. The difference in the glucopyranose units imparts different character with regards to solubility, encapsulation efficiency, complexation mechanism, and the properties of final complex.

Based the conclusions elucidated from previous studies, we observed that the size difference between the hydrophobic cones of α - and β -cyclodextrin has a significant effect on the interaction with HEUR polymer solution. The rheological behavior of HEUR polymer solution in the presence of α -CD shows different characteristics. The special viscosity-temperature relationship was explored and the possible mechanism of α -cyclodextrins HEUR polymer complexation is proposed. This mechanism is further confirmed by ITC and DLS results.

The scope of this study includes investigating the effects of α -CD concentration on the steady shear and viscoelastic properties of 2.0 wt % model

HEUR polymer containing hydrophobic $C_{16}H_{33}$ alkyl chain. The dilute HEUR solution properties in the presence of α -CD were also investigated using a U-tube viscometer, isothermal titration calorimeter, and dynamic light scattering techniques. A model polymer, which is 100 % capped with hydrophobic $C_{16}H_{33}$ alkyl chain was synthesized, and the rheological properties were systematically investigated and compared. The observed different temperature-viscosity dependence of these two polymeric systems was elucidated due to the competitive complexation of PEO/cyclodextrin and hydrophobe/cyclodextrin in the HEUR/ α -cyclodextrin system.

5.2 Interaction between α -CD and HEUR

5.2.1 Effect of α -CD on the transient network of HEUR

Effect of CDs on solution viscosity. The steady shear viscosities of 2.0 wt % HEUR- C_{16} -51K aqueous solution in the presence of different amount of α -CD were determined over a wide deformation regime. The result is shown in Figure 5.1. The HEUR solution without cyclodextrin exhibits Newtonian behavior at low shear rates. It shear-thickens at moderate shear rates, and then shear-thins at high shear rates. With the addition of cyclodextrin, the low shear viscosity decreases significantly, and the characteristic shear-thickening and shear-thinning become less dominant with increasing α -CD concentration. It is also clear that the onset of shear-thickening and shear-thinning shift to higher shear rates as α -CD concentration is increased. When the molar ratio of α -CD/hydrophobe exceeds 1.0, the system exhibits predominantly Newtonian behavior, confirming that the network structure has been fully destroyed by α -CD. When the α -CD/hydrophobe molar ratio is greater than 5.0, negligible

changes in viscosity were observed, which is similar to the results observed for m- β -CD/HEUR system [Liao et al., 2004].

Figure 5.1 Dependence of shear viscosity on shear rate for 2.0 wt % HEUR-C16-51K in different α -CD concentrations (Numbers represent the molar ratio of α -CD to hydrophobic end-group)

The dependence of low shear viscosity η_0 on α -CD concentration is shown in Figure 5.2. The viscosity of m- β CD/HEUR was also plotted for comparison. Both α -CD/HEUR and m- β CD/HEUR systems show similar trend: The interaction between α -CD and HEUR can be divided into 3 regimes. At very low CD concentrations (CD/hydrophobe molar ratio < 0.1), the solution viscosity decreases marginally with increasing CD concentration, which indicates that the presence of α -CD molecules does not have significant effect on the 3-D network structure. However, the solution viscosity decreases drastically over the α -CD/hydrophobe

molar ratio range from 0.1 to 5.0. When the molar ratio of α -CD/hydrophobe exceeds 5.0, the low shear viscosity becomes independent of α -CD/hydrophobe molar ratio. Subtle differences between the viscosity-concentration profiles of HEUR in these two types of cyclodextrin systems are observed in Figure 5.2. The low shear viscosity at high α -CD/hydrophobe ratio (α -CD/hydrophobe molar ratio greater than 1.0) is lower than m- β CD/HEUR system. Since the effect of PEO chain entanglements within experimental concentration range is insignificant [Liao et al., 2004], the viscosity of HEUR solution is directly related to the interaction of hydrophobic end-groups. For α -CD/HEUR system, the asymptotic viscosity is almost identical to the unmodified PEO solution at similar α -CD concentration, suggesting that α -CD is more effective in deactivating hydrophobic interaction than m- β CD. It is also observed that at low CD concentrations (CD/hydrophobe molar ratio < 1.0), m- β CD is more efficient in reducing the low shear viscosity since the viscosity of m- β CD/HEUR solution is lower than α -CD/HEUR solution at identical CD/hydrophobe molar ratios. This is also evident for the γ -CD/HEUR system, where the capability to reduce the low shear viscosity is weakest. Therefore, there are two trends in the viscosity depend on the CD/Hydrophobe molar ratio; namely at high ratio, α -CD is more efficient in reducing the shear viscosity and at low ratio the trend reverses. Such subtle difference may be attributed to the different binding interactions of HEUR and α -CD or m- β CD, and a detailed study on the temperature dependence may provide further information for elucidating the above phenomenon.

Figure 5.2 Low shear viscosity of 2.0 wt% HEUR-C16-51K solutions in the presence of different cyclodextrins

5.2.2 Dynamic rheological properties of HEUR/CD solution

Figure 5.3a shows the storage $G'(\omega)$ and loss $G''(\omega)$ moduli of 2.0 wt% solutions of hexadecyl terminated HEUR polymers in the presence of different concentrations of α -CD. It is evident that the viscoelastic properties of α -CD/HEUR solution follows single Maxwell model and the plateau modulus can be fitted by Cole-Cole plot (Figure 5.3b). The plateau modulus can be accurately determined from the intersection of the semicircle with the horizontal x-axis, which was discussed in chapter 4. At low frequencies, $G'(\omega)$ and $G''(\omega)$ possesses a slope of 2 and 1 respectively. At higher frequencies, $G'(\omega)$ increases and reaches an entanglement plateau region. Addition of α -CD into HEUR solution reduces the storage and loss moduli, and when the α -CD/hydrophobe molar ratio exceeds 1.0, $G'(\omega)$ decreases to the point where it is not accurately detectable by the rheometer. The higher

dependence of the modulus on the frequency at intermediate α -CD concentrations is an indication of a weaker network structure.

Comparing the Cole-Cole plot of different CD/HEUR system, it is evident that when CD/HEUR ratio increases, α -CD/HEUR system shows a sharp decrease in the G_N^0 while m- β CD system shows an almost constant G_N^0 prior to the disruption of the transient network. This suggests that α - and β -CDs exhibit different inclusion characteristics when they form complexes with HEUR chains. The difference may arise from the different diameter of the cavity, which is 0.57nm and 0.78nm for α - and β -CD respectively. This alters the selectivity and molecular recognition of guest molecules and the binding site of the guest moiety. The relative cavity size of CD and the cross-sectional area of hydrophobic group must be fit hence produce stable complex. For example, α -CD form complex with PEO, but it does not form complex with PPO..In contrast, β -CD form stable complex with PPO but can not form complex with PEO [Harada et al, 1997].

5.2.3 Temperature dependence of low shear viscosity

Previous studies [Liao et al. 2004] indicated that the temperature dependence of solution viscosity for m- β CD/HEUR complex can be described by Arrhenius equation:

$$\eta = A \exp^{E_a / RT} \quad (5-1)$$

where η is the solution viscosity at low shear rate, A is a constant, E_a is the activation energy (J/mol), R is gas constant (8.314 J/molK), and T is the temperature (K). From the temperature scan of the low shear viscosity, the activation energy E_a could be determined, and information on the strength of the overall HEUR network junctions at various CD concentrations can be deduced.

Figure 5.3a Shear moduli of 2.0 wt% HEUR- C_{16} -51K aqueous solution with different amount of α -CD. The number corresponds to the molar ratio of α -CD/hydrophobe. Open symbols are G'' and filled symbols are G' .

Figure 5.3b Cole-cole plot of 2.0 wt% HEUR- C_{16} -51K aqueous solution with different amount of α -CD. The number corresponds to the molar ratio of α -CD/hydrophobe.

Figure 5.4 Viscosity profile of 2.0 wt% HEUR-C16-51K solution in the presence of α -CD at CD/Hydrophobe molar ratio 1:1 at different temperatures.

When the temperature studies were extended to the α -CD/HEUR system, we observed that at low and high CD concentrations, the viscosity-temperature can be described by the Arrhenius equation. But over a prescribed concentration range, unusual viscosity-temperature dependence was observed. Figure 5.4 presents the viscosity profile of 2.0% HEUR solution in the presence of α -CD under different temperature. As an example, at 15 °C and α -CD/hHydrophobe molar ratio of 1, the solution exhibits a Newtonian behavior. With increasing temperature, the low shear viscosity starts to increase, and shear-thickening was observed at moderate shear rates. At temperature 35 °C, the low shear viscosity reaches a maximum, and then decreases when the temperature exceeds 40 °C. Therefore, the Arrhenius equation cannot adequately describe this viscosity-temperature relationship.

When α -CD/hydrophobe molar ratio is lower than 0.8, the viscosity data obey the Arrhenius relationship (i.e. $\ln(\eta_0)$ vs. $1/T$), and E_a can be extracted from the linear slope. It was found that the activation energies at α -CD/hydrophobe molar ratio of 0.25 and 0.5 are 67 and 30 kJ/mol respectively, which are lower than the activation energies for m- β CD/HEUR system at similar molar ratios (78 and 76 kJ/mol respectively). This reinforces our earlier conclusion that α -CD is more effective in disrupting the associative junctions of HEUR chains.

Figure 5.5 shows the temperature dependence of low shear viscosity of HEUR solution in the presence of different amount of α -CD. The E_a at higher α -CD content (CD/hydrophobe molar ratio > 5) is ~ 20 kJ/mol, which is identical to the E_a of unmodified PEO solution at similar concentration. Within the molar ratio ranges from 1.0 to 5, the viscosity data do not obey the Arrhenius equation (i.e. $\ln(\eta_0)$ vs. $1/T$). Instead, the viscosity profile of $\ln(\eta_0)$ vs. $1/T$ at α -CD/hydrophobe molar ratio of 0.8 can be fitted by two straight lines at the low and high temperature regimes (as shown by the unfilled diamonds), which produces two activation energies. At low (5 to 25 °C) and high temperature (30 to 50 °C) regimes, the activation energies, E_{a1} and E_{a2} were determined to be about 20 and 80 kJ/mol respectively.

When α -CD/hydrophobe molar ratio increases to 1.0, the viscosity–temperature relationship is totally different from the system at low molar ratios, where the viscosity at low temperatures showed a larger decrease compared to the molar ratio of 0.8. For example, at 5 °C, the viscosities are 2.5 and 0.07 Pa.s at the molar ratio of 0.8 and 1.0 respectively, while the viscosities at 35 °C are 0.91 and 0.54 respectively. The viscosity vs. temperature profile exhibits two slopes: one at 5 to 15 °C and the other from 45 to 50 °C. At the temperature range of 20 to 40 °C, a non-linear behavior was observed. The slope at temperature range of 5 to 15 °C yields an

activation energy of about 20 kJ/mol, which corresponds to the activation energy of unmodified PEO solution. The activation energy at high temperature is about 80 kJ/mol, which is close to the activation energy of pure HEUR solution. The above observation implies that the transient network is completely disrupted at low temperatures. As temperature increases to 30 °C, the increase in the viscosity suggests that the transient network is being restored due to the increase in the proportion of bridging hydrophobic chains, which is confirmed by dynamic oscillation experiments, where G' increases with increasing temperature for α -CD/HEUR molar ratio of 0.8. When the molar ratio exceeds 1.0, the viscosity decreases with increasing temperature before it reaches a transition temperature T_α , where $\ln(\eta_0)$ vs. $1/T$ can be fitted by the Arrhenius equation to yield an activation energy of ~ 20 kJ/mol. At temperature greater than T_α , the viscosity starts to increase and then decrease. With increasing molar ratio, T_α shifts to higher temperature as evident from Figure 5.5. When the molar ratio exceeds 5.0, the linear relationship was re-established with E_a value of ~ 20 kJ/mol, which is similar to the activation energy of unmodified PEO solution. This is a indication that hydrophobic association is completely suppressed by cyclodextrin at high concentration.

Figure 5.5 Temperature dependence of low shear viscosity of HEUR-C16-51K 2.0 wt% in the presence of α -cyclodextrin. The number corresponds to the molar ratio of α -CD/hydrophobe

It was reported by Harada and coworkers [Harada et al., 1995] that β -CD does not form inclusion complex with PEO, because the relative cavity size of β -CD and the cross-sectional area of PEO chain is incompatible. For β -CD, The diameter of cavity is 0.6 to 0.65nm, but cross-sectional area of PEO is around 0.4nm, which is relatively small and thus can thread in and out freely. Hence, the interaction between m- β CD/HEUR is dominated by the hydrophobic interaction between m- β CD and hydrophobic segments at the terminus of the HEUR chains. However, Harada [Harada and Kamachi, 1990] also reported that α -CD interacts strongly with PEO to produce a crystalline compound. In addition, the interaction between hydrophobic $C_{16}H_{33}$ alkyl chains and α -CD was confirmed previously [Karlson et al., 2002]. So far there is no report on the competitive interaction between α -CD/PEO and α -CD/hydrophobe.

The study of α -CD/PEO mainly focus on the characterization of crystal complex while α -CD/hydrophobe interaction mainly affect the rheological properties of the solution. For α -CD/HEUR mixed system, the two possible interaction mechanisms may co-exist, depending on the temperature, and they can be described by Equation (5-2) and (5-3):

where m and n are the possible stoichiometric numbers for α -CD/hydrophobe and α -CD/PEO respectively. K_1 and K_2 are the equilibrium constants for each reaction respectively. According to Equation (5-2) and (5-3), there are five possible species in the α -CD/HEUR solution; i.e. α -CD, $(\alpha - CD)_m - C_{16}H_{33}$, $HO - (C_2H_4O)_{186}$, $(\alpha - CD)_n - HO - (C_2H_4O)_{186}$ and $C_{16}H_{33}$, and only the hydrophobic segments, $C_{16}H_{33}$ accounts for the enhancement of the solution viscosity via transient network of hydrophobic association.

Hydrophobic interaction of α -CD and hydrophobe is stronger than m- β CD and hydrophobe as demonstrated by Abdala and co-workers [Abdala et al., 2003]. It was also evident from Figure 5.2 and 5.3b that the solution viscosity of α -CD/HEUR system is always lower than m- β CD/HEUR system at CD/hydrophobe molar ratio exceeding 1.0, and the plateau modulu is always lower in α -CD/HEUR system at same CD/hydrophobe molar ratio. because diameter of α -CD is 4.7nm, which is fit for the size of alkyl hydrophobe of 4nm, thus alkyl hydrophobe is easily thread into the hydrophobic cavity for stable complex. The deactivate the mechanical active chain and reduce the plateau modulus significantly. The reversed viscosity trend as observed at CD/hydrophobe molar ratio lower than 1.0 is attributed to the presence of

these uncapped PEO chains. But the proportion of uncapped PEO is relatively small, with functionality of 1.7, the uncapped PEO is 15%. This coincident with the result from Figure 5.2 that at molar ratio lower than 0.2, the effect of cyclodextrin on viscosity is insignificant. Since PEO ($\text{HO}-(\text{C}_2\text{H}_4\text{O})_{186}\sim$) also interacts with α -CD, the presence of 15 % uncapped PEO segments in the HEUR polymer shifts the equilibrium of α -CD/hydrophobe system to the left (Equation 5-2). Thus, the effect of α -CD on rheological properties of HEUR is not as significant as that of m - β CD at low CD concentrations since a portion of α -CD are consumed in the complexation of α -CD/PEO system. The main difference between complexation of α -CD/alkyl hydrophobe and m - β CD/alkyl hydrophobe is that α -CD/alkyl hydrophobe complexation deactivates the mechanical active chain by forming stable complex, the transient polymer network is disrupted at low α -CD concentration. But m - β CD/alkyl hydrophobe complexation is relatively weak therefore the transient polymer network is weakened at low β -CD concentration.

The deviation from Arrhenius equation for the systems with α -CD/HEUR molar ratio between 1.0 and 5.0 implies that temperature plays an important role in controlling the balance between the interaction of α -CD/hydrophobe and α -CD/PEO. Since the viscosity enhancement is solely attributed to the hydrophobic association of bridging HEUR chains, the amount of bridging chain is the major factor controlling solution viscosity. At low temperatures, the viscosity is low and the activation energy is close to that of aqueous PEO solution, which implies that α -CD/hydrophobe is the dominant interaction. At elevated temperatures, viscosity increases with increasing temperature, suggesting that the concentration of bridging chain increases, which is consistent with the dynamic oscillation results. Thus,

increasing temperature promotes α -CD/PEO interaction, which shifts the equilibrium in Equation (5-2) to left. As a consequence, more bridging chains are produced, which enhances the solution viscosity.

In order to examine the effect of temperature on the equilibrium behavior in Equations (5-2) and (5-3), dynamic oscillation experiments were performed at different temperatures. The results provide insights into the transient network structure upon the addition of α -CD. Figure 5.6a shows that the storage modulus of 2.0 wt% HEUR-C16-51K solution in the presence of CD/hydrophobe of 0.8 moles of α -CD. G' increases with increasing temperature. The relaxation time (λ) was extracted from the intersection of G' and G'' , and plateau modulus (G_N^0) was extracted from the Cole-cole plot, and plotted in Figure 5.6b.

Figure 5.6a G' of α -CD/2.0 wt% HEUR-C16-51K at CD/hydrophobe molar ratio of 0.8 at different temperature. Numbers correspond to the testing temperature.

Figure 5.6b Plateau modulus (G_N^0) and relaxation time (λ) of α -CD/2.0 wt% HEUR-C16-51K whit CD/Hydrophobe ratio = 0.8, at different temperatures. Open symbols represent α -CD/HEUR mixing complex and filled symbols represent 2.0 wt% HEUR solution. Square: G_N^0 . circle: λ .

Comparing the temperature dependence of relaxation time (λ) and plateau modulus (G_N^0) of 2.0 wt% HEUR solution and in the presence of 0.8 mole of α -CD, it was observed that in the absence of α -CD, relaxation time λ decreases more significantly than the plateau modulus, suggesting that increasing temperature enhances the exit rate of hydrophobes from the micellar core, which weakens the micellar structure and the overall network structure. In contrast, the solution with α -CD/hydrophobe molar ratio of 0.8 exhibits characteristics that are unusual and which have not been reported before. The plateau modulus increases while the relaxation time decreases with increasing temperature. Since G_N^0 is proportional to

the density of mechanically active chain number, ν based on the classical theory of rubber elasticity described by Equation (5-4):

$$G_N^0 = \nu RT \quad (5-4)$$

where R is the gas constant and T is the absolute temperature. From Figure 5.6b, it is evident that the number of bridging chain for the α -CD/HEUR complex solution increases with increasing temperature (open squares). Therefore, it can be concluded that the interaction between α -CD and PEO is dominant at higher temperatures, while α -CD and $C_{16}H_{33}$ interaction dominates at low temperatures. This hypothesis is demonstrated later by ITC studies that α -CD/PEO interaction is weak endothermal but α -CD/hydrophobe interaction is exothermal. As a result, the probability of hydrophobes being encapsulated by α -CD is reduced at higher temperatures. Thus, increasing temperature promotes the interaction between PEO and α -CD, and inhibits the interaction between $C_{16}H_{33}$ alkyl chains and α -CD. It should be noteworthy that the reduction in the viscosity does not mean that the disruption of transient network, like the example at CD/hydrophobe molar ratio 0.8 (Figure 5.7). The network in fact strengthens with increasing temperature since G_N^0 increases even though the low shear viscosity decreases. In contrast, dynamic mechanical properties is more reasonable to characterize the network because plateau modulus is proportional to the number of mechanical active chain and relaxation time is related to the strength of network.

In HEUR solution, the polymer chains in the flower micelles are constantly exchanging their position as dictated by their “life-time” or exit time of the hydrophobes in the micelles. The hydrophobic alkyl segments reside in the hydrophobic core, while the PEO segments are located at the outer surface of the micelles. Since 15 % of the PEO chains are not capped by the hydrophobic alkyl

groups and the free PEO chain dangles in solvent which is easily approached by cyclodextrin, it is more likely that α -CD would first encapsulate these free PEO segments rather than the hydrophobic alkyl groups which are hidden in the core and surround by PEO chain. This is proved by ITC studies [Liao et al, 2007] that the titration curves of α -CD/HEUR represent the typical profile for two site bind interaction. Such interaction destabilizes the flower micelles, as demonstrated by the reduction in relaxation time. As a result, more hydrophobes are released from the hydrophobic junctions, which are then encapsulated by α -CD molecules presented in the bulk solution. The two competitive processes, i.e. α -CD/PEO and α -CD/hydrophobe interactions, co-exist in solution. Since increasing temperature favors α -CD/PEO interaction over the α -CD/hydrophobe interaction, encapsulation of the hydrophobes by α -CDs can only be accomplished at higher α -CD concentrations. Thus, for a given α -CD/hydrophobe molar ratio, increasing temperature results in the apparent increase in the concentration of hydrophobe as higher proportion of the α -CD formed complexes with PEO chains. This is corroborated by the rheological measurements, which show an increase in bridging chains as confirmed by the increase in the plateau moduli for α -CD/hydrophobe ratio of 0.8 to 5. The mechanism of α -CD and HEUR interaction is presented schematically in Figure 5.8. This 15% uncapped PEO is introduced deliberately in the process of synthesis. In order to demonstrate the hypotheses a 100% capped polymer is synthesized for comparison.

Figure 5.7 Low shear viscosity and plateau modulus of α -CD/2.0 wt% HEUR-C₁₆-51K solution at CD/Hy molar ratio of 0.8

5.2.4 The effect of hydrophobe length on the α -CD/HEUR interaction

The length of hydrophobic alkyl chain should have significant effects on the rheological properties. Three polymers have similar molecular weight (M_w : about 50,000 g/mol) and concentration of 2.0 wt% but different length of alkyl chain. The HEUR-C16-51K possesses C₁₆H₃₃ end group, HEUR-C12-51K with C₁₂H₂₅ and HEUR-C0-51K without hydrophobe. The comparison of low shear viscosities between associative polymer solution and control polymer solutions shows the effect of hydrophobic end group on solution viscosity. The low shear viscosity of HEUR-C16-51K solution is 4 orders in magnitude higher than their corresponding counterparts without hydrophobic modification. Shear-thickening was not observed with HEUR-C12-51K, and the solution exhibits a characteristic Newtonian flow within experimental shear rate range. But HEUR-C12-51K shows higher viscosity

than HEUR-C0-51K, which does not possess end-capped alkyl hydrophobic chain. Therefore, it is evident that even though hydrophobe $C_{12}H_{25}$ does not exhibit association as strong as $C_{16}H_{33}$ hydrophobe, there are still interactions among these hydrophobes, which produce different microstructure, namely open association in the solution [Dai et al., 2004]

Figure 5.8 Schematic representation of the interaction mechanism between α -CD and HEUR. The bold line represents PEO without hydrophobe and the fine line represents the hydrophobically capped PEO. The interaction mechanism of m- β -CD with HEUR is plotted in Figure 4.12.

As discussed previously, addition of α -CD effectively removes the hydrophobic interactions among the alkyl end-groups of the polymer chains. Though it interact with PEO competitively, the effect of PEO is relatively small because the relatively small quantity of free PEO in the solution. Excess α -CD reduces the solution viscosity to that close to the viscosity of similar molecular weight PEO solution. (Figure 5.9). It is evident that insignificant effect of α -CD for the HEUR-C0-51K system. At the same time, for $C_{16}H_{33}$ hydrophobe, the viscosity reaches a minimum when the CD/hydrophobe molar ratio exceeds 4.0. However, for $C_{12}H_{25}$ hydrophobe, the viscosity does not show any significant reduction when the ratio is greater than 2.0. The difference may be attributed to following two reasons: (1) $C_{12}H_{25}$ hydrophobic interaction with α -CD is weaker than that of $C_{16}H_{33}$, therefore the hydrophobic interaction of $C_{12}H_{25}$ is completely suppressed with lower amount of cyclodextrin, compared to $C_{16}H_{33}$. (2) the length of $C_{12}H_{25}$ is shorter than $C_{16}H_{33}$, hence fewer cyclodextrin molecules can be thread onto the hydrophobe.

Figure 5.9 The effect of hydrophobe size on low shear viscosity of α -CD/HEUR solutions. The concentration of HEUR solution is 2.0 wt%.

By comparing the temperature dependence of these three polymers at CD/Hydrophobe ratio of 1 and 2, new insights into the competitive complexation of hydrophobe and PEO chain with α -cyclodextrins can be determined. For HEUR without hydrophobe, the viscosity of HEUR-C0-51K obeys the Arrhenius relationship. Addition of different amounts of α -CD has negligible effect on the viscosity and temperature dependence (Figure 5.10). HEUR-C12-51K, which is end-capped by $C_{12}H_{25}$ hydrophobe, the viscosity only shows a reverse trend at high temperature with α -CD/hydrophobe ratio of 1.0. When ratio is equal to 2, the viscosity-temperature profile exhibits similar trend as the PEO solution. Hence, it is evident the hydrophobic interaction between α -CD and $C_{12}H_{25}$ is also affected by the competitive complexation of PEO/ α -CD, which is enhanced by increasing temperature. This is proved by ITC studies [Liao et al, 2007]. But the hydrophobic association of $C_{12}H_{25}$ is much weaker than that of $C_{16}H_{33}$, hence the magnitude of viscosity recovery is not as significant as $C_{16}H_{33}$.

Figure 5.10 The effect of hydrophobe on the temperature dependence of viscosity in α -CD/2.0 wt% HEUR solution.

- : HEUR-C0-51K - CD/Hydrophobe molar ratio of 1;
- △: HEUR-C12-51K - CD/Hydrophobe molar ratio of 2;
- ▲: HEUR-C12-51K - CD/Hydrophobe molar ratio of 1;
- : HEUR-C16-51K - CD/Hydrophobe molar ratio of 2;
- : HEUR-C16-51K - CD/Hydrophobe molar ratio of 1.

5.2.5. The effect of molecular weight of HEUR on the interaction of α -CD/HEUR

The interactions between α -CD and different molecular weights' HEUR polymers were examined. Three HEUR polymers were compared, with molecular weight 17500, 51000 and 85000 g/mol respectively. The viscosity vs. CD concentration was plotted in Figure 5.11. Before the addition of α -CD, the solution with higher molecular weights HEUR displays lower viscosity for 2.0 wt % HEUR solution. The concentration of end-capped hydrophobes determined the total number of elastically active chains, or the density of cross-linking junctions and the functionality of the junctions of the self-associative network. Therefore, the effect of

HEUR molecular weight on the viscosity of solution mainly comes from the polymer's ability to modify the topology of the associative structure, for example, the functionality of the cross-linking junction and the association energy of the terminal hydrophobe in the junction. The cross-link junction is form in the aqueous phase through self-association of hydrophobic end-groups in the micelle-like junction by the linear hydrophobically modified polymer. This has been discussed by Li [Li, 1995].

Figure 5.11 the effect of M_w on the interaction between HEUR and α -CD. Concentration of HEUR solution is 2.0 wt%,

Figure 5.11 indicates that the addition of certain amount of α -CD significantly reduces the low shear viscosity of HEUR solution, where the α -CD influence on the viscosity of lower molecular weights HEUR is more significant than that of higher molecular weight, mainly because the low proportion of hydrophobe in high molecular weight HEUR. It is concluded that the lower the M_w and the stronger the CD/HEUR interaction, because the higher the M_w , the lower the number of

micelles and junction points in solution. In addition, the higher the M_w , the weaker is the hydrophobic interaction. When α -CD/hydrophobe molar ratio exceeds 5, no further reduction in solution viscosity was observed. It is interesting to note that at α -CD/hydrophobe molar ratio greater than 5, the solution of higher molecular weight HEUR possesses a higher viscosity.

Figure 5.12 Temperature dependence of viscosity for α -CD in 2.0 wt% HEUR solution of different molecular weights. Numbers represent HEUR molecular weight. CD/hydrophobe molar ratio equals to 1.0.

This phenomenon is in contrast to HEUR solution, but it follows the same trend as unmodified control PEO polymer, which reinforces that the hydrophobic association has been completely suppressed when α -CD/hydrophobe molar ratio exceeds 5. In HEUR polymer solution, the viscosity is mainly attributed to two factors; i.e. hydrophobic interaction and length of polymer backbone. Previous studies have shown that HEUR associative thickeners established the viscosity enhancement solely

by hydrophobic association. In comparison, the contribution from the polymer backbone is negligible. The addition of α -CD dissociates the hydrophobic association by threading onto the hydrophobe and weakening the hydrophobic interaction. But α -CD has no effect on the viscosity of PEO even there is strong interaction between α -CD and PEO since PEO has low viscosity and negligible interaction, which is confirmed by the fact that α -CD has no effect the viscosity profile of PEO solution. When the hydrophobic interaction is sufficiently weak, the effect of polymer backbone becomes significant. It is also observed that regardless of the molecular weight, all the viscosity profile reaches a minimum at ratio of 5, which implies the equilibrium constant for α -CD and $C_{16}H_{33}$ hydrophobe is not affected by the molecular weight of PEO segment concentration of the hydrophobe.

The temperature dependence of low shear viscosity of the three polymers with different molecular weights was investigated. Figure 5.12 shows that all the polymers exhibit similar trend. When the α -CD/hydrophobe molar ratio equals to 1, the viscosity increases with increasing temperature and reaches a maximum when it then starts to decrease. The general trends observed from Figure 5.12 are: (1) the viscosity increases more significantly for HEUR with low molecular weights, (2) the temperature corresponding to the maximum viscosity T_c , corresponding to the maximum conversion of α -CD/ hydrophobe to α -CD/PEO does not change significantly. For all the α -CD/HEUR system, maximum viscosity is still lower - compared to the HEUR solution without CD, which implies that the conversion from α -CD/hydrophobe to α -CD/PEO complexation is not yet complete. Instead, we achieved an equilibrium between the hydrophobe, PEO chain and α -CD. By combining Equation 5-2 and 5-3, we obtain the followings:

The temperature dependence of the binding equilibrium can be discussed using Equation 5-4. As discussed previously, lower temperature favors the interaction between hydrophobe and α -CD, where the hydrophobes mainly interact with α -CD. Increasing the temperature promotes α -CD/PEO interaction because the complexation is endothermal, this is later demonstrated by ITC studies. resulting in a higher proportion of α -CD/PEO complex and a corresponding reduction in the α -CD/hydrophobe complex. The equilibrium constant, K is more sensitive to temperature than the molecular weight of PEO. Therefore, the molecular weight does not affect critical onset temperature, T_c . In this experiment, the polymer concentration was set at 2.0 wt% for all the three HEUR polymers, hence the moles of hydrophobic moiety for the three polymers are different. The higher the molecular weight, the lower is the concentration of hydrophobe. At identical α -CD/hydrophobic molar ratio, the concentration of hydrophobic alkyl chain is higher in the low molecular weight HEUR solution, yielding a higher viscosity.

5.3 Interaction between α -CD and fully capped PEO system

Commercial hydrophobically-modified ethoxylated urethane (HEUR) polymers were prepared by step-growth process and they also exhibit a heterogeneous mixture of molecular weights with various degrees of hydrophobic modification [Kaczmariski and Glass, 1992]. In this study, the synthesis, characterization and solution rheology of a well-defined hydrophobically modified PEO (HM-PEG-IPDI) is described, and the rheological behavior was compared with the less well-defined commercial HEUR described in the preceding sections. The characterization of HM-

PEG-IPDI series is given in chapter 9, which is 100% end-capped. The model HEUR materials provide a basis for the interpretation of more complex HEURs prepared by a traditional step-growth polymerization.

The phase behavior of HEUR polymers have been studied theoretically by Semenov and coworkers [Semenov et al., 1995], where they predicted the bridging of neighboring aggregates to yield an effective attractive potential between the flower micelles. When the attractive energy is larger than the thermal energy, phase separation is observed. The phase separation of fully capped PEO system was previously reported by Karlson and coworkers [Karlson et al., 1999]. Such behavior was also observed for our fully capped PEO system (HM-PEG-IPDI) at solution concentration lower than 2.5 wt%. Because of phase separation, the top liquid layer is isotropic comprising of a homogeneous polymer solution, while the bottom layer consists of an opaque liquid of condensed micellar aggregates .

Complete steady shear viscosity profiles as shown in Figure 5.13, for a concentration of 2.5 wt%, where a homogeneous single phase solution was obtained. The viscosity profiles resemble those reported previously for the same class of HEUR polymer [Liao et al, 2004], consisting of a low shear plateau, slight shear-thickening and shear-thinning at high shear rates. The shear-thinning is much more abrupt and the change in viscosity with shear rate is steeper and exhibit time-dependent property, which is consistent with the findings reported by Pham [Pham et al., 2000]. The possible reason for the abrupt shear-thinning is probably related to shear induced phase separation. With increasing temperature, the degree of shear-thickening becomes less significant. Analysis of the viscoelasticity of this polymer solution using the Cole-cole plot suggests that the viscoelasticity can be explained by a single mode Maxwell model.

Figure 5.13 Viscosity profile of 2.5 wt% HM-PEG-IPDI-C16-20K solution at different temperatures. (Numerical values correspond to temperatures.)

Addition of α -CD to this polymer solution also causes an abrupt reduction in the viscosity, which is similar to that observed for α -CD/HEUR system. The low shear viscosity for the α -CD/HM-PEG-IPDI solution were extracted from the Newtonian plateaus and plotted in Figure 5.14, which exhibits a similar trend with some minor differences. Following analogous classification as α -CD/HEUR interaction described previously, α -CD and HM-PEG-IPDI interaction can also be described by 3 identifiable regimes. The difference between these two systems is that the onset for the abrupt reduction in the low shear viscosity for α -CD/HM-PEG-IPDI occurs at a much lower α -CD concentration. However, the asymptotic viscosity at the molar ratio of 4 for both systems is identical. Since the only difference between HEUR and HM-PEG-IPDI is the functionality (100% for HM-PEG-IPDI and 70% for

HEUR), the 15% of un-capped PEO competes with the hydrophobe for their binding interaction with α -CD. For HM-PEG-IPDI polymer, $C_{16}H_{33}$ is the only group that interacts with α -CD. Due to the fact that the increase in HEUR solution viscosity arisen from hydrophobic interaction, α -CD is more effective in reducing the viscosity of HM-PEG-IPDI.

Figure 5.14 Low shear viscosity of α -CD/2.0 wt % HM-PEG-IPDI-C16-20K solution at different α -CD concentration. HEUR-C16-17K was plotted as dotted line for comparison.

Figure 5.15 illustrates how the viscosity of α -CD/HM-PEG is affected by temperature. Our experimental results indicate that the low shear viscosity exhibit an exponential dependence on temperature, which was predicted by Tanaka and Edwards [Tanaka and Edwards, 1992]. In their transient network theory, Tanaka and Edwards defined a bonding potential for a hydrophobe in an associative junction that is characterized by a well depth W and an activation energy for disengagement, E . In

general, these two terms are different, $E=W-f_r\alpha$, where f_r is the additional force transmitted along the chain in the direction of the other end of the chain, and reflects the free energy stored in the water-soluble polymer chain, where α is the size of segment. The bonding potential W is a characteristic of hydrophobic association. The probability for dissociation process to occur is proportional to $\exp(-E/kt)$, and hence the dissociation rate per unit time takes the form of;

$$\beta_0 = \omega_0 \exp(-W / kT) \quad (5-5)$$

$$\beta_r = \omega_0 \exp(-E / kT) \quad (5-6)$$

where subscript 0 and r refer to the polymer chains that are free subjected to a elongation force respectively, ω_0 is the natural frequency of the thermal vibration of the reactive group in isolated state. The time scale dominating the molecular motion is the junction dissociation time τ :

$$\tau = \omega_0^{-1} \exp(E / kT) \quad (5-7)$$

and the zero shear viscosity takes the form,

$$\eta_0 = f_N \frac{\nu_0 kT}{\beta_0} \quad (5-8)$$

where f_N is a numerical prefactor and can be safely replaced by unity, ν_0 is the equilibrium number of the mechanically active chains in a quiescent state free from external forces, and is expressed by the following equation:

$$\nu_0 = \frac{p / \beta_0}{1 + p / \beta_0} n \quad (5-9)$$

where p the chain recombination probability of the sticky dangling ends, and n the total number of the chains in a unit volume. Equations 5-7 and 5-8 reflect the activation process: the solution relaxation time and zero shear viscosity depend exponentially on the temperature.

Figure 5.15a $E_a(\eta_0)$ and $E_a(\lambda)$ of a 2.5 wt% HM-PEG-IPDI solution

Figure 5.15b Temperature dependence of α -CD/ 2.0 wt % HM-PEG-IPDI solution at different molar ratio of α -CD/hydrophobe

In a physically cross-linked network, the decrease in the number of cross-links (proportion to v_0) with temperature is usually more profound than the increase in the rigidity due to the entropic change (proportional to kT), so that the decrease in viscosity may be more significant than the solution relaxation time λ with increasing temperature, which is evident in Figure 5.15a.

When α -CD was added to the HM-PEG-IDPI solution, it interacts with the sticky dangling ends and prohibits them from re-entering the hydrophobic core. According to Equation 5-9, the equilibrium number of the mechanically active chains decreases accordingly. The bonding potential W decreases because the hydrophobic interaction is weakened by the action of cyclodextrin molecules. Figure 5.15b shows that when α -CD/hydrophobe ratio was increased from 0 to 10, the activation energies decrease in correspondence with the low shear viscosity. In stage 1, when α -CD concentration is low, the activation energy decreases marginally since the associative network has not been destroyed. At moderate CD concentrations, the activation energy decreases abruptly, an indication of the disruption of transient network. At high CD concentrations, where the hydrophobic junctions are completely deactivated, the activation energy approaches an asymptotic value that is close to the activation of PEO solution. The different temperature dependence characteristics between HEUR and HM-PEG-IDPI strongly suggests that the unique viscosity-temperature profiles of α -CD/HEUR solution are attributed to the competitive complexation between the 15% uncapped PEO chain ends and the 70% $C_{16}H_{33}$ alkyl chain ends.

5.4 The α -CD/HEUR interaction in dilute solution: intrinsic viscosities and Huggins parameter of associative polymers in the presence of α -CD

Figure 5.16 compares the dependence of the reduced viscosity on the concentration for PEO chains containing hydroxyl and hexadecyl groups. As revealed in Figure 5.16, the reduced viscosity of a hydroxyl terminated HEUR system varies linearly with concentration over the measured concentration range, with a Huggins constant K' of approximately 0.35, which is the typical value for most polymer-solvent systems. In contrast, the HEUR polymers with hydrophobic alkyl chain ends interact at extremely low polymer concentrations to produce a rapid increase in reduced viscosity showing a deviation from linear behavior predicted by the Huggins equation. Such characteristic signifies the formation of an extensive associative network in solution, and shows that the rate of addition of associative polymer to the network with respect to polymer concentration increases as the length of the hydrophobic end-group relative to the polymer backbone increases. The Huggins parameter K' for the polymer with hexadecyl has a value of ~ 6.0 , which is extremely high.

Addition of α -CD to dilute solution of model associative polymers imparts different characteristics on polymer with different hydrophobic end groups. The intrinsic viscosity of HEUR-C0-51K in the presence of α -CD or β -CD remains essentially constant because there is no hydrophobic association, thus the addition of cyclodextrin does not affect the intrinsic viscosity and Huggins parameter K' . However, for HEUR-C16-51K, which possesses hexadecyl end groups at both ends of the PEO chain, the Huggins constant shows significant decreases with increasing CD concentration. The reduced viscosity at low polymer concentrations decreases with increasing CD concentration, and reaches an asymptotic value when the CD

concentration exceeds 22 mg/dL. In this region, the relationship between reduced viscosity and concentration becomes linear, and the Huggins parameter approaches about 0.3, which is the classical value for most conventional polymer-solvent pairs.

Figure 5.16 Reduced viscosity of HEUR-C16-51K solution (solid line) in the presence of different concentration of α -CD. Dotted line is the reduced viscosity of HEUR-C0-51K solution in the presence of α -CD.

As discussed by Hoy [Hoy, 1984], the driving force for forming and sustaining intermolecular associations increases as the chemical potential of the hydrophobic groups becomes more negative. Thus, the Huggins parameter is an indicator of the degree of intermolecular association. Addition of cyclodextrin into HEUR solution increases the solubility of polymers since the hydrophobes are threaded into the hydrophobic cavity of cyclodextrin molecules. Such phenomenon decreases the driving force for the formation and sustenance of hydrophobic associations to yield

flower micelle in dilute solution. Even when the Huggins constant is decreased to 0.3 when α -CD concentration increases to 44 mg/dL, the micelle does not dissociate into single polymer chain, which was later confirmed by the dynamic light scattering measurement. Jenkins [Jenkins, 1991] has reported the difference caused by distribution of aggregates and unimers.

5.5 Isothermal Titration Calorimetric (ITC) Studies

The titration curve of 10.5 mM α -cyclodextrin solutions into 0.2 wt% HEUR-C16-51K solution was plotted in Figure 5.17. For comparison, the titration curve of α -cyclodextrin into water and into PEO with molecular weight of 60K was also plotted on the same figure. We were not able to measure 100% hydrophobically modified PEO with ITC because of the phase separation at 0.1 wt%. The dilution curve of α -cyclodextrin into water exhibits negligible change in enthalpy. It has been reported that α -cyclodextrin aggregates at very low concentration. Therefore, it seems that the dilution of α -cyclodextrin does not affect the aggregate. A pronounced exothermic peak for the titration of α -cyclodextrin into HEUR-C16-51K solution is observed. Due to the fact that ITC detects the isothermal enthalpy changes after titrating cyclodextrin solution into water or aqueous polymer solution, the difference between the ITC curves of titrating into polymer solution and that into water is attributed to the polymer/cyclodextrin interaction [Olofsson and Wang, 1994; Persson et al., 1994]. However, the α -cyclodextrin/PEO titration curve is different, and very weak endothermal enthalpy peak was observed for the titration of α -cyclodextrin into PEG-20K. It has been reported by Harada [Harada and Kamachi, 1990] that precipitates were produced when PEO was added into saturated α -CD solution. The properties of crystalline precipitates will be studied and will be discussed in Chapter 7.

Therefore, PEO/ α -CD interaction is evident even though very weak enthalpy change is observed in the titration curve.

Figure 5.17 Calorimetric titration curves of 1.0 wt% α -CD into HEUR-C16-51K solution (0.1 wt%) at different temperatures. Number corresponds titration temperature. $\diamond$ is the titration curve of 1.0 wt% α -CD into water at 25 °C; $\blacklozenge$ is the titration curve of 1.0 wt% α -CD into 0.1 wt% PEO solution at 25 °C

Figure 5.17 shows that the titration curves of cyclodextrin/HEUR systems represent the typical profile for two sites binding interaction. For example, for the profile at 25 °C, the enthalpy initially decreases to a minimum at α -CD concentration of 0.05 mM, where it then increases again until an asymptotic value at high α -CD concentration. This phenomenon differs from the ITC profile for m- β CD/HEUR system, which exhibits a standard S curve. For m- β CD/HEUR system, only alkyl hydrophobes at both ends of the polymer backbone interact with m- β CD. Yet in α -CD/HEUR system, two possible binding sites are present, i.e. PEO segment and alkyl hydrophobe. The initial decrease in enthalpy is attributed to the competitive binding

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of PEO/cyclodextrin and hydrophobe/cyclodextrin, which occurs simultaneously. The concentration of uncapped PEO chain end (30 %) is much smaller than hydrophobic modified PEO (70 %), hence the uncapped PEO chain ends become saturated at α -cyclodextrin concentration of 0.05 mM. When α -CD concentration exceeds 0.05 mM, the hydrophobe/cyclodextrin interaction dominates giving rise to a change in the slope and it reaches an asymptotic value at α -CD concentration of 1.0 mM, where the hydrophobes are saturated by cyclodextrin molecules and no further binding occurs. It is observed that the impact of temperature on the binding equilibrium is significant. The exothermic peak becomes less significant with increasing temperature. The concentration of α -CD corresponding to minimum ΔH increases significantly, suggesting that the equilibrium for the competitive binding of PEO/cyclodextrin and hydrophobe/cyclodextrin is altered with increasing temperature. Increasing temperature favors α -CD/PEO interaction but weakens the interaction between α -CD and hydrophobe.

By fitting the curve with a two-site model, the ΔS , ΔH , ΔG , stoichiometry and reaction constant K for the hydrophobe/cyclodextrin interaction at different temperatures were determined and summarized in Table 5.1.

Table 5.1 Thermodynamic parameters for α -CD titration into HEUR

Temp. (°C)	ΔH (kCal/mol)	K	ΔS (Cal/mol)	N
15	-5.25	8482	-0.2	4.8
25	-3.27	6187	6.5	6.4
35	-2.78	2512	6.6	8.8
40	-2.32	1543	7.0	16.0

From Table 5.1, it is evident that ΔH and K decrease with increasing temperature. Since the reaction is exothermic, increasing temperature does not favor interaction between the hydrophobe and α -CD. As shown in Figure 5.17, the ΔH for PEO/cyclodextrin is almost 0 (filled diamonds), hence increasing the temperature will favor this interaction. It is noteworthy that the stoichiometry is large, suggesting that the chain ends are encapsulated by several cyclodextrin molecules. Since, the height of cyclodextrin is 0.78 nm, therefore a complete coverage of the $C_{16}H_{33}$ alkyl chain requires about 3 to 4 cyclodextrin molecules. However, our results as indicated in Table 5.1 show that even at 15 °C, the stoichiometry is larger than 4, which is evident that at the beginning, uncapped PEO chain ends also participate in the complexation reaction.

DLS of different concentrations of α -CD solution in HEUR solution was conducted and shown in Figure 5.18a. It is obvious that α -CD molecules self-aggregate even at very low concentrations, which has also reported by Coleman [Coleman et al., 1992].

Addition of α -CD into 0.1 wt% HEUR-C16-51K solution alters the size of the micelle. The relaxation time distribution functions of 0.1 wt% HEUR-C16-51K aqueous solution in the presence of α -CD are shown in Figure 5.18b. When α -CD concentration is low, only one peak is observed, which corresponds to the HEUR micelles. The relaxation time of this peak increases slightly with CD concentration. The relaxation distribution function broadens when α -CD concentration was increased. When the concentration of α -CD exceeds 6 mol per hydrophobe, two relaxation modes are present; a slow mode corresponding to the aggregation of α -CD complex and a fast mode corresponds to HEUR unimers encapsulated by α -CDs. The relaxation time of the fast mode decreases with increasing α -CD concentration and

when α -CD increases beyond 20 mol per hydrophobe, it approaches a constant value. However, the relaxation time of the slow mode does not change with α -CD concentration, which is identical to that observed for α -CD in water [Bonini et al., 2006]. In comparison, the relaxation time of α -CD/HEUR and m- β CD/HEUR system is almost identical when CD concentration is 40 times of hydrophobe, but their binding processes are different.

The relationship of the apparent hydrodynamic radii of the fast mode, which represent the HEUR-C16-51K/cyclodextrin aggregates, and cyclodextrin concentration is shown in Figure 5.19. The main difference between these two cyclodextrin/HEUR interactions is that the apparent hydrodynamic radii of HEUR micelle decrease gradually with increasing α -CD concentration. But for m- β CD/HEUR system, R_h remains almost constant (about 40 nm) up to CD/Hy molar ratio of 8. It then decreases abruptly to the size of HEUR unimer (about 10 nm). From the light scattering data, a microstructure for HEUR-C16-51K/cyclodextrin aggregates based on the aggregation mechanism as depicted in Figure 5.20 is proposed.

Figure 5.18 Decay time distribution functions of α -CD and α -CD /0.1 wt% HEUR-C16-51K complex solution: (a) α -CD; (b) α -CD/HEUR

Figure 5.19 Cyclodextrin concentration dependence of R_h of fast modes of 0.1 wt% HEUR-C16-51K in cyclodextrin aqueous solution.

Figure 5.20 Schematic representation of the interaction mechanism of m- β -CD/HEUR and α -CD/HEUR in dilute solution.

For m- β CD/HEUR system, the dissociation of hydrophobic micelle results in a progressive extraction of the hydrophobically modified chains from the micelle by m- β CD. This destabilizes the micelles, which then dissociate into unimers. It is evident from previous ITC studies that m- β CD/HEUR interaction is weaker than α -CD/HEUR, thus the reduction in the apparent hydrodynamic radii occurs at higher CD/hydrophobe ratio. For α -CD/HEUR system, the dissociation of hydrophobic micelle goes through a transition phase, which changes from flower micelle to intermediate micelle and finally become HEUR unimers that are end-capped by α -CDs. When the cyclodextrin concentration is increased to CD/hydrophobe molar ratio of 6, HEUR micelles break into smaller intermediate aggregates as indicated by the two peaks in the distribution function. The fast mode corresponds to the smaller intermediate aggregate and the slow mode corresponds to the aggregation of α -cyclodextrin [Bonini et al., 2006]. With increasing CD/hydrophobe ratio, the size of the micelle gradually decreases. When the ratio reaches 20, the size approaches a minimum of about 10 nm, which is very close to size of PEO unimer of similar molecular weight.

5.6 Summary

The complexation of α -CD/HEUR is different from m- β CD/HEUR. In α -CD/HEUR system, competitive binding of α -CD/hydrophobe and α -CD/PEO coexist in the solution. High temperature enhances the α -CD/PEO interaction because of its weak endothermal properties and weakens α -CD/hydrophobe interaction because of the strong exothermic properties, which causes the concentrated HEUR solution to exhibit a unique viscosity recovery at elevated temperature. The transient hydrophobic network, which is suppressed by the addition

of α -CD is partially restored with increasing temperature, which is evident by dynamic oscillatory measurements. Studies on the complex interaction in dilute solution using ITC and DLS confirmed the different complex mechanisms; m- β CD/HEUR complexation results in a gradual reduction in the size of micelle, while α -CD/HEUR complexation results in an increase in micelle size followed by a reduction in the micelle size with increasing α -CD concentration, suggesting that a star to micelle transient structure at medium α -CD concentration.

Chapter 6 Interactions between Sodium Dodecyl Sulfate and Cyclodextrin/HEUR Complex

6.1 Introduction

In most latex paint formulations, HEUR offers the best balance of application rheology and dry film performance. However, this type of associative thickeners is also difficult to use in coating formulation comprising of more than ten different components. HEUR associative thickeners depend strongly on their hydrophobic association characteristics to achieve efficient thickening and the desired rheological behavior. The rheology of HEUR solution is sensitive to additives, such as surfactants. Since surfactants are organized by the same hydrophobic association and adsorption mechanism, they can form mixed micelles or aggregates with hydrophobic moiety of associative thickener in aqueous phase, thereby hindering or enhancing the association between hydrophobes of HEUR chains. It has been demonstrated previously (see Chapters 4 and 5) that the transient associative network held together by physical linkages of assembled hydrophobic groups can be suppressed by α - and β -cyclodextrins. Interestingly, the reduction in the viscoelasticity of the polymeric system in the presence of CD is restored with the addition of surfactant as first reported by Eisenhart et al. [Eisenhart et al., 1992]. Such strategy can be adopted, resulting in the elimination of organic cosolvents that were introduced to suppress the viscosity of the thickener prior to the coating formulation.

Despite the technical importance of this topic, very few experimental studies on this subject have been reported. One such study is by Abdala [Abdala, 2003] who described briefly this phenomenon when he studied the viscoelasticity of HASE solutions. However, his study is somewhat limited, and the mechanism of

complexation between cyclodextrin and associative polymer is still not fully understood. Therefore it is necessary to systematically study the effect of the addition of surfactant on the rheological behavior of cyclodextrin/HEUR system with the hope that the competing interaction between cyclodextrin and SDS with HEUR will be elucidated.

6.2 Addition of SDS into m- β CD/HEUR system

In order to study the effect of SDS on cyclodextrin/HEUR system, it is important to understand the interaction between each binary system such as SDS/HEUR, SDS/cyclodextrin and cyclodextrin/HEUR. Based on the understanding of interaction in the binary system, the interaction and chemical equilibrium in the ternary system can be understood.

6.2.1 SDS-HEUR interaction

Figure 6.1 shows the effects of sodium dodecyl sulfate (SDS) on the viscosity of a 2.0 wt% HEUR-C16-51K solution. At low surfactant concentrations, the presence of SDS increases the viscosity of HEUR solution. However, after the maximum viscosity is reached, the viscosity begins to decrease with further addition of SDS. When the SDS concentration was increased to 8 mM, which is close to the critical micelle concentration of SDS, the solution exhibits Newtonian behavior and approaches the viscosity of PEO solution of similar molecular weight. This suggests that SDS has the ability to completely disrupt the transient network of hydrophobic associations in HEUR polymer solution.

Figure 6.1 Solution viscosity profiles of 2 wt% HEUR-C16-51K in the presence of different concentrations of SDS, numbers corresponding to the concentration of SDS in mM.

As discussed previously (Chapters 4 and 5), the rheological properties of HEUR solutions depend on two characteristics of the association network, namely plateau modulus and relaxation time, which correspond to the number of mechanically active chains and the strength of hydrophobically association, respectively. The viscoelasticity of HEUR solutions may be approximately described by the Maxwell model, as verified by Cole-Cole plot for the system. The advantage of using the Cole-Cole plot is that the plateau modulus can be accurately determined from the intersection of the semicircle with the horizontal x-axis. Figure 6.2 shows the plateau modulus (G_N^0), relaxation time (λ) and low shear viscosity (η_0) of HEUR solution dependence on SDS concentration. It is interesting that the addition of SDS does not significantly increase the plateau modulus at low SDS concentration, while the low shear viscosity exhibits an abrupt increase. The relaxation time displays a

similar trend as the low shear viscosity, which suggests that the viscosity is mainly attributed to the enhancement of the strength of the transient network. Therefore it is evident that this strong $\lambda - \eta_0$ correlation starts with pure 2.0 wt% HEUR solution and continues up to 3 to 4 mM of added surfactant. The low shear viscosity, plateau modulus and relaxation time approach an maximum at the SDS concentration of about 2 mM. When the SDS concentration was increased further, these three physical parameters start to decrease sharply. Thus, it can be concluded from the viscoelastic properties that low concentration of SDS may enhance the HEUR hydrophobic association and strengthens the transient network, thus increasing the relaxation time. However, at high SDS concentration, the strength of HEUR hydrophobic associations is weakened by excess of SDS, which decreases the proportion of physical cross-linked junctions and relaxation time. Finally the transient network is completely disrupted when the SDS concentration exceeds CMC.

Figure 6.2 Effect of SDS concentration on the storage modulus (G_N^0), relaxation time (λ) and low shear viscosity (η_0) of 2 wt% HEUR-C16-51K solution

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To investigate the thermodynamic and binding mechanism of this system, ITC was used to provide the thermodynamic parameters for the binding process. Figure 6.3 (filled circle) shows the isothermal titration curve of 0.2 M SDS in 0.1 wt% HEUR-C16-51K solution together with the dilution curve of 0.2 M SDS in water shown by open circles. A large deviation between these two titration thermograms is observed. The difference is attributed to the interactions between SDS and HEUR.

There is only one weak transition at 8.3 mM in the SDS dilution curve and this corresponds to the CMC of SDS, which is close to the literature value [Rosen, 1980; Wang and Olofsson, 1998]. In comparison, the interaction between SDS and HEUR is more complicated. The interaction process is separated into 4 stages according change of enthalpy, which has been reported earlier. [Dai et al., 2001 and 2004]: [SDS]<2.7mM, At low SDS concentration, the titration curve for HEUR/SDS system begins to deviate from the SDS/water curve, but the enthalpy change is not significant. The slight increase in enthalpy may be due to the non-cooperative hydrophobic interaction between HEUR end groups and monomeric SDS hydrophobic tails. However, the enthalpy changes also include those arising from the change in the solvent environment caused by the presence of HEUR chains.

- 1) [SDS] <2.7mM, At low SDS concentration, the titration curve for HEUR/SDS system begins to deviate from the SDS/water curve, but the enthalpy change is not significant. The slight increase in enthalpy may be due to the non-cooperative hydrophobic interaction between HEUR end groups and monomeric SDS hydrophobic tails. However, the enthalpy changes also include those arising from the change in the solvent environment caused by the presence of HEUR chains.

- 2) $2.7\text{mM} < [\text{SDS}] < 8.0\text{mM}$, When the SDS concentration reaches 2.7 mM, ΔH increases sharply and reaches a maximum at 5.4 mM and then decreases. This endothermic peak correlates to the formation of SDS mixed micelles on the HEUR chains (or HEUR/SDS aggregation complex) and the solubilization of both the HEUR end groups and the dehydrated PEO segments from water phase into the hydrophobic core of mixed SDS micelles. The onset point for the sharp increase of ΔH is characterized by CAC. For the PEO/SDS system, the aggregation number of SDS inside the aggregation complex at CAC is much lower than that of free SDS micelles. With increasing SDS concentration, the aggregation number of SDS in the PEO/SDS complex continues to increase [van Satam et al., 1993]. However, as the aggregation number of the bound SDS micelles increases, the binding rate decreases due to electrostatic repulsions of these SDS head groups, which result in a decrease in ΔH beyond the maximum value. The titration curve then intersects with the SDS/water curve, and continues to decrease to a minimum. The minimum exothermic peak is attributed to the structural reorganization of the HEUR/SDS complex.
- 3) $8.0\text{mM} < [\text{SDS}] < C_2$, With further addition of SDS, the degree of the rehydration becomes more rapid. It slows down after the minimum in the ΔH value and approaches another critical concentration designated as C_2 ($C_2 = 18\text{mM}$ in this system), where the HEUR chains become saturated by SDS molecules.
- 4) Beyond C_2 , no further bindings between HEUR and SDS molecules can be detected and the titration curve merges with the dilution curve of SDS in

water at C_m , where free SDS micelles are present and co-exist with HEUR/SDS complex.

Figure 6.3 Calorimetric titration curves for titration of 0.2 M SDS into water (open circle) and 0.1 wt% HEUR-C16-51K (filled circle) at 25°C [Dai et al., 2001]

DLS of HEUR-C16-51K and SDS mixtures were examined with relaxation time distributions at different concentrations of SDS as shown in Figure 6.4. Only one peak in the relaxation time distribution is evident when the SDS concentration is less than 2 mM. The peak corresponds to the translational diffusion of HEUR-C16-51K micelles. With increasing SDS concentration, the relaxation time distributions exhibit two distinct peaks. The relaxation time of slow peak increases with SDS concentration until the SDS concentration reaches 8 mM. The relaxation time of the fast peak does not change with increasing SDS concentration. A very fast mode appears when SDS concentration reaches 10 mM. In this concentration range, the relaxation time of the fast and the slow peaks are independent of SDS concentration. But the very fast peak decreases with increasing SDS concentration until SDS

concentration reaches 25 mM. The fast and the slow peaks in the relaxation time distributions are attributed to the translational diffusions of the SDS bound HEUR unimers and the HEUR/SDS micellar aggregation complexes respectively. The very fast peak at higher SDS concentration corresponds to the hydrodynamic radius of 1.5 nm, which is identical to the size of free SDS micelles.

Figure 6.4 The relaxation time distribution functions of 0.1 wt% HEUR-C16-51K in different concentrations of SDS at 25°C. [Dai et al., 2001]

Combining the results from rheological studies, ITC and DLS, the possible mechanism of SDS/HEUR interaction was proposed by Dai et al. [Dai et al., 2001]. In the absence of SDS, the 0.1 wt% HEURC-16-51K is in the form of micelles as shown in Figure 6.5a. At SDS concentration lower than the CAC, SDS

monomers un-cooperatively bind to the core of HEUR micelles (Figure 6.5b). The relaxation times and the hydrodynamic radii remain constant. This is consistent with rheological results that no significant change of storage modulus is observed when SDS concentration is low. With increasing SDS concentration, more and more SDS monomers are bound and the aggregation number of the synergism core increases. Since the aggregation number at 25 °C is 70 for SDS and lower than 70 for $C_{16}H_{33}(OC_2H_4)_xOH$ (x is larger than 21), the aggregation number in the hydrophobic HEUR core cannot continue to increase. Later, small amounts of $C_{16}H_{33}$ alkyl groups will be displaced by the hydrophobic groups of SDS monomers. Some HEUR chains are only replaced one end group and the other end group is still in the HEUR core, while small amount of HEUR chains are separated from the micelles with one ends exposed to the water phase (Figure 6.5c). When the SDS concentration exceeds the CAC of 2.7 mM, HEUR unimers are dehydrated from the water phase and solubilized into the SDS micellar core to form SDS bound HEUR unimers. This is represented by the fast relaxation mode with an apparent hydrodynamic radius of 9 nm which is fairly close to the hydrodynamic radius of ~ 9.5 nm for PEO chain of similar molecular weight. (The R_h of the PEO chain can be determined from $R_h = 0.0145M_w^{0.571}$.) [Alami et al., 1996] For the HEUR micelles, these exposed hydrophobic groups and the dehydrated PEO segments are solubilized by the polymer induced SDS mixed micelles, which form aggregates that grow in size yielding clusters of a few HEUR micelles as depicted in Figure 6.5d. The HEUR/SDS aggregation complex corresponds to the slow relaxation peak in the relaxation time distribution. Since the HEUR is in the dilute solution regime and the electrostatic repulsion from SDS micelles is strong, free HEUR end-groups are not able to form bridges with

other HEUR micelles directly. In concentrated HEUR solution, the transient network is weakened and number of mechanical active chains decreases with increasing SDS concentration, which results in a significant reduction in the viscosity and storage modulus. Thus, the formation of the aggregation complex must be driven by the solubilization of several “exposed” HEUR hydrophobic end groups by one SDS micelle. The CAC value determined from light scattering agrees with that determined from ITC technique. With increasing SDS concentrations, the SDS aggregation number will increase, giving rise to the increase in the relaxation times and the hydrodynamic radii for both fast and slow modes. When the SDS concentration exceeds 8 mM, the solubilized PEO segments re-hydrate and bind to the SDS micelles via ion-dipole association, and the structure re-organizes into a necklace-like conformation where the PEO chains wrap around the head groups of SDS micelles as indicated in Figure 6.5e. This re-organization results in the continuous increase in the SDS aggregation number. The cluster size increases from 150 to 220 nm when the SDS concentration is increased from 8 to 15 mM. At SDS concentration of 20 mM, all the HEURs are saturated by SDS micelles and free SDS micelles appear in the solution. This concentration is closed to the value of C_m as determined from ITC measurements. After that, both the hydrodynamic radii are independent of the SDS concentration.

Figure 6.5 The schematic diagram describing the binding interactions between SDS and HEUR at different concentrations of SDS. [Dai et al. 2001]

6.2.2 The effect of SDS on m- β CD/HEUR system

The rheological properties of m- β CD/HEUR systems have been investigated systematically in Chapter 4. It was proven that when m- β CD/hydrophobe molar ratio exceeds 5.0, the viscosity approaches a minimum and possesses a characteristic Newtonian behavior. Starting with m- β CD/HEUR system consisting of 2.0 wt% HEUR and m- β CD/ hydrophobe molar ratio of 5, SDS was added into the system and the rheological properties were monitored. The results are shown in Figure 6.6.

Figure 6.6 Effect of SDS concentration on the solution properties of m-βCD /2.0 wt% HEUR-C16-51K solution: (a) Steady Shear viscosity and (b) Dynamic elastic (G') and viscous (G'') moduli.

Before the addition of SDS, the solution possesses a low Newtonian viscosity at all shear rates. Upon the addition of SDS, the solution viscosity begins to increase. When SDS concentration is lower than 4 mM, no viscoelasticity is observed and the increase in viscosity is not significant. When the SDS concentration exceeds 4 mM, the low shear viscosity is significantly enhanced, but no shear-thickening and shear-thinning is observed up to a shear rate of 100 s^{-1} . At SDS concentration between 6 to 8 mM, the solution exhibits shear-thickening behavior at moderate shear stresses, followed by a shear-thinning at higher shear rates. The low shear viscosity reaches a maximum at SDS concentration of 6 mM, and beyond this the viscosity starts to decrease abruptly, while the shear-thickening and shear-thinning behavior are less apparent. The solution becomes Newtonian again possessing a low viscosity identical to that of PEO solution of similar molecular weight at high SDS concentration.

From the oscillation shear experiments, it is evident that the transient network recovers upon the addition of SDS. The viscoelastic property becomes accurately measurable when the SDS concentration exceeds 4 mM. At SDS concentration of between 6 to 8 mM, the plateau modulus and relaxation time is significantly enhanced, indicating the strengthening of the transient network and formation of larger number mechanically active chains. Beyond 6 mM of SDS, the plateau modulus and relaxation time start to decrease again and the viscoelastic property is not measurable when SDS concentration exceeds 10 mM.

We noticed that the viscosity cannot be completely recovered by the addition of surfactant, for e.g., the η_0 of 2 wt% HEUR-C16-51K solution is 6 Pa.s, and with the addition of SDS the achievable maximum viscosity is 12 Pa.s. In contrast, the maximum achievable viscosity of HEUR/m- β CD (CD/hydrophobe molar ratio=5) by adding SDS is only 3 Pa.s. Figure 6.7 shows the dependence of low shear viscosity of

HEUR/cyclodextrin system with different m- β CD/hydrophobe content in the presence of different concentrations of SDS. It is clear that with increasing m- β CD concentration, more SDS is required to achieve the maximum viscosity. The magnitude of maximum low shear viscosity decreases with increasing cyclodextrin concentration.

Figure 6.7 The effect of SDS concentration on low shear viscosity of HEUR-C16-51K/m- β CD systems. Numbers correspond to CD/hydrophobe molar ratio

When SDS was added into mixtures of HEUR and cyclodextrin, a number of possible competitive interactions are present in the system, where SDS molecules can interact with β -cyclodextrins or HEUR chains. Depending on the types of interactions, the recovery of the viscosity varies. The basic principle for the restoration of the solution viscosity of HEUR is the removal of the hydrophobes from HEUR/m- β CD complex and the restoration of the transient network. The issue that needs to be

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resolved is whether the HEUR/m- β CD solution can recover its viscoelasticity and if yes, to what extent? The possible reaction can be described by;

Abdada et al. [Abdada et al., 2003] attempted to recover the viscosity of HASE/cyclodextrin system with a macromonomer that resembles that of a nonionic surfactant containing a hydrophobic C₂₂H₄₅ alkyl chain and a hydrophilic segment containing 40 EO units. They proposed that initially a fraction of the macromonomer added was encapsulated by CD, others interacted with the polymer, and the remaining remained as free macromonomer. Beyond a critical concentration, the macromonomer has a negative effect on the bulk property of the polymer solution, resulting in a reduction in the viscosity and viscoelastic properties. Our current studies on the anionic surfactant SDS revealed some differences for the interaction between cyclodextrin and HEUR, where SDS restores m- β CD/HEUR viscosity to about 50% of the viscosity of 2 wt% HEUR-C16-51K solution. Therefore it is probably that the interaction between SDS molecules and m- β CD is not strong enough to completely remove hydrophobes in HEUR chain from HEUR/cyclodextrin complex.

The probable interactions for the system are shown below;

If K₁ is sufficiently large, SDS and m- β CD, interaction will dominate, and the hydrophobic moieties of HEUR can be released from CD-HEUR complex resulting in the complete recovery of the viscosity to original HEUR solution. However, if K₂ dominates the reaction, it is possible to recover the viscosity by extracting the

hydrophobic moiety of HEUR from the CD-HEUR complex. In order to confirm which interactions dominate, isothermal titration calorimetry was used to examine the thermodynamic properties of the system.

Figure 6.8 compares the thermograms for the titration of SDS into water and SDS into m- β CD solution of different concentrations. There is only one weak transition at 8.3 mM for the SDS dilution curve, which corresponds to the CMC of SDS. A large deviation between these two titration thermograms is attributed to the interactions between SDS and cyclodextrin. The interaction of β -CD and SDS has been extensively studied by various techniques such as surface tension, conductivity and ITC [Puglisi and Ventura, 1992]. It was found that β -CD and SDS form stable complex with a large equilibrium constant (6.3×10^3), and the complexation is characterized by one site binding mechanism with a binding stoichiometry of 1.0 [Park and Song, 1989; Saski et al., 1989; Funasaki et al., 1992]. Thus far, there is no reported study on the complexation of m- β CD and SDS. From the thermogram, it seems that the complexation is rather complex, suggesting that the additional methyl group on the cyclodextrin has a significant effect on the binding interaction between SDS and m- β CD. At low SDS concentration, a small difference between the titration curves of cyclodextrin/SDS and SDS/water system. The slightly larger enthalpy at very low SDS concentration may be due to the non-cooperative hydrophobic interaction between SDS end groups and the hydrophobic cavity of cyclodextrin. However, the enthalpy changes also include those arising from the change in the solvent environment caused by the presence of cyclodextrin molecules. After the hydrophobic cavity of cyclodextrin is saturated by SDS molecules, the enthalpy change approaches the SDS/water system at SDS concentration ranging from 2 to 7 mM. Since the enthalpy change is positive, it can be deduced that the process is

entropy controlled. Fitting the first region using the non-linear least-squares algorithm, we determined that the binding stoichiometry is equal to 1.0, which is identical to the stoichiometry for SDS/ β -CD system. The equilibrium constant, K is found to be about 1.5×10^3 , which is small and this might be related to the steric hinderance of the methyl group on the exterior of cyclodextrin molecule.

Figure 6.8 Calorimetric thermograms for the titration of 0.2 M SDS into m- β CD solution at 25°C with. Numbers correspond to concentration of m- β CD. The inset figure is Calorimetric thermograms for the titration of 0.2 M SDS into m- β CD solution deduced by Calorimetric thermograms of the titration of 0.2 M SDS into water.

It is observed from Figure 6.8 that when the hydrophobic cavity of cyclodextrin is saturated with SDS molecules at 2 mM, the SDS/m- β CD titration curve merges with the SDS/water curve, suggesting that negligible interaction is present up to the SDS concentration of 7 mM. When SDS concentration reaches 7 mM, the titration curve for SDS/m- β CD system begins to deviate from the SDS/water curve, where the ΔH is less positive than SDS/water system. This endothermic peak

correlates to the formation of SDS mixed micelles with the cyclodextrin molecules, and the solubilization of the cyclodextrin from water phase into the hydrophobic core of mixed SDS micelles. The onset point for the sharp increase of ΔH is characterized by CAC, which is similar to the definition of CAC in HEUR/SDS system [Dai et al. 2004]. As the aggregation number of the bound SDS micelles increases, the binding rate decreases due to electrostatic repulsions of these SDS head groups, which result in a decrease in ΔH beyond the maximum value. With further addition of SDS, the m- β CD molecules become saturated by SDS molecules, and no further bindings between m- β CD and SDS molecules can be detected and the titration curve merges with the dilution curve of SDS in water.

Based on a complete understanding on the interaction for the HEUR/cyclodextrin, HEUR/SDS and SDS/cyclodextrin systems, it is possible to examine the characteristics of a ternary system, i.e. HEUR/SDS/cyclodextrin and to elucidate the manner in which SDS interacts with HEUR/cyclodextrin system. The thermograms for the titration of SDS into various compositions of HEUR/cyclodextrins were plotted in Figure 6.9. From the titration curve of SDS/HEUR, there is a positive enthalpy peak at the beginning of the titration which is quite similar to SDS/m- β CD titration curve (Figure 6.9b). The peak increases with increasing cyclodextrin concentration, confirming that the positive enthalpy peak is most likely to be related to the non-cooperative hydrophobic interaction between SDS and cyclodextrin. Such binding releases some HEUR end-groups from HEUR-cyclodextrin complex to the bulk solution. When the SDS concentration was increased to 1 mM, all the cyclodextrin molecules are bound to SDS to form a 1:1 complex, and the interaction between cyclodextrin and monomeric SDS ceases.

The titration curve of SDS/HEUR/m- β CD merges with the SDS/HEUR titration curve at [SDS] = 1 mM. Between SDS concentration ranging from 1.0 to 5.4 mM, ΔH increases sharply and reaches a maximum at 5.4 mM and it then decreases. This endothermic peak correlates to the formation of SDS mixed micelles on HEUR chains (or HEUR/SDS aggregation complex) and the solubilization of both hydrophobic moiety of HEUR chains and dehydrated PEO segments from water phase into the hydrophobic core of SDS mixed micelles. The onset for the sharp increase of ΔH is characterized by the CAC, which is not altered by the presence of cyclodextrin. For PEO/SDS system, the aggregation number of SDS inside the aggregation complex at CAC is much lower than free SDS micelles. With increasing SDS concentration, the aggregation number of SDS in the PEO/SDS complex continues to increase [van Satam et al., 1993]. However, as the aggregation number of bound SDS micelles increases, the binding rate decreases due to electrostatic repulsions of SDS head groups, which result in a decrease in ΔH beyond the maximum value. The titration curve then intersects with the SDS/water curve, and continues to decrease to a minimum. At this stage, only the interaction between HEUR chains and SDS is present. This is deduced from the observation that the ternary titration curves do not change in the presence of cyclodextrin, which is identical to HEUR/SDS titration curve within this concentration regime. It is also evident from the titration curve of SDS/m- β CD (Figure 6.8) that there is no interaction between SDS and cyclodextrin in the SDS concentration of between 1.0 to 7.0 mM. The minimum exothermic peak is attributed to the structural reorganization of the HEUR/SDS complex (Dai et al. 2001). Dai studied this structural reorganization and this reorganization and rearrangement of the necklace-like PEG structure from one to two SDS micelles, the structural reorganization is due to the limited segment chain length. With further addition of

SDS, the titration curve deviates from HEUR/SDS curve again. The critical concentration C_2 , which is characterized by saturation of the HEUR chains by SDS molecules, becomes less significant with increasing cyclodextrin concentrations. This suggests that both HEUR and cyclodextrin participate in the interaction. Because of the large negative enthalpy observed in Figure 6.8 (insert figure), it is likely that cyclodextrin/SDS interaction dominates in the system. It is also observed from Figure 6.9 that these four titration curves approaches each other with increasing SDS concentration, but these curves do not merge with the dilution curve of SDS in water, instead, they merges into the titration curve of SDS/m- β CD (indicated by filled triangles). Due to the consumption of SDS bound with CD, it is also evident of the increase in the saturation concentration for the HEUR/CD/SDS system.

Figure 6.9 a) Calorimetric titration curves for titration of 0.2 M SDS into HEUR/m- β CD solution at 25°C with HEUR concentration of 0.1 wt%. The numbers correspond to concentration of m- β CD.

Figure 6.9 b) Part of a) where SDS concentration varied from 0 to 4 mM .

In order to further confirm the proposed mechanism for SDS/HEUR/ β -CD system, DLS of HEUR₁₆51K, $m\text{-}\beta\text{CD}$ and SDS mixtures were conducted and the relaxation time distributions at different SDS concentrations are shown in Figure 6.10 for CD/hydrophobe ratio of 10 and 20 respectively. The number on the figures represents the SDS concentration in the HEUR polymer and CD mixed solutions.

Figure 6.10 The relaxation time distribution functions of HEUR-C₁₆-51K/m-βCD in different concentrations of SDS at 25°C. [HEUR]= 0.1 wt%; (a) CD/hydrophobe ratio of 10, (b) CD/hydrophobe ratio of 20.

The effect of m-βCD concentration on the relaxation time distribution of HEUR solution was discussed in section 4.6.7. Only one peak in the relaxation time distribution is evident when m-βCD/hydrophobe molar ratio is lower than 6. The peak corresponds to the translational diffusion of HEUR-C16-51K micelles. At molar ratio of 10, two peaks were observed. The fast mode corresponds to HEUR aggregates, but the size is smaller than original HEUR micelle of about 15 nm, which is attributed to the partially dissociated HEUR micelles with lower N_{agg} . The slow mode is attributed to the aggregation of m-βCD. When SDS was added to the system, the relaxation times of the fast mode increase slightly when the SDS concentration is lower than 3

mM. The fast mode starts to decrease when SDS concentration was further increased. When the SDS concentration was increased to 15 mM, a very fast mode appeared. In this concentration range, the relaxation times of the fast and slow peaks are independent of SDS concentration. Addition of SDS into HEUR/m- β CD mixture solution with m- β CD /hydrophobe molar ratio of 20 (Figure 6.10b) yielded similar result. However some subtle differences were evident, even though initially the location of the fast mode is different for different m- β CD /hydrophobe ratio system. When [SDS] = 1mM, the location of the fast mode is identical for the two systems which m- β CD /hydrophobe ratio equals to 10 and 20. R_h corresponding to this peak is about 25 nm, which is smaller than R_h of pure HEUR micelle. This is consistent with previous result that the hydrophobic association is only partially recovered when SDS was added into m- β CD/HEUR system. Based on the results from ITC and DLS, a probable binding mechanism for the SDS/HEUR/m- β CD system is proposed (Figure 6.11).

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Figure 6.11 Schematic representation of the interaction mechanism of SDS and m-βCD/HEUR complex in dilute solution.

In the absence of SDS, m-βCD dissociates HEUR micelle to single polymer chain by threading on both ends of the PEO chains. Because this reaction is relatively weak, m-βCD needs to be in excess to form HEUR unimeric chain. Upon the addition of SDS in the solution, a portion of SDS bind to the free m-βCD, which perturbs the equilibrium between m-βCD and HEUR. With increasing SDS concentration, SDS monomers bind to m-βCDs that are encapsulating the hydrophobes within the HEUR-cyclodextrin complex, resulting in the dissociation of the HEUR chains. These hydrophobic moieties are then free to form HEUR flower micelles mixed with SDS monomers. Because the equilibrium constant K is relatively low, SDS must be in excess to bind with m-βCD molecules. When the m-βCDs are completely bound to SDS molecules, the size of HEUR micelle approaches an optimum. As a result of the physical equilibrium condition, monomeric SDS also exists in solution at relatively

high concentration and the monomeric SDS will simultaneously bind to the HEUR micelle. At SDS concentration lower than the CAC, SDS monomers bind uncooperatively to the core of HEUR micelles. When the SDS concentration exceeds the CAC of 2.7 mM, HEUR unimers are dehydrated from the water phase and solubilized to the SDS micellar core. This is represented by the fast relaxation mode with an apparent hydrodynamic radius of 10 nm, which is fairly close to the hydrodynamic radius of ~ 9.5 nm for PEO chain of similar molecular weight. When SDS concentration is increased further, cyclodextrin molecules also dehydrated from water phase and dissolved in SDS micelles.

6.3 Addition of SDS to α -CD/HEUR system

6.3.1 Rheological studies

The viscosity profile of HEUR/ α -CD (with CD/hydrophobe molar ratio equals to 5) in the presence of different amounts of SDS is shown in Figure 6.12a. It is evident that upon the addition of SDS, the solution viscosity of HEUR/ α -CD mixture starts to increase. Prior to the addition of SDS, the 2 wt% HEUR/ α -CD solution (with CD/hydrophobe molar ratio of 5) possesses a Newtonian low viscosity over the entire shear rates. When SDS concentration was increased to 2 mM, the low shear viscosity increases significantly and the solution exhibits shear-thickening behavior at moderate shear rates, followed by a shear-thinning region at higher shear rates. The low shear viscosity reaches a maximum at SDS concentration of 5 mM. When the SDS concentration was further increased, the low shear viscosity decreases sharply, and the shear-thickening and shear-thinning behavior becomes less significant. At SDS concentration higher than 10 mM, the solution becomes Newtonian with a very low viscosity of 0.1 Pa.s.

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Figure 6.12a. The viscosity profile of HEUR/α-CD complex solution in the presence of different concentrations of SDS. The number corresponds to the concentration of SDS.

Figure 6.12b Effect of SDS on the viscosity of HEUR/α-CD solution. [HEUR]=2 wt% α-CD/hydrophobe molar ratio=5

Figure 6.13 G' and G'' of ternary system corresponding to maximum η_0 , dotted line is G' and G'' for 2 wt% HEUR solution

The zero shear viscosity (η_0) as a function of SDS concentration is shown in Figure 6.12b. Comparing the three systems: HEUR/SDS, HEUR/m- β CD/SDS and HEUR/ α -CD/SDS, it is evident that the low shear viscosity $\eta_0 \sim$ CD concentration relationship follows a similar trend; initially η_0 increases with increasing CD concentration. It reaches maximum recoverable viscosity and then starts to abruptly decrease with increasing CD concentration. The maximum recoverable viscosity appears at SDS concentration of 5 mM for HEUR/ α -CD/SDS system, which is higher than the original viscosity of 2 wt% HEUR solution and very close to the maximum viscosity of HEUR/SDS system. In comparison, the magnitude of maximum low shear viscosity of HEUR/m- β CD/SDS is much lower and appears at higher SDS concentrations (i.e. at [SDS] = 7 mM).

From the oscillatory shear experiments, it is also evident that the transient network is completely restored upon the addition of SDS. Before the addition of SDS, the solution is Newtonian, and it changes to viscoelastic when SDS concentration is increased to 2 mM. When SDS concentration is increased further, the plateau modulus and relaxation time both increase, signifying the strengthening of the transient network. At SDS concentration of 5 mM, the plateau modulus and viscosity reaches a maximum, and it then decreases with further addition of SDS. Beyond SDS of 10 mM, the viscoelasticity cannot be experimentally measured. Figure 6.13 shows the storage $G'(\omega)$ and loss $G''(\omega)$ moduli of 2.0 wt% solutions of hexadecyl terminated HEUR polymers in the present of α -CD (α -CD/hydrophobe molar ratio=5) and SDS (concentration of 5mM). G' and G'' of 2.0 wt% HEUR solution and HEUR polymers in the presence of m- β CD (m- β CD/hydrophobe molar ratio=5) and SDS (concentration of 7mM) were also plotted for comparison. It is evident that the transient network of HEUR/ α -CD/SDS system is more stable with longer relaxation time than that of 2 wt% HEUR solution, while the transient network of HEUR/m- β CD/SDS system is less stable with a smaller relaxation time. It is also interesting that the difference of G_N^0 is not significant among three HEUR solution systems, and this implies that number of mechanically active junctions is identical, but the life-time or the residence time of the hydrophobes in the hydrophobic domain is different for different cyclodextrin systems. Thus, we noted that SDS can restore the transient network for both HEUR/ α -CD and HEUR/m- β CD solution mixtures. Due to the weaker interaction between SDS and m- β CD, the transient network is restored at higher SDS concentration.

In order to completely suppress the transient network of 2 wt% HEUR-C16-51K solution, the minimum α -CD concentration is 5 mol per mol of hydrophobe,

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which corresponds to a total α -CD concentration of 3 mM. It is interesting that in the HEUR/ α -CD/SDS ternary system (CD/hydrophobe molar ratio is 5), the low shear viscosity is almost identical to the 2 wt % HEUR solution when SDS concentration is 3 mM. In other words, the ternary systems require an additional 3 mM SDS to offset the effect of α -CD. The interaction is in fact a displacement reaction, with one SDS molecule displacing one α -CD molecule from CD-HEUR complex, resulting in the release of free HEUR chain from HEUR/ α -CD complex. As previously discussed, addition of cyclodextrin into HEUR solution deactivates the mechanically active chains, resulting in the disruption of the transient network. But in HEUR and α -CD inclusion complex system, the addition of SDS deactivates α -CD from binding to HEUR. We observed that the ternary SDS/HEUR/ α -CD system shows a lower maximum viscosity than SDS/HEUR system, which indicates that SDS/ α -CD interaction is the dominant reaction in the three components system.

6.3.2 Dilute solution behavior

In order to investigate the interaction of SDS and HEUR/ α -CD complex in dilute solution, we need to explore the interaction of SDS/HEUR and SDS/ α -CD by conducting ITC experiments.

Figure 6.14 shows the thermogram for the titration of 0.2 M SDS into different concentrations of α -CD solutions together with the dilution curve of 0.2 M SDS in water (shown by the line). When SDS was titrated in α -CD, a large deviation between these two titration thermograms is evident. An extremely large negative enthalpy was observed at low SDS concentrations. This exothermic peak correlates to the binding of SDS hydrophobic tail to the hydrophobic cavity of cyclodextrin. ΔH increases with increasing α -CD concentration until 0.5 mM, where the titration curve merges with titration curve of SDS/ water.

It is observed from the above figure that the interaction between α -CD/SDS and m- β CD/SDS is completely different. Non-linear least-squares fitting was used to fit the ITC isotherms. We assume that a single SDS/CD complex is in equilibrium with the surfactant and cyclodextrin molecules, where the interaction between SDS and cyclodextrin can be described by Equation (6.5):

The corresponding equilibrium constant (K) can be written as;

$$K = \frac{[S \bullet CD_{\alpha}]}{([S] - [S \bullet CD_{\alpha}])([CD] - \alpha[S \bullet CD_{\alpha}])^{\alpha}} \quad (6.6)$$

where [S] and [CD] are the stoichiometric concentration of the surfactant and of the cyclodextrin, $[S \bullet CD_{\alpha}]$ is the equilibrium concentration of the complex and α is the number of cyclodextrin molecules in the complex.

Figure 6.14 Thermogram for titrating SDS to α -CD solution. Numbers correspond to the concentrations of α -CD in mM.

Figure 6.15. Calorimetric thermograms for the titration of 0.2 M SDS into HEUR-C16-51K/ α -CD complex solution at 25°C with [HEUR] = 0.1 wt%. Numbers correspond to α -CD/hydrophobe molar ratio

The mathematical regression resulted in the fitted parameters as listed in Table 6.1

Table 6.1 Thermodynamic parameters for the interaction between CD and SDS

CD	N	K	ΔH (kJ/mol)	ΔS (J/mol)
α -CD	2.0	1.13×10^5	-32.0	-13.0
β -CD	1.0	6.3×10^3	-22.0	-2.1
m- β CD	1.0	1.5×10^3	-2.1	53.0

α -CD and SDS form stable complex with a very large equilibrium constant and a binding stoichiometry of 2. On the other hand, β -CD also bind to SDS with a large K, but the stoichiometry is unity. In comparison, m- β CD has a small negative enthalpy, which is attributed to the steric hindrance of methyl group introduced on the primary OH ring. However, the entropy is large and positive, which suggests that this reaction is entropic controlled.

Figure 6.15 shows calorimetric thermogram for titrating SDS to HEUR and HEUR/ α -CD complex solution. The figure is divided into 2 regions for visual comparison. The first part covers the SDS concentration from 0 to 3 mM, and the second from 3 to 40 mM, which was embedded in the main figure. It is evident that the difference in all the titration curves occurs at the beginning, with a significant negative enthalpy peak attribute to the reaction between SDS and α -CD. The reaction can be expressed by Equation (6.7);

By comparing ΔH in Figure 6.14 and 6.15, it is found that the ΔH for SDS/HEUR/ α -CD is lower than that of SDS/ α -CD at similar α -CD concentration.

The decrease in ΔH is attributed to the fact that HEUR and α -CD form a stable complex with a negative ΔH . To facilitate the reaction indicated by Equation (6.7), the complex has to be destroyed, which contributes partially to the ΔH between SDS and free α -CD. Fitting the thermogram for SDS concentration of 0 to 3 mM with non-linear least-squares, we obtained a stoichiometry of 2, which is identical to the stoichiometry for SDS/ α -CD. SDS starts to interact with HEUR polymer when SDS concentration exceeds 1 mM. This is evident from the embedded figure where the thermograms show no significant difference between SDS/HEUR and SDS/HUER/ α -CD system when α -CD concentration exceeds 3mM. The result is consistent with data from Table 6.1 that the equilibrium constant of α -CD/SDS is much higher than other reactions.

Figure 6.16 shows the distribution functions obtained from DLS for the SDS/HEUR/ α -CD ternary system. The effect of α -CD on the relaxation time distribution of HEUR solution was previously discussed in Chapter 5, which is significantly different from m- β CD. α -CD/HEUR complex goes through a transient process where star-like micelle is produced. With further increase of SDS concentration, the star-like micelle disintegrates into smaller loose aggregates and to single chain when α -CD concentration is sufficiently large. In Figure 6.16a, when CD/hydrophobe molar ratio is 10, two peaks were observed. The fast mode corresponds to HEUR aggregates of size smaller than the original HEUR micelle, which is about 15 nm. The partially dissociated HEUR micelle possesses a smaller N_{agg} . The slow mode is attributed to the aggregation of α -CD. When SDS was added to the system, the relaxation times of the fast mode increase slightly at low SDS concentration. It then starts to decrease when SDS concentration was increased further. When the SDS concentration approaches 15 mM, a very fast mode appears. In this

concentration range, the relaxation times of the fast and slow peaks are independent of SDS concentration. Addition of SDS to HEUR/ β -CD mixture solution (β -CD/hydrophobe molar ratio = 20), resulted in a similar trend. The only difference between β -CD/hydrophobe ratio of 10 and 20 is that at the ratio 10, HEUR chains are still associated in micellar aggregate of smaller size. In Figure 6.16b (α -CD/hydrophobe molar ratio equal to 20), more subtle features were observed. It has been demonstrated previously (section 5.5) that at this molar ratio, no HEUR aggregates are present in solution. The fast mode is related to the HEUR unimers that are encapsulated by α -CD molecules. When SDS was added to this system, the relaxation time of the fast mode increases to one that closely resembles the HEUR micelle. The relaxation time remains constant up to the SDS concentration of 6 mM, beyond which a very fast mode representing the HEUR unimer appears. When SDS concentration was increased further, the relaxation peak of the HEUR micelle disappears, while the relaxation time corresponding to HEUR unimer chain does not change with SDS concentration. When the SDS concentration exceeds 18 mM, a new fast mode appears, and this is related to the unbound SDS micelle. The slow mode, which was attributed to solubilized PEO segments re-hydrate and bind to the SDS micelles via ion-dipole association, and the microstructure re-organizes into a necklace-like conformation where the PEO chains wrap around the head groups of SDS micelles as indicated in Figure 6.5e for HEUR/SDS system.

Figure 6.16 DLS of SDS/HEUR/ α -CD ternary system. Number corresponds to SDS concentration in mM. Left graph: [HEUR]=0.1 wt%, α -CD/hydrophobe molar =10 Right graph: [HEUR]=0.1 wt%, α -CD/hydrophobe molar =20

6.4 Summary

The viscosity recovery of HEUR/cyclodextrin complex was investigated, and the addition of surfactant effectively restores the viscoelasticity of HEUR solution. Initially, the viscosity increases with increasing SDS concentration and the solution becomes viscoelastic. At the optimal SDS concentration, the viscosity, plateau modulus and relaxation time reach a maximum and then decrease and approach a lower magnitude at high SDS concentration. The magnitude of viscosity recovery depends on the types of cyclodextrins. With m- β CD, the viscosity only recovers partially, while for α -CD, the viscosity recovers almost completely. The difference between these two systems is attributed to the different binding interaction between

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CD and SDS molecules. m- β CD/SDS reaction is relatively weak, hence SDS needs to be in excess for the removal of m- β CD from CD/HEUR complex. After m- β CD is completely bound with SDS and the transient network has been restored, excessive SDS continues to interact with the HEUR aggregation and destabilises the hydrophobic association. In contrast, α -CD binds strongly to SDS molecules with an extremely negative enthalpy. Therefore, α -CDs are readily removed from CD/HEUR complex by SDS molecules, and hence the viscosity recovers completely.

Chapter 7 Interaction between Fluorocarbon HEUR and Cyclodextrins

7.1 Introduction

The fluorocarbon associative polymers are interesting systems because of their low surface energy, biocompatibility, oleo- and hydrophobic properties, and also because of the enhanced viscosity properties compared to the hydrocarbon counterparts. From previous studies, a consistent picture for the self-assembly and flow behaviors has emerged. In many respects, the phenomenon of self-assembly and network formation observed for telechelics fluorocarbon is similar to that of hydrocarbon analogues. At very low concentrations, and above the critical aggregation concentration, F-HEUR self-assemble in water to produce mono-disperse flower-like micelles. In telechelics fluorocarbon, the onset of viscoelasticity coincides with the formation of an associative network of flower micelles. One crucial difference between the hydrocarbon and fluorocarbon telechelics is the range of relaxation times that characterize the viscoelastic solutions in the network regime.

The influence of various types of amphiphilic molecules, such as surfactants has been reported [Brown et al. 1995; Lo Nostro et al. 2003; De Lisi et al. 2003; Berret et al. 2003]. However, very few studies on the effect of cyclodextrins on the associative behaviour of fluorocarbon hydrophobes have been studied. Zhang and co-workers [Zhang et al. 1998a] examined the complex formation β -cyclodextrin/perfluorocarbon modified water-soluble polymer by ^{19}F NMR, and found that the viscosity is greatly reduced by β -cyclodextrin as a result of the disruption of intermolecular hydrophobic association. In the present study, we examined the viscoelasticity of concentrated polymer solution in the presence of β -cyclodextrin and

proposed a binding mechanism according to a Multi-site adsorption model. The properties of dilute solution were also studied thoroughly by ^{19}F NMR, ITC and DLS.

7.2. Result and discussion

7.2.1. Effects of different types of cyclodextrins on the rheological properties

For 2.0 wt% F-HEUR with C_6F_{13} hydrophobe, the viscosity is almost independent of shear rates within the experiment shear rate regime. No shear thickening was observed in the high shear rate range, which is different from the behavior of telechelic associating polymers containing hydrocarbon hydrophobes. However, the viscosity increases with increasing polymer concentration, e.g. when concentration was increased to 3.0 wt %, the low shear viscosity approaches 1.0 Pa.s. In contrast, F-HEUR with hydrophobe of C_8F_{17} exhibits a typical rheological behavior similar to telechelic polymers with strongly associating end-groups. The 2.0 wt% solution appears to exhibit a slight shear-thickening before the onset of shear-thinning. The change in the hydrophobe from C_6F_{13} to C_8F_{17} groups results in an increase in the zero-shear viscosity of about 30 times, indicating a much stronger association of C_8F_{17} groups than C_6F_{13} groups.

Figure 7.1 Steady shear viscosities at 20 °C as a function of shear rate for F-HEUR with different hydrophobes. The solution concentration is 2.0 wt%.

Different cyclodextrins were used to study the interaction between cyclodextrin and F-HEUR-C₈F₁₇-35K. Figure 7.2 shows the viscosity profiles of 2.0 wt% F-HEUR in the presence of different types of cyclodextrin at cyclodextrin/F-hydrophobe molar ratio of 1:1. It is observed that the viscosity profile of α -cyclodextrin/F-HEUR system is identical to the fluorocarbon HEUR solution without α -cyclodextrin, which suggests that there is no interaction between α -cyclodextrin and F-HEUR. However, we observed that γ -cyclodextrin marginally reduces the viscosity of F-HEUR solution, and the characteristic shear-thickening and shear-thinning are preserved. In addition, the onset for the shear-thickening and shear-thinning behavior remained the same, which points to a weak interaction between γ -cyclodextrin and F-HEUR. In contrast, the non-Newtonian viscosity profile of methylated β -cyclodextrin/F-HEUR is reduced to one that exhibits a Newtonian viscosity of 0.005 Pa.s. The previously observed shear-thickening and shear-thinning

behavior have completely disappeared, suggesting that the transient network attributed to the associative junctions of fluorocarbon hydrophobes is completely destroyed by the strong interaction between m- β CD and fluorocarbon hydrophobic groups.

It has been reported by Palepu and co-workers [Palepu et al. 1989] that the relative size of cyclodextrin hydrophobic cavity is the decisive factor controlling the interaction between cyclodextrin and other host molecules. In order to form guest-host inclusion complex (IC), the size of hydrophobic cavity and the cross-section of the guest molecules must be compatible to produce a stable complex. The diameter of a CF_2 group is estimated to be 0.5 nm and that of a CF_3 group is 0.7 nm [Tiddy, 1985]. The cavity of α -CD is rather small (diameter ca. 0.5 nm) and cannot accommodate the fluorocarbon chain with a $\text{C}_n\text{F}_{2n+1}$ end-group. Therefore, it is not possible for α -CD to form inclusion complex with fluorocarbon hydrophobe. In contrast, γ -cyclodextrin has a larger cavity (diameter ca. 0.9 nm), and the fluorocarbon chain can loosely fit into the cavity. Thus, γ -cyclodextrin can easily thread in and out of the fluorocarbon segment yielding a stable complex. However, for β -cyclodextrin, the size of the inner hydrophobic cavity is 0.7 nm, which provide an excellent fit for $\text{C}_n\text{F}_{2n+1}$ group. Therefore, a fluorocarbon chain would be able to fit snugly inside the cavity of β -cyclodextrin molecule. Since the interior of the cavity is less polar than the aqueous phase, the inclusion of fluorocarbon chain into such a cavity reduces the contact between the fluorocarbon chain and the aqueous environment, which makes such inclusion energetically favorable.

Figure 7.2 Viscosity profile of 2.0 wt% F-HEUR-C₈F₁₇-35K aqueous solution in the presence of different types of cyclodextrins.

The effects of m-βCD on the steady shear viscosity of 2.0 wt% F-HEUR-C₈F₁₇-35K solution are shown in Figure 7.3. With the addition of cyclodextrin, the steady-shear viscosities of the polymer solutions decrease dramatically. The characteristic shear-thickening and shear-thinning region of HEUR solution becomes less apparent with increasing m-βCD concentrations, and the onset of shear-thickening and shear-thinning shifted towards higher shear rates. When m-βCD concentration increases to 0.5 mol of CD per hydrophobe, no shear-thickening and shear-thinning are observed within the experiment shear deformation investigated. When m-βCD concentration is further increased to 1 mol of CD per hydrophobe, the viscosity profile becomes Newtonian and possesses a very low viscosity of 0.005 Pa.s. Beyond this concentration regime, the viscosity does not show a significant reduction,

suggesting that the fluorocarbon hydrophobe is saturated with cyclodextrin molecules and no additional interaction occurs between F-HEUR and cyclodextrin molecules.

Figure 7.3. Effects of m-βCD on the shear viscosity of 2.0 wt% F-HEUR-C8F17-35K aqueous solution. The number corresponds to the molar ratios of m-βCD to hydrophobe.

Figure 7.4 Shear moduli of 2 wt% F8-HEUR-35K aqueous solution in different amounts of *m*-βCD. The number corresponds to the molar ratio of *m*-βCD/hydrophobe. Open symbols are G' and filled symbols are G'' .

Similar phenomenon was observed for the dynamic rheological behavior, where the viscoelastic properties of F-HEUR solution can be fitted by the Maxwell model. At low frequencies, $G'(\omega)$ and $G''(\omega)$ possesses a slope of 2 and 1 respectively, and with increasing frequencies, $G'(\omega)$ approaches the entanglement plateau region. Figure 7.4 shows the effect of methylated β-CD on the frequency dependence of elastic and viscous moduli of 2.0 wt% F-HEUR-C8F17-35K polymer solutions. The addition of cyclodextrin reduces both the elastic and viscous moduli and increases their dependence on frequency. The greater dependence of the moduli on the frequency is a sign of a weaker network structure due to the reduction in the number of mechanically active chains. When *m*-βCD/hydrophobe molar ratio exceeds 0.5, $G'(\omega)$ decreased to the point where it is not detectable by the rheometer.

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In order to verify whether Maxwell model is valid for m-βCD/HEUR complex solution, a Cole-Cole plot was constructed. The advantage of the Cole-Cole plot is that the plateau modulus can be accurately determined from the intersection of the semicircle with the horizontal x-axis. If the fitting to the experimental data with the model is perfect, G'' versus G' plot should form a semicircle as described by Equation (7.1),

$$G''(\omega) = [G'(\omega)G_N^0 - G'(\omega)^2]^m \tag{7.1}$$

where m = 0.5. Data which fitted the Maxwell model yielded a perfect semicircle when G'' was plotted against G'. Several sample solutions were studied using this method to examine the effect of m-βCD on the rheological properties of HEUR and the result is shown in Figure 7.5, and the numerical values are shows in Table 7.1.

Table 7.1 Plateau modulus and relaxation time for CD/F-HEUR system

[CD]/Hy molar ratio	0	0.025	0.05	0.1	0.25
G _N ⁰ (Pa)	367	320	265	167	59
m	0.492	0.490	0.488	0.488	0.485
λ(s ⁻¹)	0.095	0.087	0.071	0.056	0.029

Figure 7.5 Cole-Cole plot of the dynamic properties of 2.0 wt% F-HEUR-C₈F₁₇-35K solution and different concentrations of m- β CD with the accompany fitting of the Maxwell model. The number corresponds to the molar ratio of m- β CD/hydrophobe.

For 2.0 wt% F-HEUR-C₈F₁₇-35K solution in the absence of m- β CD, the fitting yielded $m \sim 0.492$, which corresponds to an ideal fitting to Maxwell model. When m- β CD/hydrophobe molar ratio equals to 0.25, the fitting results of m is 0.485, suggesting that the single Maxwell model can still be used to predict the viscoelastic behavior. It is also observed from Table 1 that both plateau moduli and relaxation times decreases with increasing CD concentrations. Comparing these results with the hydrocarbon HEUR system, the plateau modulus decreases more significantly than the relaxation time. At CD/[F] ([F] represent fluorocarbon end-group) molar ratio of 0.25, the magnitude of plateau modulus is only 1/6 the original modulus in the absence of cyclodextrin, while relaxation time remains at 1/3 the original value in the absence of cyclodextrin. This implies that the reduction in the viscosity is mainly

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attributed to the deactivation of the fluorocarbon hydrophobes from the domains forming the polymer network.

Karlson [Karlson et al, 2002a] attempted to interpret this phenomenon by adopting the Langmuir adsorption model. In developing the model equation for describing the relationship between viscosity and cyclodextrin concentration, he assumed that the relaxation time for the relaxation process is independent of CD concentration. However, we observed for F-HEUR/m- β CD system that the relaxation time decreases with increasing CD concentration. Therefore, it is difficult to quantitatively predict the η_0 -[CD] relationship, instead the plateau modulus G_N^0 , which is not affected by the relaxation time could be a more suitable parameter since it is also proportional to number of mechanically active chains. In order to interpret the influence of methylated β -CD on the transient network structure of F-HEUR, we proposed a model to describe the relationship between CD concentration and plateau modulus, G_N^0 of the polymeric network. Two adsorption models were examined: the Langmuir adsorption model and the Multi-sites adsorption model.

The Langmuir adsorption model was adopted to describe the interaction between cyclodextrin and hydrophobically modified ethyl (hydroxy ethyl) cellulose, and good correlation between and experiment data and theory was observed [Karlson et al, 2002a]. However, when the model was used to predict the rheological behavior of fluorocarbon associative polymer, large deviation was evident as shown in Figure 7.6. Instead, the Multi-site absorption model yields good prediction to the experiment data.

It is assumed that 1:1 “nut and bolt” complexes are formed between β -cyclodextrin and F8-hydrophobe [Zhang et al., 1998], where each complex formed deactivates one active junction. The Langmuir adsorption model assumes that the

adsorption process is based on the hypothesis that all binding sites are equivalent, and each site can hold at most one molecule of adsorbate A, and there are no interaction between the adsorbate molecules on adjacent sites of an ideal surface. The deviation of our experiment data from the Langmuir adsorption model arises from the fact that contributions of different F-HEUR polymer chains are not equivalent in the associative transient network in solution. Some fractions of the hydrophobes may contribute to the formation of transient network (bridging chains), and others may have no contribution to the network, but only contribute to the formation of loop within the micelle (loop chains). This is analogous to a rough and inhomogeneous surface. On a rough surface, there are multiple sites available for adsorption, and the contribution of adsorption varies from site to site, and the contribution to the properties from different sites is also different.

In an associative polymer aqueous solution, the distribution of hydrophobes is not homogeneous. For example, at very low concentration, F-HEUR polymer self-assembles into mono-dispersed flower micelles comprising of a dense core of insoluble $C_nF_{2n+1}(CH_2)_m$ - segments surrounded by a swollen corona of neutral PEO chains. The aggregation number N_{agg} ranges from 30 and 50, and generally it is independent of polymer concentration [Tae, 2002a]. When the concentration is increased beyond the cmc, micelles start to interact and connect to each other and form a three-dimensional network. One indication that the solution may be inhomogeneous is illustrated by the phase behavior, which has been predicted theoretically by Semenov and co-workers [Semenov et al., 1995]. This is expected since hydrophobic tails are buried in the core of micelles and only the PEG segments are exposed to the bulk water. Experimentally, the phase separation was reported by Russel and co-workers [Pham et al. 1999; Calvet et al., 2003], which confirmed the

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predictions by Semenov. According to theoretical development documented by Jenkins [Jenkins, 1991] in his Ph.D. thesis, the associative junctions are dynamic (e.g., continuously building and rupturing through Brownian processes), and hence the network is not an infinite cluster that spans the entire solution, instead it comprises of a predetermined hydrodynamic unit, whose lifetime is longer than the relaxation time of the solution.

According to the simple theory of rubber elasticity, described by the transient network theory proposed by Green and Tobolsky [Green and Tobolsky 1946], G_N^0 is proportion to the number density of mechanically active chains ν ,

$$G_N^0 = \nu RT \quad (7.2)$$

where R is the gas constant, and T is the temperature in Kelvin.

Equation 7.2 is frequently used to characterize the viscoelasticity of associative polymer solution. In the polymer network, two kinds of hydrophobic chains are present; looping and bridging chains. Looping chains constitute the well-defined flower micelle, which has no contribution to the elasticity of the system. The end-to-end distribution of Gaussian polymeric chains results in to formation of bridging chains linking polymeric micelles to produce a transient network. The end-to-end distance of bridging chains would be significantly distorted from its Gaussian distribution by the terminal hydrophobes connecting two neighboring associative junctions. This means that bridging chains continuously break and re-form and are more likely to encounter CD molecules in the bulk solution. [Karlson et al. 2002] The number density of mechanically active chain is ν , where the following relationship is obtained:

$$1 - \Theta \propto \nu = \frac{G_N}{G_N^0} \quad (7.3)$$

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where Θ is the fraction of hydrophobic polymeric segments that are capped with CD. G_N is the plateau modulus of F-HEUR/CD solution and G_N^0 represents the plateau modulus of F-HEUR solution without cyclodextrin.

According to the Multi-sites Model, it is assumed that the adsorbate can adsorb on a finite number of binding sites, each exhibiting the Langmuir adsorption isotherm [Richard, 1996.] Following the Langmuir adsorption isotherm, the total coverage of cyclodextrin, Θ summing over all the individual binding sites:

$$\Theta = \sum_i \frac{\chi_i K^i C_F}{1 + K^i C_F} \quad (7.4)$$

K^i is the binding constant for the complex formation. C_F , C_B , and C_{CD} are the free, bound, and total CD concentrations respectively, and C_{hy} is the concentration of polymeric hydrophobic segments. χ_i is the fraction of type i sites. As described earlier, there are two types of sites, χ_b and χ_l representing the bridging and looping chains respectively.

$$\Theta = \sum_i \frac{\chi_i K^i C_F}{1 + K^i C_F} = \frac{\chi_b K^b C_F}{1 + K^b C_F} + \frac{\chi_l K^l C_F}{1 + K^l C_F} \quad (7.5)$$

The contribution of looping chain to the viscoelastic of solution is negligible. Hence,

$$\Theta = \frac{\chi_b K^b C_F}{1 + K^b C_F} = \frac{\chi_b K^b (C_{CD} - C_B)}{1 + K^b (C_{CD} - C_B)} = \frac{\chi_b K^b (C_{CD} - \Theta C_{hy})}{1 + K^b (C_{CD} - \Theta C_{hy})} \quad (7.6)$$

$$\text{since } \Theta = \frac{C_B}{C_{hy} * \chi^b}$$

and we obtained;

$$\Theta = \frac{1}{C_{hy} * \chi^b} \left(\frac{K^b \chi_b C_{hy} + K^b C_{CD} + 1}{2K^b} - \sqrt{\left(\frac{K^b \chi_b C_{hy} + K^b C_{CD} + 1}{2K^b} \right)^2 - \chi_b C_{hy} C_{CD}} \right) \quad (7.7)$$

By combining Equations. (7.3) and (7.7) yields,

$$\frac{G_N}{G_N^0} = 1 - \frac{1}{C_{hy} * \chi^b} \left(\frac{K^b \chi_b C_{hy} + K^b C_{CD} + 1}{2K^b} - \sqrt{\left(\frac{K^b \chi_b C_{hy} + K^b C_{CD} + 1}{2K^b} \right)^2 - \chi_b C_{hy} C_{CD}} \right) \quad (7.8)$$

Figure 7.6 Langmuir and Multi-sites adsorption model prediction for G_N^0 of 2 wt% F-HEUR- C_8F_{17} -35K aqueous solution at different methylated β -CD concentrations.

Figure 7.7a. The effect of molecular weight on low shear viscosity of F-HEUR/m- β CD system.

Figure 7.7b Multi-site adsorption model prediction for G_N^0 of 2.0 wt% F-HEUR-C₈F₁₇-35K and F-HEUR-C₈F₁₇-20K aqueous solution at different methylated β -CD concentrations. (■-20K); (○-35K).

Figure 7.7a shows the effect of hydrophobe/CD ratio on the rheological properties of F-HEUR-C₈F₁₇-20K and F-HEUR-C₈F₁₇-35K solutions. The lower molecular weight, F-HEUR-C₈F₁₇-20K exhibits a larger viscosity in the absence of methylated β -CD, and this is attributed to the relatively higher concentration of fluorocarbon hydrophobe. At CD/[F] molar ratio of 1.0, the viscosity of F-HEUR-C₈F₁₇-20K /CD system is identical to F-HEUR-C₈F₁₇-35K/CD system, which suggests that the interaction of fluorocarbon HEUR and cyclodextrin is not related to the structure of PEO segment. Figure 7.7b shows that the plateau modulus of these two F-HEUR/cyclodextrin systems can also be interpreted by Multi-sites model, regardless molecular weights, where the fitted parameters are summarized in Table 7.2. It is interesting to observe that the binding constant is identical for the two different molecular weights F-HEUR polymeric systems. But the percentage of bridging chain increases with decreasing molecular weight due to the increasing proportions of hydrophobic end-groups concentration.

Table 7.2 Association constant K , percentage of bridging chain χ^b and G_N^0

M _w	C _{hy} (mmolal)	K	χ^b (mmolal)	G_N^0 (Pa)
35K	1.14	40	15	365
20K	2.00	40	22	900

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Figure 7.8a Temperature Dependence of η_0 , λ and G_N^0 of F-HEUR-C8F17-35K

Figure 7.8b Activation energy of three different F-HEUR systems in the presence of m- β CD

The effect of temperature on the viscoelastic behaviors of F-HEUR in the presence of methylated β -CD was investigated as a function of CD concentrations. With increasing temperature, a reduction in G_N^0 , λ and η_0 was observed, and λ decreases much faster than G_N^0 . This suggests that increasing temperature enhances the exit rate of hydrophobe from the associative junctions. At high temperature, the viscoelasticity of polymer solution exhibits larger deviation from the Maxwell model. The temperature dependence of relaxation time and low shear viscosity conforms to Arrhenius expression as shown in Figure 7.8a, and the activation energy derived from viscosity is larger than from the relaxation time. The activation energy of F8-20K and F8-35K systems is fairly identical, which suggests that the interaction by the hydrophobes is the major factor controlling the temperature dependence of the viscosity. The molecular weight of PEO chain has negligible effect on the activation energy. The effect of CD on the activation energy for the two F-HEURs is identical, which confirmed the hypothesis that the temperature dependence of viscosity is dictated by the hydrophobic interaction. At CD/[F] molar ratio lower than 0.1, the activation energy is constant, and it exhibits a sharp decrease at a molar ratio of between 0.1 to 2.0. At CD/[F] molar ratio greater than 2.0, the activation energy approaches an asymptotic value that is very close to the activation energy of water.

F-HEUR- C_6F_{13} -35K/methylated β -CD system possesses a smaller activation energy, since the hydrophobic interaction is weaker. When the CD/[F] molar ratio exceeds 1.0, the activation energy is slightly larger than the C_8F_{17} system, suggesting that C_6F_{13} system possesses some intermolecular junctions since it is likely that the aggregation is that of open association mechanism. From Figure 7.8b, we observed that the activation energy of F-HEUR- C_6F_{13} approaches a minimum at CD/[F] ratio of 1.0, while F-HEUR- C_8F_{17} series reach a minimum at molar ratio of 2, which implies

that the stoichiometry is different for different fluorocarbon end-group. To elucidate this phenomenon, ITC experiments were conducted on the dilute solutions, and the results are shown in Figure 7.9.

Figure 7.9 Calorimetric titration curves of 1 wt% m-βCD into F-HEUR solution (0.1 wt%).

The changes in the complexation thermodynamics of CDs are generally the results of several contrasting effects, originated mainly from the followings:

- (i) penetration of the hydrophobic segment of the guest molecule into the CDs cavity,
- (ii) dehydration of the guest,
- (iii) formation of hydrogen bonds,
- (iv) release of water molecules from the CD cavity to bulk water, and
- (v) conformational changes of CD upon the inclusion of the guest molecule.

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Large negative entropy changes for the titration of m- β CD into both F-HEUR containing C₈F₁₇ and C₆F₁₃ hydrophobes possess sigmoidal titration curves, which represent the typical one-site binding characteristic. The thermodynamic parameters were determined by applying a non-linear least-squares fitting to the data using an appropriate model, and the derived parameters are summarized in Table 7.3. In comparison, there is no significant enthalpy change observed for the titration α - and γ -CD to the polymer solutions, which suggests the absence of hydrophobic interaction, which is in agreement with the viscometric data.

Table 7.3. Thermodynamic parameters for the interaction between methylated β -CD and F-HEUR

Fluorocarbon	n	K	ΔG (kJ/mol)	ΔH (kJ/mol)	$T\Delta S$ (kJ/mol)
C ₈ F ₁₇	2	5.3×10^4	-26.9	-24.2	2.7
C ₆ F ₁₃	1	4.9×10^4	-26.7	-41.8	-14.9

Large negative entropy changes usually arise from the large reduction in the translational and conformational freedoms of host and guest molecules upon complexation. On the other hand, large positive entropy changes are attributable to the relatively high flexibility of guest after complexation, and the extensive desolation from the hydrophilic moieties of host and guest, or the release/restructuring of the water molecules inside and around the cavity [Rekharsky and Inoue, 2002]. From Table 7.3 it is interesting to observe that though the length of fluorocarbon hydrophobe is different, ΔG is almost the same. But entropy is positive for the longer C₈F₁₇ and negative for the shorter C₆F₁₃ hydrophobes. This difference is attributed to the different binding stoichiometry, where the C₈F₁₇ hydrophobe is completely encapsulated by two cyclodextrin molecules, thereby removing all possible

interactions between the fluorocarbon hydrophobes. Thus, a relatively high chain flexibility of guest is expected after complexation with m- β CD. However, C₆F₁₃ hydrophobe can only be encapsulated by one CD molecule with a small fraction of the hydrophobic segment exposed to the bulk water. The exposed hydrophobic segments results in a weak interaction between the fluorocarbon hydrophobes, which reduces the flexibility of F-HEUR compared to C₈F₁₇ hydrophobic system. This description is consistent with the result derived from activation energies.

The dynamic light scattering results conducted on the F-HEUR system in the presence and absence of m- β CD are shown in Figure 7.10. The decay rate is related to the translational diffusion coefficient D by:

$$\Gamma = Dq^2 = \frac{D(4\pi n)^2}{\lambda_0^2} \sin^2\left(\frac{\theta}{2}\right) \quad (7.9)$$

Figure 7.10 (a) Decay time distribution of 0.1wt% F-HEUR-C8F17-35K solution at different scattering angles, numbers correspond to scattering angles; (b) Decay time distribution of 0.1wt% F-HEUR-C8F17-35K solution in the presence of m-βCD, numbers correspond to CD/[F] molar ratio

Only one peak is evident from the distribution functions of 0.1 wt% F-HEUR- C_8F_{17} -35K solution. The linear dependence of the decay rates on q^2 suggests that the relaxation mode is a translational diffusion mode and the slope corresponds to the translational diffusion coefficient of F-HEUR micelles. Upon the addition of m- β CD, the relaxation time distributions exhibit two distinct peaks. The slow decay mode in the decay time distribution function is attributed to the aggregation of CD molecules. Coleman [Coleman et al. 1992] had examined the aggregation behavior of cyclodextrins and they concluded that the solubility is related to the interaction of aggregate structure and water. Although the amounts of CD aggregates are relatively small, their contribution to the scattered light intensity is significant due their relatively larger size. Owing to the large size of the clusters, their contribution to the overall scattered intensity is high compared to F-HEUR micelles and unimers. While the clusters are few in number, the scattered intensity scales with number of particles dictated by c and is also proportional to r^6 , where c is the concentration and r is the radius of the particle. The scattering is thus dominated by the slower component [Gaitano and Brown 1997]. The relaxation times of the fast peak decrease with CD concentration until the CD concentration reaches 2 mol CD per hydrophobe. It then becomes independent of CD concentration when $CD/[F]$ exceeds 2.0, and the size of hydrodynamic radius of 8 nm represents the size of PEO chain of similar molecular weight.

Figure 7.11 ^{19}F NMR peak assignments of the C_6F_{13} end group of F-HEUR

^{19}F NMR chemical shifts assignments were studied by Ribiero [Ribiero 1997]. These heteronuclear correlations are observed in perfluoroheptanoic acid and combined with ^{19}F -decoupled ^{13}C data and homonuclear ^{19}F , ^{19}F COSY to derive a full set of unequivocal ^{19}F assignment. It was found that the ^{19}F NMR spectra of F-HEUR- C_6F_{13} -35K are identical to that of perfluoroheptanoic acid. Therefore, the peak assignment of ^{19}F F-HEUR- C_6F_{13} -35K is analogous to perfluoroheptanoic acid (Figure 7.11).

Upon the addition of m- β CD, the CF_3 resonance due to the upfield aggregation at -82.2 ppm decreases and a new CF_3 downfield resonance at -80.3 ppm were observed. At about 1 equiv of added m- β CD, the ratio of the downfield over the upfield resonance is about 3, and at 2.0 equiv of m- β CD the resonance at -82.2 ppm has virtually disappeared. A new distinct downfield resonance is also observed for the

-CF₂ group upon the addition of m-βCD and the ratios of the two resonances at a particular α-CD concentration are identical to that of CF₃ resonances. For the other CF₂ groups, only downfield shifts are observed, but broad resonances are visible in the intermediate range that sharpen at m-βCD /F-HEUR ratios greater than 1.5. The data are thus consistent with the formation of a 1:1 m-βCD /F-HEUR-C₆F₁₃ inclusion complex that exchanges slowly with the associated form on the ¹⁹F NMR time scale. The resonance for the -CF₂ group close to the PEG segment is independent of CD concentration, which suggests that the fluorocarbon end-groups are only partially located inside the hydrophobic cavity, and one CF₂ groups remains outside the CD cavity. This CF₂ may interact with neighboring fluorocarbon, resulting in a larger activation energy as derived from the viscosity data compared to F-HEUR-C₈F₁₇ system.

Figure 7.12 Effect of addition of m-βCD on the ¹⁹F NMR spectra of F-HEUR-C₆F₁₃-35K number corresponds to the CD/[F] molar ratio

Figure 7.13 Effect of addition of m- β CD on the ^{19}F NMR spectra of F-HEUR-C8F17. Numbers correspond to the CD/[F] molar ratio.

NMR chemical shifts assignment of C_8F_{17} group in one-ended perfluorocarbon-modified poly(ethylene glycol) was determined by Boschet et al. [Boschet et al. 2002]. For F-HEUR polymer with C_8F_{17} end-groups, the ^{19}F NMR spectra are fairly identical. The ^{19}F NMR resonances of CF_3 upon the addition of m- β CD shows similar trend as CF_3 of C_6F_{13} end-group. The CF_3 resonance at -82.2 ppm decreases and a new CF_3 downfield resonance at -80.3 ppm were observed (Figure 7.13). At about 1 equiv of added m- β CD, the ratio of the downfield over the upfield resonance is about 3, and at 2.0 equiv of m- β CD the resonance at -82.2 ppm has virtually disappeared. The downfield resonance is also observed for the $-\text{CF}_2$ group upon addition of m- β CD and the ratios of the two resonances at a given concentration of α -CD are identical to that of the CF_3 resonance. The resonance for the $-\text{CF}_2$ group

next to PEG segment is a single peak before the addition of m- β CD at ratio 1, and no shift was observed. But when the molar ratio was increased to 2, a down shift peak was observed, which suggests that all the fluorocarbon end-groups are encapsulated within the hydrophobic cavity by two CD molecules, which suppress the hydrophobic interaction between fluorocarbon hydrophobes. The results are consistent with the result from ITC confirming the formation of a 2:1 m- β CD /F-HEUR-C8F17 inclusion complex.

7.2.2 The effect of surfactant on the F-HEUR/m- β CD interaction

SDS was added into 2 wt% F-HEUR-C₈F₁₇-20K solution, the steady flow and dynamic oscillation experiments were conducted to study the interaction between SDS and fluorocarbon hydrophobe. We observed similar results that are identical to that of hydrocarbon HEUR. The viscosity increases upon the addition of SDS until a maximum viscosity is reached, and the viscosity starts to decrease with further increase in SDS concentration (Figure 7.14). The plateau modulus and relaxation time follow the same trend as the low shear viscosity. However, when a detailed comparison was made between fluorocarbon and hydrocarbon HEUR systems, some differences are evident. For HEUR/SDS system, the maximum low shear viscosity was reached at very low SDS concentration of about 2 mM. However, for the F-HEUR system, the maximum low shear viscosity is observed at SDS concentration of 8 mM. In addition, G_N^0 increases more significantly than the relaxation time, with the low shear viscosity and G_N^0 following the same trend. Thus, the increase of viscosity is mainly attributed to the increase in the number of mechanically active chains. On the other hand, in the HEUR/SDS system, the increases in the low shear viscosity is mainly caused by the increase of relaxation time, which results in a more stable

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transient network. The decrease in the low shear viscosity in F-HEUR/SDS system is not as abrupt as HEUR/SDS, where even at SDS concentration of 40 mM, the viscoelasticity is still detectable, though it is somewhat low. This may be attributed to the stronger hydrophobic interaction between fluorocarbon hydrophobes than hydrocarbon hydrophobes.

Figure 7.14 Effect of SDS concentration on rheological parameters η_0 , G_N^0 and λ of 2 wt% F-HEUR-C8F17-20K

Figure 7.15 Calorimetric titration curves for titration of 0.2 M SDS into 0.1 wt% F-HEUR- C_8F_{17} -35K (open circle) and 0.1 wt% HEUR- C_{16} -51K (filled circle) at 25°C

To investigate the thermodynamic and binding mechanism of this system, ITC was used to provide the thermodynamic parameters for the binding process. Figure 7.15 (open circle) shows the isothermal titration curve of 0.2 M SDS in 0.1 wt% F-HEUR- C_8F_{17} -35K solution together with the titration curve of 0.2 M SDS in 0.1 wt% HEUR- C_{16} -51K (filled circles). It is evident that these two titration thermograms is fairly similar. Therefore, the binding interaction of F-HEUR/SDS is identical to HEUR/SDS interaction. At low SDS concentration, the slightly higher enthalpy may be due to the non-cooperative hydrophobic interaction between F-HEUR end groups and monomeric SDS hydrophobic tails. However, the enthalpy changes also include those arising from the change in the solvent environment caused by the presence of F-HEUR chains. When the SDS concentration reaches 2.7 mM, ΔH increases sharply and reaches a maximum at 5.4 mM and then decreases. This

endothermic peak correlates to the formation of SDS mixed micelles on the F-HEUR chains (or F-HEUR/SDS aggregation complex) and the solubilization of both the F-HEUR end groups and dehydrated PEO segments from water phase into the hydrophobic core of mixed SDS micelles. The onset for the sharp increase in ΔH is characterized by the CAC. For the PEO/SDS system, the aggregation number of SDS inside the aggregation complex at CAC is much lower than that of free SDS micelles. With increasing SDS concentration, the aggregation number of SDS in the PEO/SDS complex continues to increase [van Satam et al. 1993]. However, as the aggregation number of the bound SDS micelles increases, the binding rate decreases due to electrostatic repulsions of SDS head groups, which result in the reduction in ΔH beyond the maximum value. The titration curve then intersects with the SDS/water curve, and continues to decrease to a minimum. The minimum exothermic peak is attributed to the structural reorganization of the F-HEUR/SDS complex. With further addition of SDS, the degree of rehydration becomes more rapid, which slows down after the minimum in the ΔH value where the F-HEUR chains become saturated with SDS molecules. Beyond that, no further bindings between F-HEUR and SDS molecules can be detected and the titration curve merges with the dilution curve of SDS, where free SDS micelles are present and co-exist with F-HEUR/SDS complex.

Figure 7.16 DLS of 0.1wt% F-HEUR-C8F17-35K in the presence of SDS. Numbers correspond to the SDS concentration in mM

DLS of F-HEUR-C₈F₁₇-35K and SDS mixtures were examined and the relaxation time distributions at different concentrations of SDS are shown in Figure 7.16. Only one peak in the relaxation time distribution is evident when the SDS concentration is lower than 2 mM. The peak corresponds to the translational diffusion of F-HEUR-C₈F₁₇-35K micelles. However, the peak broadens with increasing SDS concentration, and two peaks appeared at SDS concentration of about 4 mM. The fast mode corresponds to translational diffusion of disrupted F-HEUR micelle which decreases with increase of SDS concentration and finally reach hydrodynamic radius of 9.5 nm, which is identical to the PEO chain of similar molecular weight. This distribution no longer changes with SDS concentration, and the observed trend is different from HEUR/SDS system. When the SDS concentration exceeds the CAC of 2.7 mM, HEUR unimers are dehydrated from the water phase and solubilized into the

SDS micellar core to form SDS bound HEUR unimers. In F-HEUR/SDS system, F-HEUR unimer only appears when SDS concentration reaches 6 mM, corresponding to the maximum ΔH in the ITC titration curve.

Viscosity recovery of F-HEUR/m- β CD system

From previous studies, we know that for 2 wt% F-HEUR solution, the viscosity is lower in the presence of m- β CD. The viscosity approaches a minimum when CD/[F] molar ratio is equaled to 2.0, thereafter it remains constant. Since the viscosity recovery has been observed for HEUR/CD system in the presence of SDS, the effect of SDS on F-HEUR/CD system was also investigated. SDS was added into the 2 wt% F-HEUR solution containing m- β CD at the ratio of 2 mole CD per hydrophobe and the result is shown in Figure 7.17.

Figure 7.17 Effect of SDS concentration on rheological parameters η_0 , G_N^0 and λ of F-HEUR-C8F17-20K/m- β CD system. [F-HEUR] = 2 wt%, CD/[F] molar ratio=5

It is evident that addition of SDS has a significant effect on the solution viscosity. When SDS concentration is lower than 3 mM, the viscosity increases marginally and no viscoelasticity was observed. When SDS concentration is increased beyond 3 mM, an abrupt increase in the low shear viscosity is observed. Shear-thickening and shear-thinning are observed at moderate shear rates. The low-shear viscosity reaches a maximum at SDS concentration of 11 mM. When increasing SDS concentration, the low-shear viscosity starts to decrease abruptly and the shear-thickening and shear-thinning behaviors become less apparent. The solution changes to Newtonian behavior when SDS concentration exceeds 31 mM and the low shear viscosity continues to decrease to an asymptotic value to that identical to pure PEO solution of similar molecular weight and concentration.

From the oscillation shear experiments, it is evident that the transient network is restored upon the addition of SDS. Before the addition of SDS, the solution possesses a Newtonian behavior, however, the viscoelastic property was restored when the SDS concentration was increased to 3 mM. Further increase in the SDS concentration results in the enhancement in the plateau modulus and relaxation time signifying the strengthening of the transient network and re-establishment of the mechanically active junctions. At SDS concentration of 11 mM, the plateau modulus and the low-shear viscosity reach a maximum, and beyond this, the plateau modulus and relaxation time start to decrease rapidly. Beyond the SDS concentration of 31 mM, the viscoelastic behavior cannot be measured.

It is noteworthy that the viscosity cannot be completely recovered by the addition of surfactant for F-HEUR/m- β CD system. In the absence of m- β CD, the viscosity of F-HEUR can increase to 70 Pa.s by adding SDS, while in the presence of

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m- β CD, the maximum recoverable viscosity is only 13 Pa.s, which is significantly lower.

Figure 7.18 compares thermograms for titrating SDS into F-HEUR/m- β CD and HEUR/m- β CD system. At very low SDS content, the ternary system titration curves deviate from the SDS/F-HEUR titration curve, and this is attributed to the interaction between SDS and free m- β CD molecules. When no free m- β CD molecules are present, SDS starts to interact with m- β CD/F-HEUR complex, releasing F-HEUR hydrophobes from this complex until the CAC of F-HEUR/SDS system, which is about 2.7 mM. Three possible binding interactions are possible, namely;

Equation 7.10 represents the disintegration of F-HEUR/m- β CD complex, where $K_3=1/K$ must be very small with a positive enthalpy (since the equilibrium constant K for the binding of F-HEUR and m- β CD is large and possesses a negative enthalpy), as shown in Figure 7.18. Because of the fact that the solution viscosity is only partially recovered, it is possible that there is a chemical equilibrium reaction among these three reactions.

Beyond CAC, the titration curves of SDS/F-HEUR/m- β CD merge with the SDS/F-HEUR curve, which suggest that the SDS and F-HEUR interaction dominates. This is consistent with previous discussion that the formation of F-HEUR/SDS aggregation complex when SDS concentration goes beyond CAC. The solubilized PEO segments re-hydrate and bind to the SDS micelles via ion-dipole association, and

the structure re-organizes into a necklace-like conformation where the PEO chains wrap around the head groups of SDS micelles.

When SDS concentration is increased beyond 11mM, the titration curve deviates from SDS/F-HEUR curve, and this suggests that no further bindings between F-HEUR and SDS molecules can be detected and the deviation is attributed to α - β CD SDS micelles interaction

Comparing the HEUR/ α - β CD(10)/SDS and F-HEUR/ α - β CD(10)/SDS ternary titration curves in Figure 7.18, it is observed that both curves are similar. When SDS concentration is lower than 1 mM, the titration curve deviates from HEUR/SDS curve, which is attributed to the α - β CD/SDS interaction, which releases free F-HEUR chains. But in F-HEUR system, the peak appears at higher SDS concentration, which suggests that HEUR/ α - β CD complex is more easily disrupted by SDS molecules, and the curve merges with HEUR/SDS titration curve at about 0.7 mM SDS while F-HEUR systems merge at 2 mM SDS, Therefore, a higher SDS concentration is required to replace F-HEUR polymer chains from F-HEUR/ α - β CD complex, which is consistent with the rheological data.

Figure 7.18 Calorimetric titration curves for titration of 0.2 M SDS into F-HEUR-C8F17-35K/m- β CD complex solution at 25°C with [F-HEUR]= 0.1 wt%. Number correspond to CD/[F] molar ratio

7.3 Summary

The interaction between methylated β -cyclodextrins and perfluorocarbon derivatives (F-HEUR) (C_6F_{13} and C_8F_{17}) of poly(ethylene glycol)s (PEGs) of molecular weights 20K and 35K g/mol was studied by rheological, dynamic light scattering (DLS), isothermal titration calorimetric (ITC) and ^{19}F -NMR techniques. The viscosity of F-HEUR solution is greatly reduced in the presence of methylated β -cyclodextrins, because of the disruption of intermolecular hydrophobic association. The results from oscillatory measurement indicate that the plateau modulus decreases with the addition of m- β CD. A multi-sites adsorption model was proposed for the first time to describe the relationship between G_N^0 and cyclodextrin concentrations. The activation energies determined from the zero-shear viscosity decreased with methylated β -cyclodextrin concentrations until a molar ratio of 2, and thereafter it

remained constant. There is a small difference between the E_a for C_6F_{13} and C_8F_{17} end-groups at high cyclodextrin concentrations, revealing some subtle differences in the complex produced by these two fluorocarbon end-groups. It is observed from ITC thermograms that the complex formation of methylated β -cyclodextrin and fluorocarbon group revealed a stoichiometry of 1 and 2 for C_6F_{13} and C_8F_{17} respectively. DLS results showed a different mechanism for C_6F_{13} and C_8F_{17} fluorocarbon hydrophobes, which are in agreement with the results determined from activation energies and ^{19}F -NMR spectra.

Chapter 8 Characterization of Solid Complex produced from α -CD and Hydrophobically Modified Polyethylene-oxides

8.1 Introduction

Over the past decade, inclusion complexes (ICs) formed with CDs and polymers have attracted special interest since the first report of IC formation between α -CD and poly(ethylene glycol) (PEG), which was reported by Harada and co-workers [Harada and Kamachi 1990]. A large number of reports have been published on ICs formed between CD and various polymers containing necklace-like supramolecular structures. Although α -, β -, and γ -CDs have similar depth for the hydrophobic cavities (ca. 7.0 Å), their internal diameters are quite different. It has been found that the size correlation between the cross-sectional areas of polymer chains and the internal cavity diameters of CDs play important roles in the IC formation.

Except for a few cases where block polymers were used, most of the studies dealt with polymers having “homogeneous” cross-sectional areas along the polymer chains. In view of the correlation between the cross-sectional areas of polymers and the cavity size of CDs, it is of interest to investigate the behavior of polymer IC formation for a polymer with “heterogeneous” cross-sectional area.

In this chapter, the solid complexes were studied by conducting DSC, TGA, XRD, ^{13}C -NMR measurements. It is found that hydrophobically modified PEO form crystalline precipitates with α -CD, but does not form complex with β -CD. For the polymer with bulky IPDI segment on the polymer backbone, no precipitation was observed.

8.2 Results and discussion

When measured the rheological properties of HEUR-C16-51K in the presence of α -CD, the solutions become turbid when stirred overnight at high CD concentration, indicating the formation of crystalline inclusion complexes, which was not observed in β -CD/HEUR system. The mixture was then continuously stirred at room temperature for 2 days. The IC formed was separated by centrifugation, washed with water, and dried in vacuum at 60 °C for 2 days. The yield is less than 5%. Instead, the as synthesized polymer HM-PEG and HM-PEG-MONO form solid precipitate at very high yield with α -CD. But no precipitate was observed when α -CD was added into HM-PEG-IPDI. Figure 8.1a shows variation in the yield of the solid complex as a function of α -CD for HM-PEG and HM-PEG-MONO polymers. The curves are identical to that of PEG of similar molecular weight. The plots show a maximum yield at 0.33 mole fraction of α -CD for HM-PEG, which has molecular weight of 5K. These results suggest that a PEG complex of 2:1 (two monomers unit per CD) is produced since the length of two ethylene glycol units, corresponds to the depth of the CD cavity (7Å). However, for HM-PEG, which has M_w of 20K, the maximum yield appears at a stoichiometry of 5:1, which suggests that CD cannot fully cover the whole polymer chain when the polymer molecular weight is relatively high. Harada [Harada et al. 1997] confirmed that the maximum yield corresponded to complex with stoichiometry of 2:1 (PEG units:CD) determined from ^1H NMR spectra for low M_w PEG even if the polymer and CD were present at all proportion. The composition of CD-HM-PEG-MONO IC was quantitatively studied using ^1H NMR spectroscopy. Figure 8.2b shows the ^1H NMR spectra of α -CD-HM-PEG-MONO IC formed at room temperature in DMSO- d_6 . All the proton signals belonging to both α -CD and

HM-PEG-MONO are identified as shown in Figure 8.1b. By comparing the integral of the peaks for CD and those for HM-PEG tri-block copolymer, the ratio of EO repeat unit to CD of α -CD-HM-PEG IC is 2, and for higher molecular weight HM-PEG, the ratio of PEG repeat unit to CD of the complex is about 5. The compositions determined from ^1H NMR spectroscopy were also found to be in good agreement with the IC yield analysis results.

Figure 8.1a Continuous variation plots for complex formation between α -CD and HM-PEG, The yields are arbitrary.

Figure 8.1b The 400MHz ^1H NMR spectrum of α -CD/HM-PEG-MONO IC

HEUR-C16-51K, was prepared by the reaction of PEG, IPDI and alkyl alcohol, which is supposed to have a structure as shown by Figure 8.2. However, 30 % of the PEG chains are not capped with the hydrophobic alkyl groups as reported in previous studies [Yekta et al. 1995]. Harada [Harada et al. 1996] reported that polyisobutylene (PIB) does not form complexes with α -CD at all molecular weights because of the steric hindrance exerted by dimethyl groups on the polymer backbone. Jiao and co-worker (Jiao et al, 2001) observed that poly(neopentyl glycol sebacate) (PNGS) was able to form inclusion complexes with α -cyclodextrin. They suggested that α -CD can “squeeze” through the bulky dimethyl groups and reside along the thinner part of the polymer chain of the complex. IPDI groups is more bulky than dimethyl groups, and in order to verify whether α -CD can “squeeze” over the bulky IPDI groups, two HM-PEG polymers were synthesized, one with the structure identical to that shown in Figure 8.2 and possesses a narrower molecular weight distribution and 100% capped

with alkyl hydrophobe. The second polymer is by reacting PEG with palmitoyl chloride, hence there is no bulky side-group in the second polymer.

Figure 8.2 Structure of HEUR polymer

The thermal properties of the complex were observed using differential scanning calorimetry (DSC) and TGA. TGA of the inclusion complex and their constituent polymers is shown in Figure 8.3.

Figure 8.3 TGA curves of HM-PEG- α -CD IC in comparison with PEG, PEG- α -CD IC and α -CD respectively.

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Pure α -CD undergoes two steps thermal degradation. The first step is attributed to the dehydration of bonded water. The decomposition of α -CD starts at 300 °C, and the pure α -CD reached an asymptotic weight percentage of about 15 % at 600 °C. On the other hand, pure PEG starts to decompose at 400 °C, and reaches a very low weight percentage of about 2 % at 600°C. The ICs undergo three steps thermal degradation, where the first two steps are attributed to dehydration and decomposition of CD, while the third corresponds to the degradation of PEG chains. The most striking feature for the PEG-CD-IC is that it exhibits a higher decomposition temperature (320 °C) than pure α -CDs. The phenomenon of a higher decomposition temperature in polymer-CD ICs may imply that the polymer chains included inside the polymer CD-IC channels can improve the thermal stability cyclodextrin. The TGA curve is similar for all the ICs, e.g. PEG/CD, HM-PEG/CD, HM-PEG-MONO/CD and HEUR-C16/CD.

Figure 8.4. Typical for DSC heating curves (10 °C/min) for the mixture of HM-PEG/ α -CD

Figure 8.4 shows the typical DSC curves of solid mixture of HM-PEG/ α -CD, which was prepared by freeze-drying of the solution. In MDSC, a sinusoidal modulation (oscillation) was superimposed on the conventional linear heating or cooling ramp to yield a profile where the average sample temperature is continuously changed with time. The net effect of imposing this more complex heating profile on the sample is the same as if two experiments were run simultaneously. Such a heating profile produces three separate thermograms; total heat flow, reversing heat flow and non-reversing heat flow. It is observed that two peaks appeared in the first cycle of heating. The sharp peak at 48 °C may correspond to the melting of PEG chains, which is reversible and identical in the second heating cycle. The second peak, corresponding to dehydration of cyclodextrin arises from the strong bonded water molecules of α -CD, and hence is not reversible, and does not appear in the first

cooling and second heating cycles. Our objective is to study the change of crystalline PEG in the presence of α -CD, thus only the reversing heat flow was studied subsequently.

Thus far, all the studies on α -CD/PEG complex were focused on the characterization of solid precipitate from solution (Figure 8.5). It had been reported previously that the melting peak corresponding to crystalline PEG disappeared in the solid complex. The absence of the peak in polymer-CD-IC DSC scans may indicate that there is absence of crystalline phase in the polymer-CD-ICs. As such, we expect that most of the polymer chains may have been included inside the channels of the orderly stacked cyclodextrin molecules. For PEG/ α -CD system, the precipitate starts to appear at a molar ratio 30, where a weak melting peak at 50 °C was observed. One thing noteworthy is that even at very low CD concentrations, e.g. at molar ratio less 1, one PEO chain is encapsulated by one α -CD molecule, and there is a significant reduction in T_m , and the intensity of the peak does not change significantly. This may imply that when α -CDs are threaded onto PEO chains, they do not affect the crystalline structure of the polymer chains, and it isolates the crystalline domains into smaller sub-domains instead. The crystalline domains become smaller and finally disappear with increasing α -CD content, resulting in the appearance of channel inclusion complex that is consistent with the result from XRD measurements. At a molar ratio of 30, the co-existence of PEG crystalline phase and PEG/ α -CD inclusion complex is observed.

Figure 8.5 Reversing Heat flow of PEG(20K) in the presence of α -CD. The numbers correspond to molar ratio.

Figure 8.6 shows the DSC scan of hydrophobically modified PEG and their complexes with α -cyclodextrin, and it is observed that for HM-PEG-Mono and HM-PEG, the reversing heat flow of the complex with α -CD is almost identical to that of PEG system. Thus, for PEG chain without bulky IPDI groups, α -CD can thread through the hydrophobic segment and reside on PEG chain segments. The endothermic peak changes significantly even when α -CD/polymer molar ratio is equal to 1. According to previous rheological studies, at molar ratio of 1, α -CD suppresses the hydrophobic association and significantly reduces the solution viscosity. The reduction in T_m at low α -CD concentrations suggests that α -CD reside on the PEG segment in solid state. In contrast, the α -CD/HM-PEG-IPDI exhibits different property. When the molar ratio of α -CD is between 1 to 4, T_m does not show a significant change, and this is attributed to the fact that α -CD only binds to

the hydrophobic alkyl segments. Because of the IPDI group separating the hydrophobic alkyl chain and PEO segment, cyclodextrin molecules are not able to squeeze through the bulky IPDI segment. Interestingly, the T_m of HM-PEG-IPDI starts to decrease when α -CD concentration was further increased to α -CD/polymer molar ratio of 30. The PEG crystalline peak disappears when α -CD concentration approaches a molar ratio of 60. This suggests that α -CD may affect crystallinity of PEG even though it is not thread on PEO chain. There are some intermolecular interactions between these two components, which disrupt PEG crystallinity even though α -CD does form solid complex with HM-PEG-IPDI. Similar result is evident for m- β CD/HEUR-C16-17K system, where previous studies have shown that no complex was produced between β -CD and PEG due to the mismatch of the cavity size of the cyclodextrin and the PEO segment. However, from the XRD spectra, we observed that the characteristic peak of PEG disappears with the addition of β -CD, showing that there is interaction between these two components. It is noteworthy that many previous reported studies used the disappearance of PEG peak in DSC scan as evidence for the formation of channel inclusion complex in the solid precipitates. It is evident from our current study that the disappearance of PEG crystalline can be caused by various types of intermolecular interactions between CD and PEG, such as hydrogen bonding between hydroxyl groups on the cyclodextrin and the PEG segments. The evidence for the formation of inclusion complex was derived from the XRD spectra, a new peak appeared at the characteristic angle of $2\theta=20^\circ$.

Figure 8.6 Reversing Heat flow of HM-PEG in the presence of cyclodextrins.

Numbers correspond to molar ratio. a) HM-PEG / α -CD

b) HM-PEG-Mono/ α -CD

c) HEUR-C16-17K/m- β CD

d) HM-PEG-IPDI/ α -CD

e) HEUR-C16-17K/ α -CD

Figure 8.7 X-ray powder diffraction patterns of HM-PEG and the complex with α -CD, numbers correspond to the α -CD/PEG (w/w) feed.

The wide-angle X-ray diffraction patterns of HM-PEG and the complex formed with α -CD are presented in Figure 8.7. For α -CD/PEG, the characteristic reflection at $2\theta=20^\circ$ means that the columnar structure is formed between α -CD and PEG, instead of a cage structure. The cage structure for α -CD does not have continuous channels and is characterized by a strong reflection around $2\theta=12^\circ$. When the ratio is less than 30, no precipitate was observed in the solution, hence the solid was obtained by drying the solution in vacuum at 60°C . For HEUR-C16-17K, there is no hydrogel or precipitate even at α -CD/PEG molar ratio of 2, hence solid samples were obtained by drying the solution in vacuum.

Comparing PEG and HM-PEG, the crystalline structure is similar, where two sharp peaks at $2\theta=19^\circ$ and 23.2° were observed for all the PEG and HM-PEG systems, which is characteristic of the reflection peak of PEG.[Ozkan et al. 2000] Addition of

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α -CD reduces the intensities of both peaks until they are not observed in solid precipitate system. In contrast, the diffraction pattern of PEG/ α -CD complex exhibits a number of sharp reflections including strong peak at $2\theta=20^\circ$ ($d=4.44\text{\AA}$) and 22.6° ($d=3.96\text{\AA}$). These peaks were assigned to the 210 and 300 reflections from the hexagonal lattice with $a=13.6\text{\AA}$. The strong {210} reflection is a typical peak observed for PEG- α -CD complex, which corresponds to the electron density distribution of the core of the α -CD molecules with a radius of $\sim 5\text{\AA}$ [Huh et al. 2001].

It is known that PEG- α -CD complex has a channel type crystalline structure due to the long-chain character of the guest molecule/polymer complex [Harada and Okada 1999]. The strong characteristic peak for channel structure appears for HM-PEG-Mono and HM-PEG (Figure 8.8), and this coincides with the results from DSC scan. Therefore it is evident that linear aliphatic alkyl hydrophobically modified PEG form complex with α -CD with a channel type crystalline structure.

HM-PEG-IPDI/ α -CD exhibits different reflection pattern. No peak is observed at $2\theta=20$ and 22.6° , suggesting that the channel type crystalline structure is not present. This is attributed to the fact that the cavity size of α -CD is smaller than the bulky IPDI segment. Thus α -CD only resides on hydrophobe and cannot squeeze through the IPDI segment to reside on PEG chain segments. We noted that in the HM-PEG-IPED/ α -CD solid mixture, a characteristic reflection peak of PEG at $2\theta=19$ and 23.2° was not observed, and this is consistent with DSC study where other types of intermolecular interactions (e.g. hydrogen bond) may affect the crystallinity of PEG.

Figure 8.8 X-ray powder patterns of the complex of different HM-PEG with α -CD

8.3 Summary

Precipitation was observed when HEUR solution was added to saturated α -CD solution. Together with other samples which have well-defined molecular weight and PDI and 100% substitution of hydrophobe, the solid complexes were studied by DSC, TGA and XRD. From the TGA curves, it is evident that the heat stability of cyclodextrin is significantly enhanced in the presence of PEG. From DSC scan, it is evident that the PEG crystalline structure is disrupted by the presence of CD, while XRD spectra indicate that α -cyclodextrin can pass through the carboxyl group and reside on PEO segment. Solid complex with channel structure was produced at high CD concentration. We observed that α -CD is not able to squeeze through the IPDI segment on the backbone of PEG copolymer. Therefore no channel structure is observed for the mixture containing HM-PEG-IPDI and α -CD.

Chapter 9 Conclusions and Recommendations

9.1 Conclusions

In this thesis, the interaction between cyclodextrin (CD) and amphiphilic polymers was examined. The transient associative network of HEUR solution was investigated by conducting steady-shear and oscillation measurements in the presence of cyclodextrins at dilute and concentrated solution regime. The effect of CD on the transient associative network of HEUR was characterized by intrinsic viscosity in dilute solution, while the steady-shear viscosity and dynamic mechanical properties at different temperatures and CD concentrations were determined for semi-concentrated solutions. Isothermal titration calorimetry (ITC) and dynamic light scattering (DLS) were used to investigate the aggregation behavior and conformation of amphiphilic polymers in aqueous solution and in the presence of cyclodextrins. SDS was added into the binary CD/HEUR system to restore the transient network and this phenomenon was also investigated by rheological, titration calorimetric and light scattering techniques. Fluoro-HEUR was synthesized and its interaction with CD was studied. In addition, ^{19}F NMR was employed to characterize the association of fluorocarbon hydrophobe. The solid inclusion complex produced using the hydrophobically modified PEO and α -CD was prepared and investigated by XRD, DSC, TGA and ^{13}C NMR.

For methylated β -cyclodextrin/HEUR system, steady shear flow and dynamic oscillation experiments were carried out to study the effect of m- β CD on the transient network formed by the association of HEUR hydrophobes. It was found that m- β CD interacts with HEUR in three progressive steps. At very low m- β CD concentrations, m- β CD encapsulates the hydrophobes on the loop HEUR chains, which reduces the

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stability of the transient network, while maintaining the number of mechanically active chains. This destabilizes the m- β CD/HEUR complexes, rendering them to be more sensitive to shear stress. At moderate m- β CD concentration, m- β CD begins to decouple the bridging chains resulting in the reduction in the number of mechanically active chains and this further weakens the transient network. The decrease in the plateau modulus and relaxation time results in a corresponding reduction in the solution viscosity. Finally, in the presence of excessive amounts of m- β CD, the network structure is completely destroyed, yielding isolated polymeric chains that are capped on both ends with CD molecules. The results from ITC and DLS measurement are consistent with the proposed mechanism.

For α -cyclodextrin/HEUR system, similar phenomenon was observed with regards to the disruption of the transient association network. However some subtle differences are evident from the experimental results obtained from light scattering and rheometry. We observed that α -CD starts to disrupt the transient network by deactivating the mechanical active chains at low α -CD concentration. At moderate α -CD concentration, the viscosity of the solution exhibits unusual temperature dependence, which deviates from the Arrhenius relationship. This is attributed to the selective binding of α -CD to alkyl hydrophobic chains and free PEO segments. Higher temperature enhances the α -CD/PEO interaction and weakens α -CD/hydrophobe interaction, which results in the recovery of the viscosity brought about by the increasing junction densities. ITC thermograms were obtained at different temperatures, which suggest that the interaction is a two-site binding process. DLS results suggest that star-like micelle exists at moderate α -CD concentration, which is different from β -CD/HEUR system.

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Both α - and β -CD have similar ability to completely suppress the hydrophobic interaction resulting in an asymptotic viscosity identical to PEO of similar molecular weight and concentration. When an anionic surfactant, such as SDS was added to the low viscosity solution of CD/HEUR, the viscosity can be partially or completely restored, depending on the types of cyclodextrins used. SDS can restore completely the viscoelastic properties of HEUR in α -CD/HEUR solution, while it can only partially restore that in m- β CD/HEUR solution. This is attributed to the competitive binding of CD/SDS and CD/hydrophobe, resulting in the release of unassociated hydrophobe from the CD/HEUR complex that associates to produce a polymer network. ITC measurements indicate that in SDS/m- β CD/HEUR ternary system, the binding affinity of CD/SDS and CD/hydrophobe binding seems to be identical, hence CD/hydrophobe complexes are only partially dissociated resulting in a partial recovery of the viscosity. However, in SDS/ α -CD/HEUR ternary system, SDS/ α -CD complexation is much stronger than α -CD/HEUR, which results in the expulsion of α -CD molecules from the CD/HEUR complex. Thus, the hydrophobes aided by SDS molecules are able to restore the polymer network resulting in the complete recovery of the viscosity. The mechanism is supported by the binding results from ITC and DLS measurements.

In comparison, fluorocarbon HEUR (F-HEUR) exhibits different characteristics in their interaction with cyclodextrin. The interaction is insignificant for α - and γ -CD due to their unsuitable cavity size, while m- β CD is more effective in reducing the viscosity of F-HEUR than its counterpart hydrocarbon HEUR. Both ^{19}F NMR and ITC results confirmed that the stoichiometry is approximately 2 for C_8F_{17} hydrophobe and 1 for C_6F_{13} hydrophobe. The dependence of the plateau modulus of F-HEUR/m- β CD solution on CD concentration was fitted using a multi-site

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adsorption model, which yielded useful physical parameters such as the reaction constant K , and the percentage of mechanically active chains. The model fitting and derived parameters corroborate with the results determined from ITC measurements. Viscosity recovery was also observed upon the addition of SDS into F-HEUR/ m - β CD solution. However, only a partial recovery of viscosity was observed, which is attributed to the competitive strong interaction between fluorocarbon hydrophobe and m - β CD and relatively weak interaction SDS/ m - β CD interaction.

In the studying of α -CD/HEUR interaction, one interesting phenomenon was observed that when concentrated HEUR solution was added to saturated α -CD, as the solution became turbid and precipitated after a few days. In order to verify if the precipitate is caused by the interaction between α -CD and uncapped PEO or hydrophobically modified PEO, three polymers with well-defined PDI and 100% substitution were synthesized. Concentrated solutions of these polymers were added to saturated α -CD solution, and no precipitate was observed for IPDI modified PEO. From DSC and XRD results, it is clear that there is no complexation in the system, which suggests that α -CD cannot squeeze through the bulky IPDI segment to reside on the PEO segments. However, for the other two hydrophobically modified PEOs without IPDI segment, the phenomenon is identical to PEO/ α -CD system. Therefore, we concluded that α -CD molecules can pass through the hydrophobes and reside on the PEO segment to produce channel structure.

9.2 Recommendations

The present study constitutes an attempt to investigate the binding behavior and mechanisms between cyclodextrin and different types of amphiphilic polymers. The competitive binding in SDS/cyclodextrin/amphiphilic polymer ternary system is

also investigated thoroughly. Greater understanding on the binding mechanisms has been gained and this forms the basis for the future studies described below. The future research work on the polymer-cyclodextrin interaction can be carried out in following directions:

(a) New Research Methodologies

Other research methods can be used to verify or improve our current understandings on the polymer-surfactant interactions. Steady fluorescence spectroscopy (SFS), surface tension (ST), ^1H and ^{13}C nuclear magnetic resonance (NMR), and time resolved fluorescence quenching (TRFQ) could provide additional information on the critical aggregation concentration, the location of the interaction, and the averaged aggregation number. TEM and AFM can be used to verify the microstructures inferred from light scattering experiments.

(b) New Polymer-cyclodextrin Systems

Cyclodextrin polymer with well-defined substitution and PDI can be synthesized. The interaction between amphiphilic polymer and cyclodextrin polymer can be carried out to investigate the effect of cyclodextrin on the rheological properties of amphiphilic polymer. At the same time, the interaction of other surfactants, such as nonionic and cationic surfactants with polymer-cyclodextrin complex can be carried out to study the effect of surfactant structure on the competitive binding process.

(c) Solid complex characterization

The interaction cyclodextrin with hydrophobically modified PEO is widely studied, but almost all the studies have focused on the dissociation of hydrophobically transit network by CD/hydrophobe complexation. Our research confirmed that the interaction action continues even after the hydrophobically association is completely suppressed. The cyclodextrin molecule resides on the PEO segment. However, the process is still unclear, therefore further ^1H and ^{13}C nuclear magnetic resonance (NMR) can be used to study the competitive complexation of CD/hydrophobe and CD/PEO.

(d) Cyclodextrin self-aggregation

It is observed that cyclodextrin self -aggregates in solution, which generates a dominant peak in the relaxation time distribution. The effect of self-aggregation is not taken into consideration when we study the cyclodextrin/HEUR interaction. To have a better understanding on the self-aggregation behaviour of cyclodextrin, dynamic (DLS) and static (SLS) light scattering can be used to characterize the aggregates. Transmission electron microscopy at cryogenic temperature (Cryo-TEM), which are ideally suited for the characterization of aggregates sized between 2 and 2000 nm. In particular, cryo-TEM experiments allowed us to determine the sample morphology at the aggregate level.

Repeatability of experimental data

In this study, two groups of data were tested. Since the most frequently used material is HEUR-C16-51K and the most frequently test method used is for the determination of rheological properties, the HEUR-C16-51K and viscosity measurement were utilized to assess the repeatability of all experimental test data obtained. Two groups of tests were conducted: Group 1 comprising pure HEUR solution, which shows high viscosity at room temperature, and Group 2 which comprised HEUR/m-βCD solution, which is a Newtonian fluid with low viscosity. Different rheometers were used for the two Groups.

Group 1: 2% aqueous solution of HEUR-C16-51K. test equipment: CSL500. Test condition temperature: 25°C.

The results are list in table 1

Table 1: Low shear viscosity of 2% HEUR-C16-51K solution

Series	1	2	3	4
η_0	5.45	5.65	5.53	5.71

Series 1: The test was conducted immediately after the sample was prepared

Series 2: The test was conducted one week after testing of series one with the same solution prepared for series 1.

Series 3: The test was conducted one month after testing of series one with the same solution prepared for series 1.

Series 4: A fresh sample prepared at under the same condition as series 1 and tested on the same date as series 3.

Appendix **Repeatability of experimental data**

Using the student t-distribution, a P value at 0.043 which had a significance of 5% of the average was obtained. From this, it can be seen that the experimental viscosity data is indeed repeatable, reliable and reproducible.

Group 2: 2% aqueous solution of HEUR in the presence of m-βCD. The molar ratio of cyclodextrin/hydrophobe=5

C16-51K. test equipment: LS40. Test condition temperature: 25°C.

Table 2: Low shear viscosity of 2% HEUR-C16-51K solution in the presence of m-βCD with CD/hydrophobe molar ration=5

Series	1	2	3	4
η_0	0. 006859	0. 006806	0. 00688	0. 007047

The sample conditions are similar to that for Group 1.

Using the student t-distribution, the P value obtained was 0.049 at a significance of 5% of the average. Therefore, the repeatability and reliability of the experimental viscosity test data was verifie.

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