

Abstract

TALWAR, SACHIN. Hydrophobically Modified Associative Polymers: Solution Rheology and Applications in Electrospinning. (Under the direction of Prof. Saad Khan.)

Hydrophobically modified associative polymers are generating considerable research interest owing to their ability to be used in a variety of applications ranging from paints and coatings to drug delivery. These polymers have pendant hydrophobic groups that form a reversible physical network in an alkaline solution comprising of both intra- and inter-molecular hydrophobic junctions resulting in a unique thickening mechanism. The present study can essentially be divided into two parts. In the first part, we discuss how nonionic surfactants, both individually and in binary surfactant mixtures, can be effectively used to modify the rheology of associative polymers *via* formation of free as well as bound micelles incorporating polymer hydrophobes. We also demonstrate the applicability of nonionic surfactants in modulating hydrophobic associations in these polymers in the presence of inclusion compounds called cyclodextrin.

Electrostatic spinning or electrospinning of nanofibers has drawn considerable research attention in recent years. It involves the application of an electric field to a polymer solution or melt to facilitate production of fibers in the sub-micron range. The scope and utility of associative polymers can be broadened further by incorporating them in precursor electrospinning solutions due to their ability to alter solution rheology. In the second part of this study, we focus on gaining insights into the role of rheology on fiber formation by including associative polymers in electrospinning solutions. We further illustrate how the concept of using surfactants to control viscoelasticity of these polymers can be extended to fabricate electrospun nanofibers. Finally, we establish the utility of associative polymers in

improving the morphology of electrospun fibers through significant changes in viscosity and viscoelasticity of precursor solutions. This concept of using associative polymers is extended further to other associative polymers that interact *via* mechanisms other than hydrophobic associations.

Hydrophobically Modified Associative Polymers: Solution Rheology and Applications in Electrospinning

by
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Biography

Sachin Talwar was born on December 25, 1979 in Patna, India to his parents Shiv and Renu. After graduating from high school, he moved to Roorkee to pursue Chemical Engineering at the Indian Institute of Technology (IIT) Roorkee (formerly known as University of Roorkee). Upon completion of his Bachelor's degree in 2003, Sachin joined the PhD program in Chemical Engineering at North Carolina State University. His dissertation research was guided by Prof. Saad Khan. In March 2008, Sachin will join DuPont as a Research Engineer in Richmond, VA.

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CHAPTER 1

Motivation, Goals and Background

1.1 Motivation and Goals

The overarching objectives of this study are to i) modulate molecular interactions and rheology in associative polymers using surfactants, and ii) extend the scope of these polymers to develop electrospun nanofibers.

Hydrophobically modified associative polymers have drawn considerable research interest in recent years owing to their unique rheological properties. These are macromolecules consisting of a water-soluble polymer backbone to which hydrophobic groups such as alky chains are attached. Depending on the site of attachment of the hydrophobic groups on the backbone, these polymers are broadly classified as telechelic (two end sites) and comb-like (along the backbone) associative polymers. A schematic representation of these two types of associative polymers is shown in Figure 1.1. In aqueous formulations, the hydrophobic groups interact with each other giving rise to a transient or reversible network of both intra- and inter-molecular hydrophobic junctions. The formation of this transient network imparts distinct rheological characteristics to the formulations in terms of enhanced solution viscosity, shear thickening behavior and a pronounced shear thinning profile¹⁻³. These characteristics justify the use of these polymers in several industrial applications including paint formulations, adhesives, paper coatings agrochemicals, ceramics, pharmaceuticals and personal care products². Additionally, they have potential to be applied in applications as diverse as oil recovery (e.g. drilling fluids, mobility control, and profile modification)⁴, triggered drug delivery⁵, and glycol based anti-icing aircraft fluids⁶⁻⁸.

Hydrophobically modified alkali-soluble emulsion (HASE) polymers are one class of comb-like associative polymers possessing an anionic backbone and pendant hydrophobic groups spread throughout the backbone. Figure 1.2 shows a schematic representation of the interactions between polymer molecules in an aqueous solution. They possess significant performance and cost advantages over other associative polymers with linear chains⁹⁻¹² in terms of thickening efficiency, biostability and wide formulation latitude¹³. The use of surfactants provides a powerful and potent tool to further manipulate the rheology of these systems. Interaction of HASE polymers with surfactants exhibit an entire range of interesting complex behavior, controlled by a number of variables related to the macromonomer composition of the HASE polymer as well as to surfactant composition. Interest in these systems also arises from the fact that surfactants or other amphiphilic species are present in most aqueous formulations that employ these associative polymers. The surfactant affects the dynamics of these solutions by forming free as well as bound micelles incorporating the polymer hydrophobes. One of the parameters that play a key role in determining the effect of nonionic surfactants on HASE polymer is surfactant hydrophilic-lipophilic balance (HLB). Studies on HASE polymer/nonionic surfactant systems, despite its industrial relevance, have been limited to a model HASE polymer with nonionic surfactants that have either a low¹⁴ or high¹⁵ hydrophilic-lipophilic balance (HLB), or a complex macromonomer HASE polymer and nonionic surfactants that have intermediate to high HLB¹⁶. The results obtained from these studies are either very specific in nature^{14,15} or too intricate¹⁶ to be carried over in a general way. Our **first goal** in this study is to systematically investigate the role of surfactant

HLB on HASE polymers by studying surfactants encompassing an entire range of HLB, from low to high.

In industry, it is common practice to employ surfactant mixtures instead of individual surfactants mainly due to the enhanced properties and performance of the final product in case of surfactant mixtures, attributable to an existence of synergism between the surfactants in the mixture. While binary mixtures of surfactants are well documented and are known to present a synergistic effect in several cases, no studies exist on the effects of mixed nonionic surfactants on the rheology of HASE polymers. Our **second goal** in this study is to investigate the effect of binary surfactant mixtures on the rheology of HASE polymers, as opposed to individual surfactants, by mixing surfactants of different HLBs.

From a practical standpoint, it is often desirable to eliminate the hydrophobic associations at one stage and recover them at a later stage, thus controlling the viscosity at various steps. An effective route to “deactivate” hydrophobic associations is *via* addition of doughnut-shaped inclusion compounds called cyclodextrin that have a hydrophilic outer shell and a hydrophobic cavity. This unique structure imparts them the ability to encapsulate pendant hydrophobic groups of the polymer inside their cavity thereby preventing the hydrophobes from participating in junction formation (Figure 1.3). This translates into a drastic reduction in the viscosity as well as viscoelastic properties of the polymer system. An interesting feature of cyclodextrin/polymer-hydrophobe complexation is its reversibility when there is a shift in equilibrium away from these complexes in the presence of another amphiphilic guest molecule such as surfactant. This in turn “frees” the polymer hydrophobes

to reassociate and form the original network hence, recovering the original solution viscosity. Despite the relevance of such systems, to the best of our knowledge, no studies have been undertaken to decipher the role of surfactant amphiphilicity, as given by its HLB, on the scope and extent of recovery of rheological properties in associative polymer/cyclodextrin systems. Our **third goal** is to determine the role of nonionic surfactant HLB on the rheological recovery and molecular interactions of HASE polymer solutions in the presence of cyclodextrins with different cavity sizes.

Our **final goal** in this study is to extend the scope and utility of these associative polymers into electrospinning which is the most commonly used technique employed for nanofiber production. The use of nanofibers, especially in nonwovens, presents an exciting opportunity for the development of materials with novel and functional performance. Such desirable attributes stem in part from the intrinsic dimensional characteristics of nanofibers, i.e., typical diameters between 10 – 500 nm. The high surface to volume ratio provides possibilities to embed or coat functional moieties onto the fibers rendering them useful in potential applications ranging from membrane technology, to reinforced composites, smart textiles and functional coatings/sensors¹⁷⁻¹⁹. Although many different polymers have been electrospun so far, to our knowledge no studies on the electrospinning of hydrophobically modified associative polymers exist. Employing associative polymers in electrospinning solutions can not only lead to the development novel fibrous networks, but also provide useful insights into the role of rheological modification of polymer solutions on electrospinning. The presence of associative polymers, even in small amounts, can drastically affect solution rheology which in turn is expected to affect the final fiber quality.

1.2. Background

This section briefly discusses the general background aspects and specific objectives of our study that should prove helpful in understanding the topics subsequently covered in this dissertation. Each subsequent chapter includes a detailed discussion related to the background of the specific issues addressed therein.

1.2.1 HASE polymer

The molecular structure of a model HASE polymer used in our study is shown in Figure 1.4. It consists of a copolymer backbone comprising of randomly arranged ethyl acrylate and methacrylic acid repeat units. The methacrylic acid group neutralizes upon the addition of a base and imparts solubility and a polyelectrolyte nature to the polymer backbone. The hydrophobic groups are comprised of alkyl chains attached to the backbone via a urethane linkage and separated from the backbone by a poly(ethylene oxide)(PEO) spacer; the entire structure being referred to as a macromonomer. In an alkaline solution, the hydrophobes associate via intra- and inter-molecular interactions to form a network of hydrophobic junctions resulting in substantial viscosity enhancement of the solution^{1,20}. Recent experimental studies of HASE polymers have addressed several relevant issues related to their synthesis, their flow behavior in parallel superposed steady dynamic shear as well as the effect of the backbone composition on flow dynamics²¹⁻²⁵. The effects of the hydrophobic size and side-chain length, and of the ethylene oxide (EO) group number and ionic strength on solution rheology have also been explored^{15,26-31}.

1.2.2 Role of Surfactants

Surfactants and water-soluble polymers are usually present together in many formulations and industrial processes. Interactions between these two components can bring about interesting changes in the final properties of the system. Experimental studies^{14,32} have shown that the presence of surfactants can significantly affect the dynamics of the HASE solutions by strongly influencing the rheological properties of the system depending on the surfactant concentration and type. Surfactant-induced factors that change the extent of interactions in the hydrophobic junctions thus play a major role in changing the solution rheology.

Addition of ionic surfactants to HASE polymer solutions generally result in an increase in solution viscosity up to a maximum at a critical surfactant concentration followed by a decrease up to a point where the surfactant concentration exceeds its critical micelle concentration (CMC). The viscosity enhancement upon addition of surfactants is generally attributed to an increase in both the number and the average lifetime of hydrophobic junctions present in the HASE solution³². The viscosity decrease at higher surfactant concentrations is associated with the decrease in both the number of hydrophobic junctions and the associative network strength.

Nonionic surfactants impart a more complex behavior when added to HASE solutions depending on the surfactant Hydrophilic-Lipophilic Balance (HLB) as well as on the molecular architecture structure of the surfactant hydrophobic tail relative to that of the polymer hydrophobe. HLB is a measure of surfactant amphiphilicity and is usually defined as

20 times the fraction of molecular weight of the hydrophilic portion to overall molecular weight of surfactant molecule. A higher HLB value denotes higher water solubility of surfactant and a higher CMC, and *vice versa*³³. Tirtaatmadja *et al.*¹⁴ studied the concentration effect of nonionic surfactant Rhodasurf L-4 ($C_{12}EO_4$, HLB = 9.7) on 0.5% HASE polymer (macromonomer comprising of 35 EO units and $C_{20}H_{41}$ alkyl hydrophobe). In contrast to the effect of ionic surfactant concentration where a maximum in low shear viscosity is usually observed, the viscosity of the system monotonically increased by almost five decades as the nonionic surfactant concentration was raised to 0.1 M. The continuous increase in viscosity even at high surfactant concentration was attributed to the formation of large bilayers or vesicles which considerably reinforce the associative network. The morphological transition of surfactants from spherical micelles to large vesicles has also been observed for the same HASE polymer/nonionic surfactant system with increasing temperature¹³. The effect of temperature on nonionic surfactant co-thickening has been further explored by Wu *et al.*³⁴ on 0.5% HASE polymer (macromonomer with 40 EO units and a $C_{18}H_{37}$ alkyl chain) in the presence of Brij 97 ($C_{18}EO_{10}$, HLB = 12.4) nonionic surfactants. They observed an increase in solution viscosity with increasing temperature to a maximum at 45°C and a gradual decrease in solution viscosity at higher temperatures. According to the authors, the trend of solution viscosity with increasing temperature is most likely related to changes in size and structure of surfactant micelles which affect the number and strength of hydrophobic junctions. Tam *et al.*¹⁵ studied the rheological properties of a 1 % HASE polymer - whose macromonomer hydrophilic and hydrophobic parts consist of an approximately 25 EO chain and a $C_{20}H_{41}$ chain respectively- in the presence of nonionic surfactant Brij 35 ($C_{12}EO_{23}$,

HLB = 16.9) systems and observed that both the steady state viscosity and the dynamic moduli exhibit a maxima at a critical surfactant concentration. The concentration corresponding to the observed maxima was approximately 17 times the CMC of surfactant. English *et al.*¹⁶ studied the effects of two nonylphenol ethoxylate surfactants NP6 (C₉ΦEO₆, HLB = 10.9) and NP10 (C₉ΦEO₁₀, HLB = 13.2) – where Φ stands for phenol group- on the rheological properties of 0.6% and 1% HASE polymer solutions. The HASE polymer used in this study was very different in its macromonomer structure and composition (80 EO units and bis-NP hydrophobic part). While addition of NP10 surfactant caused a reduction in low shear viscosity of HASE solutions, the opposite behavior was observed with increasing NP6 surfactant concentration. The decrease in solution viscosity with increasing NP10 surfactant concentration was ascribed to the formation surfactant micelles incorporating polymer hydrophobes which in turn decreased the number of polymer hydrophobes per hydrophobic junction. On the other hand, the increase in solution viscosity upon NP6 addition was explained in terms of the formation of complex microstructures of partially water-soluble NP6 surfactant.

The results obtained from these studies are either very specific in nature or too intricate to be carried over in a general way. Several scientific challenges exist for the expanded use of HASE/nonionic surfactant system, and form the basis of the first part of this study. They include:

- How do nonionic surfactants affect the rheology of HASE polymer solutions? Is there a surfactant concentration at which the zero shear viscosity of a model HASE

polymer/intermediate HLB nonionic surfactant system exhibits a maximum? If yes, how does variation in HASE polymer concentration affect the zero shear viscosity maximum?

- How do the interactions between HASE polymer and nonionic surfactant vary with increasing surfactant EO chain length i.e., increasing the surfactant hydrophilic-lipophilic balance (HLB)? Depending on the HLB, the structure of surfactant aggregation may vary from spherical micelle for intermediate to high HLB surfactant, to lamellar phase for low HLB surfactants thereby the interactions between HASE polymer and nonionic surfactant, and hence the solution rheology is expected to change.

The study of surfactant mixtures is of practical significance in commercial applications as most applications employ surfactant mixtures instead of individual surfactants. This is partly due to synergism in physio-chemical properties that is frequently observed in such mixed systems³³. Specifically, the properties of binary nonionic surfactant mixtures with a large difference in surfactant HLB are frequently different from those of the analogous individual surfactant. While binary mixtures of nonionic surfactants are well documented, no studies exist on their effect on the rheology of HASE polymers. The mixture of a high and a low HLB surfactant in HASE solution may either form an intermediate structure between those corresponding to the high (spherical micelle) and the low (lamellar) HLB surfactants or maintain the structure of the dominant surfactant. Moreover the molar

ratio of the surfactants in the mixed systems is expected to significantly affect the solution rheology. The next part of this study deals with addressing the following issues.

- What is the role of mixed nonionic surfactants on solution properties of HASE polymers? Is the effect of mixed surfactants synergistic or antagonistic as compared to NPe surfactant with equivalent EO chain length?
- Is the effect dominated by a particular surfactant in the mixture and is it dependent on surfactant concentration?

1.2.3 Surfactant-Cyclodextrin complexation

From a practical standpoint, it is desirable to modulate the rheological characteristics and in particular viscosity of the aqueous solutions of associative polymers at different stages of processing. This can be achieved by eliminating or reducing the hydrophobic interactions at one stage and recovering them at a later stage. An effective strategy to diminish hydrophobic associations in HASE polymer solutions is by incorporating inclusion compounds called cyclodextrin (CD)^{35,36}. These are ring-shaped sugar molecules with possessing a hydrophobic cavity and a hydrophilic exterior which imparts them water solubility. There are three main types of naturally occurring cyclodextrins namely α - β - and γ - CD which have 6, 7 and 8 member rings, respectively. Owing to their hydrophobic interior, cyclodextrin molecules encapsulate hydrophobic groups present on the HASE molecule rendering them incapable to participate in hydrophobic junctions resulting in a drastic reduction in both viscosity as well as viscoelastic properties of the aqueous

formulation. Abdala *et al.*³⁵ reported a substantial reduction of hydrophobic associations in HASE solutions upon cyclodextrin addition as reflected in the decrease in both viscosity of and dynamic moduli by several decades. The authors verified the CD-polymer hydrophobe complexation by ¹H NMR and thermogravimetric analyses and additionally confirmed the absence any interactions between cyclodextrin and polymer backbone.

An interesting feature of CD–hydrophobe complexation in associative polymers is the reversibility of hydrophobic associations that can be achieved by utilizing surfactants. Surfactants are known to form complexes with cyclodextrins and extensive literature exists on this subject. Addition of surfactant to HASE solutions serves to move the CDs away from the polymer hydrophobes and subsequently bind with the surfactant³⁵. The unmasking of polymer hydrophobes promotes the “reactivation” of hydrophobic junctions resulting in a recovery of macroscopic properties. Despite the importance of such systems, very few studies have been undertaken to investigate the scope and utility of surfactants in recovering solution rheology in such systems^{35,37}. A detailed investigation to explore and understand the role of surfactant amphiphilicity on the feasibility and extent of recovery in associative polymer solutions is still missing and forms the basis of our work. This is particularly relevant as the complexation of CD-nonionic surfactants has been reported to be affected by surfactant HLB³⁸. Specifically, we address the following issues:

- Is the surfactant amphiphilicity, as measured by its HLB, a parameter affecting the extent of low shear viscosity recovery in HASE solutions containing cyclodextrin?
Are the viscosity profiles of the original and recovered solutions similar?

- Is the type of cyclodextrin, as categorized by diameter of its cavity, a factor to be considered when employing nonionic surfactants for viscosity recovery in such systems?

1.2.4 Electrospinning

Electrospinning is a facile technique to produce nanofibers that has drawn huge interest in recent years³⁹⁻⁴⁴. It involves the application of a strong electric field to a polymer solution or melt which gets charged and forms a cone commonly referred to as Taylor cone. The electrospinning jet subsequently undergoes uniaxial stretching followed by a “whipping” phenomenon, the solvent being evaporated in the process, and is finally deposited on to a grounded collector as fibers. Polymeric nanofibers produced via electrospinning have potential to be used in numerous applications due to their size advantage in terms of smaller fiber diameter. The typical fiber diameter usually ranges from 10 – 500 nm which is substantially lower than those produced using conventional fiber spinning techniques such as melt or solution spinning⁴⁵. The resulting nonwoven fiber mats possess a high surface to volume ratio and a high degree of porosity along with small pore sizes. These features render them immensely useful in a host of applications including filtration devices, tissue scaffolds, protective clothing and reinforced composites^{40,46,47}. The electrospinning process can be applied to a wide array of polymer/solvent systems as well as polymer melts and a variety of inorganic materials can be successfully incorporated into the final fibers either by directly

adding them to the polymer solution or by using sol-gel precursor solution techniques to obtain fibers with well-defined functionalities¹⁷.

A large number of studies have been published dealing with electrospinning different polymer systems either individually or in conjunction with a second polymer. - as well as in understanding the role of various process and solution parameters on the electrospinning process¹⁷⁻¹⁹. Nonetheless, several challenges remain in broadening the scope of electrospinning to include polymers with advanced functionalities. In particular, the role of rheology on fiber formation is still poorly understood. In most cases, a change in solution viscosity is achieved by changing the polymer concentration in solution and hence it becomes difficult to decouple their respective roles. Employing rheology modifiers such as associative polymers in electrospinning solutions can therefore provide useful insights into the effects of rheological modification. The addition of surfactants to these polymer solutions can further affect their rheological properties by modulating the hydrophobic interactions in solutions. Moreover, a recurring issue in the area of electrospinning is the poor spinnability of polymer solutions that exhibit low viscosity and viscoelastic properties. Empirical evidences suggest a lack of entanglements as the reason behind this phenomenon⁴⁸⁻⁵¹. By employing associative polymers in such systems, even in small amounts, their rheological properties are expected to be enhanced substantially due to the presence of extensive hydrophobic associations. This in turn is expected to influence the morphology of the final fibers. Specifically, we focus on the following issues:

- How does addition of associative polymers to electrospinning precursor solutions affect their rheology? Does this translate to significant differences in the morphology of final fibers?
- Does modulation of hydrophobic interactions through surfactant addition play any role in electrospinning, and, what is the role of viscosity and viscoelasticity in obtaining nanofibers?
- Can associative polymers be employed as rheology modifiers to aid in electrospinning of poorly spinnable systems?

1.3 Organization of Dissertation

Chapter 2 deals with the role of nonionic surfactants in modulating hydrophobic associations and resulting rheology in associative polymer solutions. The effect of binary surfactant mixtures as opposed to individual surfactants on rheological properties is discussed in Chapter 3. The scope and utility of employing a combination of surfactants and cyclodextrin to tailor flow characteristics of associative polymers is presented in Chapter 4. Chapters 5 and 6 describe the role of rheology modification in fiber formation from electrospinning and the efficacy of using associative polymers to improve the morphology of electrospun fibers. Chapter 7 summarizes the key findings of this study and identifies areas of future research.

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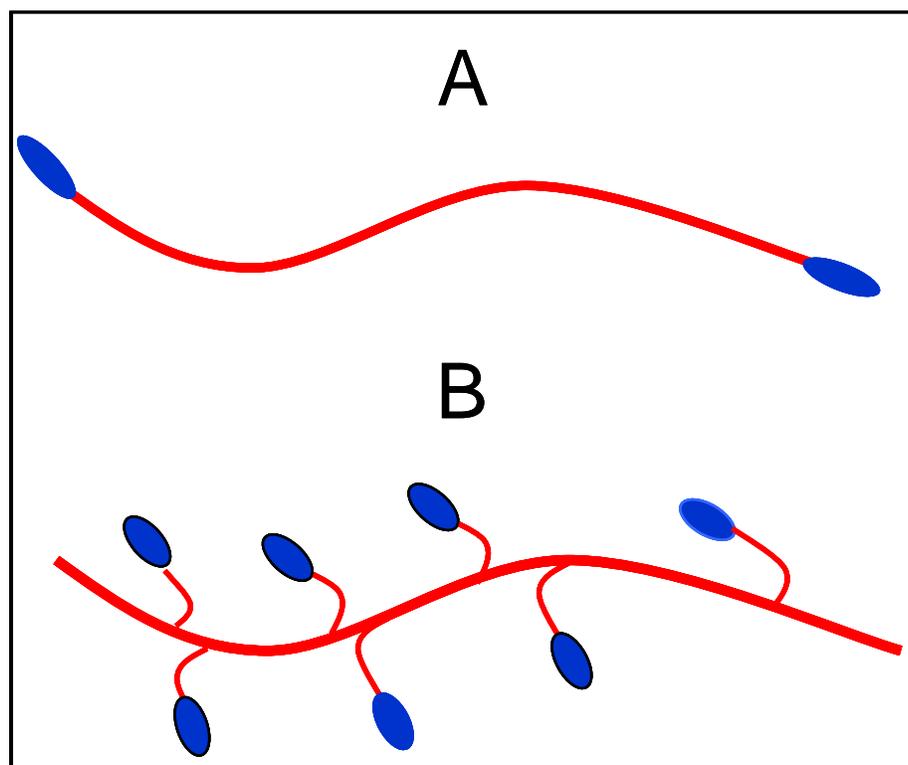


Figure 1.1: Schematic of A) telechelic and B) comb-like associative polymers

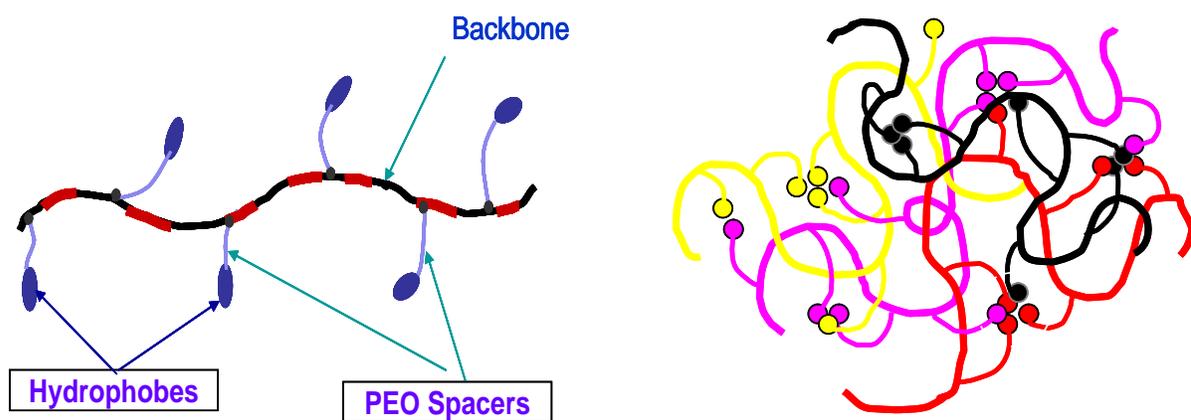


Figure 1.2. Schematic of a comb-like associative polymer and its network formation in solution showing inter- and intra-molecular association of the hydrophobes.

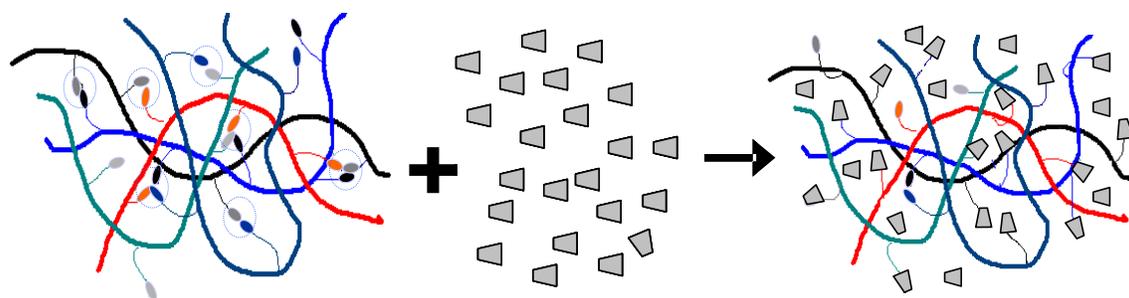


Figure 1.3. Schematic of encapsulation of polymer hydrophobes on HASE polymers in solution by cyclodextrin inclusion compounds.

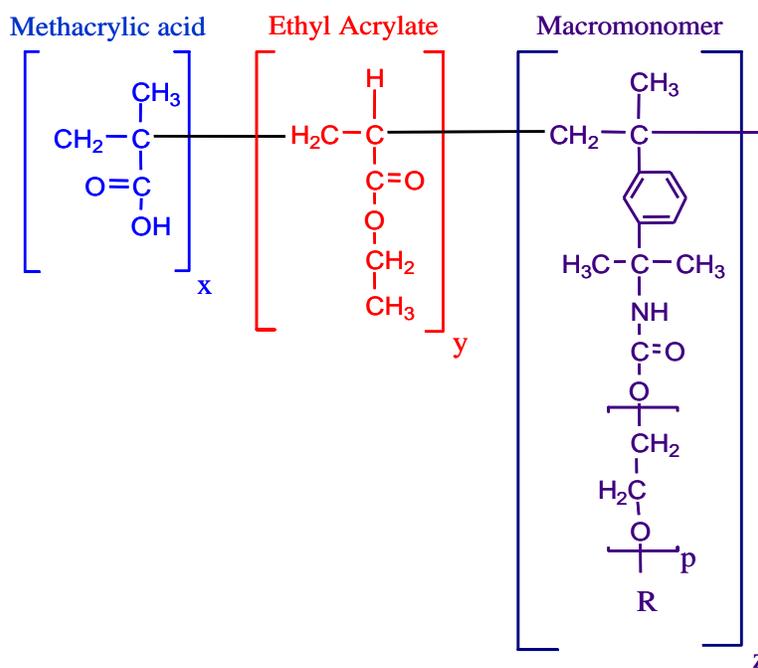


Figure 1.4. Molecular structure of the model HASE polymer. R: C22 alkyl chain polymer hydrophobe, P: 40 EO polyethylene oxide spacer, $x/y/z = 43.57/56.21/0.22$.

CHAPTER 2

Hydrophobic Interactions in Associative Polymer/Nonionic Surfactant Systems: Effects of Surfactant Architecture and System Parameters

Chapter 2 is essentially a manuscript by Sachin Talwar, Lauriane F. Scanu and Saad A. Khan published in the *Journal of Rheology* (Volume 50, pp.831-847 (2006))

Hydrophobic Interactions in Associative Polymer/Nonionic Surfactant Systems: Effects of Surfactant Architecture and System Parameters

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Abstract

The rheological behavior of a comb-like associative polymer with pendant hydrophobes in the presence of nonylphenol polyethoxylate (NPe) nonionic surfactants is examined. In particular, the effects of surfactant concentration, polymer concentration and surfactant's hydrophilic-lipophilic balance (HLB) are investigated with the latter being varied by using surfactants with different number of ethoxylate units ($e=6, 8, 12$ and 15). Steady shear and dynamic measurements are performed and the zero/low shear viscosity (η_0), the number and average life time of the hydrophobic junctions, and the numbers of polymer hydrophobes and NP8 surfactant molecules per hydrophobic junction are determined. The trend of zero/low shear viscosity with increasing NP8 surfactant concentration exhibits four distinct regions, each of them related to molecular-level changes: (1) surfactant addition to the hydrophobic junctions (no change in η_0 from that of pure HASE polymer solution); (2) formation of mixed micelles containing surfactants and several polymer hydrophobes (η_0 increases);

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(3) saturation of each polymer hydrophobe by individual surfactant micelles (η_0 decreases), and (4) formation of free surfactant micelles (η_0 is constant). The viscosity trend of the polymer / NP8 surfactant systems with increasing surfactant concentration does not change upon increasing polymer concentration from 0.5 wt.% to 1 wt.%. Moreover, the number of surfactant molecules bound to the polymer hydrophobes at the viscosity maximum is the same for both polymer concentrations. In terms of the effects of surfactant HLB on polymer / NPe surfactants systems, we find essentially similar trends of zero/low shear viscosity with increasing surfactant concentration for systems containing surfactants of higher HLB (NP12 and NP15). However, the viscosity maximum is lower, and the viscosity in the fourth region gradually decreases for systems containing higher HLB surfactant. In contrast, systems containing a surfactant with lower HLB (NP6) exhibit a different behavior with a continuous increase in zero/low shear viscosity with increasing surfactant concentration.

2.1 Introduction

Hydrophobically associating polymers are macromolecules consisting of a polymer backbone with hydrophobic groups attached either at the ends (telechelic associating polymers) or along the polymer backbone (comb-like associating polymers)¹⁻⁵. In aqueous formulations, the hydrophobic groups interact to form a transient network giving unique rheological properties to the solutions. As such, these polymers are typically used as thickeners in many industrial applications that include paint formulations, paper coatings, adhesives, agrochemicals, ceramics, pharmaceuticals and personal care products⁶. Their scope has further broadened with their potential applications in oil recovery (e.g., drilling fluids, mobility control, and profile modification)⁷, triggered drug delivery⁸ and glycol based anti-icing aircraft fluids⁹⁻¹¹. The wide industrial and also potential applications of associative polymers, coupled with their environmentally benign nature create an obvious research interest.

Hydrophobically modified alkali-soluble emulsion (HASE) polymers are one class of comb-like associating polymers. They consist of a copolymer backbone with pendant hydrophobic groups, also named polymer hydrophobes. The polymer hydrophobes are alkyl groups attached to the backbone through a urethane linkage and separated from it by a polyoxyethylene (PEO) spacer; the entire structure is referred to as a macromonomer as applied to the monomer used in polymerization¹². The transient network formed in the solution will be hereon referred to as an associative network. Over the past decade, HASE polymers have drawn considerable research interest due to their significant advantages in terms of cost, biostability and wide formulation latitude¹³ over other hydrophobically associating polymers with

simpler architectures such as telechelic polymers^{2,14-17}. Studies on HASE polymers include their synthesis¹⁸⁻²⁰, their flow behavior in parallel superposed steady and dynamic shear²¹, their nonlinear rheology²², the effects of the backbone composition on flow dynamics^{23,24}, and the influence of the hydrophobic size and side-chain length^{12,25,26}, and of the ethylene oxide (EO) group number and ionic strength²⁷⁻³¹ on solution rheology.

Since most hydrophobically associating polymers are employed in formulations containing surfactants or other amphiphilic species, the interactions of HASE polymers with surfactants have also received considerable attention. HASE polymer/surfactant systems exhibit a range of interesting and complex behavior, controlled by a number of variables, thereby providing a powerful and potent tool to manipulate further the rheology of these systems. The variables can be (i) component-related, i.e., the polymer itself particularly its macromonomer composition, and the surfactant type, and/or (ii) composition or condition-related, i.e., the component concentration and the temperature. Experimental studies³²⁻³⁴ have shown that the presence of surfactants can affect the dynamics of the solutions by monotonically increasing, decreasing or exhibiting a maximum in the system viscosity depending on the surfactant concentration and type. Surfactant-induced factors that change the number and strength of hydrophobic junctions as well as their functionality (or the number of polymer hydrophobes in a hydrophobic junction) thus play a major role in changing the solution rheology.

The interaction of HASE polymers with ionic surfactants generally result in an increase in the solution viscosity to a maximum at a critical surfactant concentration c^* , followed by a decrease in viscosity. Although the reasons for the viscosity enhancement upon

addition of surfactants up to c^* have been debated, it is well accepted now that such an increase is related to an increase in both the number of intermolecular hydrophobic junctions and the average lifetime of these junctions³³. The viscosity decrease upon further addition of ionic surfactants is associated with the decrease in both the number of intermolecular hydrophobic junctions and the associative network strength.

HASE polymer/nonionic surfactant systems exhibit a more complex behavior depending on the surfactant hydrophilic-lipophilic balance (HLB) and the structure of the surfactant hydrophobic tail relative to that of the polymer hydrophobe. HLB value gives a quantitative measure of the amphiphilicity of the surfactants. For the case of nonionic surfactants, it is generally defined as

$$20 \times \frac{M_H}{M_H + M_L}$$

where M_H is the molecular weight of the hydrophilic portion of the surfactant molecule while M_L is the molecular weight of the hydrophobic or lipophilic portion³⁵. A higher HLB value thus indicates higher water solubility and a higher cmc and vice versa. The concentration effect of nonionic surfactant Rhodasurf L-4 ($C_{12}EO_4$, HLB = 9.7) on a 0.5 wt.% solution of associative polymer, with macromonomer hydrophilic and hydrophobic parts consisting of approximately 35 ethylene oxide (EO) units and a $C_{20}H_{41}$ chain respectively, have been studied³². In contrast to the effect of ionic surfactant concentration, a monotonic increase in low-shear viscosity by up to five orders of magnitude was observed as the nonionic surfactant concentration was increased to 0.1 M. The authors attributed the viscosity

enhancement at high surfactant concentration to the formation of mixed cylindrical bilayers or vesicles which considerably reinforce the associative network. The morphological transition of the surfactants from spherical micelles to large vesicles results in a stronger associative network and hence a higher solution viscosity has also been observed for the same HASE polymer-nonionic surfactant system with increasing temperature¹³. The effect of temperature on nonionic surfactant co-thickening has been further explored by Wu *et al.*³⁴ using Brij 97 surfactant ($C_{18}EO_{10}$, HLB = 12.4) and 0.5 wt.% associative polymer with macromonomer composed of 40 EO units and a $C_{18}H_{37}$ chain. A maximum in solution viscosity with increasing temperature was observed at 45°C. The authors attributed the trend in solution viscosity to changes in size and structure of surfactant micelles, which in turn affect the number and strength of hydrophobic junctions.

Tam and coworkers³⁶ studied the rheological properties of a 1 wt.% HASE polymer (macromonomer with 25 EO units and $C_{20}H_{41}$ alkyl hydrophobe) with nonionic Brij 35 surfactant ($C_{12}EO_{23}$, HLB = 16.9) and observed that both the low shear viscosity and the dynamic moduli initially increase with surfactant concentration, $c > CMC$, reach a maximum at a critical concentration c^m (about 17 times the CMC of $C_{12}EO_{23}$ surfactant) and then decrease with increasing surfactant concentration. According to the authors, an increase in the number of hydrophobic junctions and a strengthening of the associative network were the dominant mechanisms responsible for the viscosity increase with increasing surfactant concentration while the disruption of the associative network caused by the decrease of both the number and strength of hydrophobic junctions was responsible for the viscosity decrease. English *et al.*³⁷ studied the effects of two nonylphenol ethoxylate surfactants NP6 ($C_9\Phi EO_6$,

HLB = 10.9) and NP10 ($C_9\Phi EO_{10}$, HLB = 13.2) – where Φ stands for phenol group- on the rheological properties of 0.6% and 1 wt.% HASE polymer solutions. The HASE polymer used in this study was vastly different in its macromonomer composition and structure from that in the above mentioned studies, i.e., the macromonomer hydrophilic and hydrophobic parts consisted of approximately 80 EO and bis-nonylphenol units, respectively. The authors observed a decrease in low shear viscosity with increasing NP10 surfactant concentration from 0.3 to 0.8 g dL⁻¹ but an increase in low shear viscosity with increasing NP6 surfactant concentration from 0.1 to 1.5 g dL⁻¹. They attributed the decrease in solution viscosity with increasing NP10 surfactant concentration to the formation of NP10 surfactant micelles surrounding the hydrophobic junction concurrently decreasing the number of polymer hydrophobes present in a given hydrophobic junction. The increase in solution viscosity with increasing NP6 surfactant concentration was explained by the formation of complex microstructure of partially water-soluble surfactant in HASE polymer solution.

Studies on HASE polymer-nonionic surfactant systems to date have thus dealt with either a complex macromonomer HASE polymer and nonionic surfactant having intermediate to high HLB³⁷ or a simpler macromonomer HASE polymer and nonionic surfactants having either a high³⁶ or a low HLB³². In the latter case involving polymers with simpler macromonomer, the polymer-surfactant combinations used are different in each case making it difficult to generalize the results. To the best of our knowledge, no systematic attempt has been made to obtain a detailed account of the effects of surfactants with different HLB on the rheological behavior of HASE polymers. The goal of this study is to examine how the interactions between HASE polymer and nonionic surfactants vary with changes in

the surfactant HLB. We first describe the effect of increasing surfactant concentration on the rheology of HASE polymer/NP8 nonylphenol ethoxylate surfactant ($C_9\Phi EO_8$, HLB = 12.6) systems. Subsequently, the effects of increasing polymer concentration in the former system are investigated. Finally, we explore how the effects of increasing surfactant concentration on the system rheology vary with increasing surfactant HLB from 10.9 to 15. An attempt is made to provide a molecular level explanation of the different phenomena observed in the aforesaid systems.

2.2 Materials and Methods

The polymer used in this study was obtained from UCAR emulsion systems (Dow Chemicals, NC, USA). A schematic of its chemical structure is shown in Figure 2.1; the ratio of methacrylic acid, ethylacrylate and macromonomer is 43.57/56.21/0.22 respectively, in terms of mole percent. The macromonomer, which is linked to the backbone via a urethane linkage, is composed of a polyethylene oxide (PEO) spacer with 40 moles of EO units and a C_{22} alkyl group. The HASE polymer was supplied in the form of aqueous latex at a solid concentration of approximately 26 wt %. All impurities and unreacted chemicals were removed from the aqueous latex by dialyzing it against deionized water using a Spectrapore cellulosic membrane (cut off MW = 10000) for 3 weeks. The dialyzed latex was then lyophilized for 2 days under a vacuum of 100 mTorr to obtain the HASE polymer in a powder form. The pH of the subsequently prepared polymer solution was adjusted between 9 and 9.5 by adding 0.1 M NaOH. The polymer was dissolved in a 0.05 M NaCl solution to ensure controlled/negligible polyelectrolyte effect²⁴. Details on the protocol to purify and prepare the

polymer solution can also be found in several previous publications^{24,25,36-38}. Nonylphenol ethoxylates (NPe) nonionic surfactants, Tergitol[®] were supplied by Dow Chemicals (NC) and used as received. The name and chemical specifications of the surfactants used in this study are listed in Table 2.1. Once the polymer/ surfactant samples were prepared by combining the requisite amounts of HASE polymer and NPe surfactant solutions, they were put in a water bath overnight at 50°C to remove entrained air and subsequently left for 48 hrs prior to rheological measurements. Rheology of the samples was measured within three weeks of the preparation to avoid possible polymer degradation in the presence of NaOH³⁹.

All rheological experiments were performed at pH = 9 and T = 25°C in a TA Instruments AR-2000 stress controlled rheometer using primarily cone and plate geometry. Both steady and dynamic shear experiments were conducted on each sample. Since the steady shear response of HASE polymer/surfactant systems is sensitive to shear history³⁹, a preshear was applied at a strain rate of 5s⁻¹ for 180 s followed by a rest period of 120 s. A dynamic stress sweep test was performed to determine the limit of linear viscoelastic regime, which was thereafter utilized to perform the dynamic frequency sweep test. Zero or low shear viscosity was determined from the steady shear viscosity profiles by averaging over the first ten points of the Newtonian region. Each experiment reported in this study was performed at least twice and all experiments were reproducible within ± 5 %. The error is included in the symbol size.

2.3 Results and Discussion

2.3.1 Effect of NP8 Surfactant Concentration

The steady shear viscosity profiles of a 0.5 wt.% polymer solution (equivalent to 0.11 mM polymer hydrophobes) in the presence of NP8 surfactants at concentrations C_{NP8} varying from 0 mM to 27 mM are shown in Figure 2.2. For ease of viewing, only selected polymer/NP8 surfactant systems studied are presented in Figure 2.2. For polymer solutions containing NP8 surfactants at $C_{NP8} = 1.7$ mM, the steady shear viscosity is higher than that of the polymer itself. We observe a Newtonian region at low shear stresses followed by an abrupt drop at higher shear stresses. The drastic drop in steady shear viscosity with increasing shear stress is related to the disruption of the associative network in associative polymer/surfactant systems⁴⁰. In contrast, we observe no drastic decrease in steady shear viscosity for the pure polymer solution or for polymer solutions containing NP8 surfactants at $C_{NP8} = 3.4$ mM. In this surfactant concentration regime, the steady shear viscosity is lower than that of the pure polymer solution.

The effect of surfactant concentration on system viscosity is seen more clearly in Figure 2.3, in which we plot the zero/low shear viscosity from Figure 2.2 as a function of NP8 surfactant concentration. Four distinct regimes can be observed in Figure 2.3. The first region corresponds to very low NP8 surfactant concentration ($C_{NP8} = 0.1$ mM) in which the viscosity is nearly constant and equal to the viscosity of the pure polymer solution. In the second region, the viscosity of the polymer/NP8 surfactant solution increases with increasing NP8 surfactant concentration up to a maximum at $C_{NP8} \sim 0.85$ mM. The viscosity at this

point is more than an order of magnitude higher than the viscosity of the pure polymer. In the third region ($0.85 = C_{NP8} = 10$ mM), the viscosity of polymer/surfactant systems decreases with increasing NP8 surfactant concentration up to 10mM and then finally reaches the fourth region of constant low shear viscosity hereon referred to as the plateau region. We find the viscosity in the last regime to be approximately a factor of thirty lower than the viscosity of the pure polymer solution. To the best of our knowledge, a plateau region at high surfactant concentrations has not been reported before for HASE polymer/nonionic surfactant systems.

Figure 2.4 shows the effects of NP8 surfactant on the dynamic moduli of the HASE polymer solution for three representative NP8 concentrations: 0, 0.85 and 27 mM. Surfactant concentrations of 0.85 and 27 mM correspond to the maximum and low viscosity regime observed in Figure 2.3. Compared to the pure polymer, the dynamic moduli show a substantial increase at $C_{NP8} = 0.85$ mM. The characteristic relaxation time, denoted by the crossover point, also increases by an order of magnitude. Further addition of NP8 to $C_{NP8} = 27$ mM not only drops the moduli to below that of the pure polymer but also decreases the relaxation time from it by about two orders of magnitude. Such behavior, suggesting enhancement of association followed by disruption upon surfactant addition, is consistent with the observed changes in viscosity.

To better understand the possible mechanisms responsible for the different zero/low shear viscosity trends with increasing NP8 surfactant concentration, we first discuss the effect of increasing NP8 surfactant concentration both on the number and average lifetime of the hydrophobic junctions, and on the number of polymer hydrophobes and NP8 surfactant molecules per hydrophobic junction. Based on the theory by ⁴¹ on transient networks, the

number of mechanically active hydrophobic junctions, v_{eff} in a polymer/surfactant system can be related to the high frequency plateau modulus G_8 through the following expression:

$$G_8 = v_{eff} RT$$

where R is the gas constant and T is the absolute temperature. Figure 2.5 shows the effects of increasing NP8 surfactant concentration on G_8 , which is proportional to the number of hydrophobic junctions. We find that the number of hydrophobic junctions initially decreases slightly for $C_{NP8} = 0.025$ mM, increases to reach a maximum at $C_{NP8} = 0.85$ mM and then decreases with increasing NP8 surfactant concentration. We also observe that the maximum number of hydrophobic junctions is reached at the same NP8 surfactant concentration as the low shear viscosity maximum (*cf.* Figure 2.3). It should be noted that G_8 could not be determined for polymer/ NP8 surfactant systems at surfactant concentrations $C_{NP8} > 1.7$ mM because of the presence of inertial effects at higher frequencies; nevertheless, most of the relevant features are captured in the concentration regime shown in Figure 2.5.

Figure 2.5 also shows the average junction lifetime of our system as a function of surfactant concentration. Aubry and Moan⁴² proposed that the average lifetime of the hydrophobic junctions, T_c , can be calculated as the ratio of the steady shear viscosity to the shear stress at the point where a drastic drop in steady shear viscosity occurs, that is when the associative network disrupts. Because of the uncertainty in accurately identifying such a point, we determine T_c to be the point at which straight lines drawn through the Newtonian region and through the region after the steady shear viscosity drop intersect. Although T_c is an approximate value of the average junction lifetime, it is a useful parameter to compare different HASE polymer/NP8 surfactant systems which exhibit a disruption of the associative

network, i.e., for concentration range $0.025 = C_{NP8} = 1.7$ mM. We find from Figure 2.5 that as the NP8 surfactant concentration increases, the average junction lifetime initially increases and then decreases after achieving a maximum at $C_{NP8} = 0.85$ mM.

We have also estimated the numbers of polymer hydrophobes and NP8 surfactant molecules per hydrophobic junction by dividing the molar density of polymer hydrophobes in a 0.5 wt.% (0.11mM) HASE polymer solution and the number of surfactant molecules at a given NP8 surfactant concentration respectively by the number of hydrophobic junctions, v_{eff} . These calculations hold true only in the surfactant concentration range in which the NP8 surfactant molecules systematically bind onto the hydrophobic junctions up to $C_{NP8} = 0.85$ mM and assuming that all NP8 surfactant molecules and polymer hydrophobes present in the system participate in hydrophobic junctions. The numbers of polymer hydrophobes and NP8 surfactant molecules per hydrophobic junction are plotted against NP8 surfactant concentration in Figure 2.6. We observe that the number of polymer hydrophobes per hydrophobic junction continuously decreases while the number of surfactant molecules per hydrophobic junction monotonically increases with increasing NP8 surfactant concentration in agreement with fluorescence studies on similar systems containing hydrophobically modified hydroxycellulose and cationic surfactants⁴³.

In the light of the observations made in Figures 2.5 and 2.6, the low shear viscosity trend of the polymer/ surfactant system observed in Figure 2.3 with increasing NP8 surfactant concentration can be explained in terms of the schematic representations of the polymer/ NP8 surfactant interactions shown in Figure 2.7. Figure 2.7 also includes the zero/low shear viscosity with increasing NP8 surfactant concentration replotted from Figure

2.3. In the first region ($C_{NP8} = 0.1$ mM), although NP8 surfactant molecules may be binding to the hydrophobic junctions, its contribution is not large enough to be reflected on the rheology of the polymer/surfactant systems. Such observation is consistent with results obtained in a previous study by ³⁶. In the second region ($0.1 < C_{NP8} = 0.85$ mM), the surfactant molecules bind to the hydrophobic junctions to form mixed micelles with the polymer hydrophobes. The strength of the hydrophobic junctions increases further as shown by the increase in T_c with increasing C_{NP8} from 0.1 to 0.85 mM (*cf.* Figure 2.5). However, to accommodate the increasing number of surfactant molecules (Figure 2.7), the polymer hydrophobes rearrange to create more hydrophobic junctions as shown by the increase in G_8 and the decrease in polymer hydrophobes per hydrophobic junctions with increasing NP8 surfactant concentration. As a result the associative network is stronger and hence the low shear viscosity increases. At $C_{NP8} = 0.85$ mM, both the number of hydrophobic junctions and the low shear viscosity reach a maximum at which approximately eight molecules of NP8 surfactant are bound to each polymer hydrophobe. The strength of hydrophobic junctions which is determined by the balance between the polymer hydrophobe number and the surfactant molecule number per hydrophobic junctions³² also exhibits a maximum at $C_{NP8} = 0.85$ mM. In the third region, increasing NP8 surfactant concentration from 0.85 to 10 mM leads to (i) some individually surfactant-saturated polymer hydrophobes, i.e., fewer hydrophobic junctions consistent with the observed decrease in G_8 for $C_{NP8} > 0.85$ mM (Figure 2.5), and (ii) shorter average lifetime of the hydrophobic junctions to a point that no disruption of the associative network is observed for HASE polymer/NP8 surfactant systems at $C_{NP8} = 3.4$ mM (Figure 2.2). Consequently, the low shear viscosity decreases. At $C_{NP8} \sim 10$

mM all the polymer hydrophobes are individually surfactant-saturated; there is no more associative network as shown by the low shear viscosity plateau which is lower than the low shear viscosity of the pure polymer. This notion of the absence of hydrophobic interaction is consistent with the fact the viscosity of the polymer/surfactant systems in the plateau region (~ 0.3 Pa-s) is similar to that observed for the same polymer but with no hydrophobes attached³⁸. Assuming that at $C_{NP8} \sim 10$ mM, all NP8 surfactant molecules present in the system form mixed micelles around each polymer hydrophobe, the aggregation number of the mixed micelles is approximately 94, which is less than the aggregation number of pure NP8 surfactant micelles in water. Although the aggregation number of NP8 surfactant is not reported in the literature to our knowledge, it can be safely assumed to be greater than 350, the aggregation number of NP9 surfactant⁴⁴ as the aggregation number decreases with increasing HLB for nonionic surfactants. Finally, additional NP8 surfactant molecules form free micelles which do not affect the rheology of the polymer/ surfactant system since its low shear viscosity remains constant (plateau region).

An important issue to examine is the role of polymer concentration on the trends observed thus far with surfactant addition. Figure 2.8a shows the zero/low shear viscosity of polymer/surfactant systems as a function of NP8 surfactant for two different HASE polymer concentrations, 0.5 wt.% (0.11mM) and 1 wt.%(0.22mM) The viscosity trend of the polymer/ surfactant systems with increasing NP8 surfactant concentration, the presence of an initial plateau followed by a maximum and finally another low viscosity plateau, remains unchanged for the two polymer concentration. However, the initial plateau with no viscosity change seems to extend to a higher surfactant concentration for the 1 wt.% polymer solution.

In addition, the viscosity curve for the higher polymer concentration is always higher, and for some surfactant concentrations by more than an order of magnitude. Finally, we observe the viscosity maximum for the 1 wt.% polymer/surfactant system to occur at twice the surfactant concentration than that for the 0.5 wt.% polymer/surfactant system. As expected, the molar ratio of NP8 surfactant to polymer hydrophobes at the viscosity maximum is the same for both systems and approximately equal to 8 as can be seen in Figure 2.8b wherein the viscosity data in Figure 2.8a has been replotted against moles of NP8 surfactant per mole of polymer hydrophobe. In effect, the number of surfactant molecules able to bind onto a hydrophobic junction depends on the surfactant architecture (as will be shown later) and not on the polymer concentration, i.e., the number of hydrophobic junctions in the system.

2.3.2 Effect of Surfactant Hydrophilic-Lipophilic Balance (HLB)

To explore the effect of varying surfactant HLB on the rheology of polymer/surfactant systems, four different surfactants were considered: NP6, NP8, NP12 and NP15. The HLB of these surfactants is reported in Table 2.1 and ranges from 10.9 for NP6, the most hydrophobic surfactant studied, to 15 for NP15. As mentioned earlier, increasing HLB increases the cmc and decreases the aggregation number of the surfactants. The surfactant concentration studied for systems containing NP8, NP12 or NP15 surfactants ranged between 0.1 mM to 34 mM while the maximum concentration studied for systems containing NP6 surfactants was limited to 10 mM as higher concentrations of NP6 surfactant in the HASE polymer solution resulted in a non-homogeneous system. Figure 2.9 shows the zero/low shear viscosity of polymer/NPe surfactant systems as a function of NPe surfactant

concentration for different NPe surfactants. Several features are apparent from the plot. First, the zero/low shear viscosity at a given surfactant concentration decreases with increasing surfactant HLB. In effect, as the surfactant becomes less hydrophobic with increasing HLB (going from NP6 to NP15), the strength of both the hydrophobic junctions and the resulting associative network decreases and hence the zero/low shear viscosity decreases. Second, the viscosity behavior of the system containing NP6 surfactant is different from that of the other systems considered in that the viscosity increases monotonically with increasing NP6 surfactant concentration, particularly in region III ($C_{NP6} = 0.85$ mM). Third, the viscosity trend observed for systems containing NP8, NP12 or NP15 surfactants are similar in that they all exhibit a viscosity maxima in region II (0.1 mM = $C_{NP12} = 0.85$ mM). In the case of NP15 containing system, the viscosity maxima is a plateau extending from $C_{NP15} = 0.25$ mM to $C_{NP15} = 1$ mM. Finally, for NP12 and NP15 containing systems at high surfactant concentrations (region IV), we observe a gradual drop in viscosity instead of the viscosity plateau observed for NP8 containing system. Additionally, the viscosity of both systems is essentially the same in this region.

In order to obtain further insights on how the molecular interactions between HASE polymer and NPe surfactants vary with the surfactant HLB, we examine in Figure 2.10 the number (G_8) and average lifetime (T_c) of hydrophobic junctions as a function of NPe surfactant concentration for the above mentioned systems. For any surfactant system, the behavior observed for G_8 and T_c with increasing surfactant concentration is qualitatively similar to that observed for the corresponding viscosity. For HASE polymer/NP6 surfactant systems, the number and average lifetime of the hydrophobic junctions continuously increase

with increasing surfactant concentration, whereas for HASE/NPe surfactant systems containing NP8, NP12 or NP15 surfactants, the number and average lifetime of hydrophobic junctions exhibit a maximum (broad in one case) followed by a drop with increasing surfactant concentration. We note that for HASE polymer/NP15 surfactant system, the average lifetime of hydrophobic junction slightly increases from $C_{NP15} = 0.1$ mM to $C_{NP15} = 1$ mM instead of showing a plateau as for the zero/low shear viscosity and the number of hydrophobic junction. G_8 and T_c values for NP8, NP12 and NP15-based systems could not be determined for region IV because of frequency constraints of the rheometer.

Based on the observations made in Figures 2.9 and 2.10, and our explanation of the viscosity trend for polymer/NP8 surfactant systems (*cf.* Figure 2.7), we attempt to explain the various observed behavior, particularly the differences between the various NPe systems in terms of molecular interactions. For polymer/NP6 surfactant systems in region II, the surfactant molecules bind onto the hydrophobic junctions strengthening the average lifetime of the associative network (T_c increases) and forces the polymer hydrophobes to rearrange and form more hydrophobic junctions (G_8 increases). The zero/low shear viscosity strongly increases in this region. Due to the ability of NP6 surfactant to form lamellar structures in solution instead of spherical micelles³⁹, the associative network is further strengthened with NP6 addition in region III, consistent with the continuous increase in the number and average lifetime of hydrophobic junctions as well as the low shear viscosity.

The molecular interactions in region II for systems containing NP8 or NP12 are essentially the same as that for NP6, i.e., surfactant molecules bind to the polymer hydrophobes, and polymer hydrophobes rearrange to form more hydrophobic junctions. For

NP15 surfactant system, we believe that in addition to these hydrophobic interactions between the surfactant tail and the polymer hydrophobes, the EO chain in NP15 is long enough to create a hydrophilic corona with the PEO spacer of the HASE polymer by analogy to the corona formed by the surfactant hydrophilic parts of a micelle in water. Therefore the polymer hydrophobes are stabilized by both hydrophobic and hydrophilic interactions, and the thermodynamic energy penalty for a polymer hydrophobe to leave a hydrophobic junction and form a new one is high. Consequently, the number of hydrophobic junctions (G_8) increases at low surfactant concentration ($C_{NP15} < 0.25$ mM) but then remains essentially constant over a range of surfactant concentration such as $0.25 \text{ mM} = C_{NP15} = 1$ mM. Addition of surfactant molecules to the existent hydrophobic junctions strengthens the associative network and the average lifetime of the hydrophobic junctions (T_c) slightly increases.

As for region IV, we earlier hypothesized in section 2.3.1 for NP8 surfactants that all the polymer hydrophobes are screened by the surfactant micelles and further addition of surfactant leads to the formation of free surfactant micelles in solution. Based on the aggregation number of NPe surfactants in water, the number of free micelles formed at a given surfactant concentration is approximately three and six times greater⁴⁴ than that of NP8 in the case of NP12 and NP15 surfactants respectively. We believe that the presence of much higher number of free micelles causes a further breakdown of the associative network. In the case of NP12 or NP15 containing systems, the formation of additional micelles with increasing surfactant concentration act to align the polymer chains; consequently, the zero/low shear viscosity exhibits a gradual decline with increasing surfactant concentration in

region IV as seen in Figure 2.9. It is to be noted we have based our hypothesis on the rheological data but scope remains to further investigate these systems using other techniques such as light scattering or dye solubilization.

2.4 Summary

In this study, we examined the rheological behavior of HASE polymer/ nonylphenol polyethoxylate (NPe) nonionic surfactant systems under different conditions related either to the system such as the surfactant and polymer concentration, or to the surfactant architecture itself through the hydrophilic lipophilic balance (HLB). An effort was made to explain the rheological behavior in terms of the molecular interactions between polymer hydrophobes and surfactants. We first examined the effect of NP8 surfactant concentration on the rheology of HASE polymer / NP8 surfactant systems and found that the trend of zero/low shear viscosity with increasing NP8 surfactant concentration can be divided into four distinct regions. The rheological behavior in each of them was explained in terms of surfactant addition to the hydrophobic junctions formed by the polymer hydrophobes, formation of mixed micelles containing surfactants and several polymer hydrophobes, saturation of each polymer hydrophobe by individual surfactant micelles and finally, formation of free surfactant micelles. To our knowledge, the fourth or plateau region observed at high NP8 surfactant concentrations has not been reported earlier for similar associative polymer/surfactant systems. A change in the polymer concentration for the HASE polymer / NP8 surfactant systems did not affect the viscosity trend with increasing NP8 surfactant

concentration and the number of surfactant molecules bound to the polymer hydrophobes at the viscosity maximum was the same for both polymer concentrations.

We also examined the effect of surfactant HLB on the rheology of HASE polymer/NPe surfactants systems. The trends of zero/low shear viscosity were essentially similar for systems containing surfactants with higher HLB (NP8, NP12, NP15) barring two differences. The viscosity maximum for the NP15 surfactant systems showed a broad plateau. The viscosity curve for NP12 and NP15 surfactant-containing systems exhibited a gradual drop in viscosity instead of a plateau (seen for NP8 systems) in the fourth region; we attributed this to the presence of a much higher number of free surfactant micelles in these systems. Systems containing a surfactant with lower HLB (NP6), in contrast, showed a continuous increase in zero/low shear viscosity with increasing surfactant concentration which can possibly be ascribed to the formation of large lamellar structures by surfactant molecules.

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Table 2 1. Name and chemical specifications of NPe surfactants

Surfactant name (NPe)	EO moles (average number)	HLB	CMC (mM)
NP6	6	10.9	-
NP8	8	12.6	0.068
NP12	12	13.8	0.082
NP15	15	15	0.11

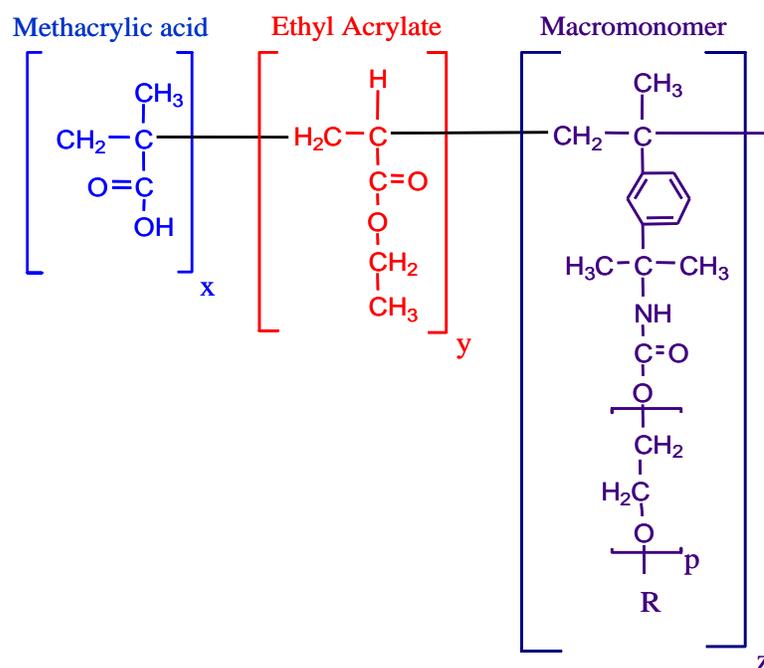


Figure 2.1. Molecular structure of the model HASE polymer. R: C22 alkyl chain polymer hydrophobe, P: 40 EO polyethylene oxide spacer, $x/y/z = 43.57/56.21/0.22$.

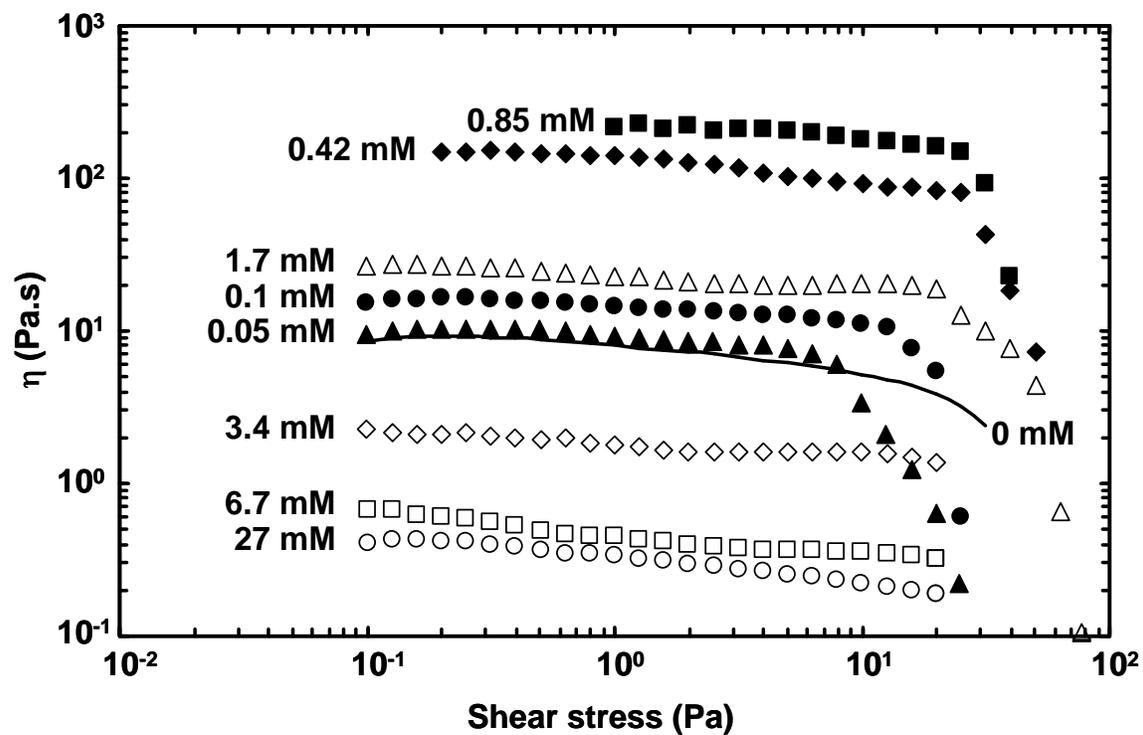


Figure 2.2. Steady shear viscosity (η) as a function of shear stress for 0.5 wt.% HASE polymer solution in the presence of NP8 surfactants at concentrations C_{NP8} varying from 0 mM to 27 mM.

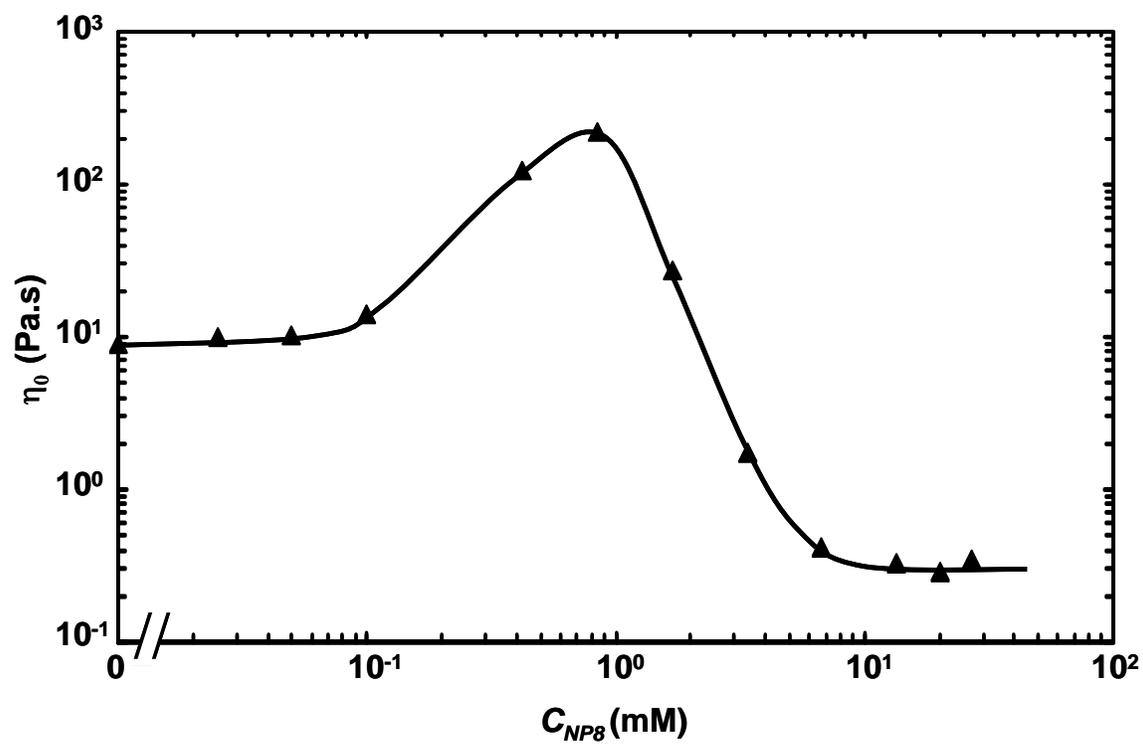


Figure 2.3. Low shear viscosity (η_0) as a function of NP8 surfactant concentration (C_{NP8}) for 0.5 wt.% HASE polymer/NP8 surfactant systems.

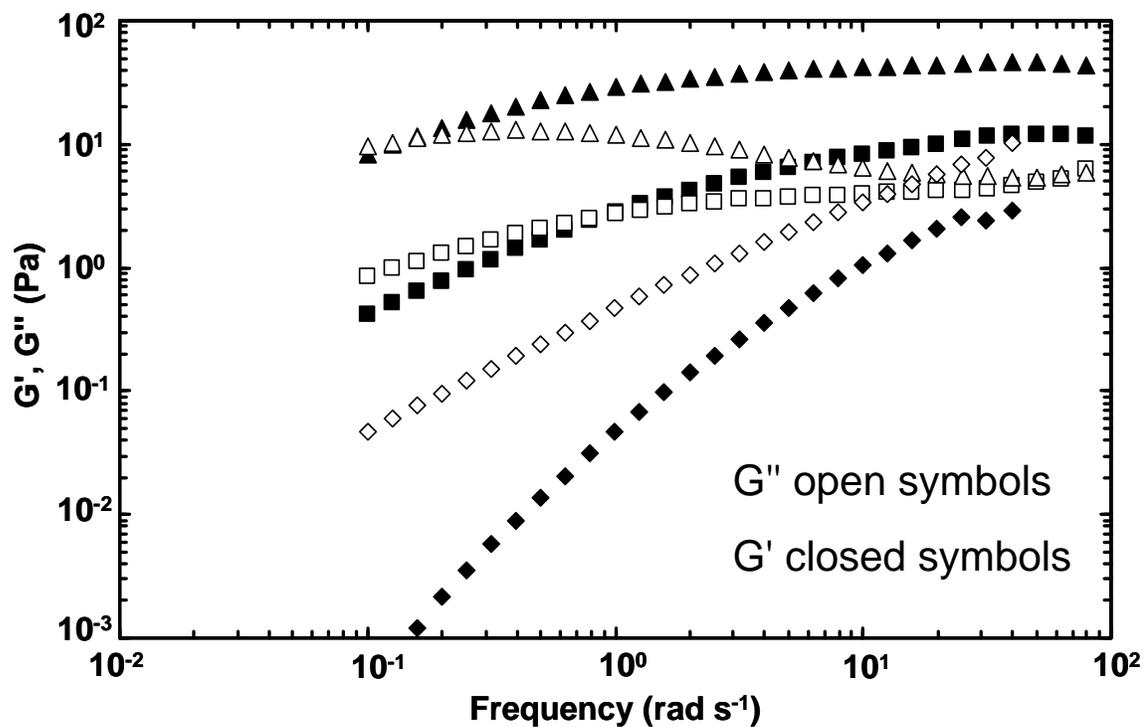


Figure 2.4. Frequency spectra of the dynamic moduli [$G'(\omega)$, $G''(\omega)$] measured for the HASE polymer solutions with different NP8 surfactant concentrations. (\square 0mM, \blacktriangle 0.85mM, \blacklozenge 27mM)

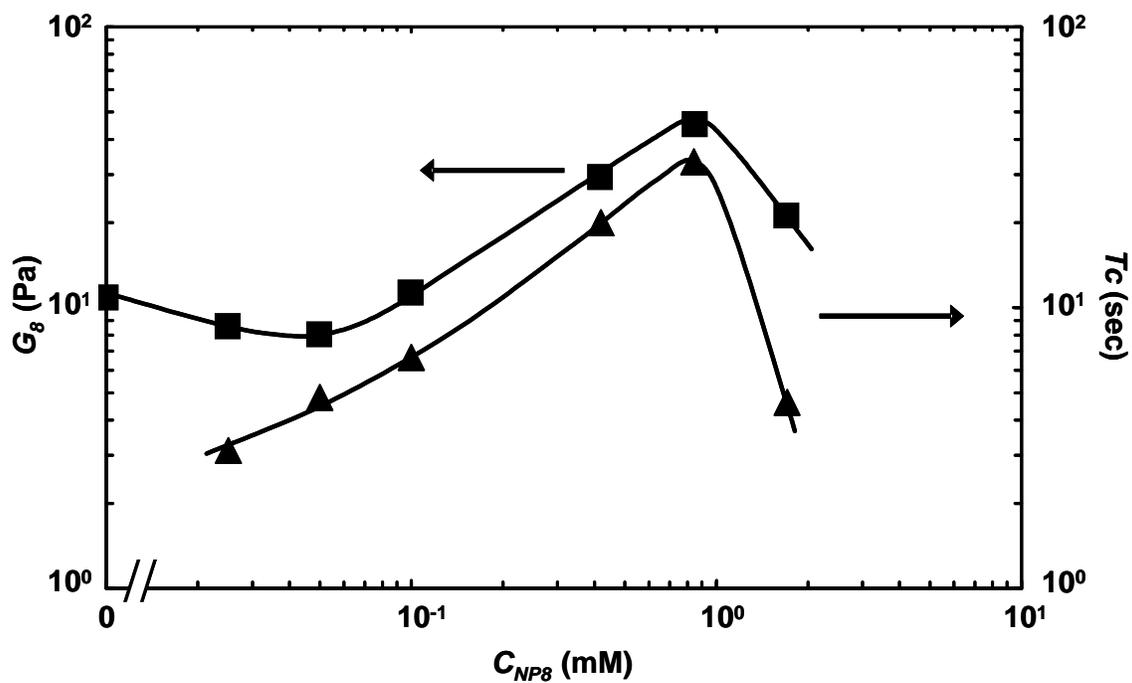


Figure 2.5. Plateau modulus G_8 (□) and average lifetime of hydrophobic junctions T_c (▲) as a function of NP8 surfactant concentration (C_{NP8}) for 0.5 wt.% HASE polymer/NP8 surfactant systems.

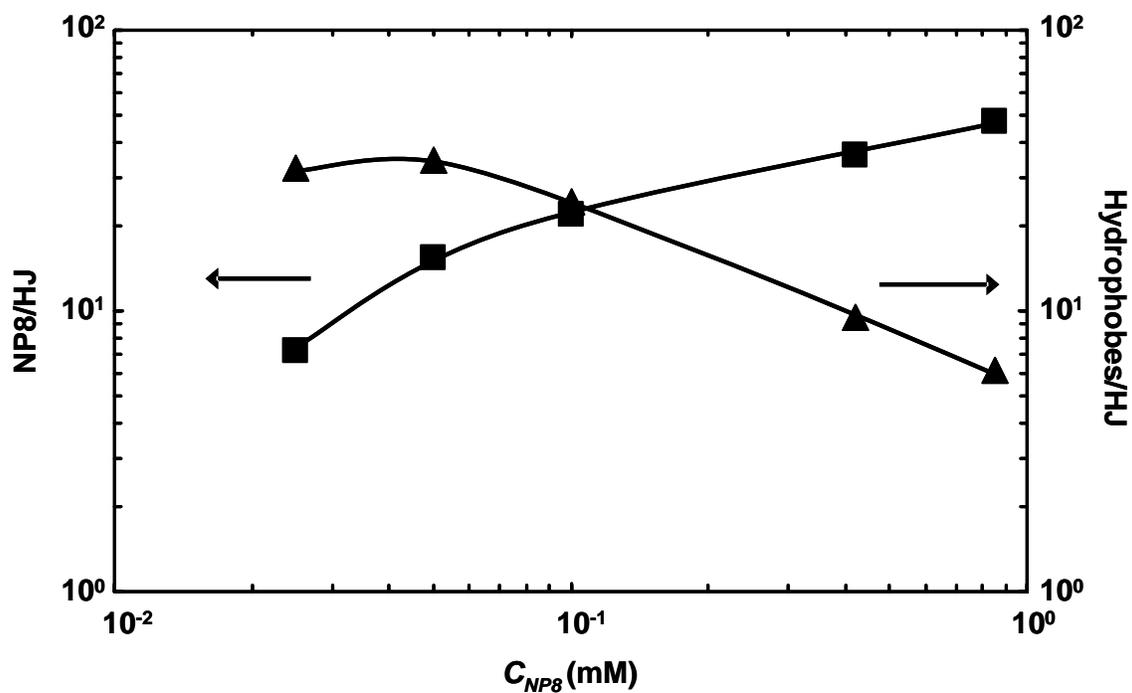


Figure 2.6. Number of NP8 surfactant molecules per hydrophobic junction (NP8/HJ) (■) and number of polymer hydrophobes per hydrophobic junction (Hydrophobes/HJ) (▲) as a function of NP8 surfactant concentration (C_{NP8}) for 0.5 wt.% HASE polymer/NP8 surfactant systems.

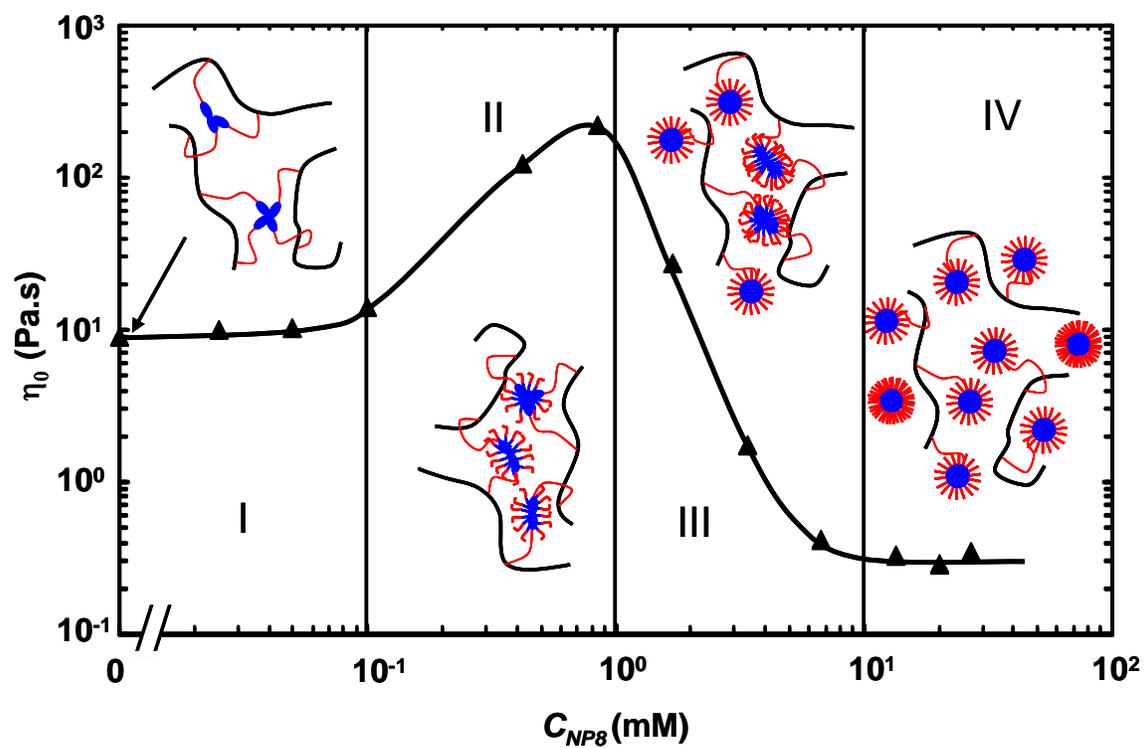


Figure 2.7. Schematic representation of HASE polymer-NP8 surfactant interactions and low shear viscosity as a function of NP8 surfactant concentration (C_{NP8}).

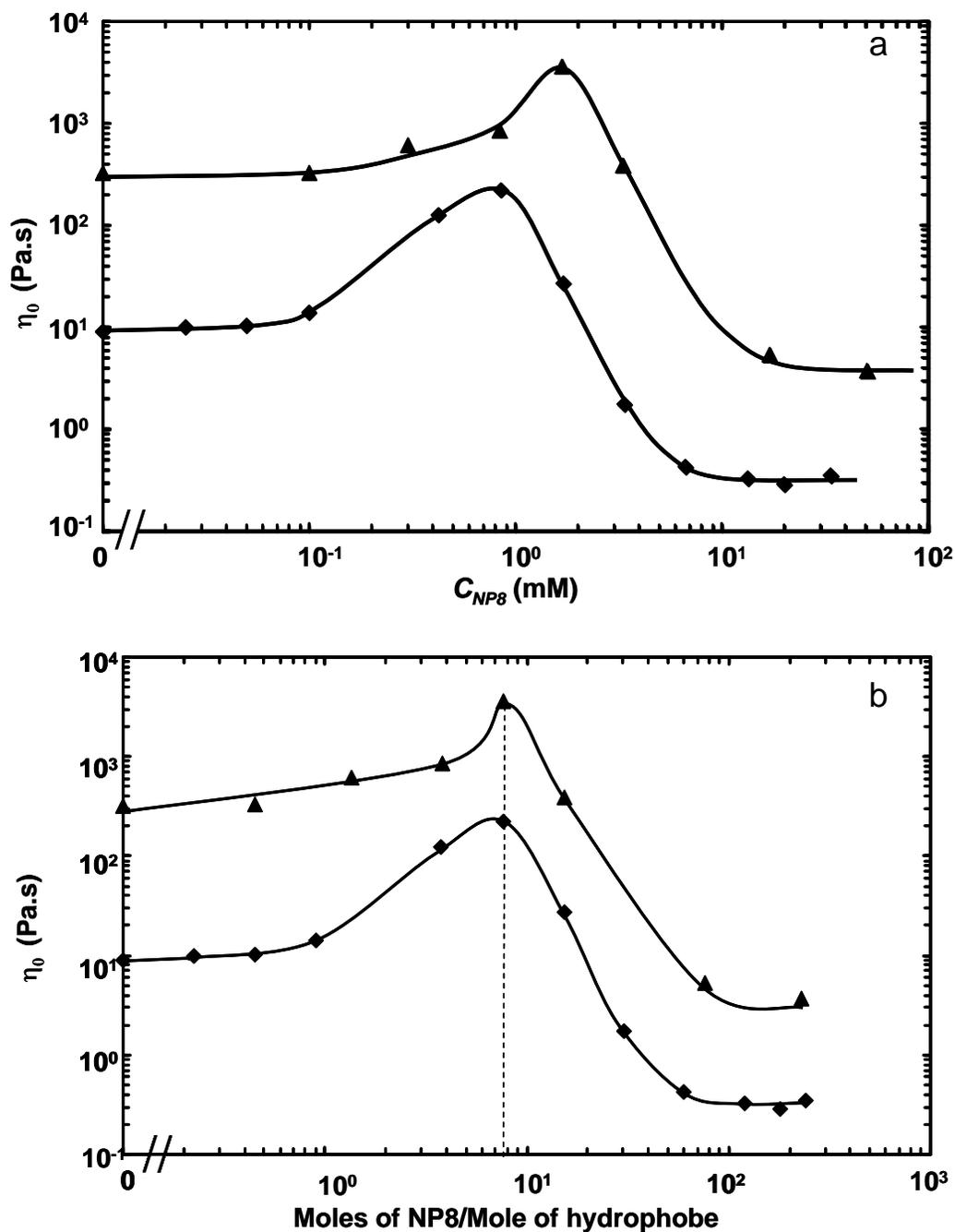


Figure 2.8 Low shear viscosity (η_0) for 0.5 wt.% (◆) and 1 wt.% (▲) HASE polymer/NP8 surfactant system as a function of **a)** NP8 surfactant concentration (C_{NP8}) and **b)** moles of NP8 per mole of polymer hydrophobe.

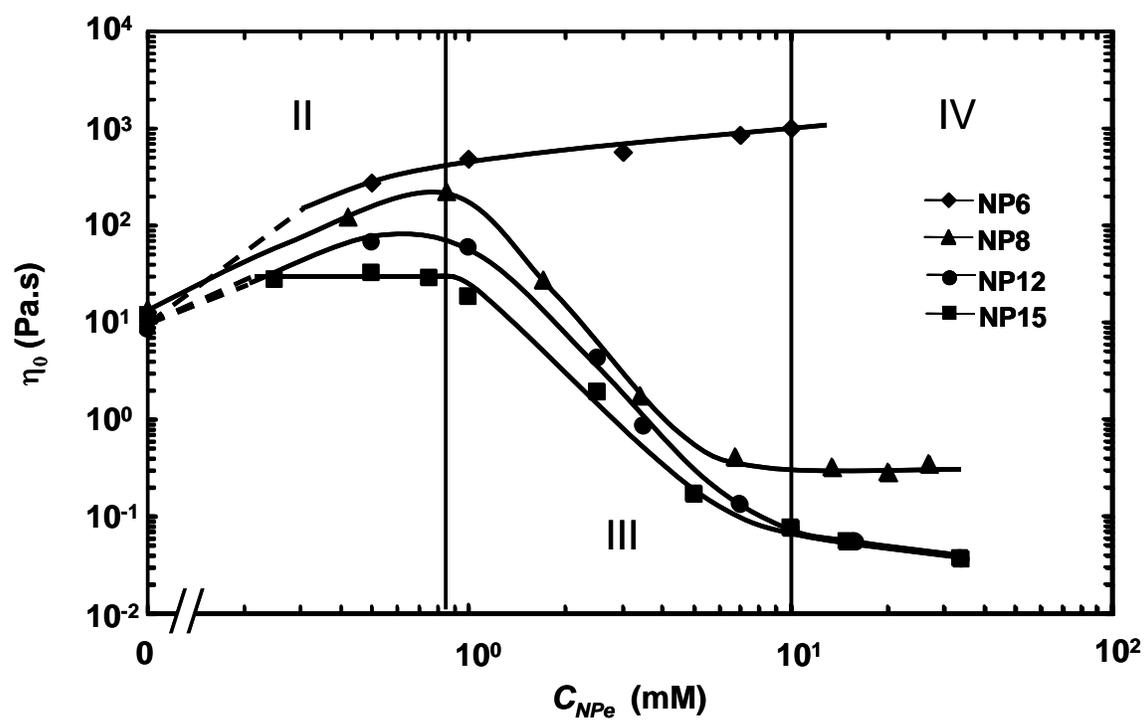


Figure 2.9. Low shear viscosity (η_0) as a function of NPe ($e = 6, 8, 12$ and 15) surfactant concentration (C_{NPe}) for 0.5 wt.% HASE polymer/NPe surfactant systems.

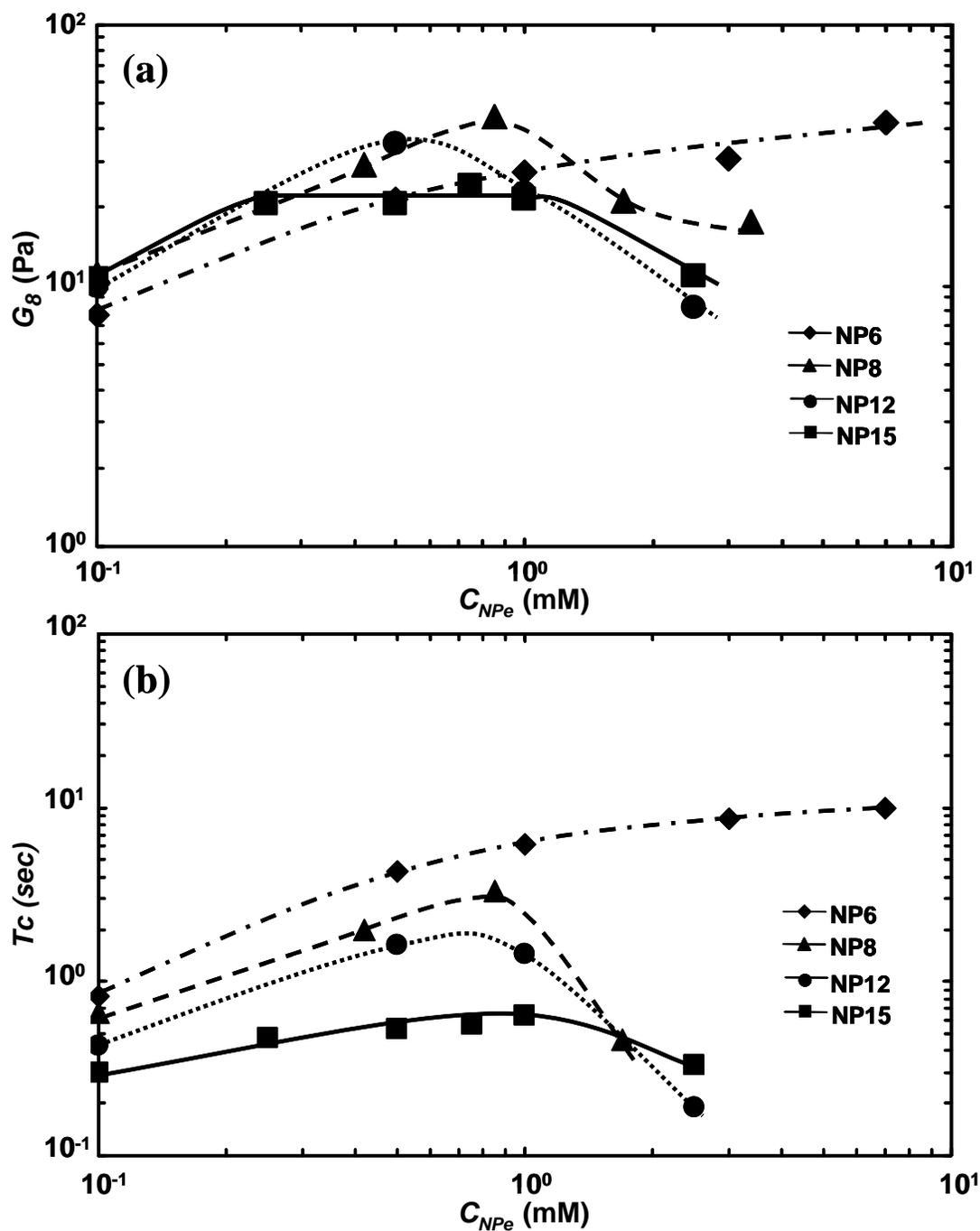


Figure 2.10. Plateau modulus G_8 (a) and average lifetime of hydrophobic junctions T_c (b) as a function of NPe ($e = 6, 8, 12$ and 15) surfactant concentration (C_{NPe}) for 0.5 wt.% HASE polymer/NPe surfactant systems.

CHAPTER 3

Complexation of Hydrophobically Modified Associative Polymer with Binary Surfactant Mixtures

Chapter 4 is essentially a manuscript by Sachin Talwar, Lauriane F. Scanu, Srinivasa R. Raghavan and Saad A. Khan prepared for submission to *Langmuir*

Complexation of Hydrophobically Modified Associative Polymer with Binary Surfactant Mixtures

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Abstract

Hydrophobically modified alkali-soluble emulsion polymers (HASE) are a class of comb-like associative polymers that can impart high viscosities to aqueous solutions. The rheology of HASE solutions can be tuned by the addition of surfactants, such as nonylphenol ethoxylates (NPe), where e is the length of the hydrophilic (ethoxylate) chain. While previous studies have considered individual surfactants, our focus here is on binary surfactant mixtures. We find that equimolar NP4-NP12 mixtures significantly enhance the zero-shear viscosities of HASE solutions compared to equivalent amounts of NP8, especially at high overall surfactant concentrations. Dynamic rheological measurements suggest that the higher viscosities are due to increases in the lifetime of hydrophobic junctions in the polymer-surfactant network. In contrast to the above results, equimolar NP4-NP8 mixtures are rheologically identical to equivalent solutions of NP6. The differences between the two sets of mixtures are further correlated with cloud point measurements and thereby with the overall hydrophilic-lipophilic balance (HLB) of the surfactant system.

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3.1. Introduction

Hydrophobically modified associative polymers are the rheology modifiers of choice in several applications including paints and coatings, personal care products, agrochemicals, enhanced oil recovery and glycol-based anti-icing aircraft fluids¹⁻⁷. Hydrophobically modified alkali-soluble emulsion (HASE) polymers are a class of associative polymers with hydrophobic alkyl groups grafted to the copolymer backbone in a comb-like fashion. The hydrophobes associate in aqueous solutions to form a transient network of hydrophobic junctions. The presence of these junctions greatly enhances the solution viscosity and gives rise to other unique rheological properties. As such these polymers have been a subject of considerable research interest owing to their broad industrial applications, and a large number of studies have been undertaken pertaining to their synthesis⁸⁻¹⁰, their non-linear rheology¹¹, parallel superposed steady and dynamic shear¹², and the effects of hydrophobic size and side-chain length¹³⁻¹⁵, ethylene oxide (EO) group number and ionic strength^{16,17} on solution rheology. Since the rheological properties of HASE polymers are primarily governed by their hydrophobic associations in solution, efforts have been made to study the effects on solution rheology of amphiphilic molecules such as surfactants, which can associate with the hydrophobes. Results show that the presence of surfactants can vastly alter the dynamics of these solutions by continuously increasing, decreasing or exhibiting a maximum in the system viscosity depending on the surfactant concentration and type¹⁸⁻²⁰.

In our previous work on associative polymers²¹, we examined the rheological behavior of HASE polymer/nonylphenol polyethoxylate (NPe) nonionic surfactant systems

with different hydrophilic lipophilic balance (HLB). The HLB was varied by using surfactants with different number of ethoxylate units ($e = 6, 8, 12$ and 15). The results revealed that the zero shear viscosity versus surfactant concentration trends were vastly different for surfactants with different HLB. In case of NP8 and NP12 surfactants, viscosity of the HASE/NPe surfactant solutions exhibited a viscosity maximum followed by a decrease. On the other hand, low HLB NP6 surfactant showed a monotonous increase in viscosity in the concentration range studied (Figure 3.1). The rheological behavior in each of them was explained in terms of formation of hydrophobic junctions in solution incorporating both surfactant and polymer hydrophobes. The increase in viscosity upon surfactant addition was attributed to the increase in the number as well as strength of these “mixed” hydrophobic junctions. The subsequent reduction in viscosity in case of surfactants that formed spherical micelles was understood to be a consequence of the saturation of polymer hydrophobes by surfactant molecules making their participation in the junctions ineffective. The presence of lamellar structures in case of low HLB NP6 surfactant was believed to be the reason behind the monotonous viscosity increase in those systems.

Most practical applications employ surfactant mixtures as opposed to individual surfactants primarily to improve properties and performance of the final product. In most cases, this improvement arises from the existence of synergism wherein the physio-chemical properties of the mixture are better than those of individual surfactants²². In aqueous solution, the surfactant molecules form micelles above the critical micelle concentration (CMC). The micellar shapes include spheres, rodlike with hemispherical ends, flat lamellar structures, and vesicles²². Changes in parameters such as temperature, additives, and

structural groups in the surfactant affect the micellar structure and aggregation number of the micelle, resulting in the transition of the structure from spherical through rodlike to lamellar in shape²³. Israelachvili *et al.*²⁴ developed a theory to predict the micellar shape using the packing parameter P , defined as:

$$P = \frac{V_H}{a_o l_c} \quad (1)$$

where V_H is defined as the volume occupied by the hydrophobic groups in the micellar core, a_o is the effective cross-sectional area occupied by the hydrophilic group at the micelle-solution interface, and l_c is the length of hydrophobic group in the micellar core. The critical packing parameter- the value of P corresponding to a transition in micellar shape- is 1/3 for the sphere-to-cylinder transition, 1/2 for the cylinder-to-bilayer and vesicle transition, and 1 for the transition to inverted micelles. For the case of NP surfactants, P values are dictated by the hydrophilic (EO) chain lengths; a longer chain entailing a larger a_o ²² and consequently a lower P value.

For the case of surfactant mixtures, the packing parameter of the mixture P_{mix} is related to the packing parameter of the different components²⁵:

$$P_{mix} = \sum x_i P_i \quad (2)$$

where x_i and P_i are the mole fraction and packing parameter of the component i in the surfactant mixture, respectively. Thus, we can expect a binary mixture of nonylphenol ethoxylates (NPe) surfactants with different EO chain lengths to form structures either

similar to any of the individual surfactants in solution, or an intermediate between the two, depending on the mole fractions of the two components. For example, on mixing an equimolar ratio of two surfactants with P_i as 0.2 and 0.6 (the corresponding individual structures being spherical and lamellar respectively), the expected structure of the mixed micelles is rodlike ($P_{mix} = 0.4$). Therefore, in principle, by varying the ratio of two surfactants in their binary mixture, the micellar structure corresponding to the critical packing parameter can be achieved.

Kuneieda *et al.*²⁶ studied the phase behavior, cloud temperatures and the molecular structures in aqueous systems of nonionic homogenous $C_{12}EO_6$, and binary $C_{12}EO_i$ - $C_{12}EO_8$ systems with varying i . The average EO chain lengths of the mixed surfactant systems were kept constant and equivalent to $C_{12}EO_6$. They reported a tighter packing of surfactant molecules i.e., lower a_o as measured by SAXS, in the hexagonal and lamellar phases in the mixed systems. Moreover, the value of a_o decreased with increasing the difference in EO chain lengths in the mixed systems, and this behavior was attributed to the reduction of repulsive forces between the hydrophilic head groups in mixtures. Zhou *et al.* observed reduction in steric self-repulsion between the bulky hydrophilic groups of $C_{12}EO_i$ surfactants as one of the causes for greater surfactant attraction²⁷ in $C_{12}SO_3Na$ - $C_{12}EO_i$ mixed surfactant systems. The attraction increased with increasing i ; a more favorable conformation with respect to self-interaction of pure surfactants, which was ascribed to an increase in steric effect in the pure surfactant with increasing EO chain length.

While binary mixtures of surfactants are well documented and are known to present a synergistic effect in several cases, no studies exist on the effects of mixed nonionic surfactants on the rheology of comb-type hydrophobically modified associative polymers. The mixture of a high and a low HLB, nonionic surfactant in HASE polymer solution may either form an intermediate structure between those corresponding to the high (spherical micelle) and the low (lamellar) HLB surfactants or maintain the structure of the dominant surfactant. Moreover, the molar ratio of the surfactants in the mixed surfactants systems is expected to significantly affect the solution rheology.

The present work attempts to address the following issues: Is the effect of mixed surfactants on associative polymers synergistic or antagonistic as compared to NPe surfactants with equivalent EO chain length? Is the effect dominated by a particular surfactant and is it dependent on surfactant concentration? Can we explain the observed rheological behavior based on changes in micellar structure with changing HLB? At first, we examine the effects of mixtures of NPe nonionic surfactants on the rheology of HASE polymers. The effect of increasing the total surfactant concentration on the rheology of HASE/binary NPe systems as compared to the individual NPe surfactant with equivalent HLB is described. Subsequently, the effect of varying the ratio of surfactant mixture – with one surfactant being partially soluble and the other being highly hydrophilic – on hydrophobic interactions in HASE is investigated. Finally, an attempt is made to correlate the observed behavior to the surfactant cloud point.

3.2. Materials and Methods

The polymer used in this study was obtained from UCAR Emulsion Systems (Dow Chemicals, Cary, NC). A schematic of its chemical structure is shown in Figure 3.2; the molar ratio of methacrylic acid, ethylacrylate and macromonomer is 43.57/56.21/0.22 respectively. The macromonomer, which is linked to the backbone via a urethane linkage, is composed of a polyethylene oxide (PEO) spacer with 40 moles of EO units and a C₂₂ alkyl group. The HASE polymer was supplied in the form of aqueous latex at a solid concentration of approximately 26 wt %. All impurities and unreacted chemicals were removed from the aqueous latex by dialyzing it against deionized water using a Spectrapore cellulosic membrane (cut off MW = 10000) for 3 weeks. The dialyzed latex was then lyophilized for 2 days under a vacuum of 100 mTorr to obtain the HASE polymer in a powder form. The pH of the subsequently prepared polymer solution was adjusted between 9 and 9.5 by adding 0.1M NaOH. polymer was dissolved in a 0.05 M NaCl solution to ensure controlled/negligible polyelectrolyte effect²⁸. Nonylphenol ethoxylates (NPe) nonionic surfactants, Tergitol[®] were supplied by Dow Chemicals (NC) and used as received. Once the polymer/surfactant samples were prepared by combining the requisite amounts of HASE polymer and NPe surfactant solutions, they were put in a water bath overnight at 50°C to remove entrained air and subsequently left for 48 hrs prior to rheological measurements. Rheology of the samples was measured within three weeks of the preparation to avoid possible polymer degradation in the presence of NaOH²⁹.

All rheological experiments were performed at $\text{pH} = 9$ and $T = 25^\circ\text{C}$ using a TA Instruments AR-2000 stress controlled rheometer fitted with a cone and plate geometry. Both steady and dynamic shear experiments were conducted on each sample. Since the steady shear response of HASE polymer/surfactant systems is sensitive to shear history, a preshear was applied at a strain rate of 5s^{-1} for 180 s followed by a rest period of 120 s. A dynamic stress sweep test was performed to determine the limit of linear viscoelastic regime, which was thereafter utilized to perform the dynamic frequency sweep test. Zero or low shear viscosity was determined from the steady shear viscosity profiles by averaging over the first ten points of the Newtonian region. Each experiment reported in this study was performed at least twice and all experiments were reproducible within $\pm 5\%$. The error is included in the symbol size.

Cloud point temperatures were determined visually as the temperatures at which clear or slightly hazy surfactant solutions turned opaque on heating and clear on subsequent cooling. Each measurement was done thrice to ensure accuracy.

3.3. Results and Discussion

3.3.1. Effect of binary surfactant mixtures

The effect of overall surfactant concentration on zero shear viscosity of equimolar binary surfactant mixtures of NP4 and NP12 in 0.5 wt.% HASE solution is shown in Figure 3.3 and is compared with plots of NP8/0.5 wt.% HASE and NP12/0.5 wt.% HASE systems. The average EO chain length for the mixture is equivalent to that of NP8. Since the NP4

surfactant is insoluble in water, rheological measurements could not be performed on NP4/HASE systems as the samples were non-homogenous even at low NP4 concentrations. For the same reason, the maximum overall surfactant concentration studied for NP4-NP12/HASE systems was 13.6mM. As alluded to in the Introduction, NP4 and NP12 surfactants in HASE solution are expected to exhibit entirely different trends on viscosity i.e. a monotonous increase for NP4 and an increase followed by a decrease for NP12 with increasing concentration. The difference in trends is a consequence of different molecular structures formed by the surfactants; lamellar in case of NP4 and spherical for NP12. As can be seen from Figure 3.3, the binary surfactant mixture follows a trend similar to that of NP8/0.5% HASE system, *i.e.*, an increase up to a maximum followed by a decrease. The two curves overlap at lower concentrations and up to the concentration at which the viscosity exhibits a maximum for the NP8 system ($C^* = 0.85 \text{ mM}$). Then, two differences between the systems are observed. First, the viscosity maximum for the NP mixture system occurs at a slightly higher surfactant concentration. It is important to recall here that this surfactant concentration corresponds to the maximum number of polymer hydrophobes per hydrophobic junctions and the number of surfactant molecules able to accommodate around those²¹. Thus more surfactant molecules can be part of the mixed micelles if there is a difference on the molecule's length. Second, although the viscosity decreases at higher concentrations, NP4/NP12 systems still exhibit almost an order of magnitude higher viscosity than the equivalent NP8/polymer systems.

To further understand the underlying mechanism responsible for the viscosity trends, we measured the effect of increasing total surfactant concentration on the strength as well as

on the number of hydrophobic junctions in the solution. The longest characteristic relaxation time of a polymer system, as given by the inverse of frequency at the intersection between the elastic modulus (G') and viscous modulus (G'') curves can provide an estimate of the strength of the junctions¹⁹. Although the relaxation time obtained in this manner is applicable to Maxwell-type viscoelastic behavior which is not obeyed by our systems, nonetheless the values obtained from this treatment should be adequate for comparison purpose. The relaxation time obtained in this manner will hereon be termed as characteristic relaxation time (T_r).

Based on the theory by Green and Tobolsky³⁰ on transient networks, the number of mechanically active hydrophobic junctions, ν_{eff} in a polymer/surfactant system can be related to the high frequency plateau modulus G_8 through the following expression:

$$G_8 = \nu_{eff} RT \quad (3)$$

where R is the gas constant and T is the absolute temperature. We estimate G_8 by taking the value of G' curve at a frequency of 25 rad/sec for systems exhibiting a plateau in storage modulus, as has been done previously^{19,21}. Figures 3.4a and 3.4b show the plots of G_8 , which is proportional to the number of hydrophobic junctions, and T_r respectively for binary surfactant mixtures of NP4 and NP12 in 0.5 wt.% HASE solution at different surfactant concentrations alongside plot of NP8/0.5 wt.% HASE system. We observe from Figure 3.4a that the number of hydrophobic junctions, as given by G' at high frequencies, is not affected by the presence of mixed surfactant instead of the individual surfactant. The characteristic relaxation time however decreases more drastically at higher concentrations in case of the

individual surfactant as opposed to the surfactant mixture (Figure 3.4b). A higher characteristic relaxation time implies an increase in junction lifetime, i.e., hydrophobic junctions are more tightly packed in case of a surfactant mixture.

The difference in the rheological response of the surfactant mixture versus the corresponding individual surfactant is more evident from the dynamic mechanical spectrum (elastic modulus G' and the viscous modulus G'' as function of frequency) of a 3.4mM surfactant solution with HASE (Figure 3.5). In the case of the mixture, there is a reduction in frequency dependence of both G' and G'' and the plateau modulus becomes more well defined. Moreover there is more than an order of magnitude shift in the crossover point of G' and G'' reflecting a significant increase in T_r . These results are typical of associative polymer/surfactant systems^{19,21,31,32} and indicate the presence of a much tighter packing of hydrophobic junctions (consisting of both polymer and surfactant hydrophobes) in case of surfactant mixtures as compared to the corresponding individual surfactant.

The presence of a tighter packing in case of mixed surfactants is further validated by comparing the values of activation energy of dissociation of the hydrophobic junctions, E_a , of the two systems at high surfactant concentrations. E_a values were calculated using the method proposed by Tam and coworkers³³. The applied shear stress at a particular temperature T was first scaled to the reference temperature T_R (298K) based on $\sigma(T) = \sigma(T_R) * (T / T_R)$. The corresponding low shear viscosity was used to determine the E_a values by using the Arrhenius equation

$$\eta_0 = A \exp(E_a / RT) \quad (4)$$

where A is the Arrhenius constant and R , the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$). Figure 3.6 shows the plots of zero shear viscosity versus inverse of temperature for 0.5 wt.% HASE solutions with individual and mixed surfactants. Both the curves follow Arrhenius equation and E_a values can therefore be estimated from the slopes of these curves. The calculated values of E_a for systems with individual and mixed surfactants are 31.6 kJ/mol and 45 kJ/mol respectively thereby indicating presence of tighter junction packing in case of surfactant mixtures.

The above results clearly indicate that at high surfactant concentrations, an equimolar NP4-12 mixture behaves differently from its equivalent HLB single surfactant NP8 in terms of its effect on HASE solution. From these observations, we propose a mechanism to elucidate this synergistic effect in solution viscosity based on molecular geometry considerations. As noted earlier, the molecular geometry of the micelles in solution is dictated by the packing parameter defined as $P = \frac{V_H}{a_o l_c}$ where V_H is the volume occupied by the hydrophobic groups in the micellar core, a_o is the effective cross-sectional area occupied by the hydrophilic group at the micelle-solution interface, and l_c is the length of hydrophobic group in the micellar core. Depending on the value of P , surfactants can form different structures in an aqueous solution ranging from spheres ($P < 1/3$) to cylinders ($1/3 < P < 1/2$) to bilayers ($1/2 < P < 1$). NP12 and NP8 are known to form spherical micelles in water ($P < 1/3$) while NP4, which is slightly soluble in water, forms lamellar or bilayer structures ($P > 1/3$). We can expect mixed micelles of NP4-NP12 to have a lower effective hydrophilic

group area, a_o (with other terms remaining constant) as compared to NP8 due to reduced steric hindrance between hydrophilic head groups of NP12 and NP4 arising from a difference in their hydrophilic chain lengths³⁴. This in turn would increase the value of the packing parameter P_i which causes the transition of the micellar shape from being spherical ($P_i < 1/3$ for NP8) to a tighter packing conformation such as rodlike, in case of surfactant mixtures ($P_{mix} > 1/3$ for NP4-NP12 mixture). At the molecular level, a lower value of a_o translates into a reduced interfacial curvature – from cone to truncated cone corresponding to sphere and rodlike structure respectively as shown in the schematic in Figure 3.7. It should be noted that the rodlike conformation that we refer to in our discussion should not be confused with wormlike micelles that form entangled networks similar to polymeric chains and enhance solution viscoelasticity³⁵. No discernible change in viscoelasticity of our surfactant-only mixtures was observed at any of the concentrations studied. By referring to rodlike structures, we merely suggest a possible tighter packing conformation that mixed micelles might adopt in solution.

As the viscosity in HASE solutions is governed by both the number and strength of hydrophobic junctions that consist of surfactant and polymer hydrophobes, we believe that the presence of a more tightly packed micellar structure in case of mixed surfactants promotes an increase in the junction strength (increased T_j) while keeping the number of junctions constant (unchanged G_8). The overall effect is reflected in enhanced viscosity values for surfactant mixtures. In a related work on the viscosity behavior of hydrophobically modified hydroxyethyl cellulose (HMHEC), Nilsson *et al.*^{36,37} also noticed higher surfactant

aggregation numbers and higher viscosities upon addition of an oppositely charged surfactant to solutions containing the hydrophobically modified polymer and an ionic surfactant. This increase in aggregation number was attributed to the screening of charges on surfactant molecules hence enabling accommodation of more molecules per micelle.

Figure 3.8 compares the zero shear viscosity of an equimolar binary mixture of NP4 and NP8 (average EO chain length equivalent to NP6) in 0.5% HASE to that of an NP6/0.5% HASE system. Both solutions show a similar trend, *i.e.*, an initial increase followed by a region of near-constant zero shear viscosity. However, unlike NP4-NP12 mixtures where viscosity of surfactant mixtures differ significantly from that of individual surfactant at higher concentrations, the magnitude of viscosity difference between NP4-NP8 systems and its analogous NP6 systems does not vary much with concentration. Figures 3.9a and 3.9b show the plots of G_8 and T_r , respectively for the above systems with increasing surfactant concentration. Again in this case, the number of hydrophobic junctions does not vary on using mixed surfactants while the characteristic relaxation time for the surfactant mixture is only slightly lower than that of individual surfactant. This is also reflected in the frequency spectrum of G' and G'' (Figure 3.10), wherein the plots for mixed and individual surfactant systems with 7mM total surfactant concentration closely resemble each other. At the molecular level, these results imply the existence of similar micellar structures for NP6 as well as equimolar NP4-NP8 mixtures. The change in packing parameter on mixing is not significant enough to reach the transition boundary *i.e.*, the critical packing parameter. It has been observed previously²⁷ that mixtures of surfactants with small differences in EO chain lengths show similar micellar structures as their analogous individual surfactant.

On the other hand, it is possible that the P_{mix} is higher than P_i in this case which results in slightly faster relaxation times. NP6 is known to form lamellar or bilayer structures in aqueous solutions and presence of NP8 in the mixture of NP4-NP8 mixture might actually weaken the structure and by extension, the hydrophobic junctions. The difference in relaxation times however, is not considerable enough to be conclusive.

3.3.2. Effect of surfactant ratio in mixed surfactant systems

We studied the effect of changing the molar ratio of the surfactants in a binary mixture on the rheological behavior of HASE solution. The surfactants were selected such that one of the components is partially soluble (low HLB) while the other is completely soluble (high HLB). Figure 3.11 shows the plots of low shear viscosity vs. surfactant concentration for different NP6-NP12 molar ratios (1:0, 6:1, 3:1, 2:1, 1:1, 0:1) in a 0.5% HASE solution. Addition of NP12 to HASE solutions increases the solution viscosity up to a maximum followed by a decrease below the initial HASE viscosity. The viscosity increase has been attributed to formation of mixed micelles incorporating both surfactant and polymer hydrophobes. As NP12 forms spherical micelles in solution, beyond a certain surfactant concentration, further addition of surfactant molecules leads to the formation of individually surfactant-saturated polymer hydrophobes causing a reduction in hydrophobic associations and in turn the solution viscosity. On the other hand, successive addition of NP6 to HASE causes a continuous rise in viscosity although the rate of increase is much slower at high surfactant concentrations ($C_{NP6} > 1\text{mM}$). The difference in response is due to the ability of

NP6 to form bilayer or lamellar microstructures in solution which considerably enhances the overall strength of the hydrophobic associations. As we increase the proportion of NP6 in NP6-NP12 mixtures, viscosity increases but the trend of viscosity versus concentration resembles that of NP12- a viscosity maximum followed by a decrease- until we arrive at a molar ratio of 6:1 NP6-NP12. At this molar ratio, the viscosity does not show a dip and instead levels off at high concentrations. It is to be noted that rheological measurements could not be made at concentrations above 10mM for both NP6 and 6:1 NP6-NP12 due to the non-homogeneity of the solutions at higher concentrations. Moreover, at low surfactant concentrations ($C \leq 0.5\text{mM}$), the low shear viscosity of NP12/HASE system does not change on addition of NP6 up to a molar ratio of 3:1. At $C > 0.5\text{mM}$, the curves begin to diverge from each other with the viscosity increasing with an increase in the NP6 surfactant ratio in the mixture. These results indicate a transition in the micellar structure from that similar to NP12 (spherical) to one that resembles that of NP6 (lamellar) at 6:1 molar ratio. Figure 3.12 shows the dynamic frequency spectrum for 3.4mM overall surfactant concentration with 0.5 wt.% HASE for surfactant mixtures with different NP6-NP12 molar ratios. Both elastic (G') and viscous (G'') moduli show less frequency dependence and higher values with increasing NP6 concentration in the mixture thereby reflecting a transition to a tighter packing of the micellar structure.

3.3.3. Effect of mixing on Cloud Point Temperature

In the case of oxyethylated non ionic surfactants, an important parameter that determines their solution behavior is the cloud point temperature (CPT). It is the point at

which their aqueous solutions become cloudy upon increasing temperature. This phenomenon occurs due to the dehydration of EO groups as hydrogen bonds are broken with increasing temperature. CPTs have been found to increase with increasing EO length in the surfactant molecule^{22,38}. Hence, it is a characteristic of the surfactant hydrophilicity and can be used to determine its HLB. Table 3.1 shows the CPTs of 1 wt.% NPe (e = 6, 8 and 9) surfactants in water. As expected, we see that CPT increases with increasing surfactant HLB and by extension its hydrophilicity. Also shown in Table 3.1 are the CPTs of different mixtures of surfactants equivalent in EO chain length to the individual surfactants. We observe a 20 °C drop in CPT on mixing NP4 and NP12 surfactants as compared to NP8 in the absence of HASE. Figure 3.13 shows pictorially the cloudy surfactant mixture at 24 °C as compared to the clear NP8 solution. Similar results are observed for mixtures of NP6 and NP12 surfactants in different ratios and comparing the to the equivalent EO chain length surfactants. Thus the mixtures act like a surfactant with lower HLB when compared to the analogous individual surfactant. Similar drops in CPTs were observed on mixing nonionic surfactants with amphiphilic polymers and the effect was attributed to formation of more stabilized structures in solution³⁹. This can further explain the synergistic effect observed in Figure 3.6 where the surfactant mixtures have higher solution viscosities. Even in the presence of HASE a lowering of CPTs is observed although the values are slightly higher than surfactant-only solutions and exhibit a wide cloud point transition instead of a sharp CPT. For example an NP4-NP12 mixture in HASE shows a 20 °C drop in CPT compared to pure NP8 in HASE (Table 3.1). We could not measure CPTs for systems containing 0.5 wt. % HASE as the solution viscosity was too high for adequate stirring. The CPT of NP6

surfactant and its equivalent mixture on the other hand is below 0 °C even in the presence of 0.15% HASE and hence could not be determined. The trends seen with mixed surfactant CPTs is therefore retained in the presence of polymers leading credence to our hypothesis that surfactant mixtures have CPTs lower than corresponding individual surfactant and thus behave like surfactants with lower HLB.

3.4. Conclusions

In this study, we examined the effect of nonionic surfactant mixtures on the rheology of a comb-like associative polymer and compared it to that of analogous individual surfactants with equivalent hydrophilic chain lengths. The addition of NP4-NP12 surfactant mixtures, as opposed to NP8, to the associative polymer leads to considerably higher values of viscosity at high surfactant concentrations. On the other hand, NP4-NP8 mixtures do not exhibit any significant difference in viscosity trends when compared to equivalent NP6 surfactant. The observed behavior is explained in terms of transition in micellar structure due to difference in hydrophilic chain lengths in surfactant mixtures and is supported by the dynamic rheological results and activation energy data. The ratios of surfactants in binary mixtures are also shown to have a profound effect on the trends of viscosity with increasing concentration. Cloud point measurements further support our hypothesis that, in cases where the difference in surfactant hydrophilic chain length is large, surfactant mixtures behave similar to a surfactant with lower HLB when compared to the analogous individual surfactant.

3.5 References

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Table 3.1. Cloud point temperatures of 1 wt.% NPe surfactants and their mixtures in water both with and without HASE.

Surfactant mixture	Cloud Point (°C)	Individual surfactant w/equivalent EO	Cloud Point (°C)
NP4-NP8 (1:1)	<0	NP6	<0
NP4-NP12 (1:1)	23	NP8	43
NP6-NP12 (1:1)	36	NP9	54
NP6-NP12 (2:1)	16	NP8	43
NP4-NP8 (3:1)	<0	NP7.5	b/w 20(NP7) & 43(NP8)
NP4-NP8 (1:1) with 0.15% HASE	<0	NP6 with 0.15%HASE	<0
NP4-NP12 (1:1) with 0.15% HASE	25-26	NP8 with 0.15% HASE	45-47

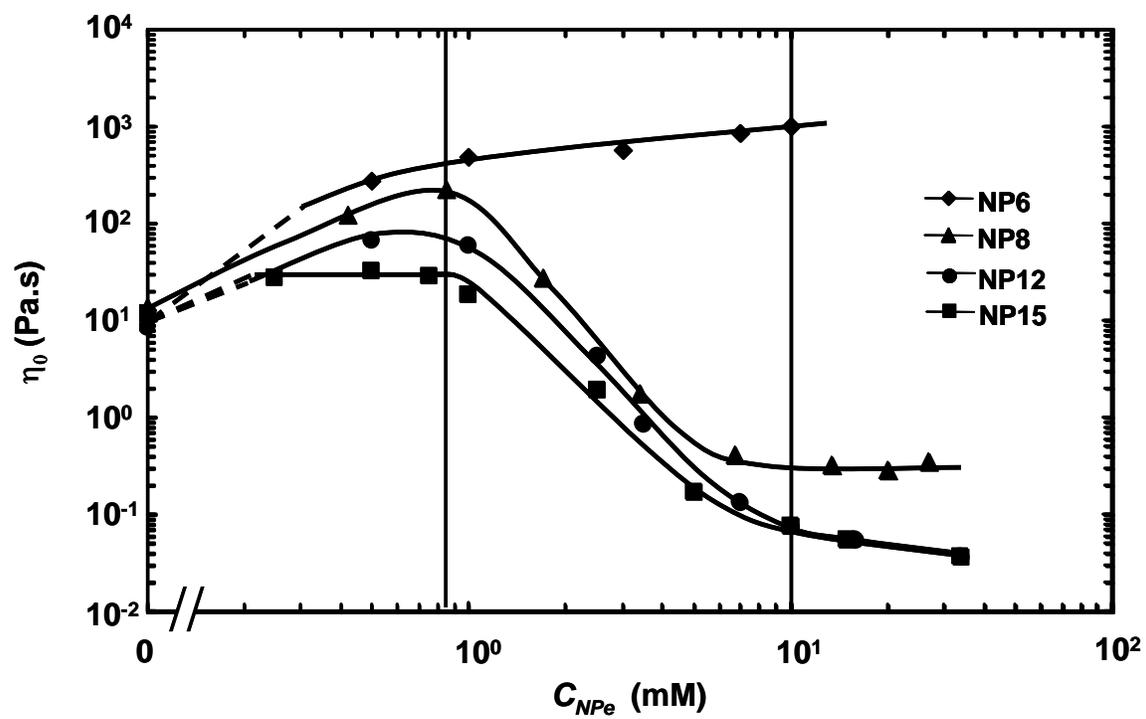


Figure 3.1. Low shear viscosity (η_0) as a function of NPe ($e = 6, 8, 12$ and 15) surfactant concentration (C_{NPe}) for 0.5% HASE polymer/NPe surfactant systems.

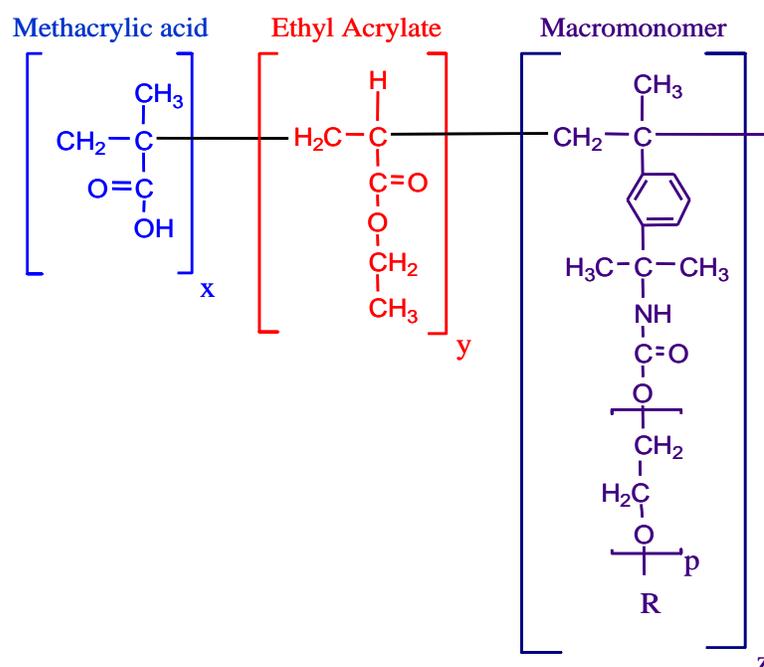


Figure 3.2. Molecular structure of the model HASE polymer. R: C22 alkyl chain polymer hydrophobe, P: 40 EO polyethylene oxide spacer, $x/y/z = 43.57/56.21/0.22$.

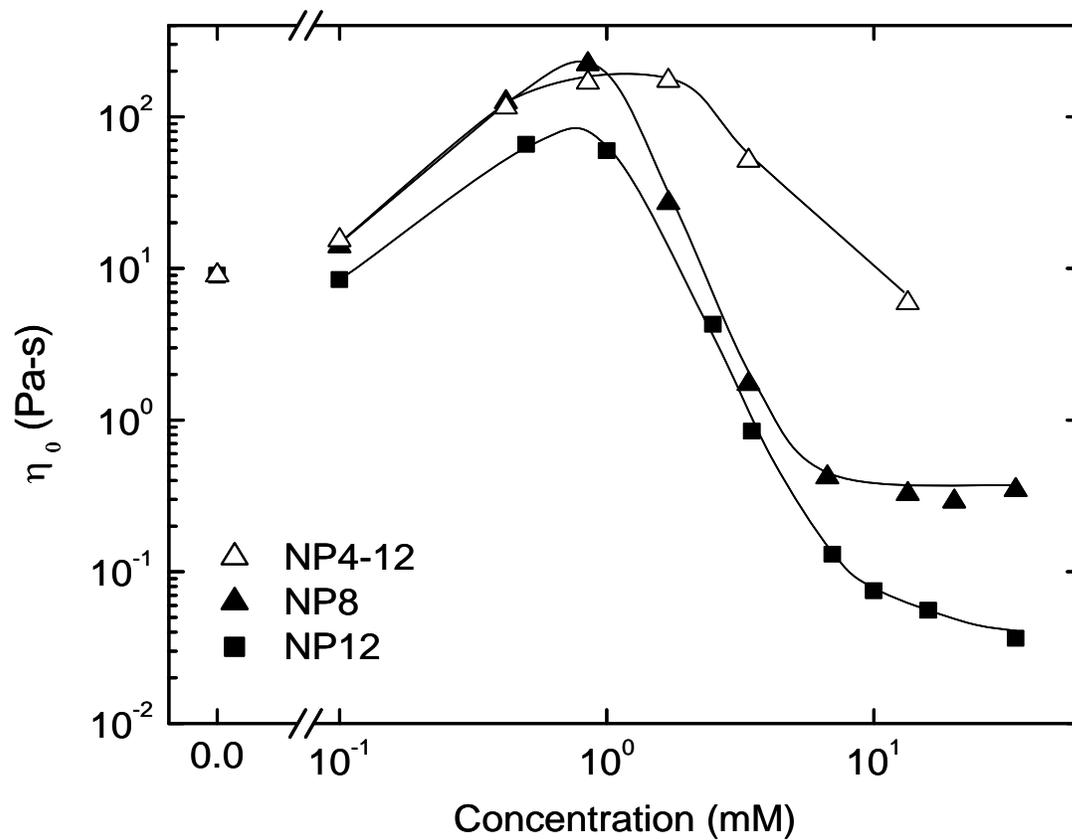


Figure 3.3. Low shear viscosity (η_0) of 0.5% HASE/NP surfactant systems as a function of surfactant concentration. NP 4-12 denotes an equimolar mixture of NP4 and NP12.

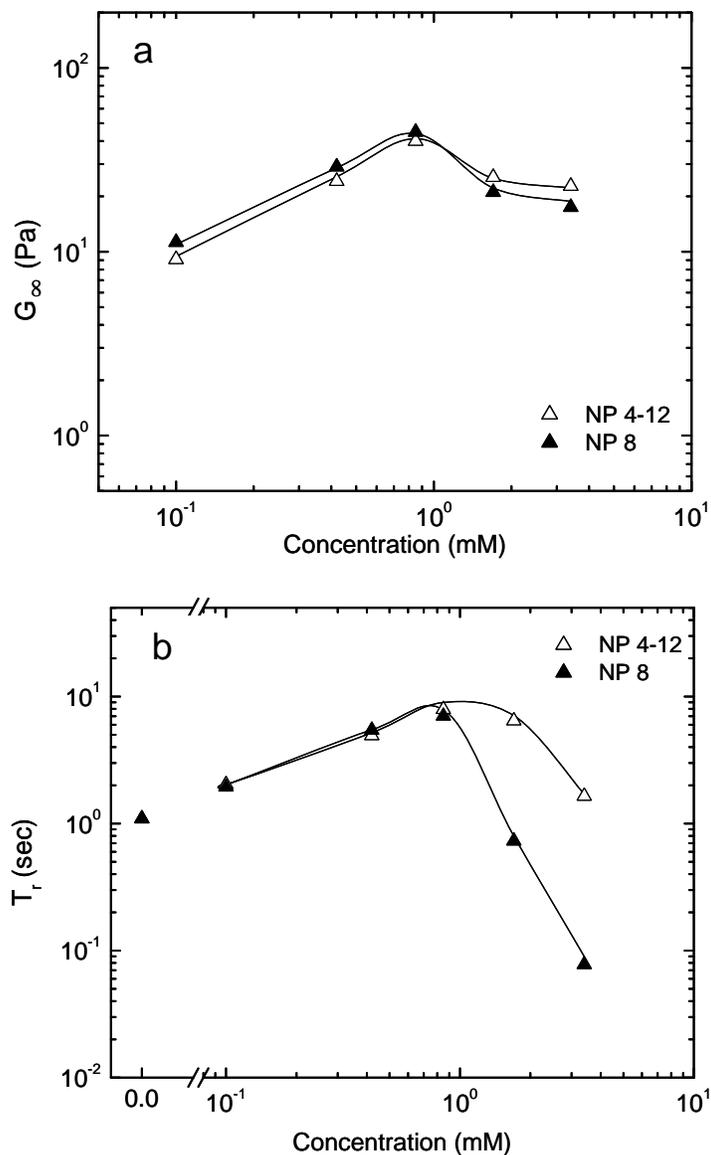


Figure 3.4. Plateau modulus G_8 (a) and characteristic relaxation time T_r (b) as a function of NPe ($e = 4, 8$ and 12) surfactant concentration (C_{NPe}) for 0.5% HASE polymer/NPe surfactant systems. NP 4-12 denotes an equimolar mixture of NP4 and NP12.

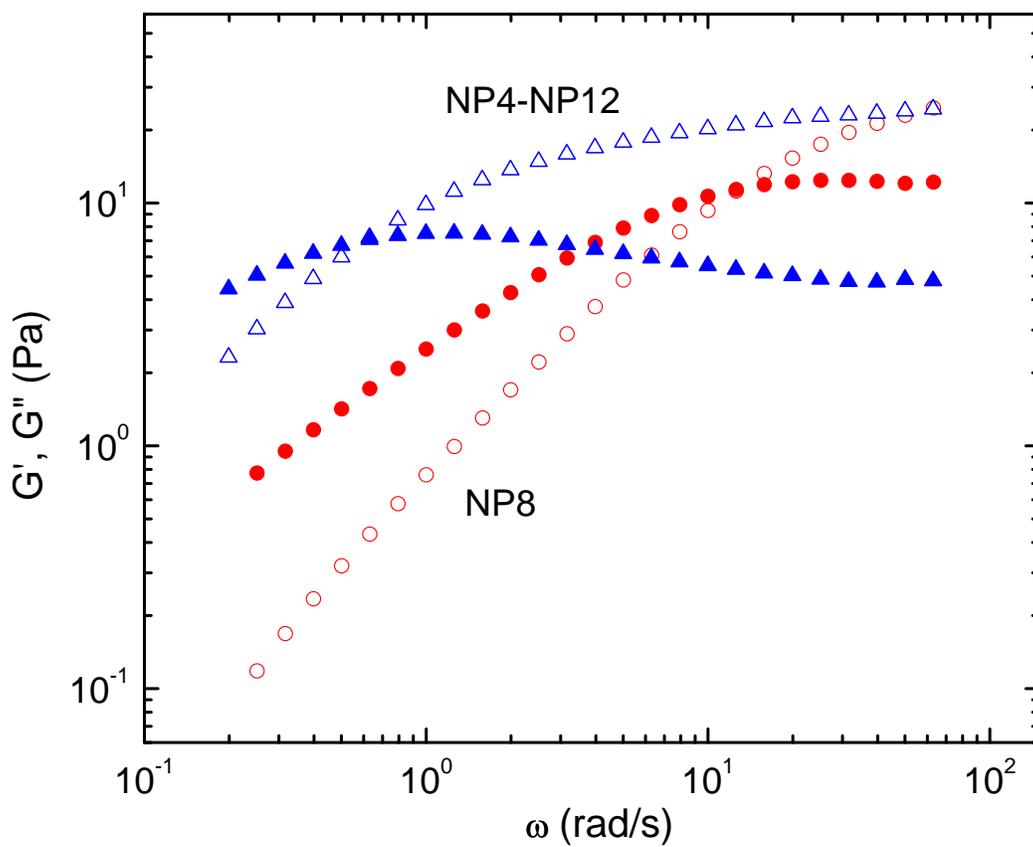


Figure 3.5. Variation of G' (unfilled symbols) and G'' (filled symbols) as a function of ω in 0.5 wt.% HASE solutions containing 3.4mM NP8 (circles) and 3.4mM NP4-NP12 (1:1 molar ratio).

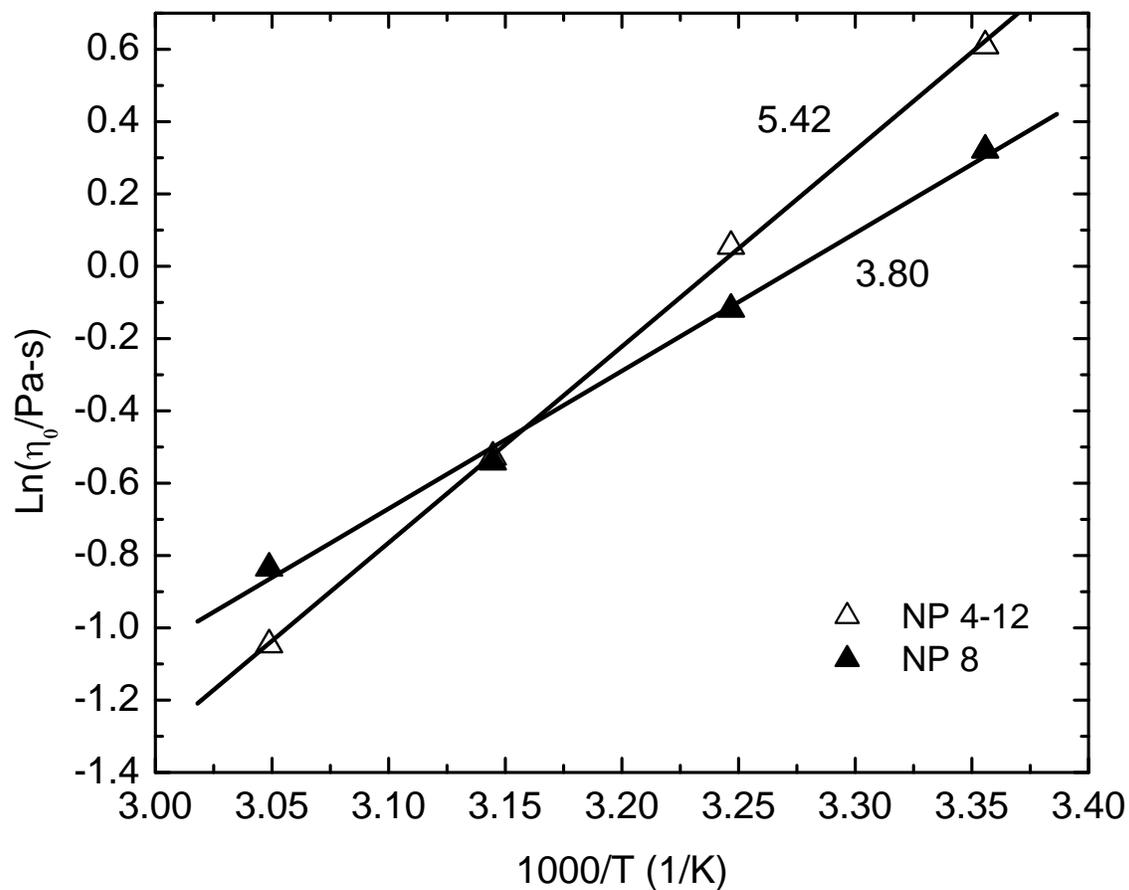


Figure 3.6. Arrhenius plots of zero shear viscosity of 0.5 wt.% HASE polymer with 5mM surfactant concentrations.

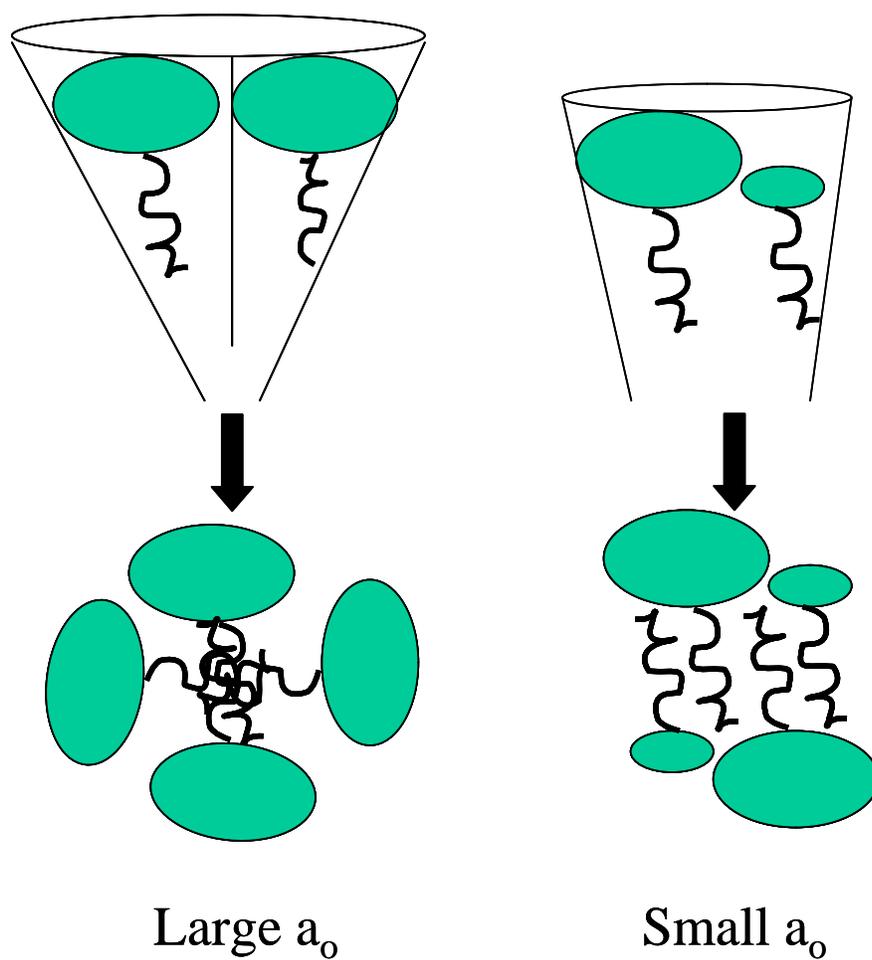


Figure 3.7. Schematic showing the formation of different micellar structures based on interfacial area, a_0 . NP8 molecule (Large a_0) by itself adopts a cone-like configuration leading to spherical micelle. NP4-NP12 (1:1) mixture (Small a_0) molecules adopt a truncated-cone shape and form rodlike micelles.

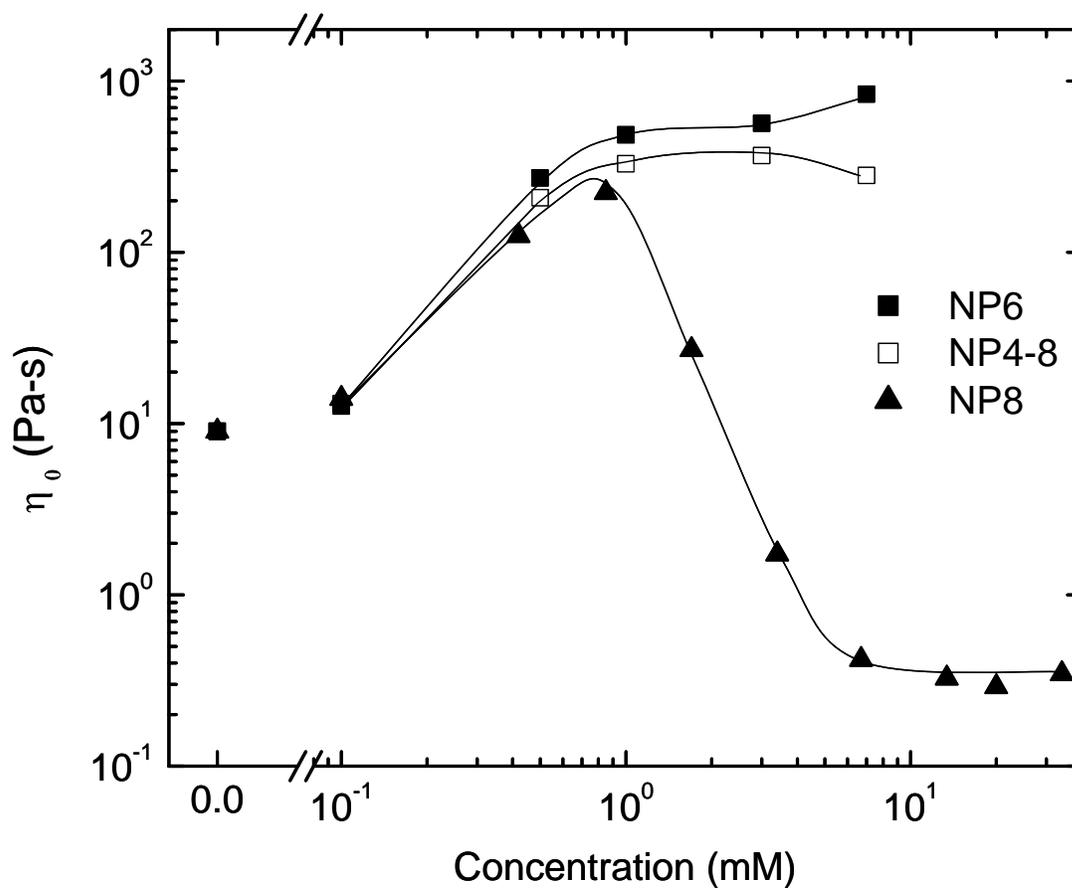


Figure 3.8. Low shear viscosity (η_0) of 0.5% HASE/NP surfactant systems as a function of surfactant concentration. NP 4-8 denotes an equimolar mixture of NP4 and NP8.

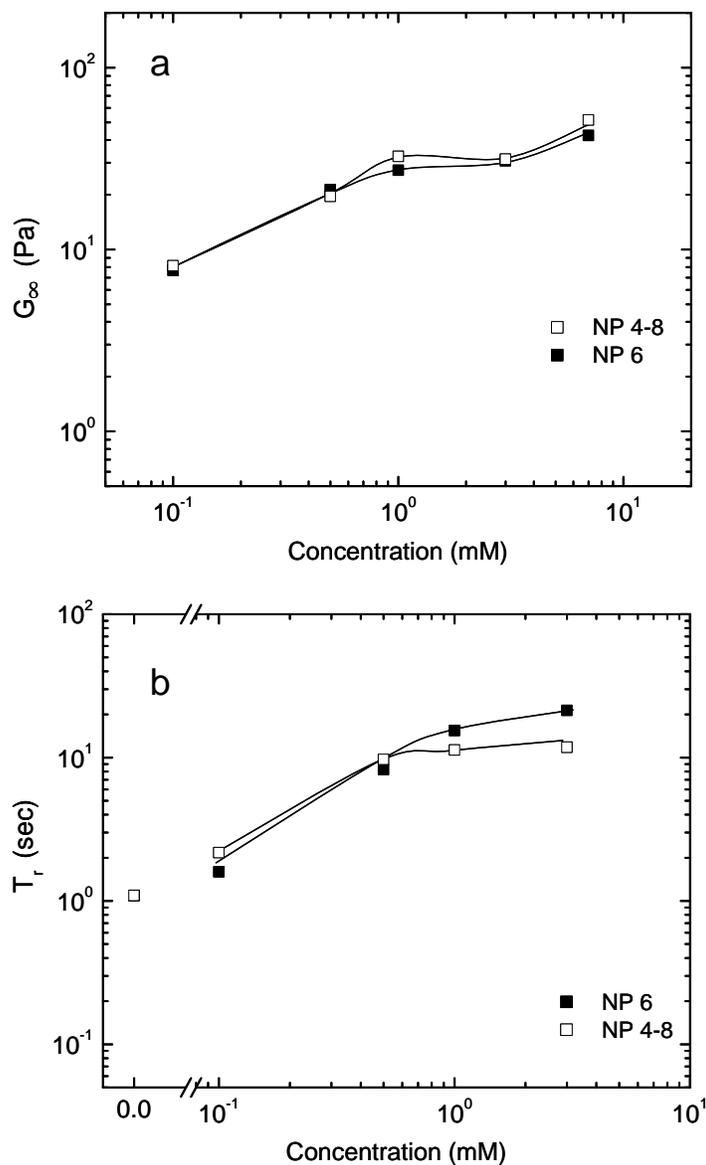


Figure 3.9. Plateau modulus G_∞ (a) and characteristic relaxation time T_r (b) as a function of NPe ($e = 4, 6$ and 8) surfactant concentration (C_{NPe}) for 0.5% HASE polymer/NPe surfactant systems. NP 4-8 denotes an equimolar mixture of NP4 and NP8.

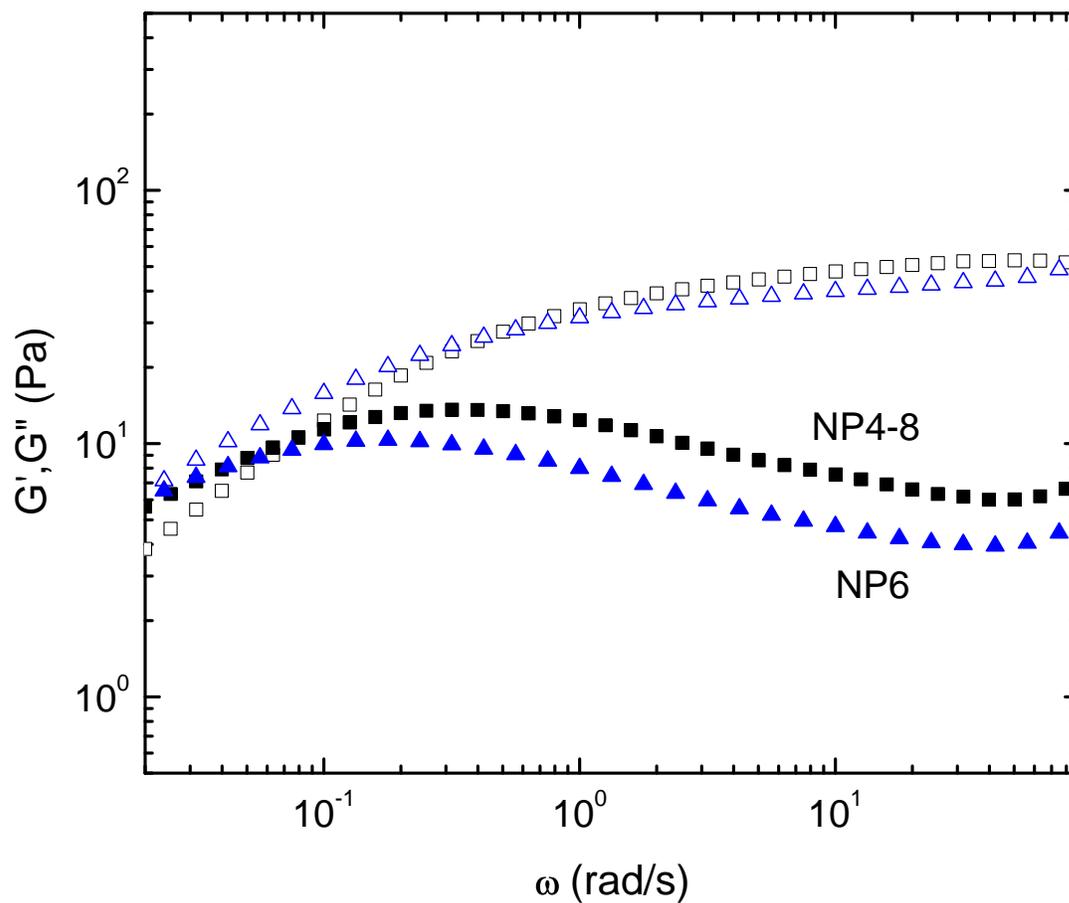


Figure 3.10. Variation of G' (unfilled symbols) and G'' (filled symbols) as a function of ω in 0.5 wt.% HASE solutions containing 7mM NP6 (triangles) and 7mM NP4-NP8 (1:1 molar ratio).

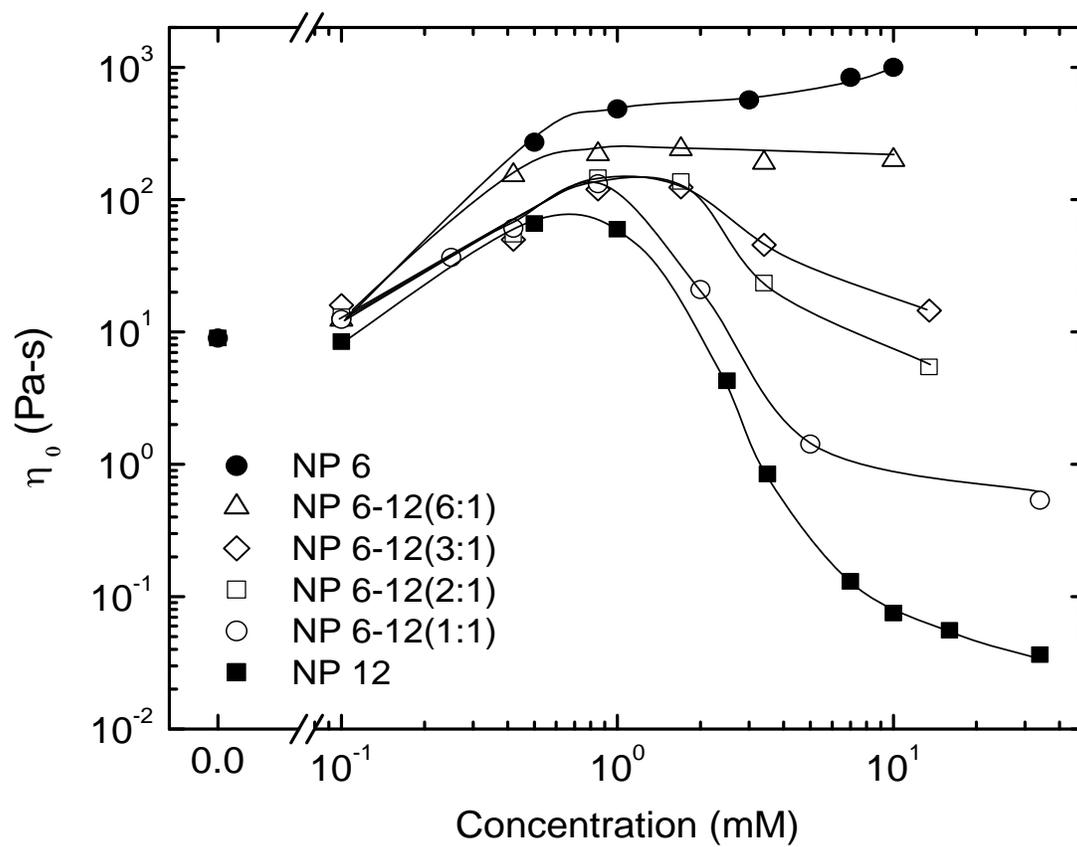


Figure 3.11. Low shear viscosity (η_0) of 0.5% HASE/NP surfactant systems as a function of surfactant concentration for different ratios of NP6-P12 mixtures.

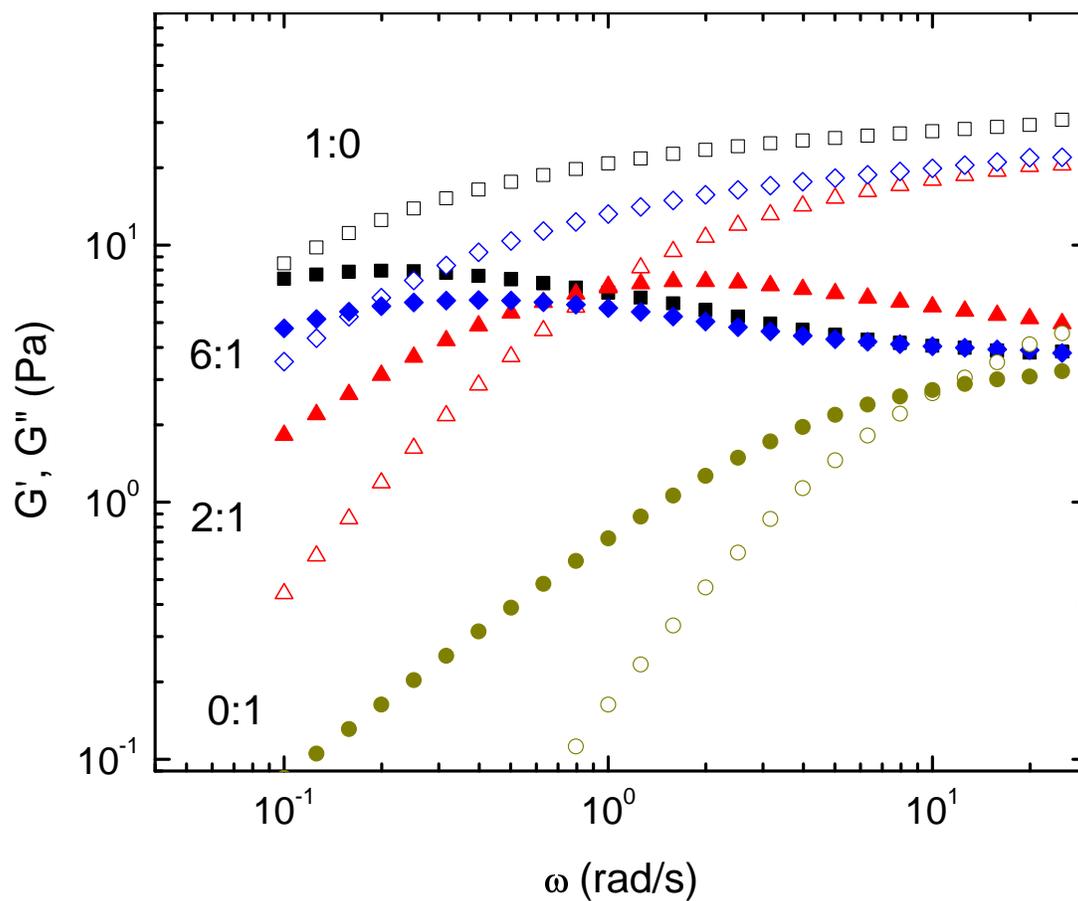


Figure 3.12. Variation of G' (unfilled symbols) and G'' (filled symbols) as a function of ω in 0.5 wt.% HASE solutions containing 3.4mM NP6-NP12 at different molar ratios.

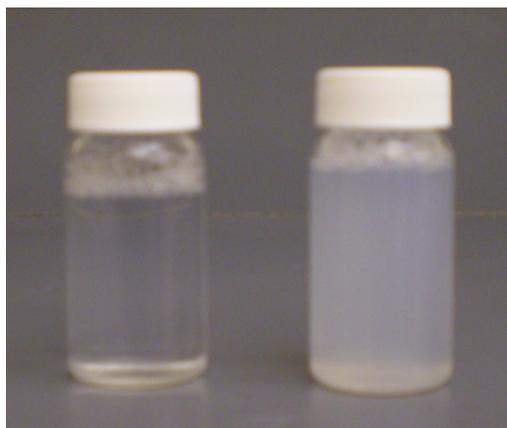


Figure 3.13: 1 wt. % aqueous solutions of equimolar NP4-NP12 surfactants (cloudy, CPT = 23°C) and equivalent NP8 surfactant (clear, CPT = 43°C) at 24°C.

CHAPTER 4

Surfactant-mediated Modulation of Hydrophobic Interactions in Associative Polymer Solutions containing Cyclodextrin

Chapter 4 is essentially a manuscript by Sachin Talwar, Jonathon Harding and Saad A. Khan prepared for submission to *Journal of Rheology*

Surfactant-mediated Modulation of Hydrophobic Interactions in Associative Polymer Solutions containing Cyclodextrin

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Abstract

The ability of nonionic surfactants to modulate and recover the rheological characteristics of hydrophobically modified associative polymers solutions containing cyclodextrin (CD) is examined. A model hydrophobically modified alkali-soluble emulsion (HASE) polymer which forms a transient physical network in aqueous solutions owing to interactions between the pendant hydrophobic groups attached to the molecule is used. The presence of either α - or β - CD results in a marked decrease in viscosity and viscoelastic properties of the polymer solution due to encapsulation of the hydrophobes in HASE polymer. Addition of nonionic surfactants to such systems alters the hydrophobic interactions by competing with the polymer hydrophobes for complexation with the CDs. In this regard, nonylphenol ethoxylates (NPe) with different ethylene oxide (EO) chain lengths which determine the hydrophilic-lipophilic balance (HLB) of the surfactant, are used. Our results reveal that depending on the type of CD (α versus β) as well as the hydrophilic-lipophilic balance (HLB) of surfactant, the extent and rate of recovery of zero shear viscosity as well as dynamic moduli are vastly different. For polymer solutions containing α - CD, recovery is observed solely in the presence of low HLB surfactants (NP6 and NP8). Additionally, in

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some cases the viscosity keeps increasing monotonically beyond the original HASE viscosity. In contrast, addition of higher HLB surfactant (NP15) to such systems does not translate into any appreciable changes in macroscopic properties. On the other hand, a complete recovery as well as further enhancement of rheological properties is achieved using the above surfactants in the case of β -CD. However, the trends of viscosity modulation are dissimilar for different surfactants as we witness a monotonous increase in case of NP6 while a maximum in viscosity is observed in the presence of NP12 and NP15. The contrasting observations can be explained in terms of varying affinities of α - and β -CDs to bind with NP surfactants and the existence of different micellar structures in solution as governed by surfactant HLB. These results are further confirmed by UV-vis spectroscopy and cloud point measurements.

4.1 Introduction

Hydrophobically modified associative polymers are water soluble polymers that have drawn considerable research attention owing to their unique thickening mechanism which renders them useful in several industrial applications such as aircraft anti-icing fluid¹, paints and coatings², and personal care products³. These polymers possess hydrophobic groups grafted onto their backbones either at the ends or in a comb-like fashion⁴⁻⁹. One class of such comb-like associative polymers are hydrophobically modified alkali-soluble emulsion (HASE) that contain pendant hydrophobic groups which interact in aqueous solution to form a transient physical network consisting of both intra- and intermolecular hydrophobic junctions^{4,10-13}. The presence of these junctions imparts distinctive rheological characteristics to these solutions including enhanced solution viscosity and a pronounced shear thinning behavior⁴.

From an application standpoint, it is at times desirable to deactivate the hydrophobic associations at one stage, thereby reducing solution viscosity, and then “reactivate” them at a later stage, thus recovering viscosity. Hydrophobic interactions in HASE polymers can be controlled to a certain extent by varying different parameters such as ionic strength¹³, pH⁸ and surfactants^{10,14-16}. However, a complete reversal of the associative behavior of these polymers cannot be accomplished by varying these parameters. An effective route to deactivate the hydrophobic associations in such systems is to use inclusion compounds called cyclodextrins¹⁷⁻²². Cyclodextrins are doughnut-shaped cyclic oligosaccharides composed of α -D-glucopyranose units and have a hydrophilic exterior and a nonpolar inner cavity. Depending on the number of glucose rings, there are three types of naturally occurring

cyclodextrin; α -, β - and γ - cyclodextrin having 6, 7 and 8 member rings respectively. Studies dealing with the inclusion complexes of CDs with a variety of organic and inorganic guest molecules in solution have been widely reported in several publications²³⁻²⁶. As has been previously reported^{18,20}, both α - and β - CDs drastically affect the rheology of HASE polymers. The inner hydrophobic cavity of CD encapsulates the pendant hydrophobic groups resulting in a disruption of hydrophobic associations which translates into reduction in both viscosity as well as viscoelastic properties of polymer solutions by several orders of magnitude. The encapsulation of hydrophobic segments by CDs has been confirmed by ¹H NMR, differential scanning calorimetry and thermogravimetric analysis. Furthermore, it has been verified that CDs do not interact with the water soluble HASE backbone¹⁸.

A unique feature of CD-hydrophobe complexation in associative polymers is the recovery of hydrophobic associations that can be achieved by using surfactants that have a stronger affinity to bind with CDs as compared to the polymer hydrophobes. Despite the importance of such systems, very few studies have explored the utility of surfactants in recovering solution rheology of hydrophobically modified associative polymers in the presence of cyclodextrin^{17,18}. Abdala *et al.*¹⁸ did some initial work on exploring the scope of viscosity recovery in HASE polymer solutions containing β - cyclodextrin by using two different nonionic surfactants. They found that the addition of surfactant to the solution leads to a near complete recovery of the viscoelastic properties. Similar viscosity recovery was observed upon addition of sodium dodecyl sulfate (SDS) in solutions containing hydrophobically modified poly(acrylic acid) wherein the hydrophobic groups were completely masked by α -cyclodextrin¹⁷.

An important aspect to be considered here is that changing the amphiphilicity of the nonionic surfactant employed is expected to influence the viscosity recovery to a large extent. This hypothesis is based on two suppositions. First, surfactant amphiphilicity, as measured by its hydrophilic lipophilic balance (HLB), is an important factor that affects the binding affinity of a surfactant with cyclodextrin. For the case of nonionic surfactants, HLB is generally defined as

$$20 \times \frac{M_H}{M_H + M_L}$$

where M_H is the molecular weight of the hydrophilic portion of the surfactant molecule and M_L is the molecular weight of the hydrophobic or lipophilic portion²⁷. A higher HLB value thus indicates higher water solubility and a higher critical micelle concentration (CMC), and vice versa. Eli *et al.*²⁸ studied the effect of nonionic surfactant HLB on the association constant between triblock polyether nonionic surfactants and β -CD. They reported that the smaller the HLB values of the nonionic surfactant, the greater the association constant with β -CD. This is intuitive as a smaller value of HLB would imply a relative more hydrophobic surfactant, and hence a stronger association with hydrophobic cyclodextrin cavity.

The second supposition is derived from the influence of surfactant HLB on polymer-surfactant interaction. In a previous study on the interactions between HASE polymer and nonionic surfactants having the same hydrophobic tail but varying lengths of hydrophilic head, the authors highlighted the role of HLB of nonionic surfactant in hydrophobic associations in solution¹⁵. Depending on the HLB of the surfactant and its concentration different trends of the rheological properties of the associative polymer in solution are

observed. These considerations make it meaningful to examine the role of surfactants with different HLB on the recovery of rheological characteristics in associative polymer solutions containing cyclodextrin.

The present study explores the effect of surfactants with different HLB on the recovery of viscoelastic properties of HASE solutions in the presence of either α - or β -cyclodextrin. To the best of our knowledge, no studies on the interaction of HASE/cyclodextrin systems with different HLB surfactants exist in the scientific literature. The surfactants used in this study are part of a homologous series of nonylphenol ethoxylate (NPe) surfactants, where e denotes the number of hydrophilic ethylene oxide groups (EO) in the surfactant molecule. We first examine the effect of surfactant concentration on the steady state as well as dynamic rheological behavior of HASE solutions in the presence of either α - or β - cyclodextrin. We then explore the role of varying surfactant HLB on the rheological response in these systems. Finally, in order to address the apparent differences in the behavior of α - and β - CD, we compare cloud point phenomena of both pure surfactant solutions and polymer/surfactant systems in the presence of different types of cyclodextrin.

4.2 Materials and Methods

The model HASE polymer used in this study was obtained from UCAR emulsion systems (Dow Chemicals, Cary, NC) in the form of aqueous latex at a solid concentration of approximately 26 wt.%. A schematic of the chemical structure of the HASE molecule is shown in Figure 4.1. The macromonomer is composed of a polyethylene oxide (PEO) spacer

with an average number of EO group equal to 40 moles and a C₂₂ alkyl group which is linked to the backbone through a urethane linkage. Details about the protocol to purify and prepare the polymer solution can be found in previous publications^{10,15,29,30}. The pH of the subsequently prepared polymer solution was adjusted between 9 and 9.5 by adding 0.1 M NaOH. The ionic strength of the samples was adjusted to 0.05M NaCl to contain any polyelectrolyte effect³⁰. Nonylphenol ethoxylates (NPe) nonionic surfactants under the commercial name of Tergitol[®] were supplied by Dow Chemicals, Cary, NC and used as received. α - and β -cyclodextrins were purchased from Cerestar and used as received.

Samples prepared were placed in a water bath overnight at 40°C to remove entrained air and subsequently left standing for 48 hrs prior to rheological measurements. All rheological experiments were performed at 25°C in a TA Instruments AR-2000 stress controlled rheometer using primarily cone and plate geometry. Both steady and dynamic shear experiments were conducted on each sample. As reported in the literature³¹, the steady shear response of HASE polymer/surfactant systems is sensitive to shear history. To overcome this issue, a preshear was applied at a strain rate of 5 s⁻¹ for 180 s followed by a rest period of 120 s. A dynamic stress sweep test was performed to determine the stress value that lied within the linear viscoelastic regime. This value was subsequently used in the dynamic frequency sweep test. All rheological experiments were run at least twice to ensure reproducibility.

UV/vis spectrophotometry measurements were performed on a JASCO V550 UV/VIS spectrophotometer (JASCO Inc., Easton, MD). Cloud point temperatures were determined visually as the temperature at the first sign of complete turbidity from clear or

slightly hazy solutions on heating and clear on subsequent cooling. The surfactant/cyclodextrin solutions were prepared in vials and kept in a constant temperature water bath. The sample temperature was controlled using digital stirring hot plate (Torrey Pines Scientific, San Marcos, CA) with the thermocouple inserted in the solution. Each measurement was conducted at least thrice to ensure accuracy.

4.3 Results and Discussion

Addition of either α - or β - CDs substantially reduces the viscosity as well as viscoelastic properties of the HASE polymer. Previous work done by our group^{18,20} shows that the drop in the value of rheological properties asymptotes off at a CD concentration of 30 moles per mole of hydrophobic macromonomer irrespective of the type of CD. This concentration corresponds to 3.3mM CD for the case of 0.5 wt.% HASE, the polymer concentration used in this study. It is believed that CDs completely encapsulate the polymer hydrophobes at this concentration, thereby breaking all hydrophobic junctions present in solution. Since we intend to investigate the effect of surfactants on the recovery of rheological properties, we selected a 0.5 wt.% HASE/3.3mM CD as one of our two reference samples, the other being 0.5 wt.% HASE polymer-only solution.

Figure 4.2 compares the viscosity behavior of various surfactants on 0.5 wt.% HASE/3.3mM α -CD solution. The molar ratio of surfactant to CD is kept constant at 3:1. As shown in the figure, addition of 3.3mM CD to the base polymer causes a reduction in steady state viscosity by almost two orders of magnitude. Upon addition of surfactants, contrasting

behaviors are observed depending on the surfactant HLB. Compared to the original HASE solution, the viscosity is two orders of magnitude higher in case of NP6 while no viscosity recovery is witnessed for solutions containing NP15. NP8, which has an intermediate HLB between NP6 and NP15, exhibits a viscosity profile overlapping with the original HASE solution at low stresses. In the following sections, we probe further the observed dramatic differences by exploring the rheological behavior and clouding phenomena in HASE solutions containing either α - or β -CD at different concentrations of the abovementioned surfactants.

4.3.1 Viscosity Modulation by Incorporating NP6 surfactant

Figure 4.3 shows the viscosity versus stress profile for 0.5 wt. % HASE solutions containing α - CD in the presence of NP6 surfactant. NP6 is a low HLB surfactant and its addition to pure HASE polymer solution is known to cause a continuous increase in low shear viscosity with increasing surfactant concentration, which is ascribed to the formation of large lamellar structures by surfactant molecules^{15,31}. A systematic addition of NP6 surfactant to this HASE/CD system leads to an increase in solution viscosity. At low concentrations of NP6, the solutions exhibit a viscosity profile mimicking that of the HASE/ α -CD system; a steady decline in viscosity with increasing stress. With further increase in NP6 concentration, viscosity profile becomes increasingly shear thinning at low stresses. The low shear viscosity of the original HASE solution without any CD is completely recovered at 5mM NP6 concentration corresponding to 1.5 guest NP6 molecules per single host CD molecule. The association between surfactant and CD is apparently strong enough to remove CDs from

HASE polymer hydrophobes, thereby reactivating the hydrophobic junctions to form the transient network. Upon further increasing NP6 concentration to 10mM (or 3:1 NP6:a-CD), the viscosity becomes almost two orders of magnitude higher than the original HASE solution and the solution exhibits a sharp drop in viscosity at a critical stress. The rise of viscosity over and above the original HASE viscosity can be attributed to interactions between NP6 and “free” polymer hydrophobes to form hydrophobic junctions incorporating both surfactant and polymer hydrophobes^{15,32}. An interesting observation is the relative magnitudes of viscosity observed for 1.5:1 NP6:a-CD solution versus that of 5mM NP6 in the absence of any CD (shown in the same figure). The fact that viscosity of the latter solution is much higher than the one with CD at the same surfactant concentration suggests that a smaller number of surfactant molecules present in solution are able to participate in hydrophobic junctions with the rest forming complexes with cyclodextrin.

Another notable feature is the more pronounced shear thinning behavior in solutions containing NP6 compared to original HASE solution. A possible cause of this enhanced shear thinning is the existence of an equilibrium wherein some of the hydrophobes still remain masked by cyclodextrin and hence do not contribute to hydrophobic associations while uncomplexed NP6 molecules participate in the “reactivated” junctions. This argument gains credence from the viscosity profile of HASE/CD solution at higher NP6 concentration (3:1). We notice a drastic drop in viscosity at a critical stress which is significantly lower than that observed in pure HASE/NP6 solution. Similar drastic drop in viscosity has previously been observed in associative polymer/surfactant systems and is attributed to the disruption of the associative network when the applied stress exceeds the overall strength of

the hydrophobic junctions^{33,34}. Therefore even at high NP6 concentration, some of the hydrophobes are likely to be encapsulated with cyclodextrin resulting in a weaker network of hydrophobic junctions. Thus we expect a portion of the hydrophobes to participate in the hydrophobic junctions and interact with surfactant molecules while the remainder of it presumably stays encapsulated by cyclodextrin.

We attempt to derive additional information on the molecular interactions in solution by conducting dynamic rheological experiments on some selected systems. The dynamic frequency spectrum of 0.5 wt.% HASE/ α -CD solutions in presence of NP6 surfactants is shown in Figure 4.4. The frequency spectrum of 0.5 wt.% HASE solution displays a viscous dominated response ($G'' > G'$) at low frequencies followed by a elastic dominated behavior ($G' > G''$) at higher frequencies. The inverse of the crossover frequency – the frequency at which G' equals G'' - gives the characteristic relaxation time of these systems which is an estimate of the average strength of the mechanically active hydrophobic junctions in solution. Thus, with the formation and strengthening of a network, this crossover is expected to move to lower frequencies or longer time scales and vice versa. Moreover, transient network theory predicts that the elastic modulus at high frequencies is directly proportional to the number of mechanically active junctions^{35,36}. The addition of α -CD to the HASE solution served to reduce both elastic and loss moduli and increased their dependence on frequency as has been observed earlier¹⁸. These results imply an overall weaker network structure arising from a reduction in the number of active junctions in HASE solution due to deactivation of the hydrophobic groups.

Upon the addition of NP6, both G' and G'' values trend upwards, following the trends exhibited by the low shear viscosity of each sample. In addition, as concentration of surfactant increases, the response becomes elastic dominated with G' values surpassing those of G'' in the frequency range studied and both the moduli exhibit a lower dependence on frequency. The cross over frequency, although not observed in the frequency range studied appears to shift to lower values indicating the strengthening of polymer network. These results further support the notion that addition of NP6 removes CDs from polymer hydrophobes thereby reactivating original hydrophobic junctions and the resulting transient network. At the highest concentration of NP6 studied, the values of dynamic moduli exceed those of the original HASE solution with G' greater than G'' over the entire frequency range. This response is typical of gel-like behavior in the system and has been witnessed earlier in certain associative polymer systems³⁷. The presence of a gel-like structure is further corroborated by the viscosity profile for the above polymer/surfactant/CD system (*cf.* Figure 4.3) which displays a drastic drop in viscosity at a critical stress similar to the yield stress phenomena associated with physical gels³⁸.

Figure 4.5a shows the steady shear profile for 0.5 wt. % HASE solutions containing β - CD in the presence of NP6 surfactant. We see that the extent of viscosity reduction of original HASE solution is less in case of β - as compared to α - CD. These results are consistent with observations made by Mahammad *et al.*^{18,20} for the same polymer/CD systems, albeit for higher HASE concentrations. As in the case of α -CD, adding NP6 to mixtures of HASE and β -CD greatly increases solution viscosity, with high concentrations of NP6 leading to zero shear viscosities well in excess of an order of magnitude than that of

original HASE solution. At low NP6 concentrations, viscosity profiles match that of a HASE/CD solution without any surfactant – low viscosity, uniform shear thinning without any sudden drop at higher stresses - while at higher concentrations, considerably larger low shear viscosities are obtained that show a sudden drop at high stresses. However, an obvious difference in viscosity recovery between the two cases of α - and β - cyclodextrin lies in their rates upon NP6 addition. Whereas in case of α -CD, complete viscosity recovery of the original solution is observed at the NP6 to CD ratio of 1.5:1, the same ratio in case of β -cyclodextrin results in a viscosity over an order magnitude higher than that of original HASE solution. This reflects a stronger affinity of β - versus α - cyclodextrin towards the nonionic surfactant. The trends of dynamic moduli are consistent with those of steady state viscosity profile and the moduli exhibit a stronger recovery when compared to the case of α -CD (Figure 4.5b). We verify this aspect subsequently in later sections by exploiting the clouding behavior of NP surfactants.

4.3.2 Role of Surfactant HLB in Viscosity Modulation

Since HLB of a nonionic surfactant plays a significant role in determining both surfactant-CD and surfactant-polymer interactions, varying the nonionic surfactant HLB is expected to affect viscosity recovery in HASE solutions containing cyclodextrin. Thus far, we considered NP6 surfactant which is a water-insoluble low HLB surfactant. We now explore viscosity recovery from nonionic surfactants of the same homologous series but with longer hydrophilic parts (or higher HLB values). We select NP8 and NP15 surfactants having average ethylene oxide (EO) chain lengths of 8 and 15 respectively. Similar to NP6, the

addition of NP8 to mixtures of HASE and α -CD increases the viscosity of the solution with increasing concentration (Figure 4.6a). The recovery, however, is retarded in this case, reflecting a weaker affinity of NP8 to bind with α -CD. Moreover, unlike NP6, wherein the low shear viscosity is almost two orders of magnitude higher than original solution viscosity at 10mM concentration (3:1 NP8: α -CD), the solution viscosity did not exceed HASE viscosity at this ratio. The viscosity stabilized at values close to the original HASE solution, as both 10 mM NP8 with 3.3 mM α -CD and 19 mM NP8 with 2.2 mM α -CD (not shown for the sake of clarity) showed very similar viscosity profiles. An even more contrasting behavior to that of NP6 is observed in case of NP15 surfactants (Figure 4.6b). A systematic addition to HASE/ α -CD solution does not demonstrate any appreciable effect on either low shear viscosity or its stress profile. While viscosity does vary slightly, these variations are minimal and do not provide a meaningful trend. The viscosity of HASE/CD solution is unaffected by the presence of NP15 indicating the absence of any NP15-CD complexation or removal of α -CDs from polymer hydrophobes. Evidently, interactions between polymer hydrophobe and surfactant are subdued in case NP8 and minimal for NP15 as it would be reasonable to assume that for those interactions to exist, polymer hydrophobes would first need to be “unmasked” of CDs and be free to interact with surfactant. These results indicate a stronger affinity of α -CD to bind with nonionic surfactants with a more hydrophobic character (lower HLB). The efficacy of viscosity recovery in HASE/ α -CD solutions appears to be strongly dependent on the hydrophilic chain length and in turn HLB of the nonionic surfactant.

An entirely different trend of viscosity recovery is witnessed upon NP8 addition in case of HASE solutions containing β -CD instead of α -CD as shown in Figure 4.7a. Low concentrations of NP8 dramatically increase the magnitude of low shear viscosity, while maintaining the steady shear thinning and without a pronounced drop in viscosity at higher stresses. Instead of a monotonous increase as with α -CD, the viscosity exhibits a maximum at NP8 concentration of 3.3mM which corresponds to NP8 to CD ratio of 1:1. The low shear viscosity at this concentration is almost a magnitude higher than original HASE solution and shows a sudden drop in viscosity as seen earlier in case of NP6. Increasing surfactant concentration beyond this point lowered the viscosity of the solutions from its maximum to around that of original HASE solution at the maximum studied concentration. Another notable observation is the viscosity profile of solutions at higher concentrations show a gradual shear thinning behavior as opposed to a drastic drop. These observations can be explained in terms of negative interaction between NP8 and HASE polymer at higher surfactant concentrations. It has been reported earlier that increase in NP8 concentration in pure HASE polymer solution results in an increase in viscosity and viscoelastic properties of HASE solution to a maximum followed by a decline. The rise in viscosity has been attributed to the formation of mixed micelles incorporating both polymer and surfactant hydrophobes resulting in a stronger overall network while the ensuing decrease in viscosity is the result of saturation of polymer hydrophobes by surfactant micelles at higher concentrations^{15,32}. These surfactant-saturated polymer hydrophobes are unable to participate in hydrophobic junctions thereby weakening the overall network, which translates into a lower viscosity and gradual shear thinning as opposed to a sudden drop in viscosity. The frequency spectrum of dynamic

moduli for these systems (Figure 4.7b) further confirms the above hypothesis wherein addition of NP8 results in an initial increase in moduli above that of original HASE solution at 1:1 NP8 to β -CD ratio followed by lower values of moduli at surfactant to CD ratio of 3:1. Moreover the dynamic moduli become less frequency dependent at first and then revert back to higher frequency dependence reflecting formation and strengthening of a network structure upon NP8 addition and subsequent weakening at higher concentrations. Similar observations are made in the trend of viscosity recovery of HASE solution containing β -CD in the presence of NP15 surfactant (Figure 4.8). A notable difference however is the maximum in viscosity achieved upon NP15 addition which is greater than HASE viscosity but significantly lower than that in the case of NP8. This is not completely unexpected as NP15 addition to pure HASE solution does not result in an appreciable increase in viscosity¹⁵.

The above observations highlight the distinction in the complexation behavior of α - versus β -cyclodextrin with nonionic surfactants. In case of α -CD, increasing the surfactant HLB diminishes the formation of surfactant-CD complexes which results in either a retarded response (NP8) or absence (NP15) of viscosity recovery upon surfactant addition. On the other hand, in case of β -CD, the surfactant-CD complexation is apparently not affected much by changing surfactant HLB and the trends of viscosity appear to be dictated by interactions between surfactant and polymer hydrophobes. Nonetheless, HLB values play a vital role in these systems as the surfactant-polymer interactions are, in turn, governed by surfactant HLB as previously reported. In order to further understand the difference in the complexation behavior of α - versus β -cyclodextrin with nonionic surfactants, we investigate the clouding

behavior of these surfactants in presence of both α - and β -cyclodextrin as discussed in the next section.

4.3.3 Clouding Phenomena in NP surfactants

A unique characteristic of oxyethylated nonionic surfactants is the display of clouding phenomena due to surfactant phase-separation into micelle-rich and micelle-poor phases above a certain temperature. This behavior is explained in terms of formation of larger aggregates as well as stronger interaction between micelles owing to the dehydration of EO groups with increasing temperature²⁷. The temperature at which the aqueous solutions become visibly turbid is termed as the Cloud Point Temperature (CPT). In general, it has been observed that cloud point temperatures of polyoxyethylene surfactants decrease with increase in the number of EO units present in the molecule. For instance, above their CMC values, NP6 is cloudy at ambient temperatures while the CPT of NP15 is greater than 100°C. An interesting feature of CD-surfactant complexation is the introduction of a new equilibrium in the system that interferes with the self-assembly of surfactants into micelles or other aggregates²⁶ which in turn influences their clouding phenomena. Martinez *et al.*³⁹ studied the interaction of NP5 surfactant with β cyclodextrin in terms of its clouding behavior. According to the authors, addition of β cyclodextrin declouds NP5 surfactant solution by binding with the hydrophobic group of the surfactant molecule. This surfactant-CD complexation disrupts the surfactant aggregates and inhibits phase separation. Cyclodextrin induced shift in CPT was also observed by Na *et al.*⁴⁰ wherein addition of 2-

hydroxypropyl- β -cyclodextrin effectively raised the CPTs of a variety of nonionic surfactants, especially those having a benzene ring.

To further our understanding of the nature of CD-surfactant interactions in α - and β -cyclodextrin, we performed a series of cloud point experiments on CD-surfactant mixtures. As aforementioned, NP6 surfactants are insoluble in aqueous solutions and hence cloudy at room temperature at concentrations above their CMC and have a CPT less than 0°C. Figure 4.9 shows images of 1mM NP6 solution by itself as well as in the presence of α - and β -cyclodextrin. As can be seen in the figure, a laser beam projected through NP6 solution shows scattering in solution, presumably due to presence of aggregates. Upon the addition of cyclodextrin to surfactant solution, NP6 to CD molar ratio being 1:2, no scattering is visible in the presence of β -cyclodextrin while scattering of laser beam persists in solutions containing α -cyclodextrin. These observations clearly reflect a stronger affinity of NP6 to β -cyclodextrin as compared to α -cyclodextrin. β -cyclodextrin encapsulates the hydrophobic group of surfactant causing a disruption of aggregates and hence the declouding. On the other hand, existence of scattering in case of α -cyclodextrin implies partial or no disruption of the micellar aggregates signifying a weaker binding of NP6 with α -cyclodextrin. We followed up these qualitative measurements with quantitative UV vis spectroscopy measurements on solutions with NP6 to CD ratios of 1:1 and 1:2 (Figure 4.10). As is evident from the transmittance curves in the visible spectrum, addition of β -cyclodextrin to NP6 solution increases its transmittance significantly and approaches 100% at 1:2 NP6:CD ratio, confirming the housing of NP6 hydrophobe within the cavity of β - cyclodextrin. In contrast

to β -cyclodextrin, the transmittance curve of NP6 solutions containing α -cyclodextrin is slightly lower than that of pure NP6 solution at 1:1 NP6:CD ratio. The % transmittance increases on further addition of α -CD but the values are considerably lower than those in the presence of β -CD. These results further confirm a stronger affinity of binding of NP6 with β -CD. This dependence of degree of binding on the type of CD is generally explained in terms of the difference in their cavity diameter ($\sim 5.2\text{\AA}$ for α and $\sim 6.6\text{\AA}$ for β -CD) which affects the snugness of the fit between the host and the guest molecule^{20,21,26,41}. As a next step, we measured the transmittance in NP6/CD solutions in the presence of 0.5 wt.% HASE (Figure 4.11). The CD concentration was fixed at 3.3mM as used in the rheological studies. HASE solutions show similar high transmittance values in presence of either α - or β -CD. As NP6 is added to these solutions in 1:2 NP6:CD molar ratio, the transmittance decreases in both the cases. Here again we find a much higher transmittance in the case of β - versus α -CD upon NP6 addition. A higher transmittance corresponds to smaller number of NP6 molecules present as self-aggregates and hence less cloudiness. This in turn implies more NP6 surfactants are complexed with β -CD suggesting a stronger binding affinity.

In the case of soluble surfactants such as NP8 that are not cloudy at room temperature, we measured the CPTs of surfactant solutions with and without CDs. Addition of β -CD to a 5mM solution of NP8 in 1:2 NP:CD ratio raised its CPT from 50°C to 79°C. On the other hand, addition of α -CD causes a minor reduction of CPT to 46°C. These findings indicate that while β -CD delays the formation of micellar aggregates by encapsulating the surfactant hydrophobic groups, the interactions of α -CD with the surfactant hydrophobic

group are not strong enough to be reflected in an appreciable change in CPT. These differences in the binding affinities of CDs are reflected in the extent and the rate of viscosity recovery of HASE solutions using surfactants.

4.4 Conclusion

The modulation of hydrophobic interactions in HASE solutions in the presence of cyclodextrin is strongly affected by both the type of cyclodextrin as well as HLB of the nonionic surfactant. Entirely different trends of viscosity as well as dynamic moduli are observed in case of low water-soluble surfactant (NP6) as compared to highly soluble surfactants (NP8, NP15). Raising surfactant HLB in case of HASE/ α -CD solutions shows a transition from a monotonous increase in low shear viscosity in case of NP6 to an absence of viscosity recovery in case of NP15. On the other hand, HASE/ β -CD mixtures exhibit complete recovery and further viscosity enhancement upon addition of the surfactants studied. However, unlike NP6, addition of NP8 and NP15 leads to a lowering of viscosity at higher concentrations after attaining a maximum. These results are explained in terms of a stronger binding affinity of nonionic surfactants for α - versus β -CD as confirmed by UV-vis spectroscopy and cloud point measurements. Moreover, the binding affinity decreases with increasing surfactant HLB especially in the case of α -CD. The interaction of surfactant molecules with the polymer hydrophobes, as governed by surfactant HLB, plays a dominant role in determining the eventual viscosity values once the original HASE viscosity is recovered. These results imply that surfactant HLB is a key factor to be considered while

employing surfactants to facilitate rheological modification in HASE solutions containing cyclodextrin.

4.5. References

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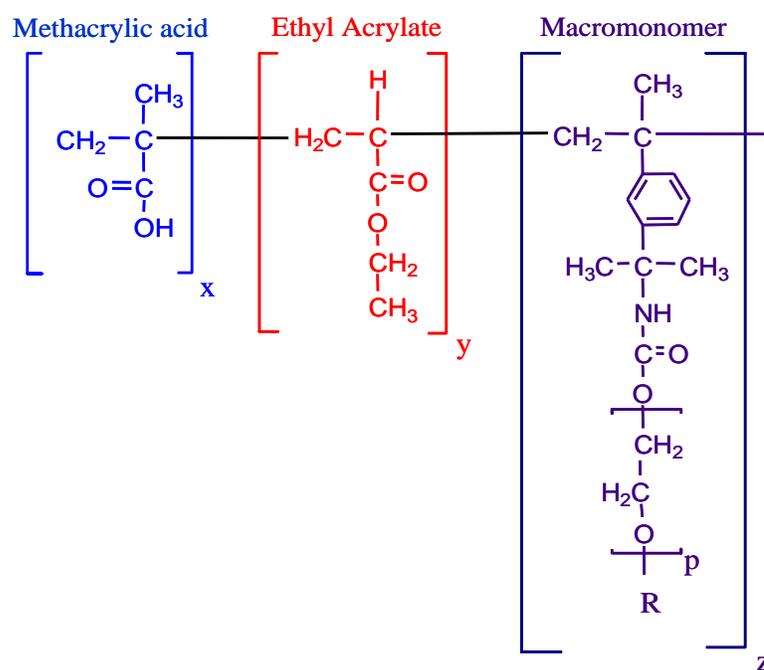


Figure 4.1. Molecular structure of the model HASE polymer. R: C22 alkyl chain polymer hydrophobe, P: 40 EO polyethylene oxide spacer, $x/y/z = 43.57/56.21/0.22$.

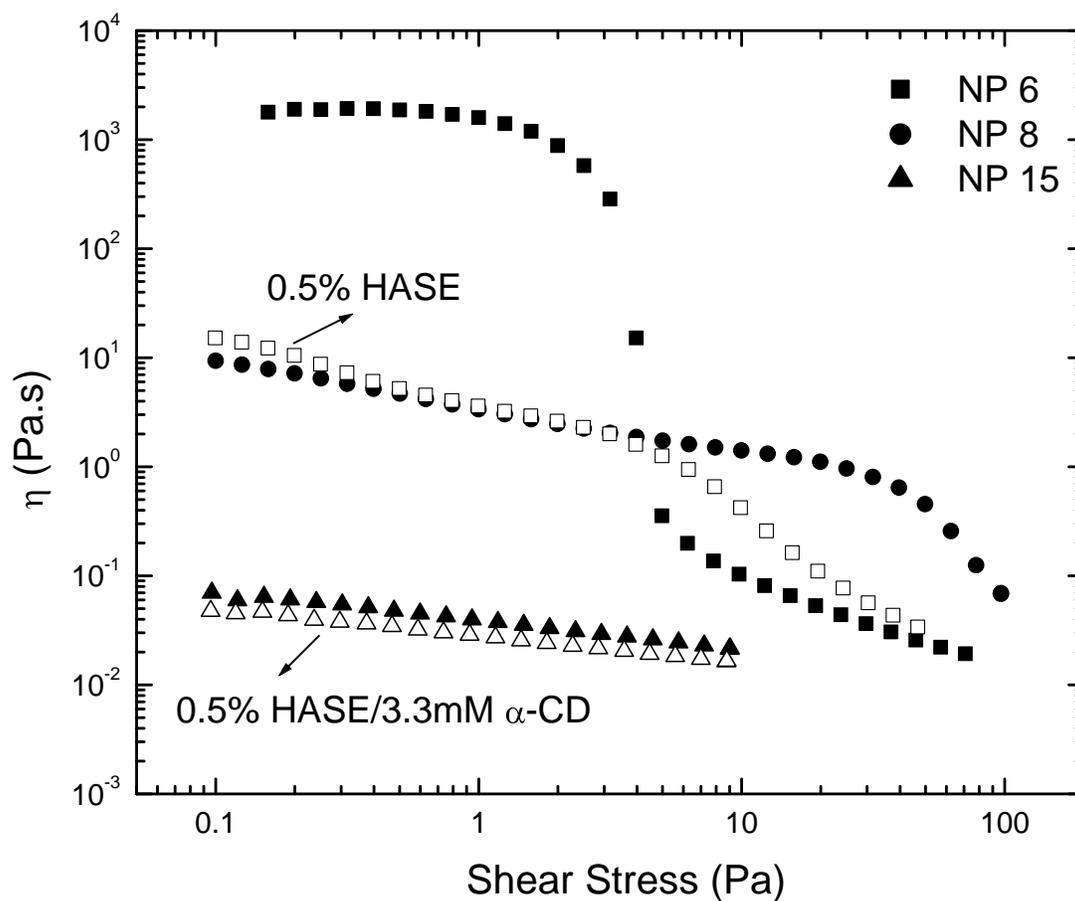


Figure 4.2. Effect of addition of various NP surfactants on steady shear viscosity of 0.5 wt.% HASE solution containing 3.3mM α -CD. The molar ratios of NP: α -CD is 3:1.

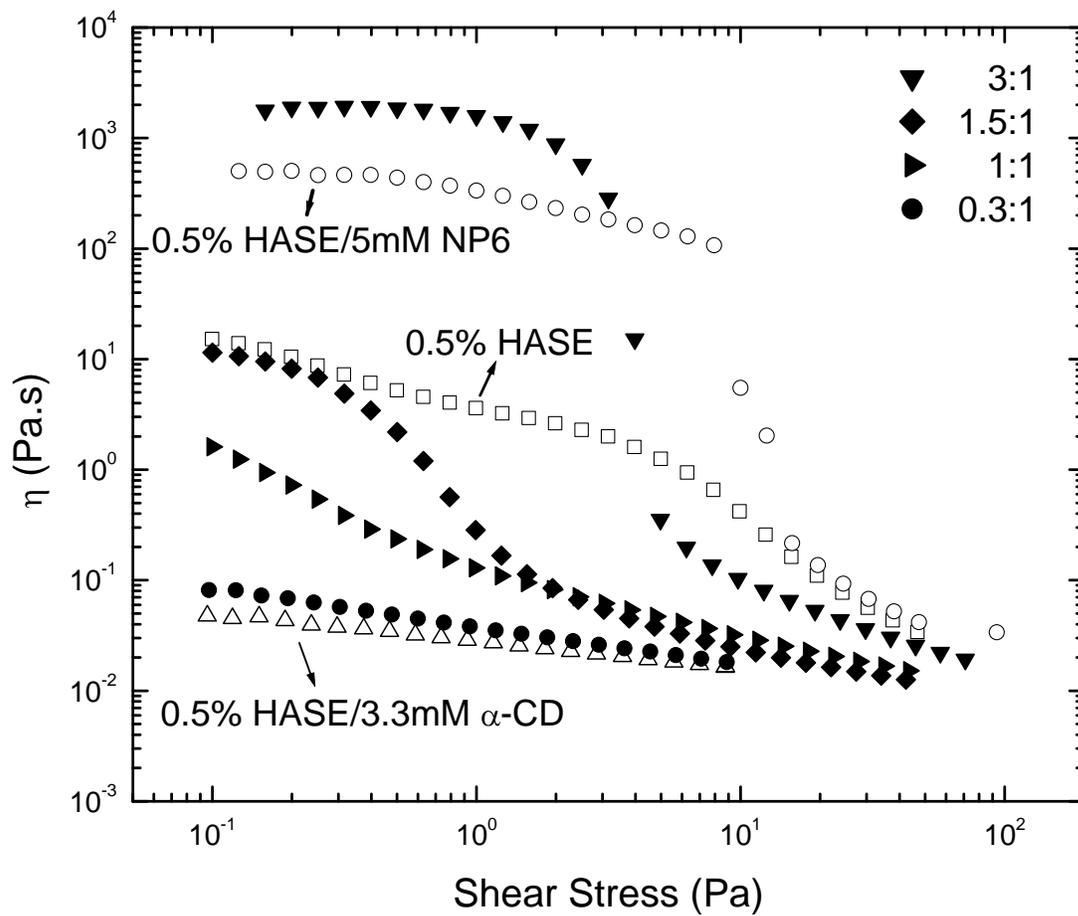


Figure 4.3. Effect of NP6 addition on steady shear viscosity of 0.5 wt.% HASE solution containing 3.3mM α -CD. The legends show the molar ratios of NP6: α -CD.

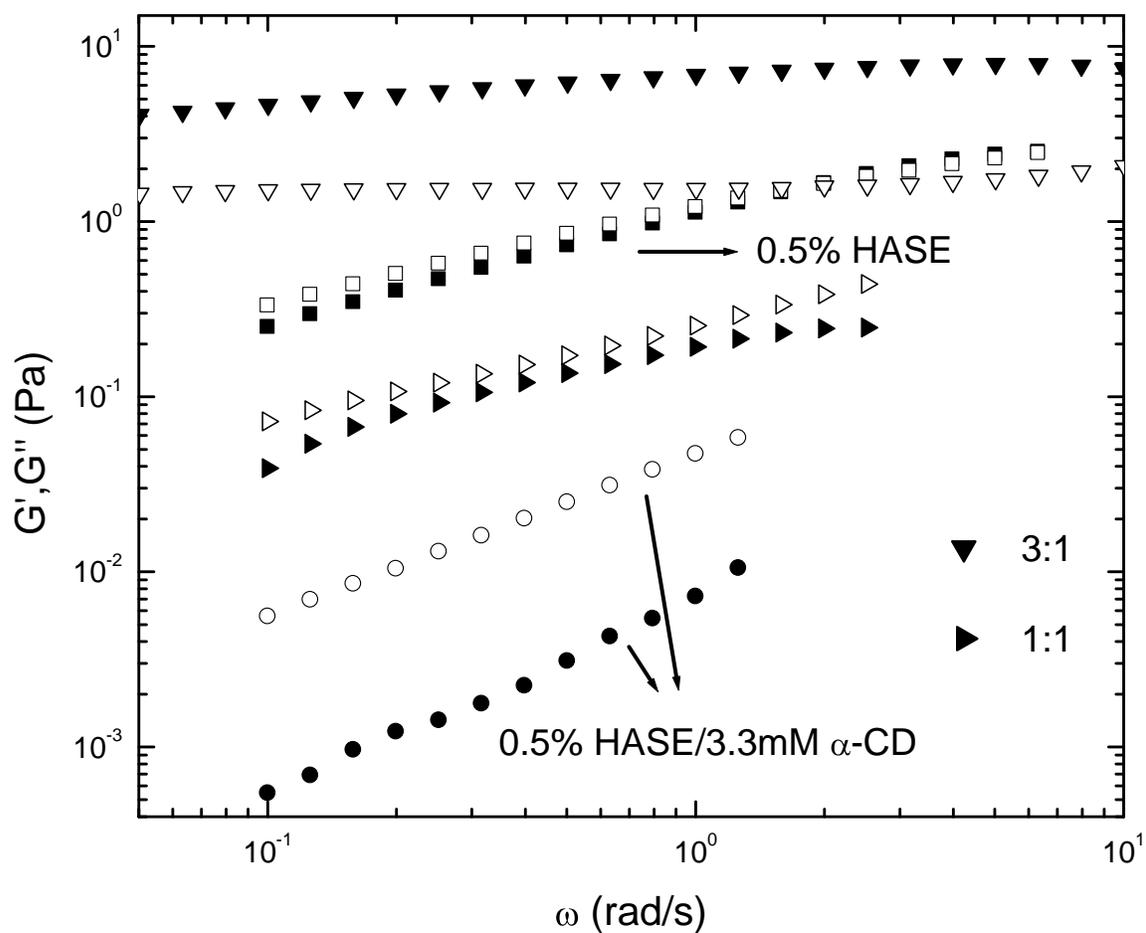


Figure 4.4. Effect of NP6 addition on dynamic elastic (G') and viscous (G'') of 0.5 wt.% HASE solution containing 3.3mM α -CD. The legends show the molar ratios of NP6: α -CD. Closed symbols denote G' and open symbols denote G'' .

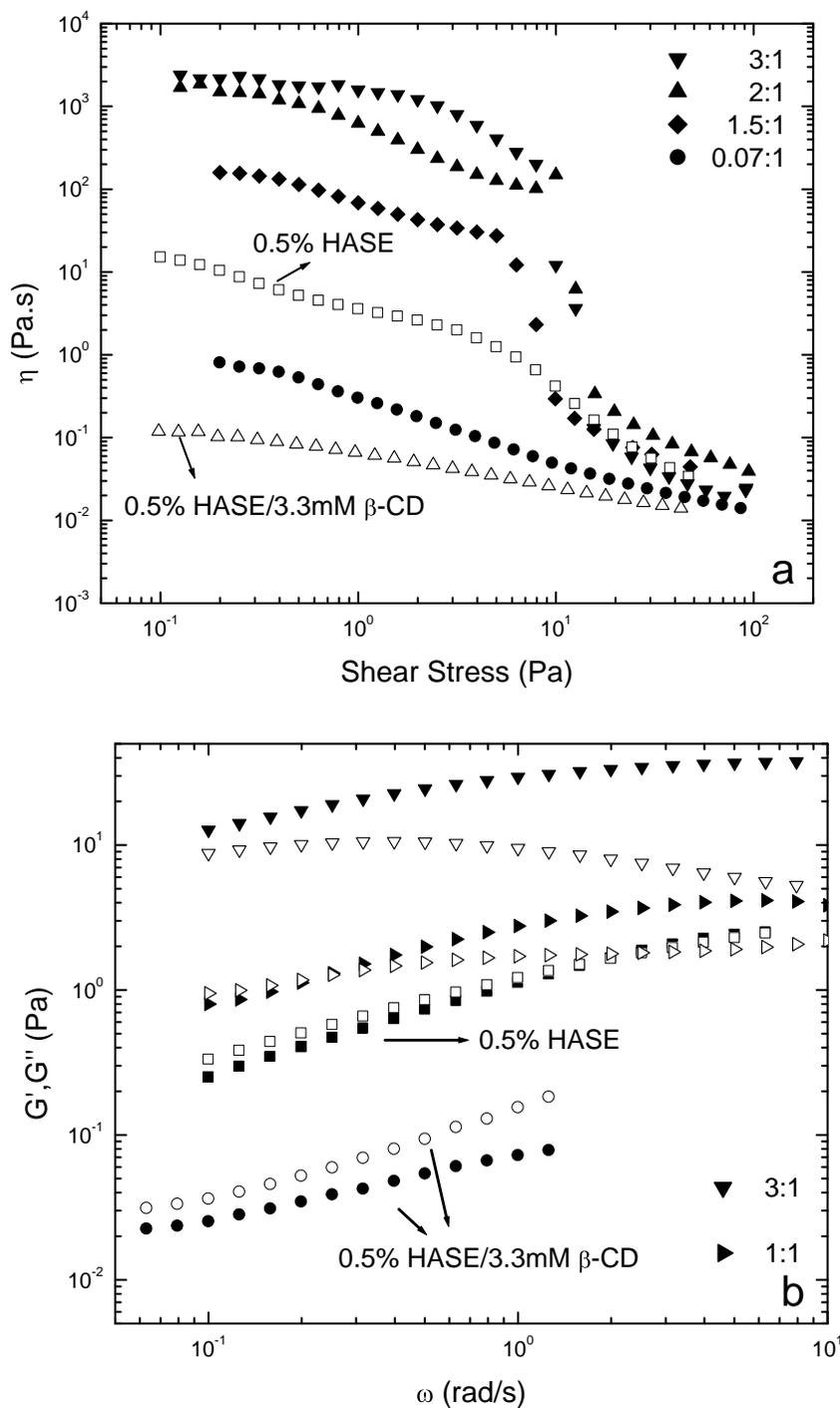


Figure 4.5. Effect of NP6 addition on a) steady shear viscosity, and b) dynamic moduli of 0.5 wt.% HASE solution containing 3.3mM β -CD. The legends show the molar ratios of NP6: β -CD. Closed symbols denote G' and open symbols denote G'' .

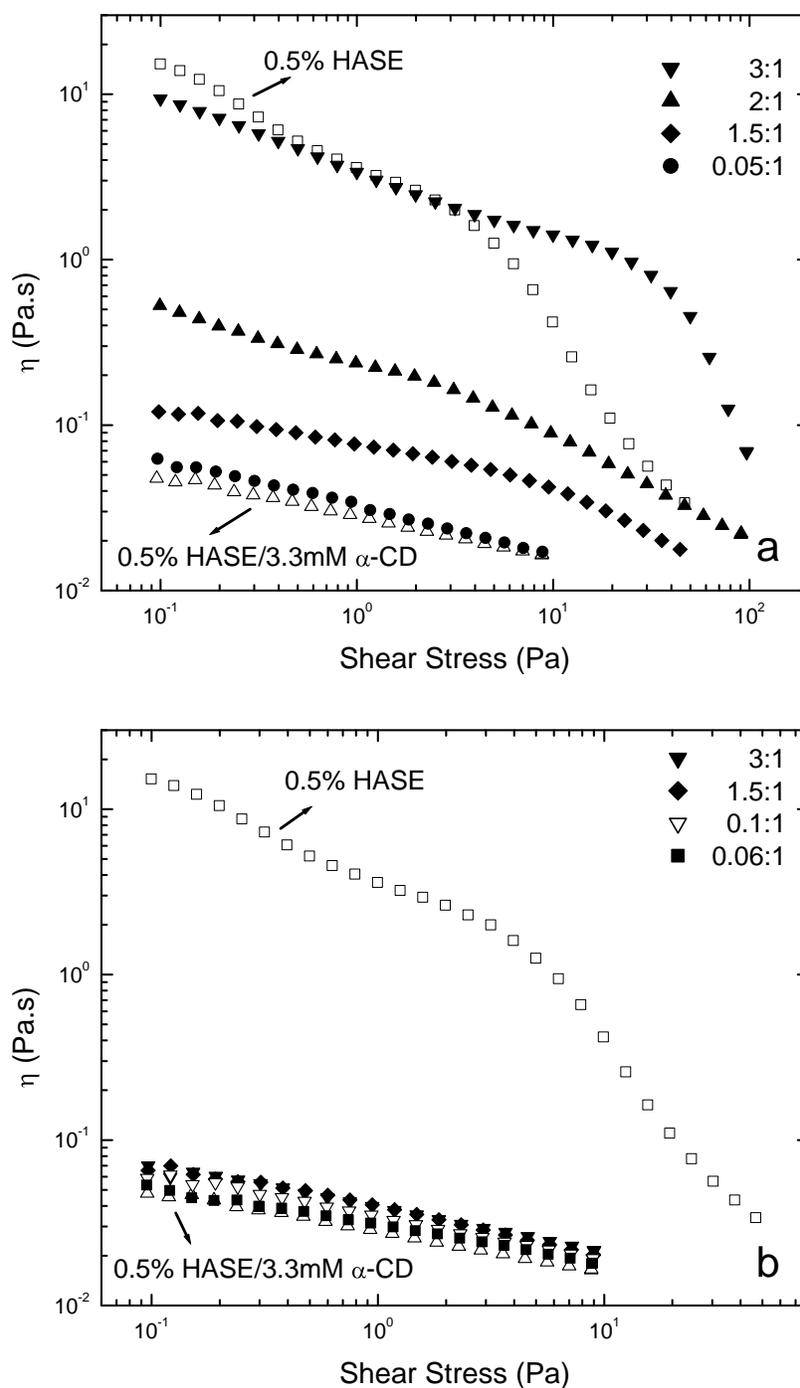


Figure 4.6. Effect of addition of a) NP8, and b) NP15 addition on steady shear viscosity of 0.5 wt.% HASE solution containing 3.3mM α -CD. The legends show the molar ratios of NP6: α -CD.

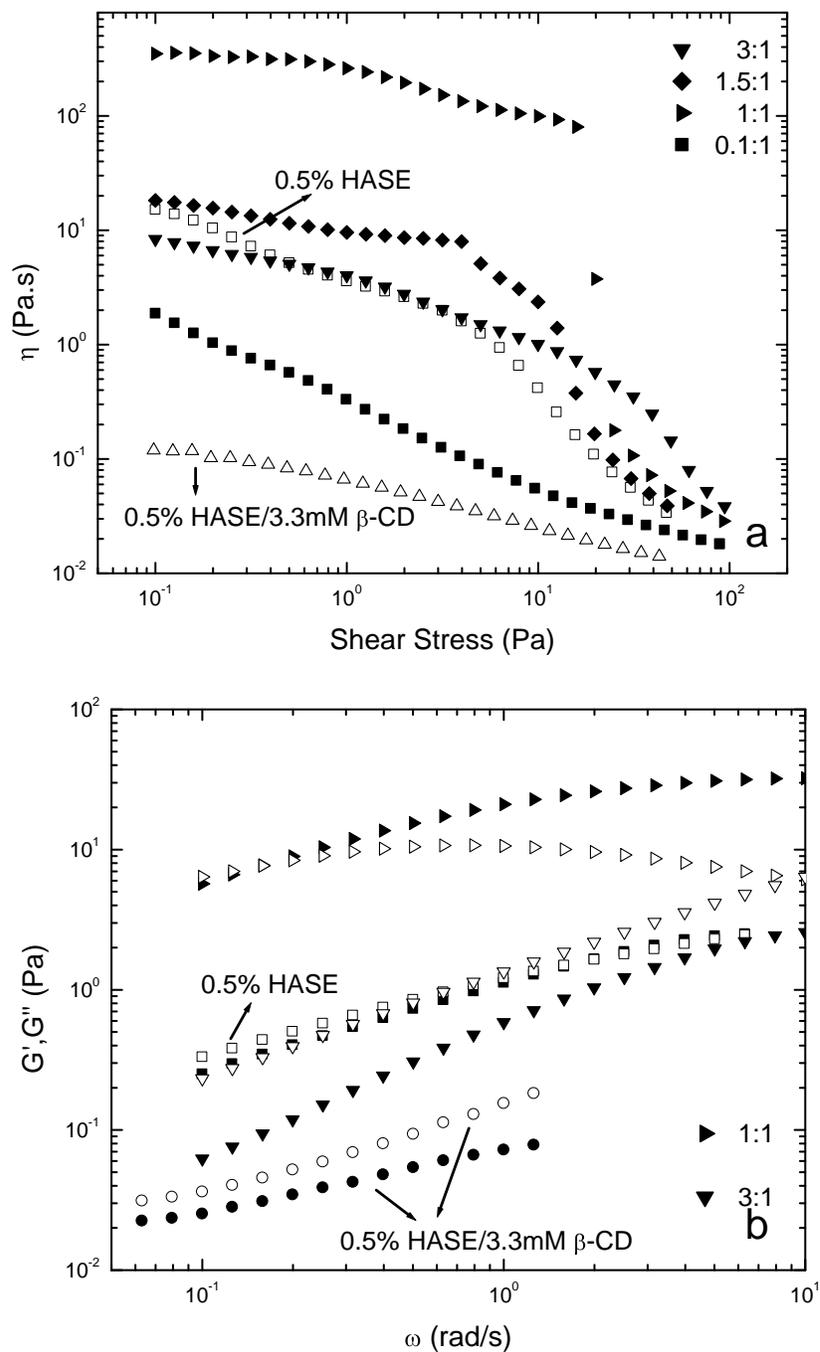


Figure 4.7. Effect of NP8 addition on a) steady shear viscosity, and b) dynamic moduli of 0.5 wt.% HASE solution containing 3.3mM β -CD. The legends show the molar ratios of NP8: β -CD. Closed symbols denote G' and open symbols denote G'' .

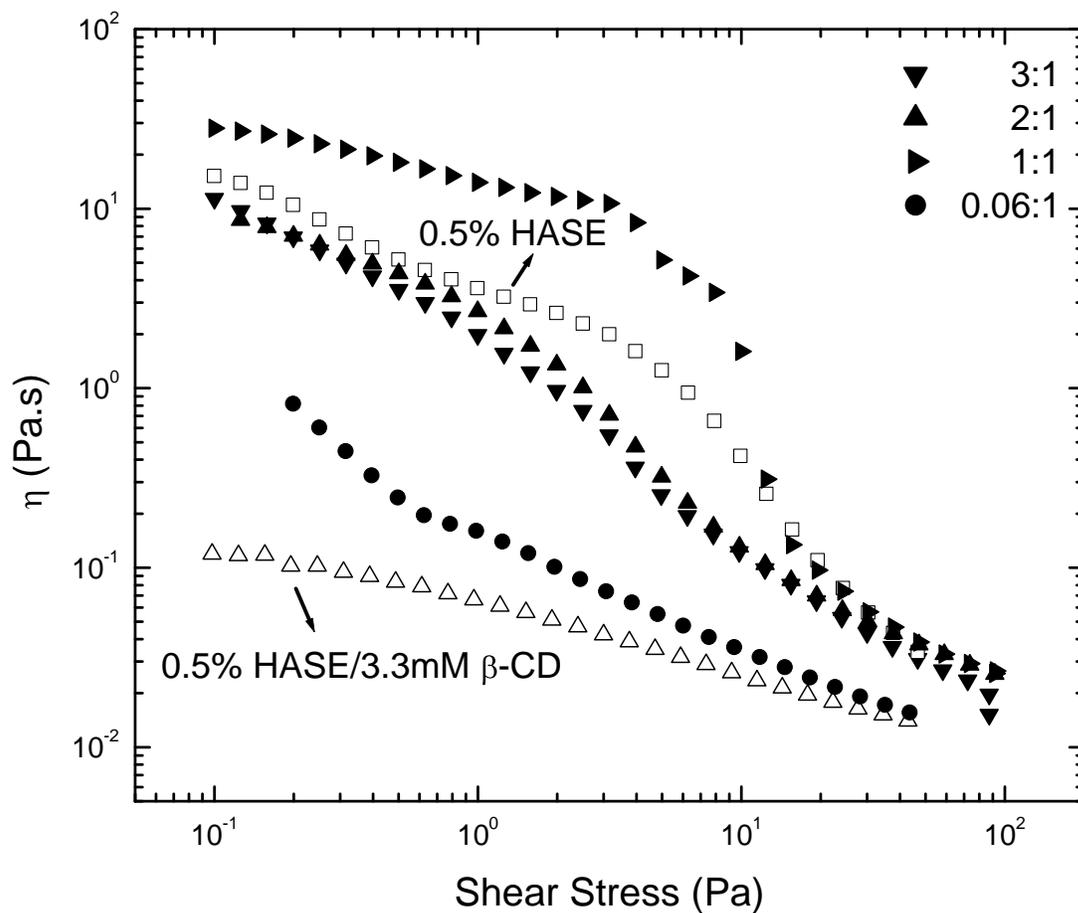


Figure 4.8. Effect of NP15 addition on steady shear viscosity of 0.5 wt.% HASE solution containing 3.3mM β -CD. The legends show the molar ratios of NP6: β -CD.

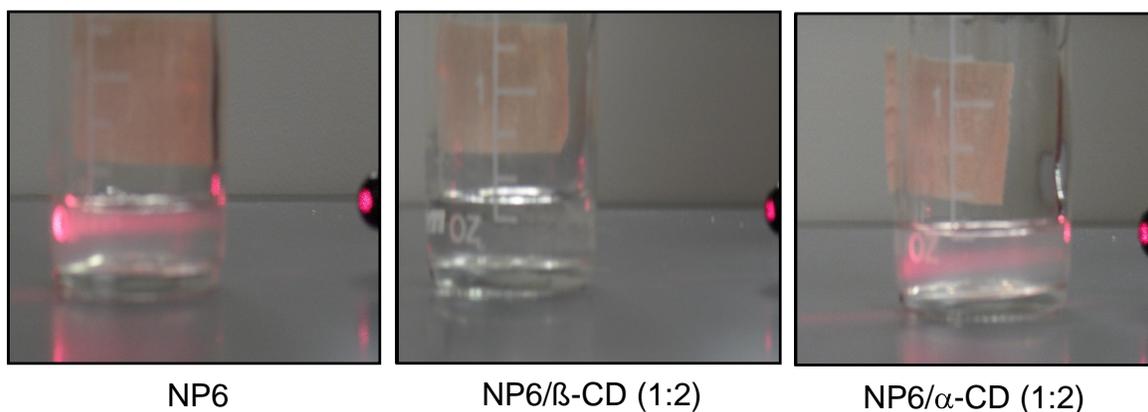


Figure 4.9. Scattering of laser beam in 1mM NP6 solution with and without the presence of α - and β -cyclodextrin in 1:2 molar ratio. Scattering disappears in the presence of β -cyclodextrin while it is still present in case of α -cyclodextrin.

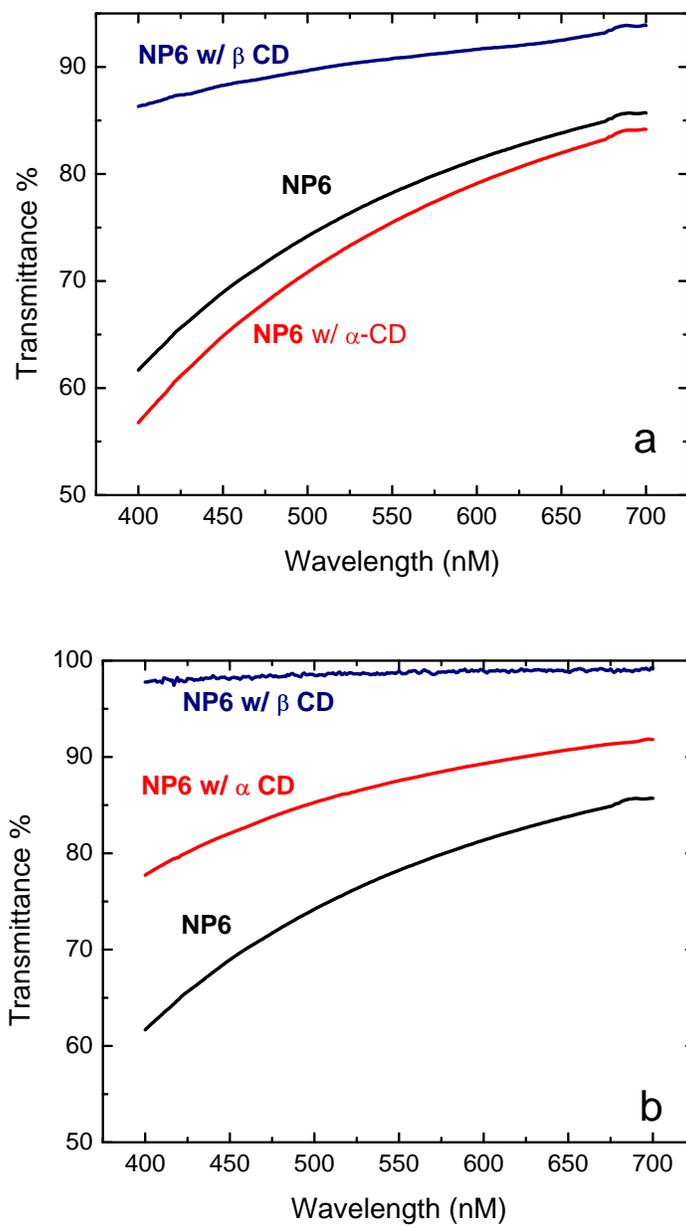


Figure 4.10. UV visible spectrum of 1mM NP6 solution with α - and β - cyclodextrin in NP6:CD ratios of a) 1:1, and b) 1:2.

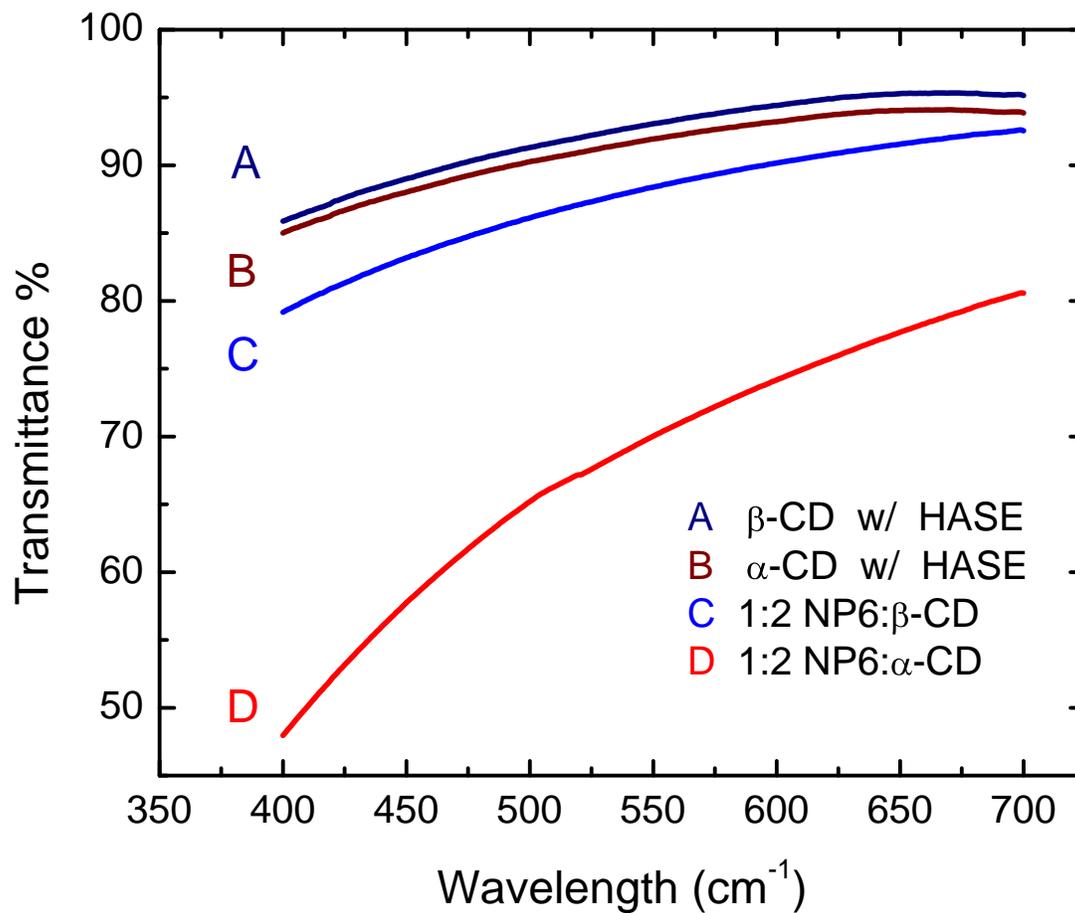


Figure 4.11. UV visible spectrum of 0.5 wt.% HASE/3.3mM CD in the presence of NP6

CHAPTER 5

Novel Electrospun Nanofibers of Associative Polymer- Surfactant Systems

Chapter 5 is essentially a manuscript by Sachin Talwar, Juan P. Hinestroza, Benham Pourdeyhimi and Saad A. Khan prepared for submission to *ACS Nano*.

Novel Electrospun Nanofibers of Associative Polymer-Surfactant Systems

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Abstract

Associative polymers are unique in their structure with pendant hydrophobes attached to their hydrophilic backbone, enabling associations between the hydrophobes and forming junctions in aqueous solutions. In this study, we report the first successful attempt in producing electrospun nanofibers of associative polymers. Scanning electron micrograph (SEM) images reveal that the solution rheology sets an upper limit to the concentration of associative polymer that can be successfully electrospun. However, addition of nonionic surfactants to the precursor solution results in significant improvement in nanofiber morphology. Through judicious use of nonionic surfactants to modulate solution viscoelastic properties we are able to obtain defect-free nanofiber morphology, and gain new insights into the fundamentals of the electrospinning process. In particular, we find that solution viscoelasticity as measured in terms of the relaxation time, rather than viscosity as typically hypothesized, control the nanofiber formation process. The presence of both associative

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polymer and surfactants in the spun fibers was found to influence the crystallinity of the resulting fibers.

5.1 Introduction

Associative polymers containing pendant hydrophobic groups are generating significant interest owing to their ability to be used in a myriad of applications ranging from paints and coatings to drug delivery. The scope and utility of these polymers can be further broadened by developing fiber-based structures for applications in nonwoven surface modification. A powerful option in this regard is to develop electrospun nanofibers of these materials, which due to their very high surface to volume ratio, would render these materials useful in many areas such as membrane technology, smart textiles and tissue scaffolds for regenerative medicine¹⁻¹¹.

Electrospinning is a versatile technique in which a charged fluid jet from a polymer solution or melt undergoes uniaxial stretching in presence of an applied electric field and is deposited on a collector as nanofibers⁵. A large number of polymer/solvent systems have been successfully spun into fibers by employing this technique^{5,6,10}. The resulting fiber diameters are usually in the submicron range as opposed to conventional fiber spinning techniques where the typical fiber diameters are in the order of microns¹². This characteristic size scale - which imparts the fiber mats a high specific surface area and small pore size - has led to significant interest in developing novel functional electrospun materials for applications including, but not limited to, filtration devices, protective clothing and reinforced composites^{2,13,14}.

However uniform fibers are not obtained from all polymer solutions. The morphology of the electrospun fibers is affected by solution properties that include viscosity, conductivity and surface tension as well as process parameters that include the precursor

solution flow rate and electric field intensity. McKee *et al.*¹⁵ have shown that a sufficient degree of overlap between polymer chains is necessary to obtain uniform fibers. They reported that the characteristics of the nanofibers produced via electrospinning are a strong function of the polymer concentration. While polymer droplets and beaded nanofibers are obtained from spinning at low polymer concentrations, electrospinning at higher concentrations results in the formation of bead-free nanofibers. The authors also found that for most of the copolymers studied, C_e , the critical entanglement concentration, was the minimum concentration required for production of beaded nanofibers, while 2-2.5 times C_e was the minimum concentration required to produce uniform, defect-free fibers. The role of entanglements in electrospinning has subsequently been recognized in several other publications^{16,17}.

Associative polymers are distinctive in their structure, with hydrophobes attached to their hydrophilic backbone, enabling associations between the hydrophobes forming junctions in aqueous solutions. We have chosen hydrophobically modified alkali-soluble emulsion (HASE) polymer, a comb-like associative polymer for this study. HASE polymers consist of a copolymer backbone with pendant hydrophobic groups, also named polymer hydrophobes (Figure 5.1). The polymer hydrophobes are alkyl groups attached to the backbone through a urethane linkage and separated from it by a poly(ethylene oxide) (PEO) spacer; the entire structure is referred to as a macromonomer¹⁸. In neutral and/or alkaline aqueous media, HASE polymers form a transient network consisting of both intra- and inter-molecular hydrophobic junctions resulting in a substantial viscosity enhancement of the solution¹⁹⁻²¹. As such, these polymers are typically used as rheology modifiers and several

studies are being undertaken to decipher the precise role of hydrophobic interactions in solution rheology. However, no effort has been made to electrospin these types of polymers. Electrospinning these polymers will not only open a route to the development of novel materials from associative polymers but also provide new insights into the role of rheology during the electrospinning process. Moreover, addition of surfactants to these polymer solutions can further affect their rheological properties by modulating the hydrophobic interactions in solution²²⁻²⁷. Depending on the concentration and the type of surfactant, the viscosity as well as viscoelastic properties of the HASE solutions either increase or decrease upon surfactant addition. These observations have been explained in terms of formation of mixed micelles incorporating both surfactant and polymer hydrophobes²⁴.

Our goal in this study, therefore, has been to examine effective strategies for electrospinning associative polymers by addressing the following issues: Can associative polymers be electrospun by itself and/or in combination with other polymers? Does modulation of hydrophobic interactions through surfactant addition play any role in electrospinning, and, what is the role of viscosity and viscoelasticity in the formation of nanofibers? Are surfactants present in the final fibers, and if so, how do they affect the crystallinity of the resulting fibers?

5.2 Materials and Methods

The HASE polymer, a copolymer of methacrylic acid, ethylacrylate and a macromonomer with a mole ratio 43.57/56.21/0.22 respectively, was obtained from UCAR emulsion systems (Dow Chemical, Cary, NC). The macromonomer is composed of a

polyethylene oxide (PEO) spacer with 40 moles of EO units and a C₂₂ alkyl group, and is linked to the backbone via a urethane linkage. The HASE polymer was supplied in the form of aqueous latex at a solid concentration of approximately 26%. All impurities and unreacted chemicals were removed from the aqueous latex by dialyzing it against deionized water using a Spectrapore cellulosic membrane (cut off MW = 10000) for 3 weeks. The dialyzed latex was then lyophilized for 2 days under 100 mTorr of vacuum to obtain the HASE polymer in a powder form. The pH of HASE solutions was set between 7.0 and 7.5 by adding 0.1M NaOH. Nonylphenol ethoxylates (NPe) nonionic surfactant, Tergitol[®] was supplied by Dow Chemical (Cary, NC) and used as received.

PEO (MW 600kDa) was obtained from PolySciences Inc., and used as received. After preparing the polymer/ surfactant samples, they were placed in a water bath overnight at 50°C to remove entrained air and then left 48 hrs at room temperature prior to rheological measurements. Rheology of the samples was measured within three weeks of the preparation to avoid possible polymer degradation in the presence of NaOH²⁸.

All rheological experiments were performed at pH = 9 and T = 25°C in a TA Instruments AR-2000 stress controlled rheometer using a cone and plate geometry. Since the steady shear response of HASE polymer/surfactant systems is sensitive to shear history²⁶, a preshear was applied at a strain rate of 5s⁻¹ for 180 s followed by a rest period of 120 s. A dynamic stress sweep test was performed to determine the limit of linear viscoelastic regime, which was thereafter utilized to perform the dynamic frequency sweep test.

The electrospinning setup consisted of two parallel aluminum plates. A Harvard Apparatus syringe pump controlled the polymer flow to a capillary nozzle attached to one of

the plates while the resulting nanofibers were collected on the other plate. A high voltage power supply (0-30KV) was used to create a potential difference between the two plates. The applied electric field strength varied from 0.9 -1.25 kv/cm. The electrospun fibers were gold sputtered and SEM images were obtained using a Hitachi S-3200 Scanning Electron Microscope. FT-IR measurements were performed on a Nicolet Magna-IR 750 FTIR spectrometer. DSC measurements on the electrospun fibers were conducted using a TA Instruments Q2000 calorimeter by heating the samples from 25°C to 90°C in a nitrogen environment at a heating rate of 10°C/min.

5.3 Results and Discussion

5.3.1 Electrospinning of HASE with PEO

The C_e for HASE polymers in water has been reported to occur around 0.85 wt.%^{29,30} at which the low shear viscosity of the solution becomes too high to allow electrospinning. Attempts to electrospin at this concentration only resulted in the electrospaying of small droplets even at high electric fields. An effective strategy to overcome similar problems is to blend the non-electrospinnable polymer with polymers that are well suited for electrospinning³¹. Based on this approach, we prepared aqueous solutions of HASE polymers with polyethylene oxide (PEO) of molecular weight (MW) 600 kDa. Initial electrospinning experiments were conducted on 4 wt.% PEO samples containing different HASE polymer amounts. Scanning electron microscope (SEM) images of the resulting fibers reveal the positive role of HASE polymer on fiber quality (Figure 5.2). An improvement is noted for

concentrations up to 0.1 wt.% of HASE. However an increase in bead-density is obvious at concentrations higher than 0.1wt.% indicating the presence of a critical HASE concentration in order to achieve defect-free nanofibers. Moreover, there exists an upper limit (0.2 wt.% in this case) of the HASE concentration at which no fibers are obtained at any values of electric fields.

Steady state and dynamic rheological experiments were conducted on the PEO/HASE polymer solutions to assess the role of low shear viscosity as well as viscoelastic properties on the properties of electrospun nanofibers. Figure 5.3a shows the low shear viscosity versus HASE polymer concentrations in 4 wt.% (600 kDa) PEO solution. We find the low-shear viscosity to increase with increasing HASE concentration and exhibit three distinct regions within the range of HASE concentration studied. In the first region, the viscosity of the solution does not vary upon the addition of HASE polymer. In the second region the viscosity of the solution increases and the slope of the viscosity curve exhibits a power-law behavior. As the concentration further increases the slope changes to a higher value and that range of concentration constitutes the third region. We found that electrospinning of precursor solutions containing HASE concentrations corresponding to those in the third region resulted in either beads or no fiber, attributable to their high solution viscosity.

The frequency spectra of the elastic (G') and viscous (G'') moduli of the polymer solutions are shown in Figure 5.3b. These spectra are typical of a reversible network with transient inter-chain interactions and the absence of any physical gelation. A transition occurs from viscous dominated response ($G'' > G'$) at low frequencies to an elastic-dominated response ($G' > G''$) at higher frequencies for both samples containing HASE polymer. We

observe that addition of HASE to the PEO solution leads to an increase in both the elastic (G') and the viscous (G'') moduli over the entire frequency range studied. The value of G' at high frequencies, which gives a measure of network connectivity or number density of elastic polymer chains in solution, increases upon addition of HASE. The values of G'' (viscous modulus) remain above those of G' over most of the frequency range studied for the sample containing 0.1% HASE concentration. This concentration was the maximum concentration at which defect-free fibers could be obtained hence indicating the dominance of the liquid-like behavior of the polymer solution. In the case of the sample containing 0.5 wt.% HASE, which was not electrospinnable, the G' values were higher than those of G'' . The characteristic relaxation time (t_R) for these polymer systems can be estimated from the reciprocal of frequency (ω) at the crossover of G' over G'' . We observe that the relaxation time increases by over two orders of magnitude as HASE concentration is increased from 0.1% to 0.5% and by about an order of magnitude when HASE concentration is increased from 0 to 0.1%. These results indicate that the viscoelastic properties, as reflected by moduli and relaxation times, along with steady state viscosity do play an important role in the electrospinning process, and they are in agreement with recent discoveries on the effect of elasticity on the formation of electrospun fibers^{32,33}.

5.3.2 Role of Surfactants

The nanofibers obtained from the solution containing 0.2 wt.% of HASE polymer are of poor quality as is evident from the SEM image in Figure 5.2. To overcome the issue of bead formation, we resorted to the use of nonionic surfactants. The motivation behind this

decision is based on previous work on associative polymers by our group^{22,24} in which nonylphenol ethoxylate (NPe) nonionic surfactants [e representing the number of ethylene oxide groups in the hydrophilic head group], were shown to have a profound influence on the hydrophobic interactions of HASE polymers. Addition of NPe surfactants to the polymer solutions leads to a slight improvement in conductivity which can be attributed to the existence of polar groups in the NPe molecule. Figures 5.4a and 5.4b show SEM images of electrospun nanofibers obtained from solutions containing 4 wt.% PEO/ 0.2 wt.% HASE with and without the presence of 20mM NP15 nonionic surfactant. We observe a significant improvement in the fiber morphology upon addition of surfactants with a considerable reduction in bead-density. The average fiber diameter ranged from 170 – 350 nm. For the sake of clarity, we will hereon refer to the 4 wt.% PEO/ 0.2 wt.% HASE solution without surfactant as w/oNP15, and with surfactant as w/NP15.

Steady state and dynamic rheological experiments were conducted on both w/oNP15 and w/NP15 samples to assess the effect of the surfactant on steady shear viscosity as well as their viscoelastic properties. Figure 5.5a shows steady shear viscosity vs. stress profile for both samples. The values of viscosity of the w/NP15 sample are lower than those of w/oNP15 except at very high stresses. Since it is unlikely that the small changes in viscosity upon surfactant addition are substantial enough to cause a drastic reduction in bead-density in the electrospun nanofibers, variations in the elastic response of this polymeric system were further examined by monitoring the evolution of G' and G'' as function of frequency.

The frequency spectra of the elastic (G') and viscous (G'') moduli of the w/oNP15 and w/NP15 samples are shown in Figure 5.5b. We observe that addition of NPe leads to a

decrease in both the elastic (G') and viscous (G'') moduli over the entire frequency range studied. The value of G' at high frequencies, which gives a measure of network connectivity or number density of elastic polymer chains in solution, decreases as surfactant is added to the solution. More importantly, the relaxation time t_R decreases by almost an order of magnitude upon the addition of NP15. These results indicate that the viscoelastic properties of the polymer solution, particularly polymer relaxation time, play a crucial role in the electrospinning of this polymeric system. We speculate that NP15 surfactant serves to alter the dynamics of the polymer solution by affecting the hydrophobic interactions of the HASE polymer in solution, resulting in lower connectivity and a lower t_R , with the eventual outcome of reduction in bead-defects.

In order to increase the concentration of HASE in the resulting fibers, we performed electrospinning experiments on solutions with 3 wt.% PEO (600kDa) and 0.5 wt% HASE. Figures 5.6a and 5.6b show the SEM images of electrospun fibers obtained from the 3 wt.% PEO/0.5 wt.% HASE solutions both with and without 20mM of NP15 surfactant. Fibers with significant amounts of beads are noted during attempts to electrospin the solution without surfactant. Upon surfactant addition, fibers with significantly-improved morphology are obtained. Here again we observe a minor reduction in viscosity upon surfactant addition a significant transformation in the trends of dynamic moduli (Figure 5.7). It appears that surfactant addition leads to a viscous-dominated ($G'' > G'$) behavior for the entire frequency spectrum studied as opposed to an elastic dominated regime for the solution without surfactants. The crossover of G' and G'' does not occur in the experimental frequency range indicating a significant decrease in t_R upon surfactant addition. These results further

corroborate the assertion that polymer viscoelasticity profoundly influences fiber morphology during electrospinning. More generally they show that nonionic surfactants can be used to obtain electrospun nanofibers of associative polymers of this class by modulating the relaxation time of the precursor solutions.

5.3.3 FTIR Spectroscopy of Electrospun Nanofibers

An important consideration in electrospinning multi-component polymer systems is to determine the presence of the polymer of interest in the resulting fibers. We sought to establish the presence of HASE polymer in the nanofibers by directly exposing the fiber mat to infrared beam in transmittance mode. The FTIR spectra of the fibers spun from pure PEO solutions are expected to exhibit characteristic peaks around 1100 cm^{-1} and 962 cm^{-1} which are associated with the stretching of the C—O—C group present in the PEO molecule³⁴. Figure 5.8 shows the FTIR spectra of the nanofibers obtained from pure PEO solutions as well as those spun from precursor solutions containing PEO and HASE. Also shown in Figure 5.8 is the spectrum of nanofibers obtained from PEO/HASE solutions containing NP15 surfactant. For the sake of clarity, the figure does not represent the entire IR spectrum but only the wavelength range where new peaks were observed upon addition of either HASE or the NP15 surfactant. The presence of HASE in the fibers from PEO/HASE solutions can be verified by the appearance of new characteristic peaks corresponding to the frequencies associated with the stretching of C=O of the ester group (1730 cm^{-1}) and COO⁻ group (1580 cm^{-1}) present in the chemical structure of HASE molecule.³⁵ In the case of fibers obtained from PEO/HASE/NP15 solutions, we notice a new peak at 1513 cm^{-1} , apparently

due to the presence of para-substituted benzene, which is a characteristic peak in the spectrum of pure NP15 surfactant. These results confirm that the NP15 surfactants are also incorporated in the fibers along with the larger polymer molecules of PEO and HASE after the electrospinning of the solutions.

5.3.4 Crystallinity of Electrospun Fibers

An intriguing issue is the effect of addition of a second polymer and surfactants on the properties of the electrospun fibers in terms of their crystallinity. The % crystallinity of the electrospun fibers was determined via differential scanning calorimetry measurements as shown in Figure 5.9. The area under the melting curve on the DSC plot provides the heat associated with melting for the polymer. This quantity when normalized by the polymer heat of fusion of 100% crystalline PEO (197 J/g³⁶) yields the % crystallinity of the specimen as presented in Table 5.1. As the crystallinity in the fibers is solely due to PEO, the proportion of weight of PEO in the fibers has been factored into when calculating % crystallinity. We find that addition of HASE to the 4% PEO solution decreases the crystallinity of the resulting fibers from 76.2% to 72.6%. The decrease in crystallinity becomes significant once NP15 surfactant is added to the precursor solution. A similar decrease in crystallinity is observed for the 3 wt.% PEO system in the presence of HASE. The melt temperature is also found to follow the same trend as that of the % crystallinity. These results indicate that the presence of HASE and surfactant molecules interferes with the crystallization of PEO molecules thereby reducing the final crystallinity of the final fibers. Moreover, the decrease in crystallinity upon HASE addition is more pronounced for fibers spun from 3% PEO solutions. An interesting

result to note from Table 5.1 is that the crystallinity of fibers electrospun from PEO-only solutions is slightly higher than that of the as received PEO powder. Similar observations of higher crystallinity in electrospun fibers have been made earlier by Kim *et al.*³⁷ in their study on electrospinning of gold nanoparticles with PEO although the reason behind this phenomena is still unclear.

5.4 Summary

In this study, we have successfully incorporated associative polymers into nanofibers via electrospinning. Steady state and dynamic, rheological experiments correlated the viscoelastic behavior of the precursor solutions with the properties of the resulting nanofibers. In particular, SEM micrographs indicate that the solution rheology puts a limit to the HASE concentration that can be electrospun. This problem can however be circumvented through use of nonionic surfactants as formation of poor quality beaded fibers could be transformed to production of defect-free nanofibers upon addition of surfactants to the precursor solution. Such significant improvement in the morphology of the nanofibers was primarily attributed to the change in solution viscoelasticity, and not the solution viscosity. FTIR spectroscopy verified the presence of associative polymer and surfactants in the electrospun fibers. The presence of surfactants in particular appeared to significantly affect the crystallinity of the resulting nanofibers.

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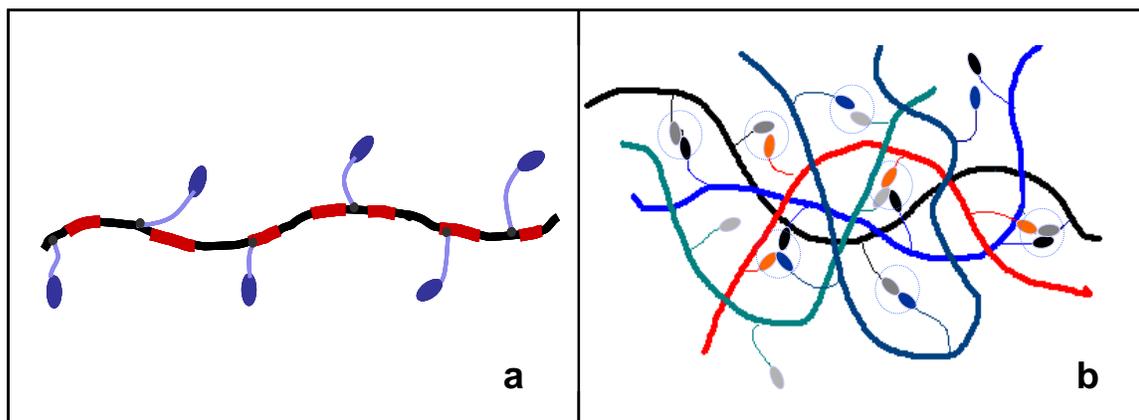


Figure 5.1. Schematic representation of HASE associative polymer. a, A polymer molecule by itself consisting of hydrophobes shown in blue. b, HASE polymer in aqueous solution showing inter and intramolecular association of the hydrophobes.

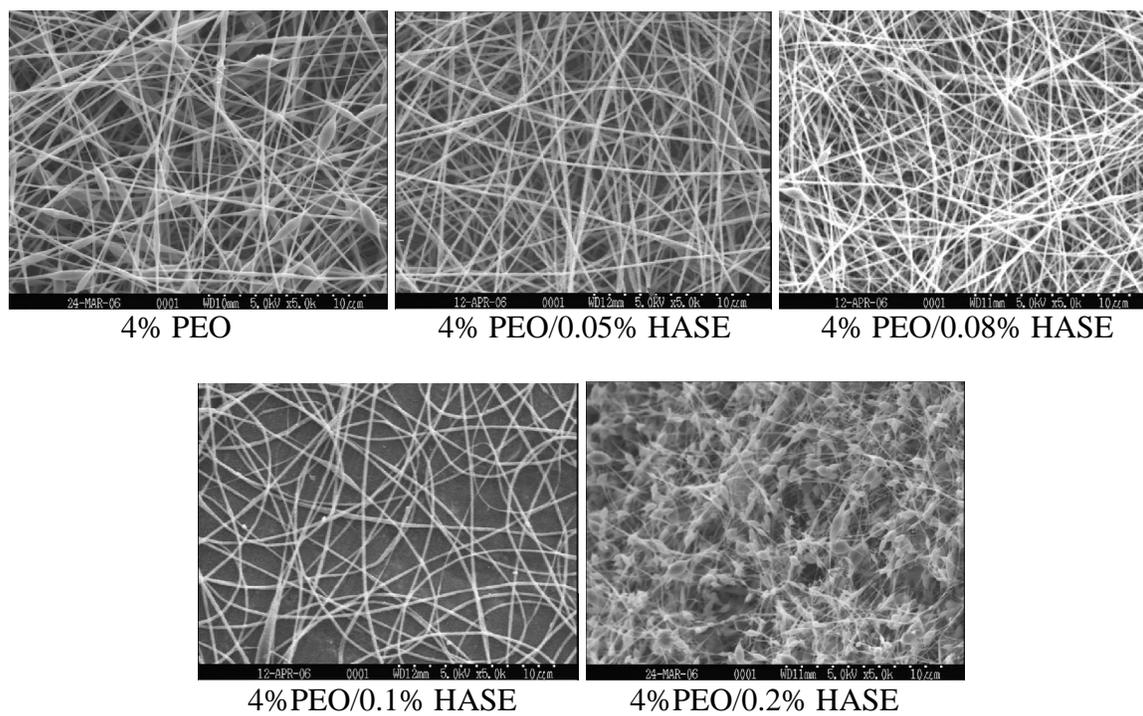


Figure 5.2. SEM micrographs of nanofibers from polymer solutions with 4 wt.% PEO with different HASE concentrations.

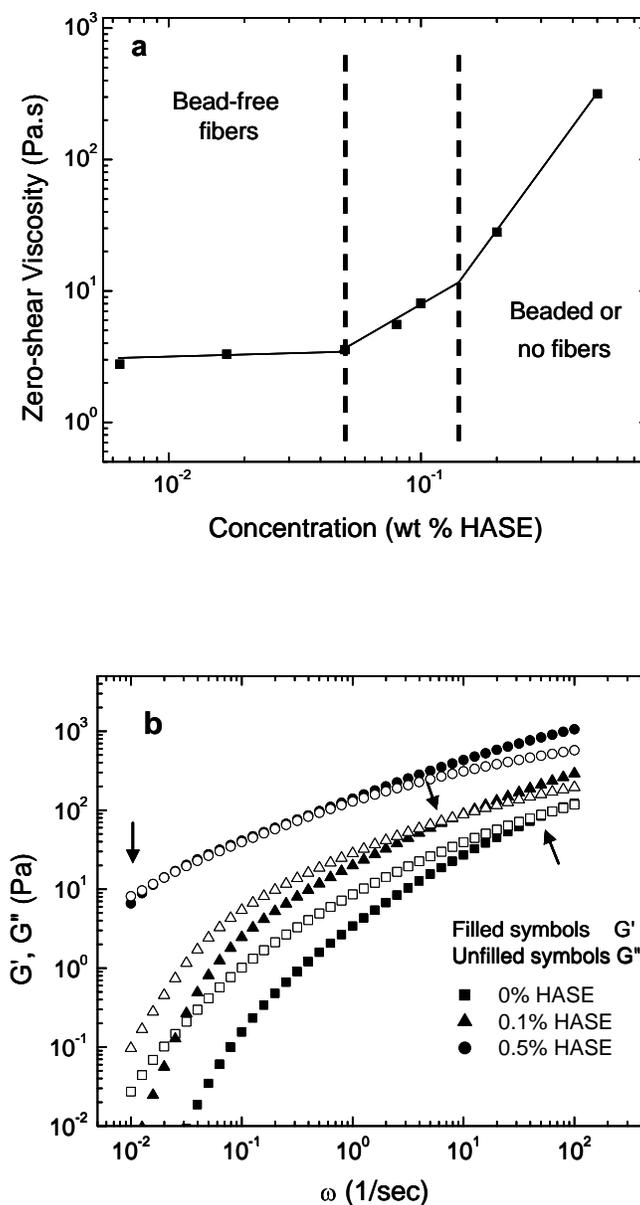


Figure 5.3. Steady state and dynamic rheology of polymer solutions that were electrospun. a, Zero-shear viscosity versus HASE polymer concentration for 4 wt.% PEO/HASE polymer solutions. b, Dynamic frequency spectrum of the elastic (G') and viscous (G'') moduli of 4% PEO/HASE polymer solutions at different HASE concentrations. The arrows correspond to cross-over points.

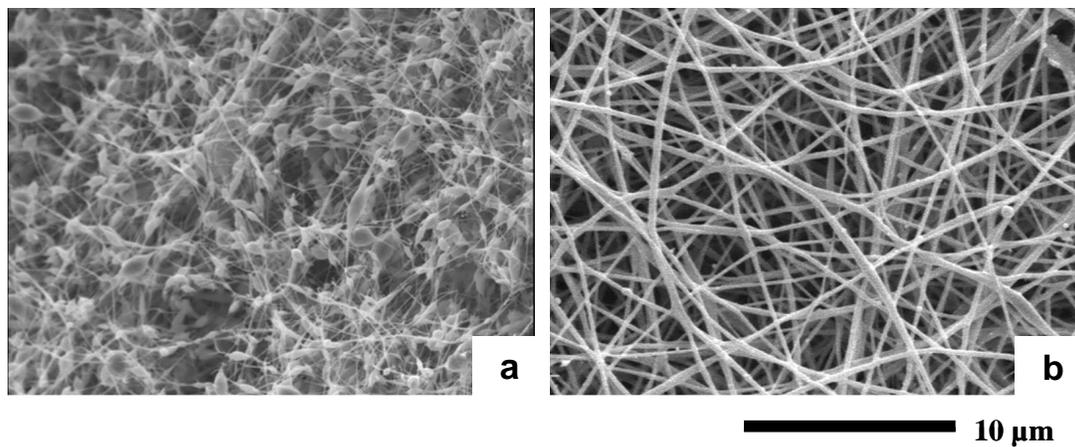


Figure 5.4. SEM images and solution rheology of nanofibers from PEO/HASE solutions. Fibers from solutions of 4 wt.% PEO/0.2 wt.% HASE both with (a) and without (b) NP15 nonionic surfactant.

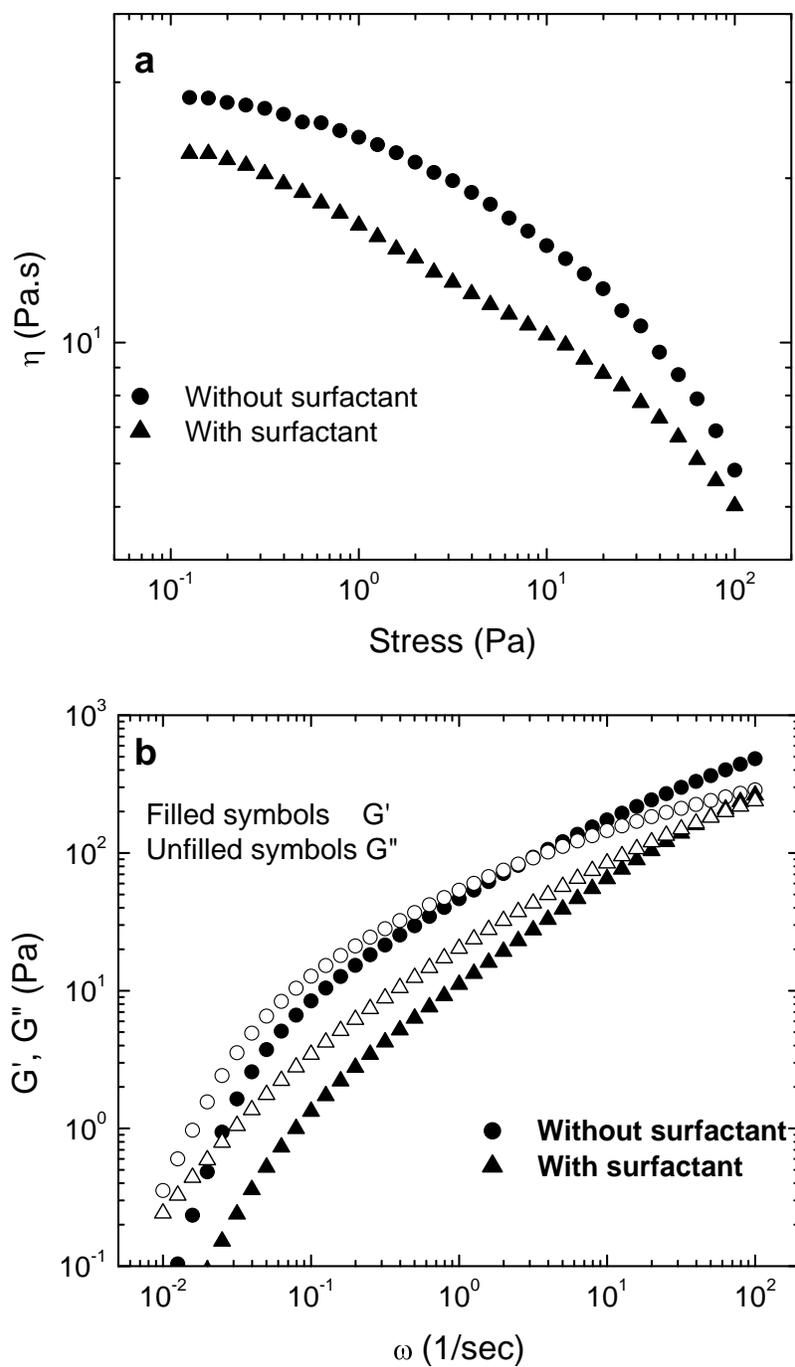


Figure 5.5. a, Steady state viscosity, and b. frequency spectrum of the elastic (G') and viscous (G'') moduli for 4 wt.% PEO/0.2 wt.% HASE solutions with and without 20mM NP15.

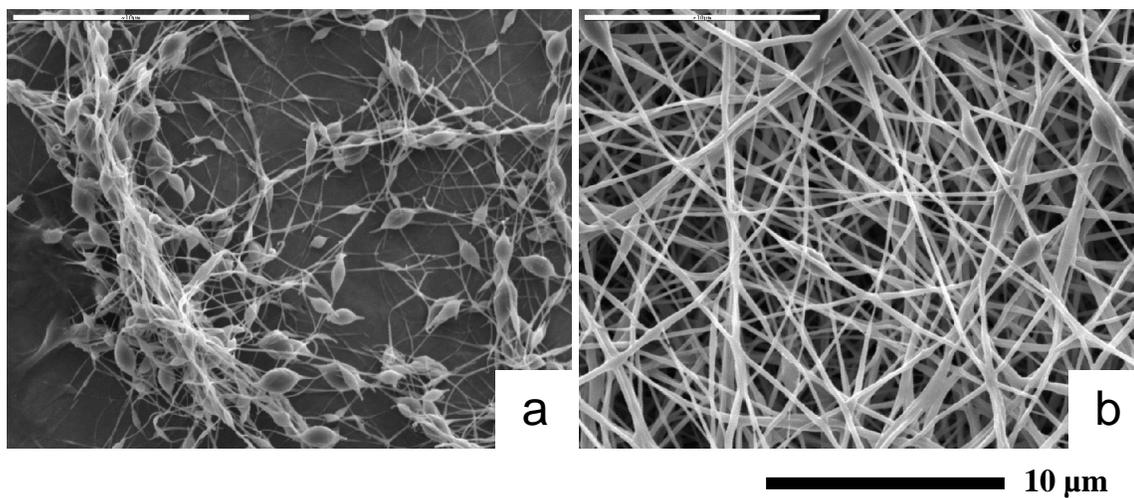


Figure 5.6. SEM images of nanofibers from PEO/HASE solutions. Fibers from solutions of 3 wt.% PEO/0.5 wt.% HASE both with (a) and without (b) NP15 nonionic surfactant.

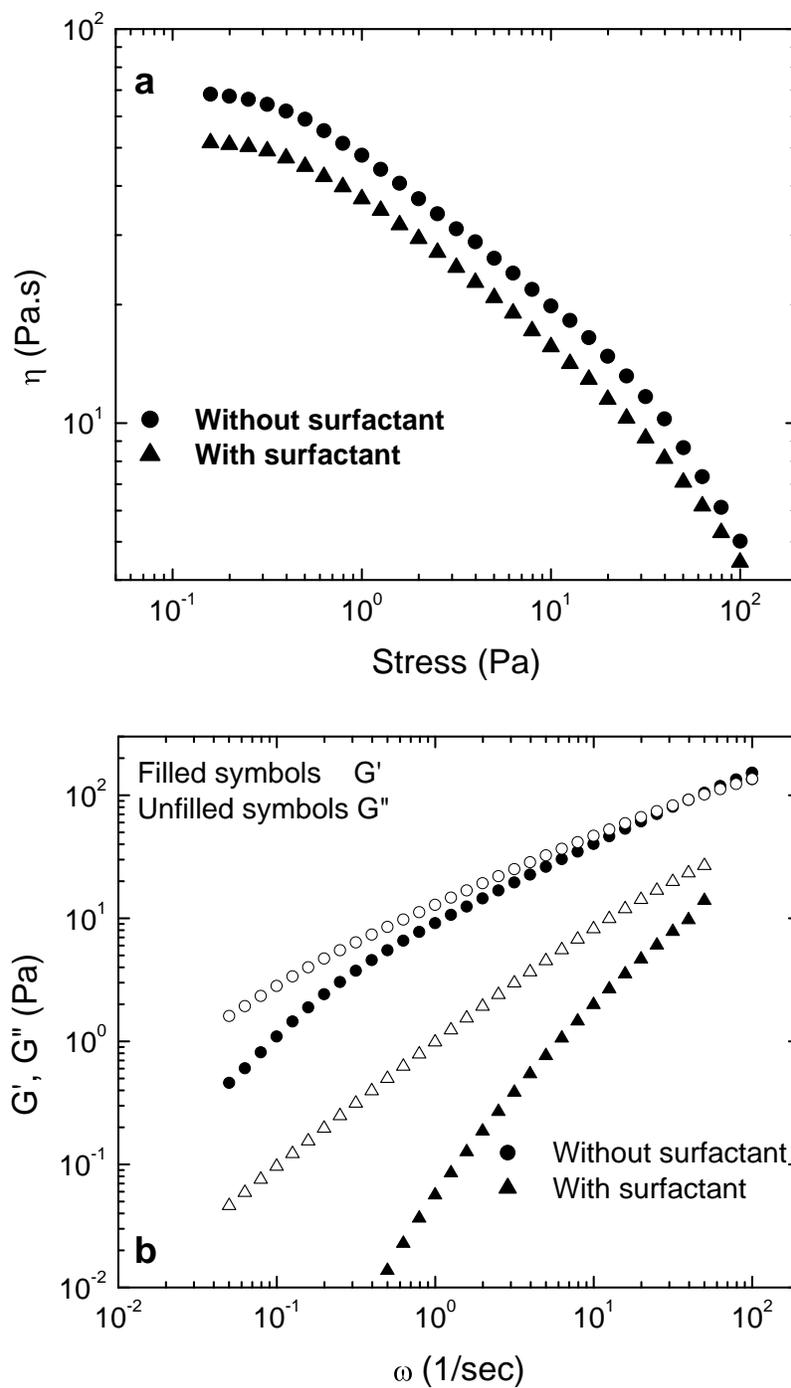


Figure 5.7. a. Steady state viscosity, and b. frequency spectrum of the elastic (G') and viscous (G'') moduli for 3 wt.% PEO/0.5 wt.% HASE solutions with and without 20mM NP15.

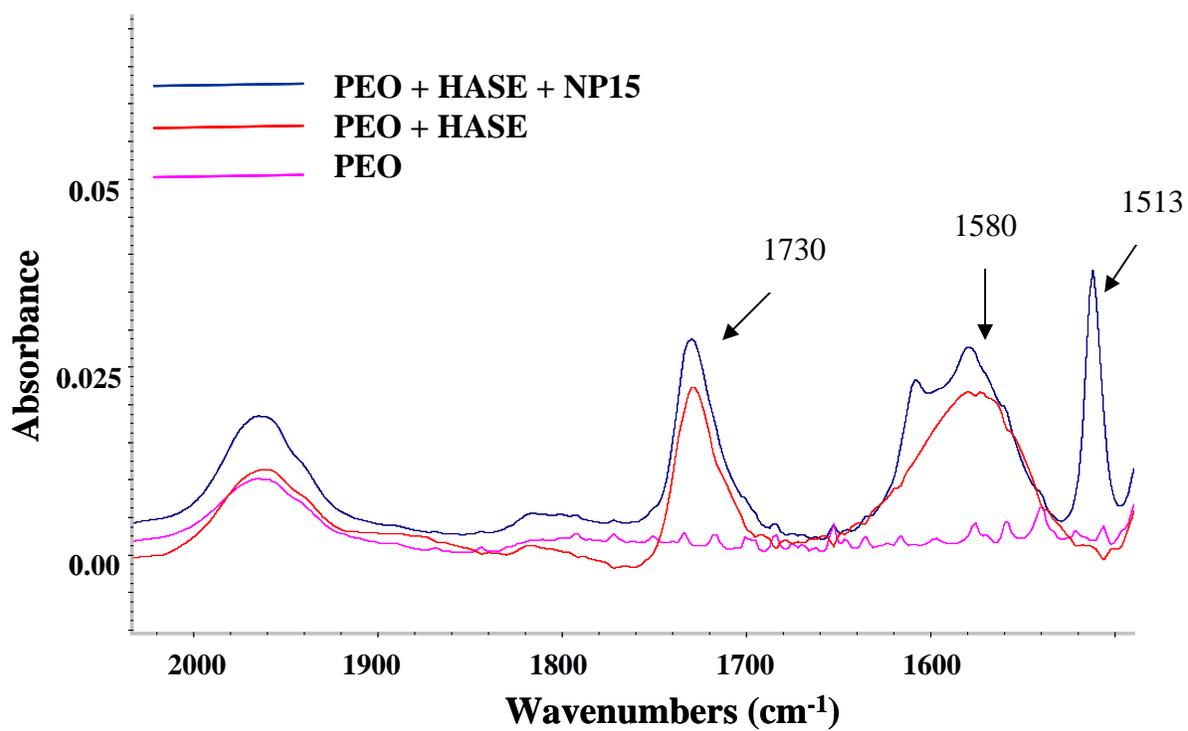


Figure 5.8. FT-IR spectrum for fibers obtained from electrospinning solutions with different components.

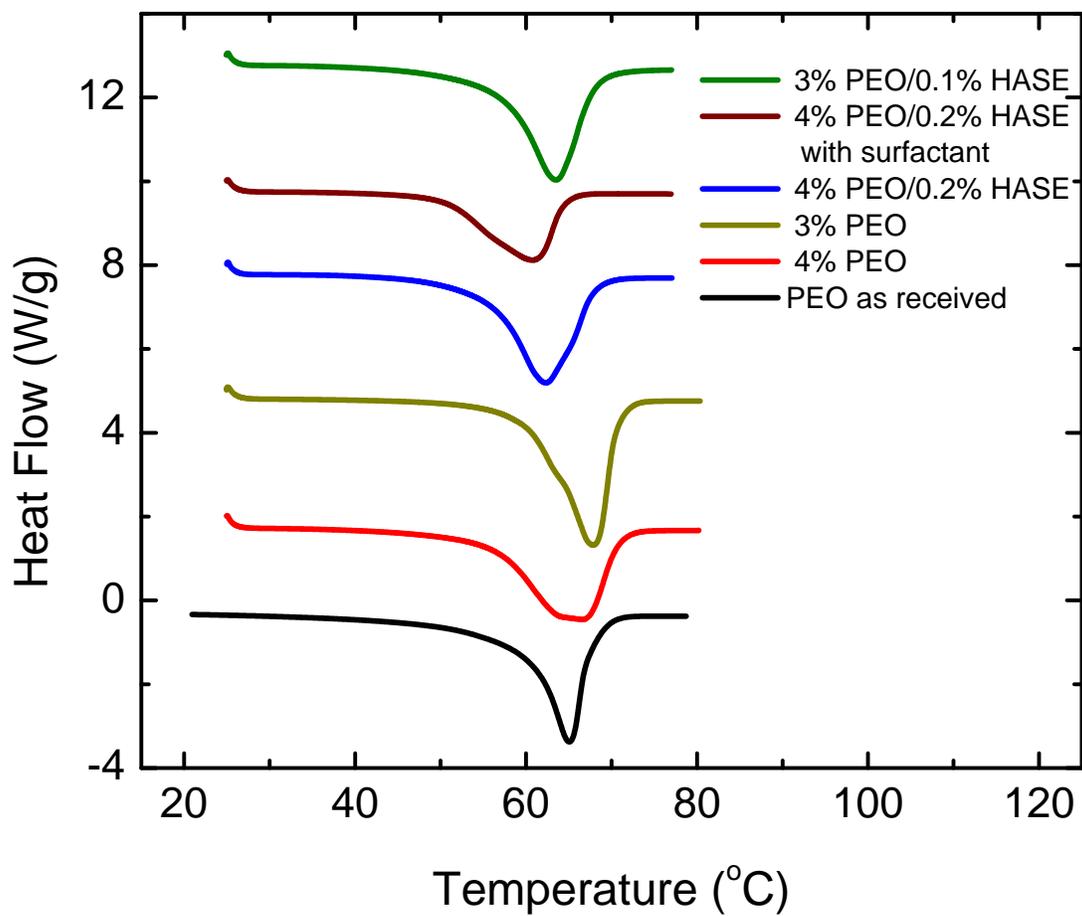


Figure 5.9. DSC melting endotherms of fibers spun from various samples along with “as received” PEO sample.

Table 5.1. % Crystallinity and Melt Peak Temperature as measured by DSC of various electrospun polymer systems.

System	Melt Peak Temperature (°C)	% Crystallinity
PEO as received	65	74.8
4% PEO	66.5	76.2
3% PEO	67.9	80.28
4% PEO/0.2% HASE	63.2	72.6
4% PEO/0.2% HASE/20mM surfactant	60.7	65.6
3% PEO/0.1% HASE	63.4	74.3

CHAPTER 6

Associative Polymer Facilitated Electrospinning of
Nanofibers

Chapter 6 is essentially a manuscript by Sachin Talwar, Juan P. Hinestroza, Benham Pourdeyhimi and Saad A. Khan submitted to *Macromolecules*.

Associative Polymer Facilitated Electrospinning of Nanofibers

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Abstract

Electrospun nanofibers present an exciting avenue for development of novel materials with well-defined functionalities; however, broadening the scope of electrospinning to a diverse range of polymers remains a major challenge. In particular, a recurring issue in this field is the inability to spin polymers at lower concentrations in order to achieve smaller fiber diameters. This work explores the use of associative polymers as a means to overcome the critical entanglement density limiting factor that prevents the electrospinning of nanofibers from low concentration polymer solutions. Hydrophobically modified alkali-soluble emulsion (HASE) polymers are comb-like associative polymers with pendant hydrophobes that form a network in aqueous media consisting of both intra- and intermolecular hydrophobic junctions. Rheological measurements reveal that addition of HASE polymers in small amounts to poly(ethylene oxide) solutions leads to considerable increase in viscosity as well as dynamic moduli of the system. More importantly, these rheological changes are translated into significant changes in fiber morphology, from beaded to uniform nanofibers, as well as reduction in fiber diameter. The concept of using rheology modifiers is further extended to another associative polymer, guar galactomannan, which associates through a

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different mechanism. Similar improvements in fiber formation are observed, thereby lending credence to the universality of this approach.

6.1 Introduction

Compared to conventional fiber spinning techniques such as melt or solution spinning, the size of fibers produced via electrospinning is at least an order of magnitude lower¹. Owing to their small diameter, the resulting nonwoven fiber mats possess a high specific surface area, a large degree of porosity and ample flexibility in tailoring the properties of these fibers to specific applications such as protective clothing², wound dressing³, filtration devices, membranes, electronic devices and reinforced composites^{4,5}.

The process of electrospinning is relatively easy to implement, and a large number of studies have been published dealing with electrospinning different polymer systems - either individually or in conjunction with a second polymer - as well as in understanding the role of various process and solution parameters on the electrospinning process⁶⁻⁸. Nonetheless, there are issues related to poor spinnability or lack of spinnability of polymer solutions at dilute concentrations. In such cases, the formation of beads or beads-on-string morphology dominates rather than the desired uniform bead-free fibers⁹⁻¹². In this study, we examine the scope of incorporating small amounts of associative polymers in such systems to facilitate nanofiber formation. We exploit the ability of associative polymers to act as rheology modifiers, and generalize the concept of using polymers having different mechanisms of association.

McKee *et al.*¹³ have shown that the morphology of fibers produced through electrospinning is a strong function of the polymer concentration. One can go from producing polymer droplets to beaded-nanofibers to defect-free nanofibers by increasing the concentration of the polymer in the precursor solution. The minimum concentration at which

the polymer can be spun into uniform fibers is limited by the entanglement density of the polymer solution, as given by critical entanglement concentration (C_e). The critical concentration is the boundary between the semidilute unentangled and the semidilute entangled regimes and represents the onset of the regime where significant overlap between the polymer chains topologically constrains the chain motion¹⁴. Based on their observations, the authors concluded that C_e was the minimum concentration required to obtain beaded nanofibers and that uniform bead-free fibers were obtained at 2-2.5 times C_e . They argued that the presence of entanglements prevents the break up of the charged fluid into droplets resulting in the formation of uniform fibers. The role of entanglements in electrospinning has been further validated in several other publications^{15,16}. In another study by the same authors on poly (methyl methacrylate-*co*-methacrylic acid) copolymers containing self-complimentary quadruple hydrogen bonding groups in the molecule¹⁷, the electrospinning behavior was found to be similar to polymers with higher molecular weight. This behavior was attributed to the presence of extensive hydrogen bonding between the molecules which essentially act as chain entanglements, hence reducing the C_e of the system. In a similar vein, lecithin, a low molecular weight amphiphile which forms cylindrical worm-like micelles in solution above a certain concentration, was electrospun from a chloroform/DMF solution¹⁸. In this case, at high enough concentrations, the worm-like micelles form physical entanglements in solution which effectively substitute for chain entanglements in polymer systems in the semidilute entangled regime.

The occurrence of beads during electrospinning is a result of the interplay between three factors namely surface tension, charge density, and the viscoelastic forces. Surface

tension tends to minimize surface area of the electrified jet, hence favoring the formation of beads, while net charge density and viscoelastic forces favor stretching of the jet, and hence favoring the formation of fibers. Therefore, additives like cationic surfactants has been shown to reduce bead-density during the electrospinning of polystyrene fibers¹⁹. The improvement in fiber formation is brought about by an increase in charge density as well as simultaneous decrease in surface tension. Similarly, addition of other ionic additives such as salts²⁰⁻²² and polyelectrolytes²³ has also been found to improve fiber formation by increasing solution conductivity.

At low concentrations however, even the presence of ionic additives in the polymer solution proves ineffective in eliminating beads⁹. This is likely due to insufficient viscoelastic forces owing to a lack of formation of entanglements²⁴. In this work, we investigate the efficacy of using associative polymers to improve fiber formation from dilute polymer solutions that lack spinnability or produce beaded fibers. An obvious advantage of spinning at low concentrations is derived from the proportional relationship between fiber diameter and polymer concentration. Keeping other parameters constant, an increase in polymer concentration results in an increase of the fiber's diameter^{7,13}.

Hydrophobically modified associative polymers are water soluble polymers with hydrophobic groups attached either to their ends or spread throughout the backbone in a comb-like manner²⁵⁻²⁹. Hydrophobically modified alkali-soluble emulsion (HASE) polymers are a class of comb-like associative polymers with pendant hydrophobes that form a transient network in an alkaline solution consisting of both intra- and intermolecular hydrophobic junctions³⁰⁻³⁷. A schematic of a HASE polymer molecule and its interactions in an aqueous

solution is shown in Figure 6.1. The presence of these hydrophobic junctions, even at small concentrations, leads to a significant increase in viscosity as well as in the viscoelastic properties of the polymer solution. Due to their unique thickening mechanism and ability to act as rheology modifiers, these water-soluble polymers find applications in paint formulations, paper coatings and oil drilling fluids³⁸⁻⁴¹. To the best of our knowledge, no attempt has been made to assess the utility of these associative polymers as an electrospinning aid for polymer systems that lack spinnability.

As such, this study is the first successful attempt of using associative polymers as an electrospinning aid for spinning polymer solutions that lack spinnability at low concentrations. We investigate the effect of addition of HASE associative polymers on the properties of the precursor solution as well as on the electrospinnability of these dilute systems. Subsequently, we discuss the various factors that can possibly influence the bead formation in these systems. Finally, we extend the concept of using HASE associative polymers to improve spinnability, to other non-hydrophobic associative polymers, thereby lending credence to the universality of this approach.

6.2 Materials and Methods

The model HASE polymer used in this study was obtained from UCAR Emulsion Systems (Dow Chemicals, Cary, NC). It is a copolymer of methacrylic acid, ethylacrylate and macromonomer, their molar ratio being 43.57/56.21/0.22 respectively. The macromonomer is composed of a polyethylene oxide (PEO) spacer with an average number of EO groups equal to 40 moles and a C₂₂ alkyl group linked to the backbone via a urethane

linkage. The HASE polymer was supplied in the form of an aqueous latex at a solid concentration of approximately 26 wt %. All impurities and unreacted chemicals were removed from the aqueous latex by dialyzing it against deionized water using a Spectrapore cellulosic membrane (cut off MW = 10000) for 3 weeks. The dialyzed latex was then lyophilized for 2 days under a vacuum of 100 mTorr to obtain the HASE polymer in a powdered form. The pH of the subsequent prepared HASE solutions was adjusted between 7 and 7.5 by adding 0.1 M NaOH. Details of this procedure are provided in previous publications^{32,33,35}.

PEO (MW 600kDa) was purchased from PolySciences Inc., Warrington, PA. Commercial PEO usually contains about 2-3 wt.% inorganic fillers in the form of calcium carbonate and silica. As the presence of these fillers can influence the molecular interactions in solution, we first purify the PEO in order to truly assess the effect of HASE on solution rheology of PEO as well as the final fiber formation. CO₂ was bubbled through a solution of 3 wt% of PEO in acetonitrile for 1 hour with constant stirring in order to facilitate the precipitation of filler particles. The solution was then centrifuged for 30 min at 4000 rpm. The supernatant from the centrifuged solution was poured into glass dishes and purified PEO was obtained after the solvent evaporated. Purified PEO was used for all the experiments in this work unless otherwise noted. Guar gum (MW 2000kDa) was purchased from Sigma-Aldrich and the sample impurities were removed using a purification procedure as reported elsewhere⁴².

The polymer solutions were placed in a water bath overnight at 40°C to remove entrained air and left in the bath for 48 hrs prior to rheological measurements. All rheological

experiments were performed at 25°C in a TA Instruments AR-2000 stress controlled rheometer using cone and plate geometry. Both steady and dynamic shear experiments were conducted on each sample. A dynamic stress sweep test was performed to determine the limit of linear viscoelastic regime and dynamic frequency sweep tests were run within this range. All rheological measurements were performed at least twice to ensure reproducibility within $\pm 5\%$.

The electrospinning set up consisted of an aluminum collector plate, a precision syringe pump (Harvard Apparatus, Holliston, MA) and a high-voltage power supply (Gamma High Voltage Research, model D-ES30 PN/M692 with a positive polarity). The syringe pump controlled the flow of polymer solution to a metallic needle which was connected to the positive electrode of the power supply. The collector plate was grounded and the fibers were collected on an aluminum foil wrapped on the collector plate. The tip-to-collector distance and solution flow rate were fixed at 15 cm and 1 ml/h, respectively and the applied voltage ranged between 7-13 kV. The electrospun fibers obtained were gold sputtered and SEM measurements were obtained on a Hitachi S-3200 Scanning Electron Microscope.

6.3 Results and Discussion

6.3.1 Electrospinning of low concentration solutions of PEO using HASE associative polymer

As a first step in determining the feasibility of using HASE associative polymers as an electrospinning aid for water soluble polymers, we selected poly(ethylene oxide) (PEO) as our model polymer system. Electrospinning of PEO having different molecular weights

(MWs) has been extensively studied in the literature⁴³⁻⁴⁶. For our purpose though, we selected a PEO concentration which does not electrospin into uniform fibers and instead forms mostly beaded fibers. A 3 wt.% PEO solution satisfies this criteria as is evident from the mostly beaded fiber SEM images observed in Figure 6.2a. Attempts to improve fiber formation from the 3 wt.% PEO solution by varying process parameters such as voltage and tip to target distance were also unsuccessful in agreement with existing published literature.

Solutions of 3 wt. % PEO with different concentrations of HASE were prepared to examine the effect of HASE on the rheological properties of the precursor solution as well as on the morphology of the electrospun fibers. No phase separation was observed in the aqueous solutions of HASE-PEO mixtures within the concentration range studied. Owing to their ability to form intra- as well as inter-molecular hydrophobic junctions, addition of HASE can considerably affect the rheology of PEO solutions. Figure 6.3a illustrates the effect of HASE addition on steady shear viscosity. The addition of HASE to the PEO solutions, even in small amounts, is found to significantly increase the viscosity of the system. For example, the shear viscosity of the solution in the presence of 0.2 wt.% HASE is more than an order of magnitude higher than that of a 3 wt.% PEO solution without any HASE. Moreover, the viscosity profile progressively shows more dependence on shear stress upon HASE addition and an absence of a Newtonian region. Both the increase in viscosity and the nonlinear steady shear response upon addition of HASE indicate the formation of a network structure presumably due to the associative nature of HASE polymer which is known to form hydrophobic junctions in solution. The above hypothesis of evolution of a polymer network in the presence of HASE is reinforced by the frequency spectra of elastic

and loss moduli of the solutions as denoted by G' and G'' , respectively (Figure 6.3b). The values of both the dynamic moduli progressively increase with the addition of HASE and become less frequency dependent. Although we do not observe a crossover of the dynamic moduli in the frequency range studied, it appears to shift towards lower frequencies with increasing HASE concentration signifying an increase in the characteristic relaxation time of the polymer system^{25,32,36}. These results are characteristic of the formation and strengthening of the polymer network in the presence of HASE. These changes in the solution rheology of the 3 wt.% PEO solution, which otherwise would result in mostly beaded fibers, translate into uniform fibers as can be seen from the SEM images in Figure 6.2. The bead-density reduces at 0.1 wt.% HASE concentration and uniform, defect-free fibers are obtained on further increasing the HASE concentration to 0.2 wt. %.

Based on the above results, we believe that the improvement in fiber morphology is primarily a consequence of the formation of a physical interaction comprising of hydrophobic junctions in solution. The C_e of purified PEO is 1.4 wt.% as obtained from the transition in the change in slope of specific viscosity (not shown here). The 3 wt.% PEO is above its C_e and hence there are sufficient entanglements in solution to form beaded fibers but not enough to obtain beads-free fibers. Upon the addition of HASE, the ensuing network of hydrophobic associations effectively substitutes for additional entanglements required to facilitate the development of uniform fibers. We refrain from delving further into this issue of “entanglement” modification as it is beyond the scope of this study.

In a related work on the effect of chitosan - a linear polysaccharide which is commonly used as a food thickener – on electrospinning of poly(vinyl alcohol) (PVA), Lin *et*

*al.*⁹ showed that the addition of chitosan improved the uniformity of fibers. However, the improvement in fiber formation was not very significant considering that even in the absence of chitosan, the minimum concentration of PVA that they explored was high enough to form beads-on-string morphology instead of predominantly beaded fibers as is usually the case when spinning from dilute concentrations. The effect of chitosan on lower PVA concentrations, which would otherwise result in mostly beads, was not reported. Moreover, as discussed by the authors, the conductivity of the solutions increased significantly on chitosan addition, due to the presence of ammonium cationic ions present in the chitin molecule, which also positively influenced the reduction in bead-density.

6.3.2 Suppressing the polyelectrolyte effect of HASE

From a practical standpoint, it is important to minimize the amount of associative polymer added to aid electrospinning because the presence of a second polymer can affect the properties of the resulting PEO fibers. A simple approach in this regard would be to suppress the polyelectrolyte effect of HASE polymers. Apart from increasing the solution conductivity which favors jet stretching, the presence of polyelectrolytes in an electrospinning solution also leads to jet instabilities caused by the lower mobility of the polyions, and poor fiber morphology. Son *et al.*⁴⁷ studied the influence of solution pH on the electrospinning of poly vinyl alcohol (PVA) solutions. They reported that electrospinning of PVA under acidic pH resulted in the formation of beaded fibers which was attributed to the protonation of the hydroxyl groups on PVA thereby rendering it a polyelectrolyte nature. According to the authors, the low mobility of protonated PVA led to local variations in

charge density which inhibited a stable jet formation. McKee *et al.*⁴⁸, in their work on electrospinning of cationic polyelectrolytes, also reported difficulties in electrospinning at lower concentrations. Unlike neutral polymers which form uniform fibers at 2-2.5 times C_e , concentrations well above C_e ($\sim 8 C_e$) were required to obtain fibers for their system. They added NaCl salts to their system to shield the electrostatic charges present on the polymer backbone and found that the minimum concentration to obtain fibers decreased as the concentration of salt increased. The authors attributed this observation to the screening of repulsive charges which in turn helped to stabilize the jet.

Thus in order to further reduce the concentration of HASE required to electrospin PEO into uniform fibers, we resorted to the use of salts that could suppress the polyelectrolyte effect of HASE by shielding the charges present on the HASE backbone. Figure 6.4 shows the SEM images of fibers spun from solutions of 3 wt.% PEO with different HASE concentrations in the presence of 0.005M NaCl. Also shown is the image of fibers spun from 4 wt.% PEO in the absence of HASE. In the presence of NaCl, we are able to obtain uniform, bead-free fibers with 0.1 wt.% HASE as opposed to 0.2 wt.% HASE in the absence of any salt (*cf.* Figure 6.2c). Reducing the polyelectrolyte effect by adding salts thus helps to improve the electrospinnability. A notable observation in Figure 6.5 is the similarity between the rheological behavior of a 3% PEO/0.1% HASE/NaCl solution and that of 4 wt.% PEO solution, which by itself is readily electrospinnable. We observe that both viscosity as well as the dynamic moduli of 3% PEO increase and become similar to that of 4% PEO upon the addition of HASE. The electrospun fibers in turn become more defect free and uniform. In essence, we are able to replicate the rheology of the 3% PEO to that of the 4% PEO

system by incorporating HASE. This observation underlines the importance of rheological modification in the fiber spinning process. The overlapping of the curves in Figure 6.5 in this particular case may be fortuitous. Nonetheless, the overarching observation is that the rheological properties of 3 wt.% PEO approach those of 4 wt.% PEO, thereby implying a change in molecular interactions in the system. For instance, in the absence of salt, the addition of HASE improves fiber formation wherein the rheological properties of 3 wt.% PEO/0.1 wt. % HASE and that of 4 wt.% PEO are similar, albeit not overlapping. These results are further validated in the next section where we report the use of another associative polymer instead of HASE.

One caveat that can possibly be associated with the above results is that reduction in bead density could be a consequence of increased conductivity upon addition of HASE. Increasing the net charge density of a precursor solution increases charge repulsion along the jet leading to stronger elongational forces which favors the formation of fibers instead of beads. This phenomenon of reduction in bead density in presence of ionic additives such as inorganic salts has been amply reported in literature²⁰⁻²². Since HASE polymer acts as a polyelectrolyte owing to its anionic backbone of carboxylate groups, the addition of HASE increases the conductivity of 3 wt.% PEO solution from 90 $\mu\text{S}/\text{cm}$ in the absence of HASE to around 1.44 mS/cm at 0.1 wt.% HASE (0.005M NaCl) concentration. Hence the formation of uniform fibers upon HASE addition may also be attributed to the increase in conductivity.

To address this issue and to establish that the improvement in the spinnability is predominantly derived from an increase in molecular associations in the presence of HASE and not due to an increase in conductivity, we prepared a 3.2 wt.% PEO solution with

conductivity similar to that of the 3 wt.% PEO/ 0.1 wt.% HASE (0.005M NaCl) solution by adding NaCl salt to the PEO-only solution. A 3.2 wt.% PEO was selected for this purpose as it represents a conservative limit when comparing fibers from both samples; one with a higher concentration (3% PEO/0.2% HASE) and the other with a higher conductivity (3% PEO/0.1% HASE with salts) as both these factors are expected to improve fiber morphology. As seen from Figure 6.6, increasing the conductivity of a 3.2 wt.% PEO solution does not result in improvement in fiber formation as mostly beaded fibers are obtained. These results affirm that the improvement in the morphology of the resulting fibers is primarily derived from increase in associations in solution.

The obvious advantage of spinning at lower concentrations lies in reduction in fiber diameters from spinning at lower concentrations. In the present work, the average fiber diameter obtained from 3 wt.% PEO (otherwise not electrospinnable into uniform fibers) in the presence 0.1 wt.% HASE and salt is ~120nm as compared to ~230nm from 4% PEO solutions and this difference is statistically significant at $\alpha = 0.05$ level.

6.3.3 Electrospinning of PEO solutions using Guar Galactomannan

The concept of using hydrophobically modified associative polymers as an electrospinning aid can be applied to other associative polymers which can modulate solution rheology. To validate this hypothesis, we used guar galactomannan, a water-soluble associative polymer which is a non-polyelectrolyte and affects solution rheology via hydrogen bonding instead of forming hydrophobic associations. Guar galactomannan is a low cost, naturally abundant polysaccharide consisting of β -1,4-linked mannose units as its

backbone with randomly attached α -1,6-linked galactose side chains⁴⁹⁻⁵³. The ratio of mannose to galactose units is roughly 2:1. Guar forms extensive hydrogen-bonding network in an aqueous solution and is therefore used as industrial thickener in several applications including food, oil recovery, drug-delivery, personal and health-care products^{52,54}. The effect of adding guar on the steady state viscosity profile of a 3 wt. % PEO solution is shown in Figure 6.7. Similar to the data obtained for HASE polymers, the presence of guar causes an increase in the PEO solution viscosity. However, the magnitude of change in viscosity is less than that compared to the effect of HASE (*cf.* Figure 6.3a). This observation is not unexpected as hydrophobic associations are much stronger than those through the formation of hydrogen bonds. The difference in their association mechanism is also reflected in dissimilarity in their viscosity profiles. Unlike HASE which shows a nonlinear steady shear response, PEO solutions in the presence of guar exhibit Newtonian behavior at low stresses. More importantly though, addition of guar does not lead to any change in solution conductivity; as such any changes in nanofiber properties for PEO-guar system can be readily attributed to entanglement effects. Figure 6.8 shows the images of electrospun fibers obtained from 3% PEO solution with increasing guar concentration. We find that a systematic increase in the concentration of guar improves the morphology of final fibers. The bead density decreases as guar content in solution is increased from 0.05 wt.% to 0.1 wt.% and at 0.2 wt.% guar, we observe uniform, bead-free PEO fibers similar to those obtained using HASE. The average fiber diameter in the presence of 0.2 wt.% guar is ~ 170 nm. These results further validate our hypothesis that associative polymers can be used effectively as an aid in electrospinning of polymers that lack spinnability, by tailoring their solution rheology.

In Figure 6.9, we juxtapose the viscosity profile of different associative polymer systems discussed so far, guar and HASE with and without salt, together with that of 3 and 4 wt.% PEO solutions, to bring together a coherent picture on the overall role of rheology on nanofiber formation. The concentrations of associative polymers in the figure correspond to the minimum concentrations at which uniform fibers were obtained. While the lowest viscosity curve of 3% PEO corresponds to a sample that is not electrospinnable, all other viscosity data corresponds to spinnable formulations. Several other features are notable. First, both the addition of either 0.2% guar or 0.2% HASE produces nanofibers with very similar average diameters (170 nm versus 180 nm). This is consistent with the fact that the total polymer concentration is same in both, and the role the associative polymer primarily being that of increasing the critical “entanglement”. However, the viscosity of the HASE sample is substantially higher because the association mechanism in HASE is much more potent than that of guar. Second, we observe that 0.2% HASE is needed to achieve electrospinnability versus 0.1% HASE with salt. This behavior is in accordance with the polyelectrolyte nature of HASE wherein a higher concentration of the polymer is required to impart jet stability. Finally, the 4% pure PEO sample and the 3% PEO containing 0.1% HASE with salt show similar viscosity, but the latter when electrospun produces a smaller fiber diameter (120 nm versus 230 nm). This behavior is in agreement with the fact that a lower total polymer concentration in the precursor solutions manifest in smaller diameter of the electrospun nanofibers^{12,55}.

6.4 Summary

In this contribution, we have demonstrated the utility of associative polymers in improving fiber formation of poorly electrospinnable polymer systems. We established that the addition of hydrophobically modified associative polymers (HASE) in small amounts to PEO solutions leads to significant changes in solution rheology and considerable improvement in the morphology of the resulting electrospun fibers. In addition, we demonstrated that the concentration of HASE required to improve the quality of fibers can be further lowered by suppressing the polyelectrolyte effect of HASE using salts. Similar changes in rheology and fiber formation were observed upon using guar associative polymer that interacts via hydrogen bonding. In both cases, hydrophobic associations or hydrogen bonding effectively substitutes for additional entanglements required to facilitate the development of uniform fibers. The reported findings have important implications as they elucidate the role of associative polymers to control hydrophobic and hydrogen-bonding interactions in dilute polymer solutions, hence adding a new degree of freedom for the production of submicron fibers via electrospinning.

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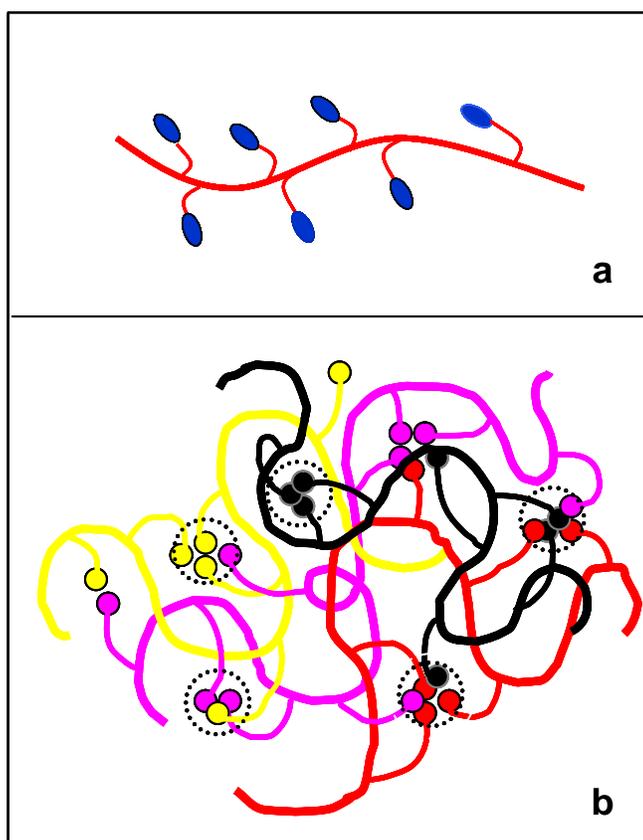


Figure 6.1. Schematic representation of HASE associative polymer. (a) A polymer molecule by itself consisting of hydrophobes shown as the tip of the pendant groups. (b), HASE polymer in aqueous solution showing inter and intramolecular association of the hydrophobes.

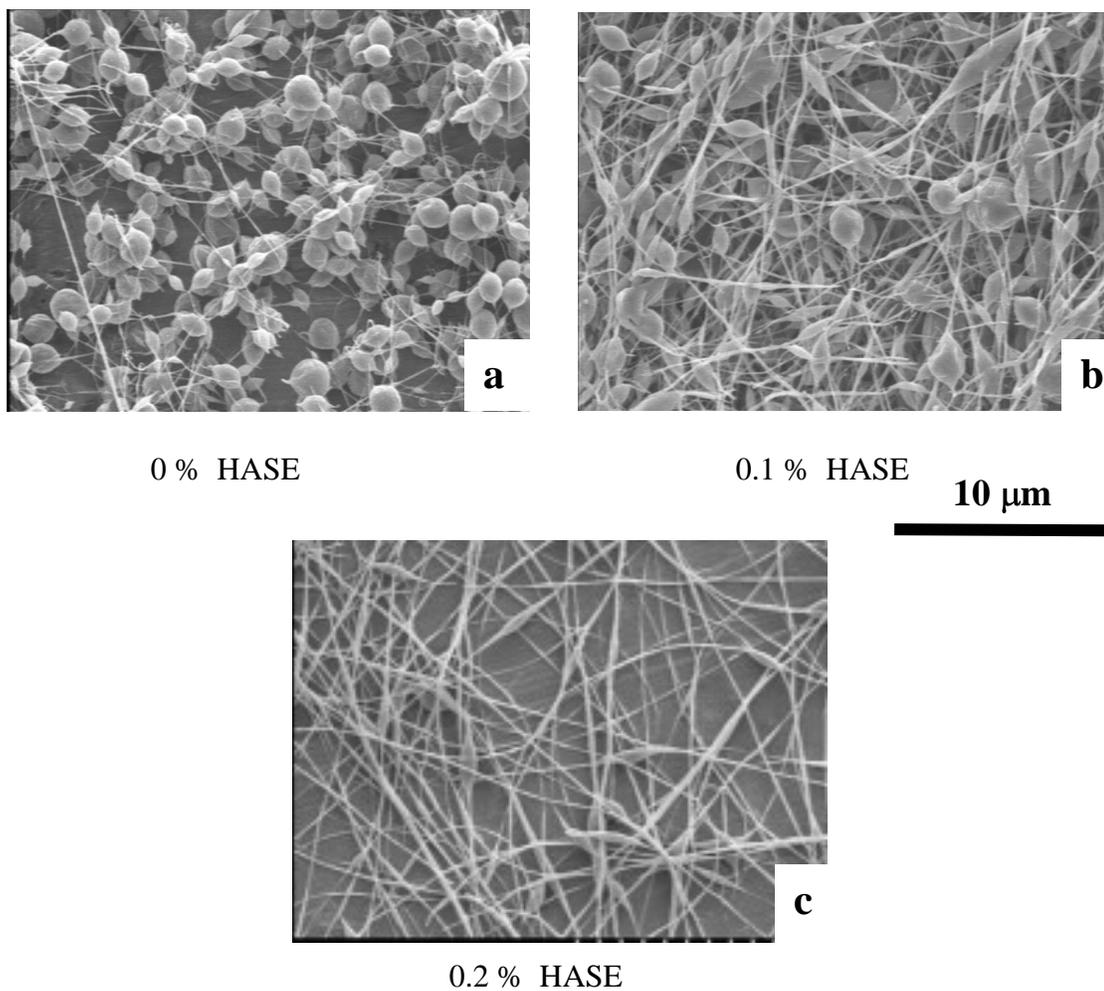


Figure 6.2. SEM images of electrospun fibers obtained from 3 wt.% PEO solution with different associative polymer (HASE) concentrations.

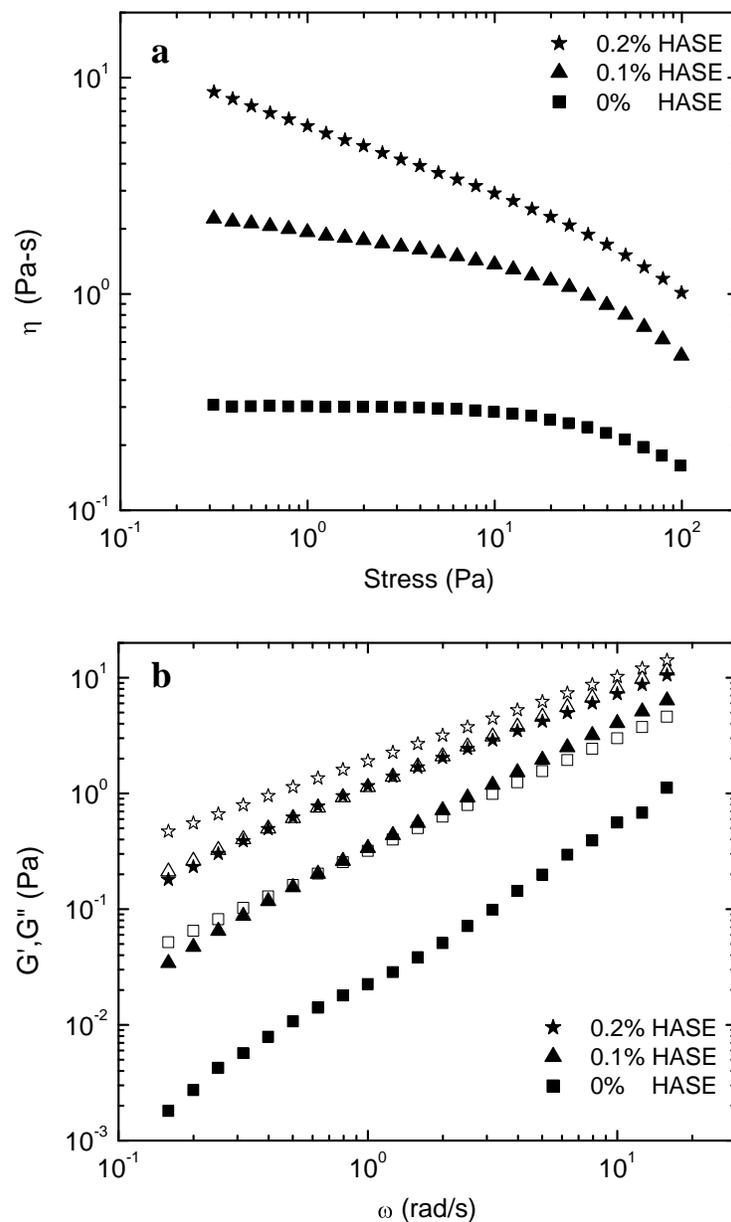
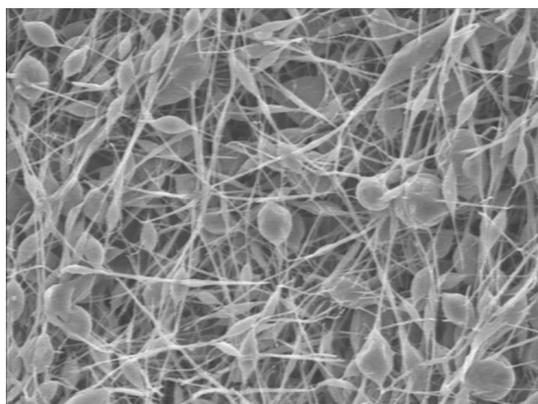
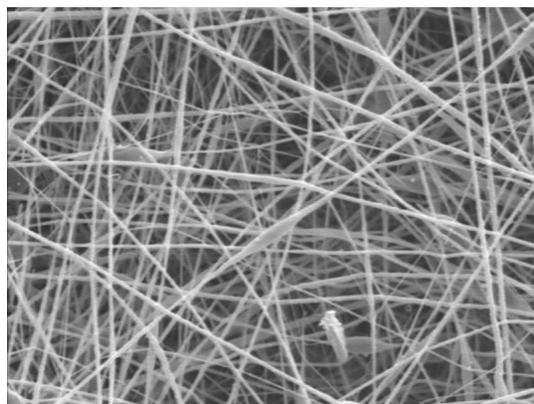


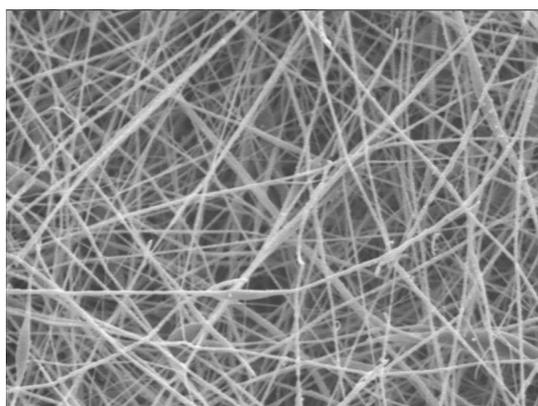
Figure 6.3. Steady shear viscosity (a), and dynamic frequency spectrum of the elastic (G' , closed symbols) and viscous (G'' open symbols) moduli (b), shown for 3 wt.% (600k MW) PEO with different HASE concentrations.



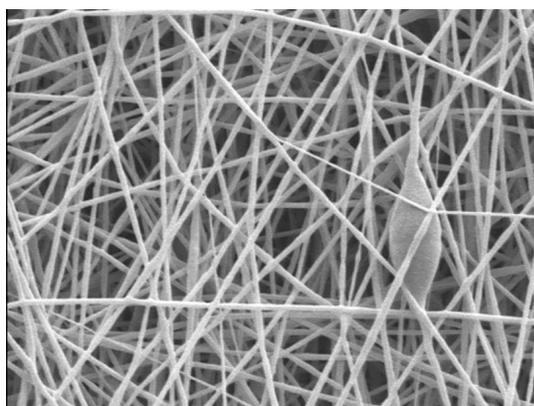
3% PEO/0.1% HASE



3% PEO/0.1% HASE (0.005M NaCl)



3% PEO/0.2% HASE (0.005M NaCl)



4% PEO

10 μ m

Figure 6.4. SEM images of electrospun nanofibers obtained from 3 wt.% PEO solution with different HASE concentrations in the presence of salt as well as from 4 wt.% PEO.

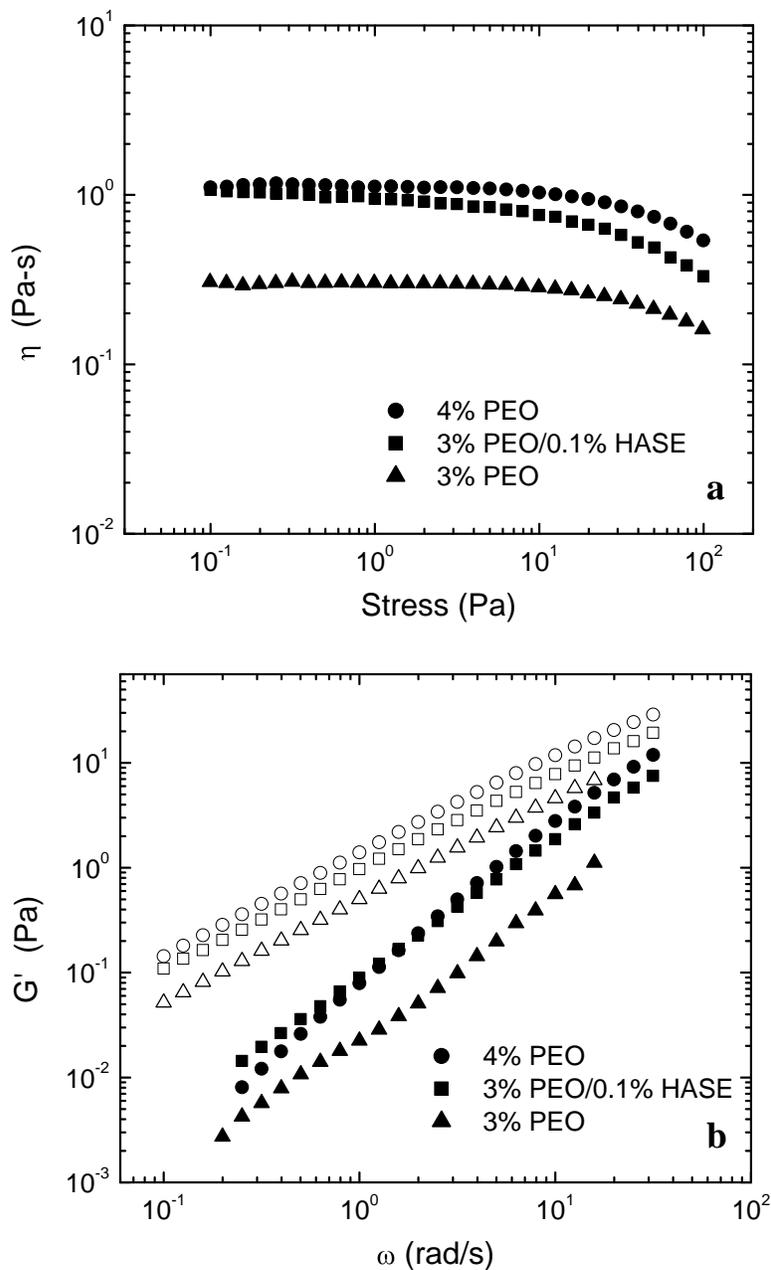


Figure 6.5. Steady shear viscosity (a), and dynamic frequency spectrum of the elastic (G' closed symbol) and viscous (G'' open symbol) moduli (b), shown for 3 wt.% (600k MW) PEO with and without 0.1 wt.% HASE (0.005M NaCl). Also shown are the profiles for 4 wt.% PEO. The figure shows how addition of HASE to 3 wt.% PEO replicates the rheology of 4 wt.% PEO.

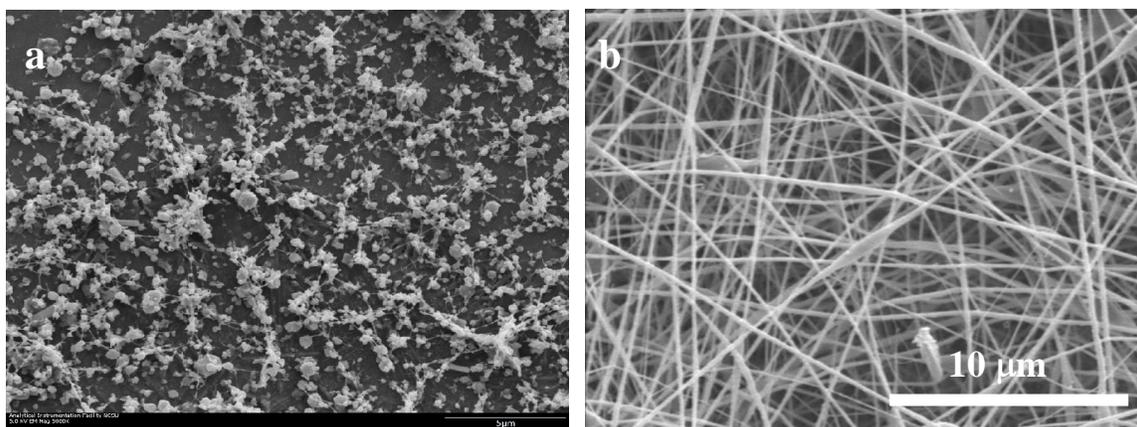


Figure 6.6. SEM images of electrospun nanofibers obtained from a) 3.2 wt.% PEO solution and b) 3 wt.% PEO/ 0.1% HASE (0.005M NaCl) with similar solution conductivities.

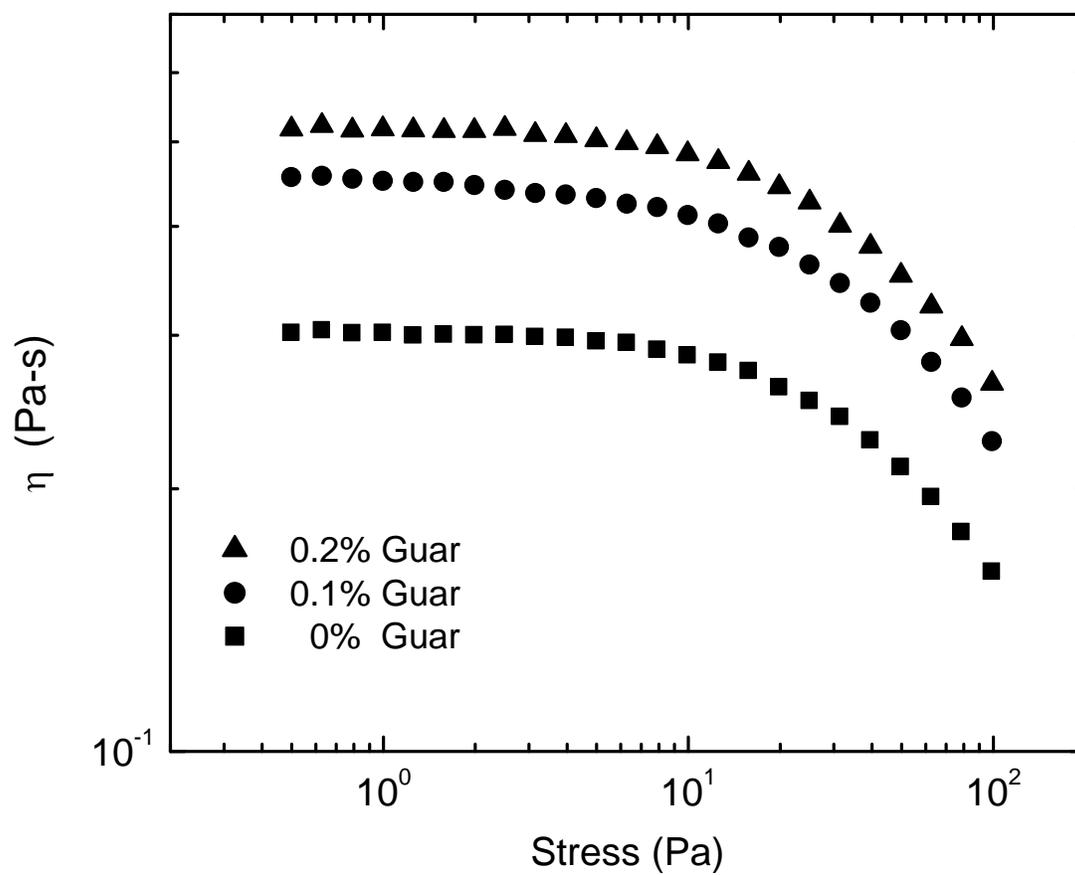


Figure 6.7. Steady state viscosity profile of 3 wt.% (600k MW) PEO with different guar concentrations.

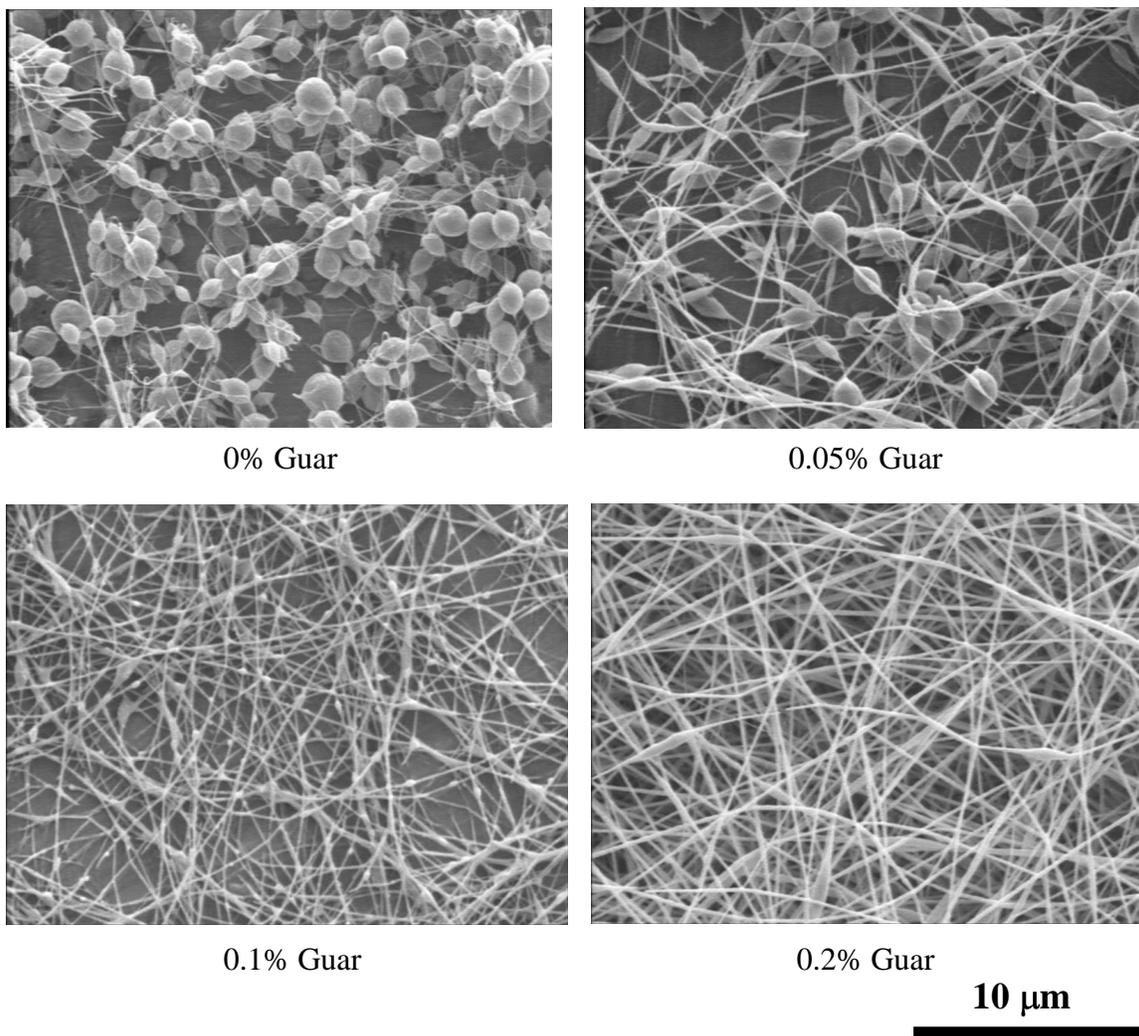


Figure 6.8. SEM images of fibers from 3% PEO with different guar concentrations.

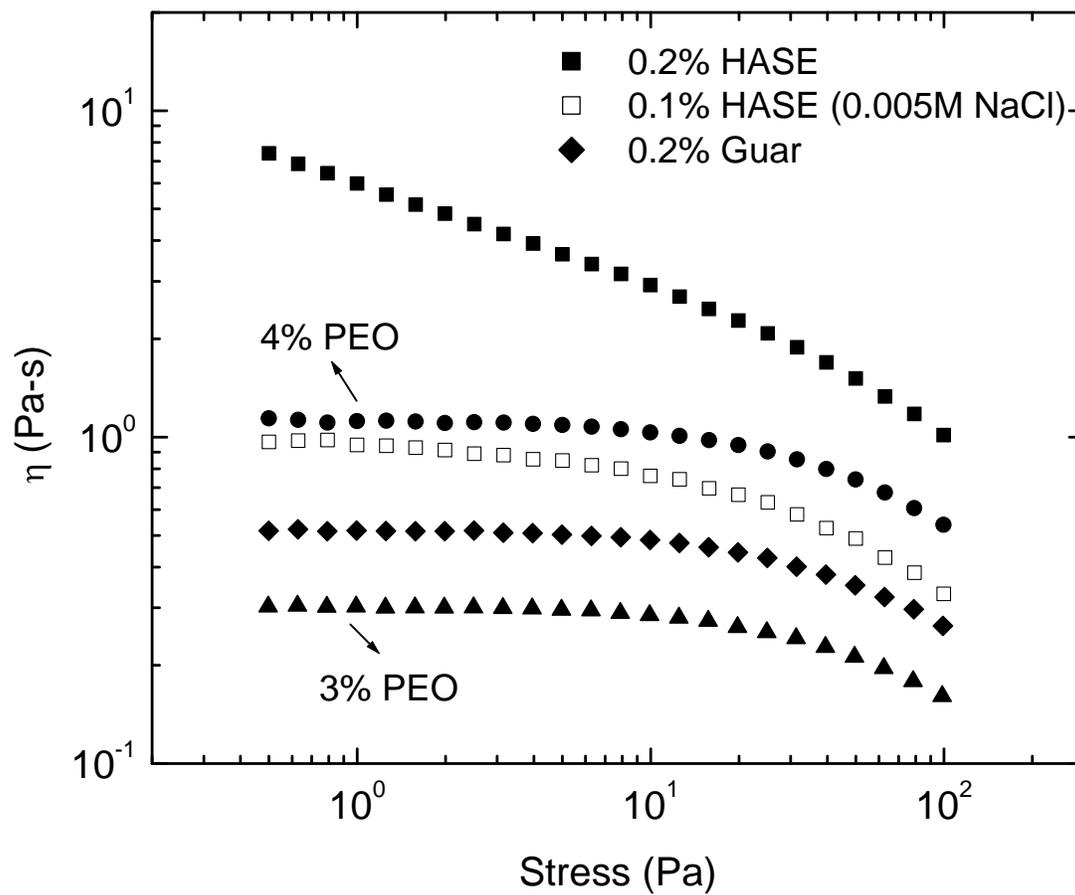


Figure 6.9. Steady state viscosity profiles of 3 wt.% PEO solution with and without different associative polymer systems. Also shown is the viscosity of a 4 wt.% PEO solution.

CHAPTER 7

Conclusions and Recommendations

7.1 Conclusions

In the preceding chapters, we explored the rheological modification of associative polymer solutions by incorporating various compounds such as surfactants and cyclodextrin. We further exploited the unique rheological characteristics of such systems to gain insights into the role of viscoelasticity in nanofiber formation *via* electrospinning and to improve the fiber morphology therein. Some of our major findings are summarized below.

- We illustrated the role of nonionic surfactants in modulating hydrophobic associations in HASE polymer solutions as reflected in their macroscopic properties. The steady state and dynamic rheological properties of the polymer solutions were shown to be dictated by both the surfactant concentration and its amphiphilicity as measured by surfactant hydrophilic lipophilic balance (HLB). In effect, the low shear viscosity continuously increases with concentration for low HLB surfactants and exhibits a maximum for intermediate HLB surfactants. Additionally, the value of this maximum gradually decreases for higher HLB values. The different behavior patterns have been explained in terms of number and average lifetime of hydrophobic junctions, and can be related to the molecular-level interactions between associative polymer and nonionic surfactants. These findings provide a better understanding of the various mechanisms of molecular interaction between nonionic surfactants and HASE polymer in solutions and should prove useful when selecting the appropriate polymer/surfactant system based on desired rheological properties.

- We examined the utility of binary nonionic surfactant mixtures, as opposed to individual analogous surfactants, in tailoring the rheology of comb-like associative polymers. We demonstrated that addition of surfactant mixtures, where the difference in surfactant hydrophilic chain length is large, to HASE polymer solutions leads to considerably higher values of viscosity at high surfactant concentrations as compared to equivalent individual surfactant. In contrast to the above results, equimolar surfactant mixtures with smaller variation in chain length are rheologically identical to equivalent solutions of single surfactant. The observed behavior has been explained in terms of transition in micellar structure due to difference in hydrophilic chain lengths in surfactant mixtures and is supported by cloud point measurements and activation energy data. The ratios of surfactants in binary mixtures are also shown to have a profound effect on the trends of viscosity versus overall surfactant concentration. These results further broaden the scope and utility of nonionic surfactants in tailoring the rheological characteristics of associative polymers to suit application requirements.
- We investigated the scope of using nonionic surfactants in recovering hydrophobic interactions and ensuing rheological properties in associative polymer solutions containing cyclodextrin. Our results reveal that depending on the type of CD (α versus β) as well as the hydrophilic-lipophilic balance (HLB) of surfactant, the extent and rate of recovery of zero shear viscosity as well as dynamic moduli are vastly different. Raising surfactant HLB in case of HASE/ α -CD solutions shows a transition

from a complete recovery of low shear viscosity in case of NP6 to an absence of recovery in case of NP15. On the other hand, HASE/ β -CD mixtures exhibit complete recovery upon addition of the surfactants studied. However, unlike NP6, addition of NP8 and NP15 leads to a lowering of viscosity at higher concentrations after attaining a maximum. These differing results have been explained on the basis of varying affinities of α - and β -CDs to bind with NP surfactants and the presence of different micellar structures in solution as dictated by surfactant HLB. These findings are of particular importance as they imply that a judicious selection of surfactant based on its HLB is critical while employing surfactants to facilitate viscosity recovery in HASE solutions containing cyclodextrin.

- We successfully incorporated associative polymers into nanofibers in conjunction with PEO. Our results reveal that the solution rheology puts a limit to the HASE concentration which can be electrospun. Our findings further suggest that polymer viscoelasticity, in addition to just solution viscosity, substantially influences fiber quality. More importantly, we have been able to achieve significant improvement in the nanofiber morphology by modulating the viscoelastic properties of the polymers using nonionic surfactants.
- We demonstrated the utility of associative polymers as electrospinning aid for poorly electrospinnable polymer systems. Addition of HASE in small amounts to PEO is shown to significantly affect the solution rheology which translates into considerable improvement in the morphology of the resulting electrospun fibers. By suppressing

the polyelectrolyte effect of HASE using salts, we were able to further lower the concentration of HASE required to improve fiber quality. Addition of guar associative polymer – that interacts via hydrogen bonding – to precursor solutions display similar changes in rheology and fiber formation. The reported findings have important implications as they elucidate the role of associative polymers to control hydrophobic and hydrogen-bonding interactions in dilute polymer solutions and establish their utility as rheology modifiers to improve fiber formation *via* electrospinning.

7.2 Recommendations

In this dissertation research, we examined the rheological properties of associative polymer solutions and applied the use of these rheology modifiers in understanding as well as in improving nanofiber formation via electrospinning. The scope of this research can be extended to other similar systems. Some of our recommendations for future research are discussed below.

7.2.1 Nanofibers from wormlike micelles

The scope of electrospinning can be extended to small biological molecules as evidenced in a recent study on electrospinning of lecithin – a naturally derived zwitterionic phospholipid – to form phospholipid membranes¹. Phospholipids are amphiphiles that form reverse micelles in non-aqueous solutions. As the phospholipid concentration is increased, the micelles show a transition from spherical to cylindrical or wormlike structure and eventually form entanglements similar to polymeric chains. The existence of these

entanglements, induced by the presence of a polar cosolvent, facilitates electrospinning in these systems^{2,3}. However, the fiber diameter formed in such systems is in the micron range owing to the high concentration of lecithin in solution. A possible route to electrospin such systems into nanofibers would be the introduction of bile salts instead of a polar cosolvent to promote entanglements at low lecithin concentrations. Raghavan and coworkers⁴ have reported the formation of wormlike micelles of lecithin in nonpolar medium at relatively low concentrations by addition of trace amounts of bile salts such as sodium deoxycholate. The authors attributed the growth of micelles to the change in molecular geometry as a consequence of interactions between salts and the phospholipid hydrophilic group. In view of these results, it is worthwhile to investigate the role of bile salts in reducing the fiber diameter in electrospinning of such systems. In a similar vein, the concept of electrospinning can be applied to other biologically and industrially relevant amphiphiles such as ionic surfactants that form wormlike micelles in an aqueous medium upon salt addition^{5,6}.

7.2.2 Facilitating associations in organic solvents

In Chapter 6 we discussed how additional interactions in aqueous solutions in the form of either hydrophobic associations or extensive hydrogen bonding effectively substitute for entanglements and promote electrospinning at lower polymer concentrations. A logical extension of this work would be to explore the scope of promoting supplementary interactions in polymers dissolved in organic solvents. Apart from scientific curiosity, it is of practical significance as a vast number of electrospinning polymer systems are non-aqueous based. In principle this can be achieved by addition of polymers that exhibit associative

mechanism in organic solvents. Examples of such polymers include, but are not limited to, graft copolymers⁷, diblock or triblock copolymers⁸ and ionomers⁹. Addition of these polymers in appropriate solvent systems results in the formation of micellar or flower-like structures. For instance, telechelic sulfonated polystyrene ionomers are known to form a transient physical network consisting flower-like micelles at low concentrations in apolar solvents like toluene¹⁰. Employing them in small quantities in electrospinning solutions of polystyrene is expected to induce additional associations due to the formation of micellar aggregates as well as increase solution viscoelasticity which in turn would aid in spinning at lower polymer concentrations. Hence a judicious selection of an associative polymer based on its rheological characteristics and its compatibility with the precursor polymer/solvent system can provide a potent tool to improve nanofiber formation from organic solvents.

7.2.3 Temperature-induced viscosity recovery in HASE solutions containing cyclodextrin and surfactants

In Chapter 3 we discussed the range of rheological behavior displayed by HASE/CD systems in the presence of surfactants, as governed by the relative affinities of binding for different complexes. An additional degree of freedom to modulate the hydrophobic associations in these systems can possibly be achieved by varying the temperature. Mahammad *et al.*¹¹ reported a decrease in the binding affinity of CD-polymer hydrophobe complexes with increase temperature. Thus increasing temperature in HASE/CD systems will have two counteracting factors affecting the viscosity. An increase in chain motion, which serves to lower viscosity, will be accompanied by an increase in hydrophobic

associations which contributes to viscosity enhancement. Additionally, with increasing temperature the binding affinity of CD-surfactant complexes reduces¹² while an increase in surfactant-HASE associations has been reported in literature for low HLB surfactants¹³. Initial work in this direction reveals that at concentrations of NP6 at which there is no viscosity recovery in HASE/ α -CD mixtures, a monotonous increase in viscosity is observed with increasing temperature up to 55°C, while no appreciable change in viscosity is observed for NP8 and NP15 surfactants. Hence, depending on the type of CD as well as surfactant concentration and HLB, a wide range of rheological behavior is expected with variations in solution temperature. A detailed examination of the rheology and microstructure of these systems would be helpful in developing aqueous formulations of associative polymers with precise rheological characteristics.

7.2.4 Mechanical properties of electrospun fibers

Although the process of electrospinning has been the focus of abundant research and a large number of studies have been undertaken to assess the effect of various parameters on fiber formation, very few reports on the mechanical properties of the final fibers exist^{14,15}. The mechanical properties of the electrospun fibers are of great significance from a practical standpoint and are expected to be considerably affected by the presence of additives in electrospinning solution. Future work in this direction should focus on a detailed investigation of the mechanical properties of the electrospun fibers obtained from solutions containing associative polymers. The research should employ differential scanning calorimetry, wide angle x-ray diffraction and atomic force microscopy to gain a

comprehensive understanding of the effect of solution properties and processing conditions on the crystallinity, crystal orientation and bending- and shear moduli- of the fibers.

7.3 References

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