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SYNTHESIS AND CHARACTERIZATION OF HYDROPHOBICALLY MODIFIED POLYACRYLAMIDE-BASED POLYMERS AND THEIR HYDROGELS

by

YI YANG

A dissertation submitted to the Graduate Faculty in Chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York

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This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philisophy.

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ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF HYDROPHOBICALLY MODIFIED POLYACRYLAMIDE-BASED POLYMERS AND THEIR HYDROGELS

by

Yi Yang

Adviser: Professor Carol A. Steiner

A series of hydrophobically modified Acrylamide-based copolymers, incorporating linear alkyl side chains containing 8-18 carbons at level of 0.75-7 mol%, hydrolysis level ranging from 0 to 65 mol%, have been prepared by micellar copolymerization and graft reaction of a precursor polymer. These polymers have been characterized by NMR for hydrophobe level, classical light scattering for molecular weight and elemental analysis for hydrolysis level. In addition, novel dispersed-phase hydrogels with hydrophobic microdomains composed of aggregates of the alkyl side chain were made from polymers containing 1.5 mol% C_8 with hydrolysis levels of 1.53 ~ 4.81 mol% acrylate and 1.5 mol% C_{10} with 2.28 ~ 23.7 mol% acrylate in aqueous systems. The hydrogel properties were investigated using

rheometry, fluorescence spectroscopy and conductimetry.

A comparison of the two synthetic routes, including the product structure, limitations and procedure of the two routes are presented in this study. Micellar copolymerization can make amphiphilic polymers by one step and is an easier procedure than the graft reaction. However, it is not possible to synthesize amphiphilic polymers with both high molecular weight and high hydrophobe level by this method. On the other hand, the graft reaction has no such structure limitation on the product. The conversions of hydrophobic modifiers are 100% for micellar copolymerization and 40 ~ 60% for the graft reaction, respectively.

Several structure/property relationships between starting polymer and the resulting hydrogel have been identified. First, the gel point (the lowest polymer concentration at which an aqueous polymer solution exhibits a rubbery plateau in the dynamic rheological spectra) increases with backbone charge and decreases with side chain length. Second, the strength of the polymeric network increases with side chain length. Third, formation of hydrophobic aggregates is favored by low hydrolysis level polymer (between 1.53 to 4.81 mol% for C_8 modified polymer) but not relatively high hydrolysis level polymer (about 24 mol%). Furthermore, the hydrogel properties may be manipulated to some extent by the addition of salt and surfactant.

To My Husband

Changdong

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CHAPTER 1. INTRODUCTION

Hydrogels are three-dimensional networks of polymers swollen with water. These networks are characterized by extensive intermolecular interactions. The links that hold the macromolecules together can be chemical bonds or physical cross-links such as crystallites, electrostatic interactions, hydrogen bonds, hydrophobic interactions etc. Polymeric gels, as a novel material, are interesting to industrial and academic laboratories because they can be used in many fields. Uses of gels, as reviewed by Tanaka [1], include super water absorbents for personal care, new wrapping sheets for fresh fish and meats, soft contact lenses that ensure air and moisture exchange with the eye, materials for continuous release of moisture to plants, and chromatography as well as other separation process. They also have potential use in pharmaceutical preparations since they can load large quantities of drug and release the drug over time.

Amphiphilic hydrogels are an interesting new class of hydrogels under development in Professor Steiner's laboratory and elsewhere. These gels are made from hydrophobically modified water-soluble polymers (HMWSPs), which are copolymers that contain a water-soluble backbone and small amounts of hydrophobic units dispersed along the backbone. In aqueous solutions above a certain polymer concentration the hydrophobic units belonging to different macromolecules aggregate to form hydrophobic microdomains. Under appropriate conditions of solvent composition, temperature, and polymer concentration, this process

results in the formation of viscoelastic networks in which the hydrophobic aggregates, or micro domains, serve as physical cross-links. These networks are called biphasic or amphiphilic hydrogels. To date, only two HMWSPs have been used successfully to fabricate this type of hydrogel. One is hydrophobically modified hydroxyethyl cellulose (HMHEC) containing either linear alkyl or nonylphenyl side chains [2-5]. The other is hydrophobically modified poly(sodium acrylate) that forms a thermal-reversible gel in the presence of nonionic surfactants [6-7]. A generalized picture of this type of hydrogel is shown in Figure 1.1. The hydrophobic microdomains, which can act as reservoirs or sinks for solutes permeating the network, are well distributed in the bulk phase. Organic solutes or drugs permeating the network partition preferentially into the microdomains. On exposure to these molecules free surroundings, the solutes or drugs exit the gel by diffusion through the bulk phase and are then restored to the bulk from the reservoirs. Therefore, these hydrogels are suitable for use in controlled drug release, chromatography and other separation processes. It is expected that the structure of the polymer will strongly influence the macroscopic and microdomain properties of the hydrogel.

The objective of this study is to establish systematic structure/property relationships between HMWSPs and hydrogels made from them. To date, no studies on this topic have appeared in the literature, although numerous studies have been conducted on structure/property relationships of HMWSPs in solution. The approach is to synthesize a series of hydrophobically modified polyacrylamide-based polymers with different side chain content, side chain length, and backbone charge and to characterize hydrogels made from

these polymers. The side chain content and side chain length may be manipulated directly during synthesis of the polymer. By incorporated different levels of backbone charge, again during synthesis of the polymer, the radius of gyration of the polymer in aqueous systems can be also manipulated. These structural parameters were chosen because they are expected to influence the rheological properties of network and properties of the hydrophobic micro domains. For example, the side chain content of the polymer will influence the total number of aggregates. The radius of gyration that reflects the flexibility of the polymer backbone will affect the number of side chains available for aggregate formation. It is expected that by adjusting the radius of gyration of the polymer, the relative concentrations of unassociated, intra-molecularly associated, and inter-molecularly associated side chains should change as well. Finally, the side chain length is expected to influence the aggregation number and packing density of the hydrophobic micro domains, and consequently the micropolarity, micromorphology and microviscosity of the hydrophobic aggregates. Thus, the results of this study are expected to provide a basis for the rational design of two-phase hydrogels for different purposes.

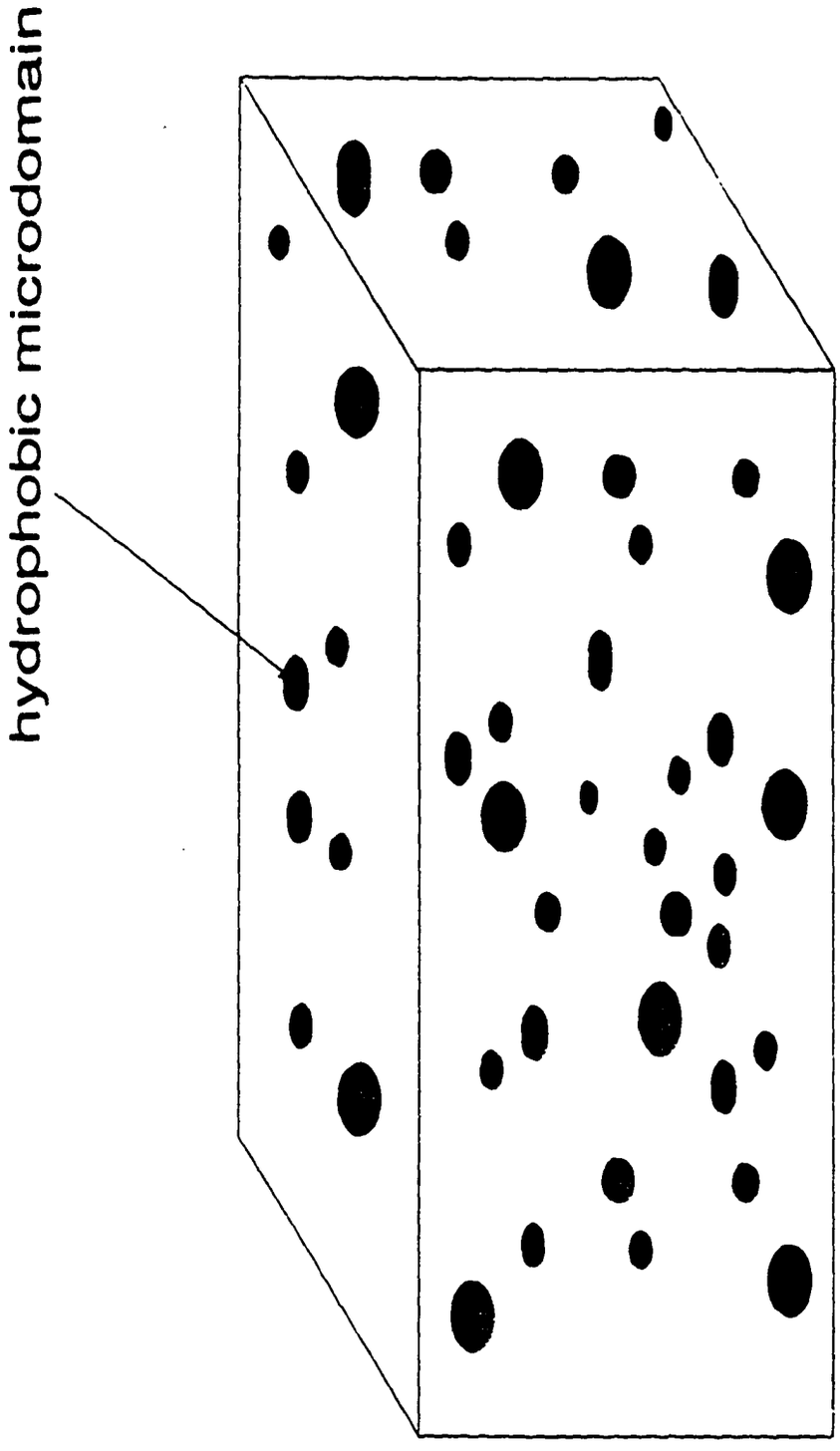


Figure 1.1 Schematic structure of three dimensional HMWSP hydrogel

CHAPTER 2. LITERATURE REVIEW

Hydrophobically modified water soluble polymers (HMWSPs) has been focus of studies in industrial and academic laboratories in recent years. Up to now, the most useful feature of HMWSPs is their unique rheological behavior in aqueous solutions. Aqueous solutions of HMWSPs have significantly higher viscosity than solutions of unmodified polymer at same concentration, because nonpolar side chains aggregate in water. The thickened aqueous medium may be employed to advantage in applications requiring viscous fluids. Such applications include rheology modifiers for latex paints [8], thickeners in enhanced oil recovery and rheology control additives in cementing operations during oil-well drilling [9]. These polymers have also been used as unique stabilizers in suspension polymerization [10] and emulsion polymerization [11], personal care formulations, flocculents and phase transfer [12]. Both nonionic HMWSPs and ionic HMWSPs have already been synthesized in numerous laboratories [13-26]. Nonionic HMWSPs possess polar, nonionic functional groups along or pendant to the backbones to which a low concentration of nonpolar side chains have been grafted. Ionic HMWSPs possess charges along or pendant to the molecular backbones. Structures of nonionic and ionic HMWSPs which have been synthesized are listed in Tables 2.1 and 2.2, respectively.

Studies of HMWSPs can be divided into three categories. First is synthetic routes for HMWSPs that include almost all available synthetic techniques of polymers. Second is

analysis of the molecular structure of HMWSPs, typically including molecular weight evaluated by light scattering or intrinsic viscosity, hydrophobe incorporation level and the chain sequence measured by UV spectroscopy and NMR techniques. The last category involves development and characterization of polymer networks or hydrophobic aggregates and the study of HMWSP solution properties.

2.1 Synthetic Routes to HMWSPs

In general, there are two different synthetic routes to HMWSPs. One is the copolymerization of a hydrophilic monomer with a hydrophobic modifier containing some polymerizable groups. The other is modification of a precursor polymer that consists of reactive groups along the WSP chain with reactive functional end groups of a hydrophobic modifier.

2.1.1 Copolymerization

Various polymerization techniques including bulk [20], solution [17], emulsion [26] and micellar polymerization [27] have been employed for the synthesis of HMWSPs. For example, poly[(maleic anhydride)-co-(n-butyl vinyl ether)] [20] and poly[1-octadecene-co-(maleic anhydride)] in which hydrophobe level was around 55 mol% [28] were made by bulk copolymerization. There have been some HMWSPs synthesized by solution copolymerization, such as, copolymer of N-isopropylacrylamide and N-[2-(1-Naphthyl)ethyl]-N-n-octadecylacrylamide synthesized in dioxane [17], poly[N-[(1-pyrenylsulfonamido)ethyl]acrylamide-co-acrylamide] in N, N-dimethylformamide (DMF) [29]

and copolymer of 2-(1-naphthylacetyl)ethyl acrylate and methacrylic acid in DMF [30]. However, in most cases, bulk and solution polymerization of copolymers composed of water-soluble and water-insoluble monomers present difficulties. Usually the copolymer is insoluble in a solvent that is a good solvent for the monomers. This leads to precipitation of the copolymer at a molecular weight too low to produce efficient viscosification. The other disadvantage is that solvents that are often employed to synthesize HMWSPs are fairly good chain transfer agents. This renders a low molecular weight of the final products. To avoid these disadvantages, emulsion copolymerization has been used to make n-alkylacrylamide modified polyacrylamide [26]. However, in this process, the droplets of water-insoluble monomer must be stabilized against coalescence. This is particularly difficult in solution containing electrolytes besides the surfactant [31]. In the past decade, a new technique, micellar copolymerization, that was developed in Exxon Research and Engineering Co. [27], became more important in HMWSP synthesis. Many of HMWSPs have been synthesized by this method [13,16,24,32].

Micellar copolymerization is a useful reaction scheme for copolymerizing water-soluble and water-insoluble monomers. The reaction takes place in a surfactant solution above the critical micelle concentraiton (cmc) of the surfactant. The concentration of hydrophobic monomer is kept low enough that the total number of hydrophobic molecules solubilzied within each micelle is of order ~10, and the system is thermodynamically stable. The hydrophilic monomer, in our case acrylamide, is solubilized in the continuous (aqueous) phase of the system and also adsorbs at the interface between the micelles and the water

because of its double bond. The initiator, in our case potassium persulfate, is dissolved in the aqueous phase. Thus the reaction between hydrophilic and hydrophobic monomers takes place in the aqueous phase in the vicinity of the micelles, and the product is water soluble. The system remains clear throughout the reaction. This system differs from more conventional emulsion polymerization schemes in that in emulsion polymerization reactions the size of the dispersed droplets is much larger, the reaction takes place in the dispersed phase, the product is insoluble in water, and the system appears milky upon completion of the reaction.

2.1.2 Modification of Precursor Polymer

Modification of the precursor polymer is a method to introduce hydrophobic side chains to water soluble polymers by the reaction of functional groups. All of the organic functional group reactions can be employed to modify water soluble polymers, as appropriate. Normally, the reaction is carried out in a solvent that can dissolve both the precursor polymer and the hydrophobic modifier. This method is very important for the modification of natural polymers such as cellulose [14]. For synthetic polymers, two steps are generally needed, namely, the polymerization of the precursor polymer and grafting the hydrophobe component to the polymer backbone. The advantage of this modification route vs. polymerization route is that the modification of precursor polymer leads to more well defined polymer structure, because functional group is added to a specific site on the chain. In contrast, the polymerization method leads to a more statistical placement of functional groups. Hydrophobically modified polyvinylpyridine [18], PAA [21], and maleic acid-ethyl vinyl ether

copolymers [33,34] have been made by this method. No kinetic data have been reported for the graft reaction of HMWSPs. However, the conversion of the hydrophobic modifier can reach 100% after 10 to 24 hr depending on the type of functional group, polymer structure and reaction conditions [21, 33-34]. The degree of polymerization of the precursor polymer should not be affected during the graft reaction [21]. ^{13}C NMR studies have shown that the hydrophobic groups distribute along the polymer chain randomly [34]. Unlike micellar copolymerization, a high molecular weight HMWSP with a desired hydrophobe level can be obtained by this synthesis method.

2.2 Characterization of HMWSPs

To date, the characterization of HMWSPs that has been reported has been focused on molecular weight, hydrophobe incorporation level and hydrophobe distribution along the polymer chain. Very few reports on the molecular weight distribution have appeared.

2.2.1 Measuring Molecular Weight

In principle, all methods that are used to determine the molecular weight of polymers could be means to measure the molecular weight of HMWSPs. However, most of them present difficulties practically, due to the interchain association induced by the hydrophobic moieties. This association is analogous to the aggregation of low-molecular-weight amphipathic species into micelles.

Classical light scattering is the most widely used method for determination of the

molecular weight of HMWSPs. It gives an absolute weight average molecular weight without requiring a standard sample. However, identification of a solvent in which intermolecular hydrophobic aggregation can't exist sometime presents difficulties. Generally, an organic solvent is a good choice for this purpose, for example, formamide for HM-polyacrylamide [32] and methanol for copolymer of dially (dimethylammonium chloride and N,N-dially(-N-(4-octyloxyberizyl)-N-methyl-ammonium chloride [36]. It is well known that addition of an organic solvent into HMWSP aqueous solutions disrupts the hydrophobic interactions. So, organic/water mixtures, such as, methanol/water (50/50 by volume) has been used as a light scattering solvent to measure the molecular weight of a copolymer of acrylamide and dimethyldodecyl(2-acrylamideoethyl)ammonium bromide [37]. Measurement of the unmodified polymer that gives the baseline of molecular weight of the modified molecules is also acceptable in cases where no solvent can completely disrupt the intermolecular interactions in HMWSPs [34,38].

The other methods that are commonly used to measure the polymer molecular weight, such as, intrinsic viscosity, gel permeation chromatography (GPC) and osmotic pressure have also been used for HMWSP molecular weight measurement. Some workers [13-14,17, 39] measured intrinsic viscosity of HMWSPs in aqueous solution instead of molecular weights. They estimated molecular weights by the Mark-Houwink equation where the two constants, K and a, for the unmodified polymer were used [13, 39]. However, the intrinsic viscosity is not only a function of degree of polymerization but also a function of hydrophobe type and hydrophobe level. The intrinsic viscosity of HMWSPs in aqueous solution is smaller than that

of the unmodified polymer with same degree of polymerization due to the intramolecular interaction of hydrophobe that leads to a more compact polymer coil. GPC is also a useful method to measure the molecular weight of HMWSPs, especially for molecular weights less than one million [17, 33, 40-41]. The molecular weight and the molecular weight distribution of HMWSPs can be determined from GPC measurements run in a suitable solvent and calibrated against polystyrene standards. However, GPC is not a good method for high molecular weight HMWSPs, because shear degradation cannot be ignored. Osmotic pressure is another method to measure the molecular weight of HMWSPs. It is reported that the number average molecular weight of poly[2-(1-naphthylacetyl)ethylacrylate-co-methacrylic acid] has been measured by osmotic pressure in DMF[30].

2.2.2 Measuring Hydrophobe Level

The method for determining the hydrophobe level of an HMWSP depends on the structure of the hydrophobe and amount of hydrophobe incorporation. UV spectroscopy is very useful for determining the hydrophobe level of HMWSPs containing UV active groups [13, 25,30, 32-34, 38]. It can detect hydrophobe levels as low as 0.75 mol% [25]. Gas chromatography has been employed to determine the amount of alkyl group incorporated in HMHEC [14]. The method is similar to pyrolysis gas chromatography. The polymer is cleaved completely and then the cleavage products are analyzed by gas chromatography. Elemental analysis is another method that is frequently used to determine the hydrophobe level [30,35,37-38,], especially for hydrophobes containing special elements. However, this is not a good method for HMWSPs containing less than 1 mol% hydrophobic component

[24].

Recently, the technology of NMR was introduced into measurement of hydrophobe levels of HMWSPs. Proton NMR has been used successfully to determine the hydrophobe level for several HMWSPs [36,35]. However, analysis by ^{1}H NMR may not be possible, sometimes, owing to broad, overlapping spectral lines resulting from high molecular weight. Solution ^{13}C NMR that gives relatively narrow spectral lines has also been employed in measurement of copolymer compositions [35]. On the other hand, solution ^{13}C NMR is time-consuming, often requiring 12-15 hr of scanning time to yield a proper signal-to-noise ratio for accurate determination of copolymer ratios. In addition, the solution technique necessitates concentrations of 5-25% by weight in solution, requiring several days for complete dissolution of high-molecular-weight polymers ($>10^{6}$ g mol^{-1}) to obtain quality solution spectra. Generally, the viscosity of HMWSP solution in such concentration is very high, which leads to broad and overlap peaks. McCormick and coworkers reported that solid-state ^{13}C direct-polarization magic angle spinning NMR has been used successfully to determine the hydrophobe level of HM-polyacrylamide [42]. This technique is much faster than the solution technique due to highly concentrated samples.

2.2.3 Measuring Chain Sequence of Comonomer

The measurement of hydrophobe distribution along the water soluble backbone is quite difficult, but, it's valuable. The chain sequence of comonomer, i.e. block or random, is an important factor that affects the HMWSPs' properties. Determination of the

microstructure of N-octylacrylamide/sodium acrylate copolymers that possess greater than 3 mol% hydrophobic groups has been performed by ^{13}C NMR in a CD_3OD/D_2O mixture [35]. The analysis was focused on the carboxyl group peaks. Good resolution of the triad peaks is required for determination of the copolymer microstructure. Deconvolutions have been used for the carbonyl peak of the acrylate group due to the overlap of peaks. Besides NMR measurement, steady-state fluorescence spectra have been used to determine the microstructure of pyrenesulfonamide-labeled polymers [16]. The excimer emission intensity of microblocky copolymer is dramatically enhanced relative to the random case.

2.3 Study of Hydrophobic Interaction

It is well known that HMWSPs associate in aqueous solution owing to unfavorable interactions between solvent and the hydrophobic moieties. The hydrophobic interaction could be an intramolecular interaction resulting in low intrinsic viscosity and a high Huggins constant or intermolecular interaction resulting significant viscosity enhancement. This review will focus on intermolecular hydrophobic interactions. The most basic questions about association of HMWSPs in aqueous solution are (1) At what concentration does the polymer begin to associate? (2) What are the bulk properties of the HMWSP aqueous solutions after aggregates form and what is the nature of the aggregates at a molecular level? (3) How many polymer molecules associate within each aggregate? This review will be divided into two parts. They are research methods for hydrophobic interaction and factors affecting hydrophobic interactions.

2.3.1 Research Methods to Determine Concentration and Composition of Hydrophobic Aggregates

The rheological properties of HMWSP systems are the best indicator of the extent of polymer-polymer association.. When aggregates form, the viscosity of an HMWSP solution is much higher than that of the unmodified polymer with similar molecular weight at same concentration [13-21,23]. Furthermore, the function viscosity vs. polymer concentration exhibits very different characteristics for HMWSPs and unmodified polymers [43]. The slope is much higher for HMWSP solutions than for the corresponding unmodified polymer. In addition, the viscosity exhibits a sharp upturn in HMWSP solutions at a concentration much lower than the critical overlap conentration of the unmodified polymer, reflecting the onset of intermolecular hydrophobic association. Under certain conditions, described below, strong viscoelastic hydrogels may be induced to precipitate from aqueous solutions of HMWSPs.

Spectroscopy is the most powerful means to study the aggregates at a molecular level. Fluorescence spectroscopy elucidates micropolarity, microviscosity and mean aggregation number of the micelle-like clusters [44]. Three types of fluorescence experiments have been carried out. Polarity-sensitive probes, of which pyrene is the most frequently utilized, can be used to determine the hydrophobicity of the probe environment and detect the onset of aggregation. The emission spectrum of the pyrene molecule exhibits five vibronic peaks in the range of 350-450 nm. The ratio of the first and third highest energy vibronic bands (I_1/I_3) may be correlated with medium polarity. The intensity ratio of I_1/I_3 drops sharply above the onset of aggregation [45]. In addition, the mean lifetime of emission that has a constant value

below the threshold of aggregation starts to increase with polymer concentration. Furthermore, there is a break in the function of intensity of pyrene emission, and the slope of the function increases significantly, at onset of aggregation. The second type of fluorescence probe is friction-sensitive probes that indicate the mobility of the probe in micelles or micelle-like clusters [46, 47-48]. The local viscosity of the dye-binding region is measured by determining the polarization of fluorescence of the dye. Because the dye is a small molecule, if there is no binding between dye and polymer, the polarization of fluorescence is found to be independent of the macroscopically measured viscosity. Fluorescence quenching experiments that allow one to determine the mean association number of the micelles or micelle-like clusters are another type of fluorescence method. Besides fluorescence study, absorption spectroscopy using pyridinium-N-phenoxide betaine [ET (30)] dye as a probe is also a simple and sensitive method to research hydrophobic microdomains of HMWSPs' aqueous solution [49]. This probe can detect the polarity of the hydrophobic microdomain surface.

2.3.2 Factors Affecting Hydrophobic Aggregation

Numerous studies on hydrophobic aggregation of HMWSPs have concentrated on the effects of polymer concentration and polymer structure on the rheological properties of dilute and semi-dilute aqueous solutions of the polymers (a semi-dilute solution is defined as one in which the polymer concentration is above the overlap concentration). The rheological properties of HMWSP solutions reflect the strength and density of hydrophobic aggregation directly. Dozens of references note that hydrophobic interaction also depends on other

conditions, such as solvents, additives, temperature, etc. Some research on HMWSPs in solution is summarized below. I will divide the discussion into three parts, as follow, effect of hydrophobe structure, effect of backbone structure and effect of solvent composition.

Effect of Hydrophobe Level and Structure

The hydrophobe level and structure influence the viscosity and solubility of the polymer. This has been demonstrated by several authors [14,23,46]. The viscosity of copolymer solutions is a direct function of both the amount and chain length of the hydrophobe [14]. It has been shown using HMHEC that as the hydrophobe content of a polymer increases, the viscosity first increases, reaches a maximum, and then decreases rapidly as the solubility of the polymer drops to zero. At a given hydrophobe level for linear alkyl side chains, the longer the side chain the higher the viscosity at constant polymer concentration. The solubility of the polymer goes down with both the amount and chain length of the hydrophobe [14].

The structure of the hydrophobic modifier also has a significant effect on the solution behavior of HMWSPs. For example, higher viscosity was found in perfluorocarbon modified polyacrylamide (PAM) solutions compared to hydrocarbon modified PAM [15]. This is probably because fluorocarbon compounds are more hydrophobic than comparable hydrocarbon ones. In addition, the viscosity of solutions HMWSPs containing branched hydrocarbon or phenyl groups [23] is higher than that containing linear alkyl groups at the same molecular weight and the same amount of incorporated hydrophobe. This may also be

the result of the higher hydrophobicity of the side chains.

Effect of Backbone Structure

Both the chemical structure and molecular weight of the backbone affect the solubility of the polymer and the rheological behavior of HMWSP solutions. Landoll [14] studied the effect of the backbone molecular weight, side chain length, and hydrophobe level in hydrophobically modified hydroxyethyl cellulose (HMHEC) on solution viscosity. At constant polymer concentration and the same hydrophobe structure, the higher the molecular weight of the polymer, the lower the hydrophobe level at which it becomes insoluble in water.

In aqueous solutions of hydrophobically modified polyelectrolytes, the competing effects of charge-charge repulsion and pendant group attraction give rise to complex behavior. For example, low charge density polymers exhibit lower viscosities below the overlap concentration (C^*) and higher viscosities above C^* than their high charge density analogues [50]. The presence of ionic groups adjacent to hydrophobic groups may result in a disruption of the hydrophobic effect because the charge increases the polarity of the solvent [40]. This may lead to an increase of solution viscosity by disrupting an intromolecular hydrophobic interactions, or a decrease of solution viscosity by disrupting an intermolecular hydrophobic interactions. The dissociation ability and steric structure of charged species also influence the rheological behavior of copolymer solutions. McCormick and coworkers studied the behavior of terpolymers consisting of acrylamide, 0.5 mol% N-(4-butyl)phenylacrylamide and 5-25 mol% one of following: sodium acrylate (NaA), sodium-2-

acrylamido-2-methylpropanesulphonate (NaAMPS) or sodium-3-acrylamido-3-methylbutanoate (NaAMB) in brine solution [51]. They found that solutions of the terpolymers containing NaA have much higher viscosities than the other two systems. They concluded that the NaNMB and NaAMPS may interfere with hydrophobic association more than the NaA since they were farther from the polymer backbone and. They also found that the terpolymers containing NaAMPS are the least affected by changing ionic strength, reflecting the difference between $-SO_3^-$ and $-CO_2^-$. Additionally, they found that low charge density polymers form gels at concentrations above 0.20 g/dl [50]. However, they did not research the properties of these gels.

Effect of Solvent composition

The hydrophobic aggregation of HMWSPs is influenced significantly by adding surfactants, salts and organic solvents into the solution.

The most significant feature of HMWSP/surfactant solutions is the presence of mixed hydrophobic microdomains comprised of aggregates of side chains and surfactant molecules. These domains have been observed by numerous workers [2-3, 6-7,52-57]. Because of the hydrophobic interaction, surfactant binding can even take place in cases where the polymer and the sufractant have the same charges [53]. The surfactant binding may facilitate aggregation of the hydrophobic moieties. These aggregates can acts as a crosslink point between different polymer chains, or may eliminate the hydrohobic interaction between chains, depending on the stoichiometry of the mixed hydrophobic domains. The relevent

stoichiometry may be either the hydrophobe stoichiometry, i.e., the ratio between surfactant chains and HMWSP hydrophobes in the mixed domains, or the charge stoichiometry, i.e., the net charge of the entire complex, including possible charges on the polymer backbone [57]. Rheology is, for HMWSP/surfactant system, predicted to be highly sensitive to concentration and composition of the mixed aggregates and the effect of surfactant will be complex due to competition between crosslink faciliting effects and an elimination of polymer-polymer association.

The addition of salt to HMWSP aqueous solutions enhances the hydrophobic associations because brine is a "poorer" solvent for the hydrophobe than is fresh water. For nonionic HMWSPs, the solution viscosity increases with the addition of salt above (C^*) [15,24,58]. This phenomenon is similar to the "salting out" effect of surfactant solution. For polyelectrolytes, the effects of salt on the viscosity of copolymer solutions are more complex because charge-charge interactions compete with hydrophobic interactions. If charge-charge interactions dominate the solution properties, the solution viscosity decreases continuously with addition of NaCl. This was found in hydrophobically modified polyacrylic acid (HMPAA) containing octyl pendant groups in solution with NaCl over the range 0 to 3% (w/v) of NaCl [52]. If the solution properties are dominated by the hydrophobic interaction, the solution viscosity increases with the ionic strength. This has been observed in solutions of hydrolyzed hydrophobically modified polyacrylamide (HRAM) containing 18 mol% sodium acrylate and 0.75-1.25 mol% N-n-octylacrylamidet [50] and solutions of HMPAA containing C_{14-18} alkyl group [52]. For example, the solution viscosity of 2% HMPAA containing 3

mol% C_{18} alkyl group increases from the order of 10^2 cp in water to the order of 10^4 cp in 1wt % NaCl solution [21].

The association of hydrophobic moieties of HMWSPs in aqueous solution can be disrupted by adding organic solvents. For example, methanol-water solutions are used as a solvent for the intrinsic viscosity measurement of HMHEC [39]. At methanol concentrations above 40%, the intrinsic viscosity of HMHEC reachs a constant value with nethanol concentration which is close to the value for the unmodified polymer at the same concentration of methanol. Zhang has also obtained a similar result [15]. He found that addition of organic solvents such as DMSO, DMF and acetone to aqueous solutions of the copolymers formed from acrylamide and fluorine-containing acrylates caused a drop in the Brookfield viscosity. The magnitude of the effect depends on the concentration of the organic solvent in water.

2.4 Gels Formation and Characterization

Professor Steiner and her coworkers [2-3,59] have investigated dispersed-phase hydrogels made from a water-insoluble hydrophobically modified hydroxyethyl cellulose (HMHEC) in aqueous systems. Two types of solvents have been used to make hydrogels. They are aqueous solutions of sodium dodecyl sulfate (SDS) below the critical micelle concentration (CMC), and mixtures of ethanol and water over the range 40:60 to 70:30 EtOH:water by volume. Under appropriate conditions, viscoelastic hydrogels precipitate out of solution and form a separate phase in equilibrium with a polymer-free supernatant phase.

In these gels, the hydrophobic microdomains serve as pseudo-crosslinks todefine the three-dimensional polymeric network. Thus, no chemical crosslinking agent is needed to fabticate this hydrogel. A generalized picture of this hydrogel is shown in Figure 1.1. The microdomains, which can act as reservoirs or sinks for hydrophobic solutes permeating the network, are well distributed in the bulk phase. These materials are being evaluated for use in controlled drug release, chromatography and other separation processes [60-61]. HMHEC gels exhibit a high (10^{3-4} dynes/cm^2) plateau values of the dynamic storage modulus. In addition, the hydrogels may be dried into films and reswollen to a constant volume without dispersing [5]. The effect of temperature and shear history on bulk and microstructural properties of HMHEC gels has also been investigated over a temperature range 25-70°C, by our group [4, 62-63]. The hydrogels exhibit an irreversible transition in both their bulk properties and the structure of the microdomians at a temperature in the range 35-50°C.

Iliopoulos and coworkers have made thermal reversible gels from hydrophobically modified poly(sodium acrylate) (HMPA) and nonionic surfactants of oligoethylene glycol alkyl ether type in aqueous system [6-7]. Gelation has been observed for this system around 23°C when the temperature is increased from 0 ° C to 60 ℃ at rate of 1℃ /minite. The temperature at which thermal gleation occurs correlated with the transition from micelles to bilayers observed in the binary water/surfactant system. Thus, it is possible to manipulate the thermal gelation temperature over a wide temperature range by using mixtures of nonionic surfactants and varing the different surfactant concentration ratio. The system exihibits a sharp increase in viscosity in the transition temperature. In addition, two different gel

structures have been found from this system. One is the micelles cross-linking the polymer network. In mixtures of HMPA and small micelles, the formation of mixed micellar aggregates, involving surfactant and the hydrophobic side chains of the modified polymer, induces an equilibrium cross-linking of the polymer network. The other is that the polymer adsorbed on the bilayer membrane of the surfactant. The polymer chain can serve as bridge between adjacent vesicles, when the surfactant forms giant vesicle aggregates, leading to an effective cross-linking of the surfactant aggregates.

In general, the characterization methods for gels include rheology, dynamic light scattering and spectroscopy. Among them, oscillatory rheological measurements are most frequently used [2-3,6-7,55]. The gel point is the polymer concentration or the temperature at which gelation starts. At this point, the storage modulus, G' is equal to loss modulus G"over a broad frequency range, in other words, the loss tangent (tanδ) is independent of frequency and equal to one. The gel point is also characterized by a sharp increase in viscosity [6-7]. Another method to determine gel point is dynamic light scattering [64-65]. The decay of the time correlation function slows down at this point. The ^{1}H NMR spectra can tell the difference between the solution and gel by a special technique [66]. For a polymer/surfactant gel, the ^{1}H NMR transverse relaxation of the surfactant protons is slightly faster in gels than in micellar solutions, analogous to solid state NMR having a short spin-spin relaxation time. Therefore, the gel point can also be determined by NMR relaxation time measurement. Besides gel point, we can obtain more information about gel properties by different methods. The mechanical properties of polymeric gel and molecular weight of the

segments between the crosslinks can be characterized by rheological measurements. The properties of hydrophobic microdomains such as polarity and aggregate size may be determined by a fluorescence and absorption spectroscopy. In addition, any liquid crystalline phase in the gel can be detected by a X-ray diffraction [65].

Table 2.1 Structure of Nonionic HMWSPs

Backbone	Side Chain	Hydrophobic Level	Refefences
Hydroxyethyl Cellulose (HEC)	n-C_8~C_{24}	0.50-4.75 wt%	[14]
Polyacrylamide (PAM)	n-C_4~C_{12}	0.25-1.25 mol%	[23]
	N,N-dialkyl (see chart 1)		[24]
	Bilinear alkyl (See chart 1)		
	N-4-alkylphenyl (see chart1)	0.75-1.25 mol%	[25]
	Nonylphenoxypoly-oxyehtylacrylate (see chart2)	3.3-16.6 wt%	[13]
	1,1-dihydroperfluoro-alkylacrylate	0.16-4.22 mol%	[15]
	Pyrenesulfonamide	0.25-0.50 mol%	[16]
Polyisopropyl-acrylamide	N-[2-(1-naphthyl)-ethyl]-N-n-octadecyl-acrylamide	0.25-0.50 mol%	[17]

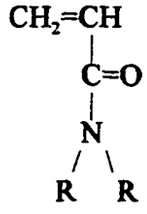
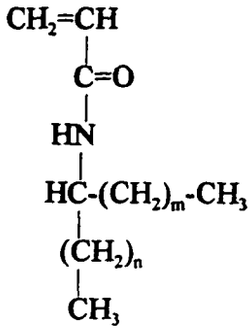
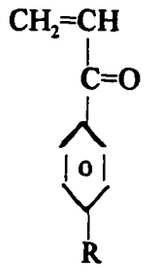
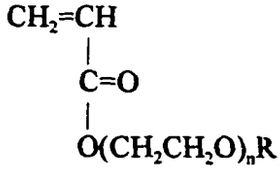
Dislkyl	Bilinear	Alkylpheny
		
$R = 1\text{-}C_3H_7 \sim C_8H_{17}$	$m + n = 5, 6, 9$	$R = C_2H_5, C_4H_9$

Chart 1. Alkylacrylamides

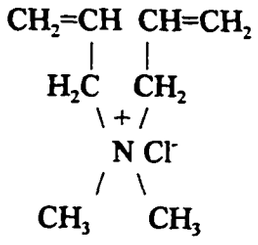


$n = 10, 20, 40;$ R = nonylphenyl

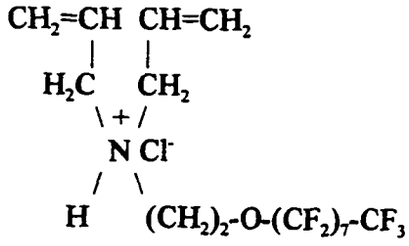
Chart 2. Nonylphenyloxy poly(etheroxy)acrylate

Table 2.2 Structure of ionic HMWSPs

Backbone	Side Chain	Hydrophobic Level	References
Hydrolyzed Polyacrylamide (HPAM)	n-C_4~C_{12}	0.25-1.25 mol%	[23]
Poly-4-Vinylpyridine	n-C_{12}	6.7-37.9 mol%	[18] [19]
Polymaleic Anhydride	n-butyl Vinyl Ether	50 mol%	[20]
	n-hexyl Vinyl Ether	50 mol%	[20]
Poly(acrylic acid)	n-C_8~C_{18}	1-3 mol%	[21]
Diallyl dimethyl ammonium chloride (DADMAC) (see chart 3)	Methyldially-(1,1dihydropentadeca-fluorooctoxyethyl) -ammonium chloride FX-15 (see chart 3)	1.062-8.22 mol%	[22]



DADMAC



FX-15

Chart 3

CHAPTER 3. EXPERIMENTAL

3.1 Materials

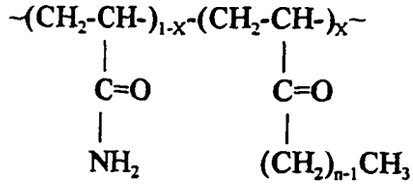
Acrylamide (AM) (99%), electrophoresis grade from Aldrich, was recrystallized twice from acetone and vacuum dried at room temperature prior to use. Acryloyl chloride (98%, Aldrich) and linear C_8, C_{10} and C_{12} alkylamines (98% Aldrich) used for micellar copolymerization were distilled prior to use, and n-octadecylamine (98%, Aldrich) used for the graft reaction was used as received. Triethylamine (99%, Aldrich) used in the synthesis of hydrophobic monomer was used as received. Potassium persulfate, reagent grade from MCB Manufacturing Chemists Inc., was used as received. Sodium dodecyl sulfate (SDS), from Polysciences, was used as received. Polyacrylamide (PAM) with a manufacturer specified molecular weight 5 - $6x10^6$ (DP = $6.94x10^4$ ~ $8.33x10^4$), purchased from Polysciences Inc., was used without further purification. Formamide (99+% spectrum grade), 1-methyl-2-pyrrolidinone (NMP) (99+% HPLC grade), alkylamine (98%) and dicyclohexylcarbodiimide (DCC) (99%), ether (anhydrous), dioxane (99+%), purchased from Aldrich, were used as received. Sodium bicarbonate (99.7+% A.C.S reagent, Aldrich) and magnesium sulfate (99%, Aldrich) were used as received.

3.2 Synthesis and Purification - Part I: Micellar Copolymerization

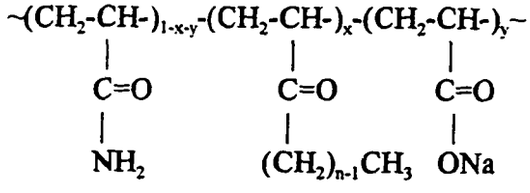
Micellar copolymerization was employed to make acrylamide and linear alkylacrylamide copolymes (RAM) incorporating linear alkyl side chains containing 8 ~ 12

carbons at level of 0.75 and 1.5 mol%. In order to improve the solubility of the RAMs and investigate the effect of sodium acrylate (NaA) level on the polymer properties, some RAMs were hydrolyzed in NaOH aqueous solution. The hydrolyzed RAMs, called HRAMs, have the same hydrophobe components as the corresponding RAMs, because no chemical reaction occurs involving hydrophobic side chains. The polymer structure and nomination is given below:

RAMn/x



HRAMn/x-y



where n, x and y are the number of carbons in side chains, hydrophobe level and NaA level, respectively. In this section, I will describe the method used to synthesize RAMs and HRAMs. It includes three steps, which are, 1-synthesis of hydrophobic monomer, 2-copolymerization of acrylamide and linear alkylacrylamide, and 3-hydrolysis of RAMs.

3.2.1 Synthesis of Linear alkylacrylamide Monomers

The chemical reaction equation for making alkylacrylamide monomer from acryloyl chloride and alkylamines is given below:

$H_2NR + CH_2=CH-C(=O)Cl \dashrightarrow CH_2=CH-C(=O)(NHR) + HCl$

alkylamine acryloyl chloride alkylacrylamide

($R=C_8H_{17}$, $C_{10}H_{21}$, $C_{12}H_{25}$)

The molar feed ratio of alkylacrylamine to acryloyl chloride was 0.5:0.54. The excess of acryloyl chloride was used because this reagent decomposes easily in the presence of moisture. Triethylamine was used to react with HCl generated in the main reaction to form a salt that is insoluble in organic solvents.

An example of the synthesis procedure for monomeric N-alkylacrylamide is as follows: A 2 liter, four-neck flask was equipped with a thermometer, mechanical stirrer, N_2 inlet (with a drying tube on N_2 line) and an addition funnel. After purging with N_2 for half hour, the alkylamine (0.5 mol) was added to the flask followed by 0.54 mole triethylamine and 1 liter ether. The solution was then cooled to -5°C in an ice/brine bath. Acryloyl chloride (0.54 mole) was dissolved in 150 ml ether and then slowly added to the reactor over a period of 1 hour at such a rate that the temperature did not exceed 10°C. The resulting mixture was warmed up to room temperature over a period of 2 hours, and then cooled down to about

0°C. A HCl aqueous solution (200ml, 5wt%) was added to the reaction mixture to extract the triethylamine salt from the organic layer. The organic layer was washed with a 5% sodium bicarbonate aqueous solution and distilled water, and then dried over $MgSO_4$. The ether was removed by rotary evaporator. The crude product was twice recrystallized from acetone at -30°C. The products were characterized by melting point, FTIR and NMR.

3.2.2 Synthesis of Acrylamide-alkylacrylamide Copolymer

The recipe for RAM copolymerization is shown below [20]:

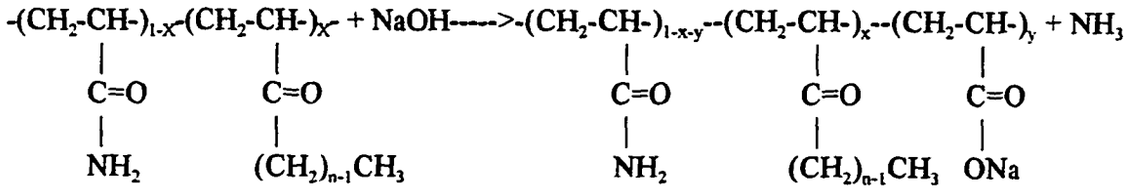
H_2O	470 ml
SDS	15.85 g (= 117 mM; critical micelle concentration (CMC) = 8 mM)
Acrylamide	0.208 mol
Alkylacrylamide	0.00157 mol (hydrophobe level = 0.75 mol%)
	0.00314 mol (hydrophobe level = 1.5 mol%)
$K_2S_2O_8$	3.7×10^{-5} mol

Synthesis of RAM8/0.75, as an example, was carried out as follow [27]. A one liter resin flask was equipped with mechanical stirrer, reflux condenser, thermometer and inert gas inlet and outlet. The flask was flushed with N_2 for a half hour. Then 0.288 g (1.57 mM) of octylacrylamide, 14.76 g (0.208 mol) of acrylamide, 15.85 g (0.177 mol) sodium dodecyl sulfate and 470 ml distilled water that had been degassed with bubbling N_2 for 0.5 hour were added to the reaction flask. The solution was heated to 50°C and 0.01 g of potassium persulfate was added. The reaction mixture was kept at 50 ± 2°C under nitrogen for 18

hours. It was then cooled to room temperature. Deionized water (200 ml) was added into the reaction mixture to dilute it. The diluted solution was introduced into acetone and the copolymer, RAM, precipitated out. The polymer was dried under vacuum at room temperature over night. The result was 15 g of white solid. The yields of various RAMs were close to 100%.

3.2.3 Hydrolysis of Acrylamide-alkylacrylamide Copolymer to Incorporate Charges of NaA in Polymers

The chemical reaction equation for hydrolysis of RAMs is given below:

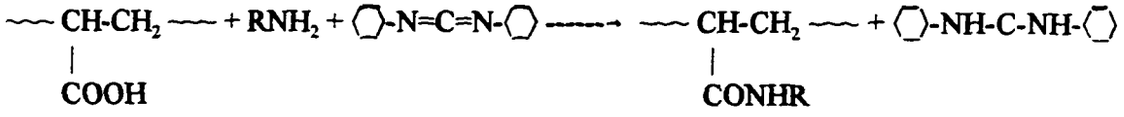


Synthesis of HRAM10/1.5 with a hydrolysis level of 10 mol% (feed ratio), as an example, is described below: The previously synthesized RAM10/1.5 (3 g, 0.0422 mol amide group) was dissolved in a mixed solvent containing 200 ml water and 80 ml EtOH for 24 hours at 50°C. After that 1.69 g NaOH (0.0422 mol) dissolved in 30 ml water was introduced into the polymer solution. The reaction mixture was stirred for 1 hour at 50°C, then the hydrolyzed copolymer solution was dialyzed (molecular weight cut off of dialysis membrane is 6000 to 8000) against liter frequently changed distilled water over a week [34] and was freeze dried. Elemental analysis for sodium was conducted by atomic absorption spectrometry at E+R

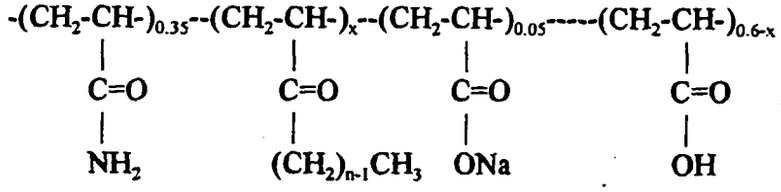
Microanalytical Laboratory Inc., NYC, NY.

3.3 Synthesis and Purification - Part II: Graft Reaction

Graft reaction is a method to produce tetra-polymers (HRAM-AA) of acrylamide, acrylic acid, sodium acrylate and linear alkylacrylamide by connecting hydrophobic side chains to a water soluble backbone by the functional group reaction. Starting from PAM (MW ~$6x10^6$), a hydrolysis reaction was carried out in NaOH solution giving a product with NaA groups, then, HCl aqueous solution was added to the reactor to change most of NaA into carboxylic acid groups. Resulting precursor polymer has 35 mol% amide, 60 mol% carboxyl acid and 5 mol% NaA groups. Hydrophobic side chains were grafted to precursor polymers by an amidation of small portion of carboxyl acid groups on the polymer backbone with amine groups in the hydrophobic modifiers. The chemical reaction equation is given below:



The structure of resulting polymer HRAM-AAn/x, where n and x represent number of carbons in hydrophobic side chain and hydrophobe level, respectively, is shown as follow:



In order to optimize the reaction condition, model reactions using small molecules with the same functional groups as the precursor polymer and hydrophobic modifier were carried out before running the graft reaction. In this section I describe the model reaction, the hydrolysis of polyacrylamide and the graft reaction of the precursor polymer.

3.3.1 Model Reaction for Graft Reaction

To investigate the reaction rate of amidation of carboxyl with amine in different solvents, a reaction of lauric acid and octylamine as a model reaction is conducted. These two compounds both have linear hydrocarbon chain, which is analogy to polymer backbone, and same functional groups with precursor polymer and hydrophobic modifier. DCC used here is a dehydrating agent that drives the reaction into the product direction. The model reaction results determine the selection of solvent and the reaction time for the graft reaction. The chemical reaction equation of the model reaction is given below:

$$CH_3(CH_2)_{10}COOH + CH_3(CH_2)_7NH_2 + DCC \text{ -------} \rightarrow CH_3(CH_2)_{10}CONH(CH_2)_7CH_3 + DCU$$

lauric acid octylamine amide

Three solvents of different polarities are used in this study. They are dioxane, NMP and formamide whose polarity increases from the first one to the last one. A model reaction using NMP as a solvent, as an example, is carried out as follows. Lauric acid (3.2 g, 0.016 mol), octylamine (2.07 g , 0.016 mol), DCC (3.3 g, 0.016 mol) and 200 ml NMP are put into a two-neck flask, equipped with a mechanical stirrer and thermometer. The reaction mixture

is stirred at 60°C for 21 hours. The solution is then cooled to room temperature. Dicyclohexylurea formed from DCC during the reaction is filtered out from solution. The crude product is twice recrystallized from acetone at -30°C. The reaction products are characterized by melting point and FTIR for purity and structure determination, respectively.

3.3.2 Hydrolysis of PAM

The purpose of hydrolyzing PAM is to change the amide groups of PAM to carboxyl acid groups that can react with the amine groups of the hydrophobic modifier, and to modify the water solubility of the final products HRAM-AA. The hydrolysis of PAM is carried out in a 2 liter three neck flask equipped with a thermometer, mechanical stirrer and reflux condenser. PAM (12 g, 0.169 mol amide groups) is dissolved in 1 liter of water under stirring at 60 °C for 1 hour. Then, a NaOH solution containing 67.5 g NaOH (1.69 mol) and 200 ml water is added to the viscous polymer solution under stirring to convert amide groups into NaA groups. The use of excess of NaOH renders a high reaction rate. The reaction is conducted at 60 ± 1 °C for 24 hours. After that, the polymer solution is cooled to room temperature. Concentrated HCl (36 - 38%, about 160 ml) is dropped into the polymer solution from an addition funnel to convert the sodium acrylate groups to acrylic acid groups. The final pH of the reaction mixture is 2 as tested by pH paper. The polymer solution is dialyzed against 4 liter distilled water over a week to remove the excess HCl and NaCl formed in the reaction. The water is changed twice per day. A $AgNO_3$ aqueous solution is dropped into the polymer solution after dialysis, and no precipitation is found. This indicates that no Cl^- is present in the product solution. After freeze drying, hydrolyzed polyacrylamide

(HPAM), 11.5 g, is obtained. The products of the hydrolysis reaction are analyzed by titration and elemental analysis. The mole fraction of acrylic acid (AA) was determined by the titration of a 0.1 g sample in 50 ml 10 mM brine with 0.1 N NaOH using phenolphthalein as an indicator [66]. The salt was included in order to sharpen the endpoint of titration by reducing the solution viscosity. The nitrogen and sodium content of HPAM were determined by elemental analysis conducted by E+R Microanalytical Laboratory Inc (Corona, NY). The sodium content of HPAM was determined by a Perkin Elmer Atomic Absorption Spectrophotometer and nitrogen content was determined by a Carlo Erba Elemental Analyzer.

3.3.3 Graft Reaction to Form HRAM-AA

A series of HRAM-AAs with a M_w $3.1x10^6$, 5 mol% NaA, 53~58.8 mol% acrylic acid and 1.2 ~ 7.0 mol% linear alkyl side chains containing 12 to 18 carbons were synthesized for this study. The following description for a copolymer with 3 mol% hydrophobe (based on the feed ratio of hydrophobe to repeat units in the backbone, HPAM) is typical of all graft reactions conducted for this report. HPAM (3.5 g, 0.0489 mol repeat units, 0.029 mol AA) is dissolved in a mixed solvent composed of 280 ml NMP and 110 ml formamide under stirring at 60°C over night. This solvent is selected based on the results of the reaction rate and solubility of the precursor polymer (see chapter 4 for the discussion of solvent selection). Dodecylamine (0.272 mg, 0.00148 mol) and DCC (0.303 g, 0.00148 mol) are dissolved separately in 40 ml NMP and introduced successively into the polymer solution under stirring after the precursor polymer had dissolved completely. The reaction mixture is stirred at 60°C for 24 h, then, the product solution is cooled to room temperature. The reaction byproducts

and unreacted modifier are extracted 3 times in a total amount of 188 ml ether. Then 1 liter of acetone is added to the polymer solution and the polymer precipitates out. The hydrophobically modified polymer is separated from the solution by centrifuge. The HRAM-AA is washed by warm MeOH (45°C) to remove the remaining free amine, after that HRAM-AA is dried by a vacuum oven for overnight. For some 7 and 10.5 mol% C_{12} modified HRAM-AAs that remained in the organic solvent, the polymer solution, consisting of NMP, formamide, acetone and methanol, is dialyzed against 4 liter frequently changed distilled water over a week and freeze dried.

3.4 Characterization of HMWSPs

The HMWSPs were characterized with respect to hydrophobe level and molecular weight. The methods used to determine these two parameters are NMR and light scattering respectively.

3.4.1 NMR Measurements to Determine the Hydrophobe Level

NMR analysis requires a relative high polymer concentration ($\geq$1 wt%) in order to obtain a good signal-to-noise ratio. However, the aqueous solution presents a very high viscosity in such concentration due to intermolecular hydrophobic interaction. A High viscosity generates broad peaks in NMR spectrum, which prevents the polymer structure analysis. Therefore, solvent selection for NMR samples preparation is very important. A D_2O/CD_3OD (Aldrich) mixture or DMSO-d_6 (Aldrich) were used as solvents for NMR analysis to limit the hydrophobic interaction.

Proton spectra were recorded on a Varian Unity Plus 500 spectrometer operating at 500 MHz. The measuring temperature was kept at 40 ^{0}C to optimize the solubility of the polymer in the solutions. Polymer concentrations were about 1 wt% in a D_2O/CD_3OD mixture or DMSO-d_6. A spectral width of 10,000 Hz and a pulse width 3.0 μsec (30^0) were used; the acquisition time was 1.2 s and the delay time was 2 s.

The integral of the ^{1}H signal is a powerful tool to determine the microstructure of a polymer chain. However, it does need to be careful to use the information of peak integral because it is dependent on the spin-lattice relaxation time. If the resonating nuclei have no sufficient time to allow them to return the equilibrium state, the resonance intensity of the nuclei is smaller than what it should be. It is found that the intensity difference between the signals measured with a delay time of 8 s and 2 s was less than 3%. Therefore, it can safely be said that a pulse repetition time of 3.2 s (delay + acquisition) is long enough for the spin to recover equilibrium.

3.4.2 Light Scattering Measurements to Determine the M_w

The molecular weight of each RAM sample in formamide solution was determined by classical light scattering. Data points were taken at multiple angles with a DAWN DSP-F laser photometer (Wyatt Technologies, Santa Barbara, CA) operating at 632.8 nm. The photometer is interfaced with a personal computer. Zimm plots were constructed using the software, named DAWN (version 2.06), provided by the manufacturer. The values of the refractive index increment, dn/dc, used to calculate M_w of RAMs were equal to that of PAM

in formamide solution (dn/dc = 0.109), which was found in the Polymer Handbook [67]. This was justified as it has been shown [32] that the refractive index increment of copolymers of acrylamide and N-(4-ethylphenyl)acrylamide in formamide did not change with hydrophobe content ranging from 0 wt% to 12 wt% [32]. The weight molecular weight, M_w of RAMs was also measured by a Brookhaven Instruments model BI 9000AT automatic goniometer at Exxon R&E Co.(New Jersey) interfaced with a personal computer. The molecular weights of PAM and HPAM were determined from small angle light scattering using a single angle spectrometer (KMX-6). The refractive index increment of HPAM in 80 mM brine, measured by a KMX-16 laser differential refractometer, is 0.163.

3.5 Measurement of HMWSP Solution and Gel Properties

The properties of HMWSPs in aqueous solvent were investigated by several methods. The viscosity of bulk solutions and the mechanical stability of the gels were measured by viscometry and rheometry, respectively. The hydrophobicity of the hydrophobic clusters was determined by fluorescence spectroscopy. The conductivity of the polymer aqueous systems was also measured to evaluate the effect of hydrophobic interaction on the degree of dissociation of the polyelectrolyte and the mobility of free ions. This section will discuss each of these methods separately.

3.5.1 Solution preparation

Before being used in the preparation of solutions, the copolymer samples were dried for 24 hours at 50°C to eliminate any residual moisture. Polymer solutions were prepared by

adding an appropriate amount of polymer into 5 ml aqueous SDS or NaCl solutions of known composition, or deionized water saturated with pyrene. Polymers were dissolved under very mild stirring at room temperature over 24 hours. Samples were allowed to stand at least 72 hours before making measurements in order to obtain a stable structure.

3.5.2 Solubility

The solubility of the polymers was defined as the highest concentration of the polymer that produced a clear solution or gel (based on visual inspection) in water after stirring at room temperature for 48 hours. Above this concentration the solutions appeared cloudy or were characterized by suspended polymer particles. For polymers that were insoluble in water, the minimum concentration of ethanol required to solubilize the polymer at a level of 0.1 g/dl is also determined in ethanol/water mixed solvents. Ethanol was added in increments of 5 v% each time in the mixed solvents.

3.5.3 Dynamic Mechanical Measurements

Below is the discussion of explaining the fundamental of viscoelasticity of fluids and gels which has been excerpted from Ferry's book [68]. A system's response to stress perturbation may be monitored in a rheological experiment. A variety experiments, such as stress relaxation after sudden strain, stress relaxation after cessation of steady shear flow, stress growth after initiation of a constant shear rate, creep after sudden stress and dynamic experiments can be used, depending on such factors as rigidity, timescale and sample geometry. Stress relaxation and creep experiments are usually used to monitor slow

processes (seconds to days), whereas oscillatory shear experiments typically are used for faster motion (milliseconds to seconds). The oscillatory experiment is based on driving one surface with known periodic displacement and measuring the periodic force at the surface on the other side of the gap with a sensing device of negligible motion. The force is proportional to stress and the displacement to strain, so monitoring these sinusoidal functions is equivalent to tracing out the sinusoidal variation of stress and strain with time. The stress developed within the sample by the oscillating strain is sinusoidal and it is in phase with the strain for a purely elastic material. On the other hand, for a viscous material, the stress and strain are 90° out of phase.. Thus, the relations between stress, strain, and their time dependencies for a viscoelastic material whose behavior is intermediate between that of an ideal elastic solid and that of a purely viscous liquid are usually described by the following equation. The storage and loss moduli, G' and G", are obtained from the stress, σ, in an oscillatory deformation at angular frequency ω,

$$\sigma = \gamma_0(G'\sin\omega t + G''\cos\omega t) \qquad (3.1)$$

where γ_0 denotes the strain amplitude and t is time. The modulus G' is defined as the stress in phase with the strain in sinusoidal shear deformation divided by the strain. It is a measure of the energy stored and recovered per cycle, when different systems are compared at the same strain amplitude. The modulus G" is defined as the stress 90^0 out of phase with the strain divided by the strain; it is a measure of the energy dissipated or lost as heat per cycle of sinusoidal deformation, when different systems are compared at the same strain amplitude.

The viscoelastic response of a polymeric system is directly related to the network structure on a molecular level and the modes of molecular motion. The magnitude of G' is not only a measure of the mechanical stability of the network, but is also a measurement of the apparent molecular weight between the crosslink points based on equation (3.2):

$$M_1 = \rho\phi RT/G_1 \qquad (3.2)$$

where M_1 is molecular weight between the linkages, ρ is the density of the polymer, ϕ is the volume fraction of the polymer in solutions or gels, R is the universal gas constant, T is the temperature of the measurement and G_1 is the storage modulus in the rubbery plateau.

In the present dynamic mechanical measurements of the polymeric mixture were performed using a Haake (Fisons Instruments, Edison, NJ) rotovisco RV-20 rheometer fitted with parallel-plate sample cell operating in an oscillating mode. The frequency range of the measurements was from 0.136 to 60.4 rad/s. The rheometer is interfaced to a personal computer and driven by a software package named OSC20 supplied by the manufacturers. The torque and phase angle were measured and the storage and loss moduli of the polymeric mixture were obtained. All measurements were conducted at 25°C.

3.5.4 Rotary Viscosity Measurements

Viscosity-shear rate measurements were performed using the Haake rotovisco RV-20 rheometer fitted with a parallel-plate sample cell. The rheometer is interfaced to a personal

computer and driven by a software package named ROT22 supplied by the manufacturer. Viscosity measurements for polymer solutions with viscosity lower than 150 cp at shear rate 10 s^{-1} were conducted using a Brookfield viscometer equipped with a cone and plate sample cell.

3.5.5 Fluorescence Spectroscopy

Fluorescence spectroscopy of the polymer solutions and gels using pyrene as a probe was conducted to detect the existence of hydrophobic clusters in polymer solutions and gels and to determine the relative hydrophobicity of the clusters. Pyrene is a strongly hydrophobic probe and its solubility in water is very low ($6x10^{-7}$M) [69]. In aqueous micellar solutions of a surfactant, pyrene is preferentially solubilized in the hydrophobic regions [70]. The fluorescence spectrum of the pyrene molecule can yield information about the polarity sensed by the probe in its solubilization site (micropolarity) [69].

The emission spectrum of pyrene exhibits five vibronic peaks in the range 350 – 450 nm. The ratio of the third and first highest energy vibronic bands (I_3/I_1) has been shown to be a direct function of the dielectric constant of the medium [71]. For example, I_3/I_1 ranges from 0.64 in water to 1.65 in hexane. Values of 0.91 to 0.83 are typical of simple aqueous micelles. This parameter has been successfully used as a microenvironmental polarity indicator for micelles [70] and surfactant/polymer aggregates [2-3,72]. Steady-state fluorescence measurements of polymer solutions and gels were performed on a Spex Fluorolog-2 Model 112A Fluorescence Spectrophotometer (Spex Industries, Inc., Edison

NJ). The pyrene spectra were obtained by exciting the solutions at 310 nm and recording the emission over the range 350 ~ 450 nm at room temperature.

3.5.6 Conductivity Measurement

Conductivity of polymer solutions was measured by a WPA CM 35 Conductivity Meter (WPA Scientific Instrument, Linton Cambridge, England) at room temperature. The equivalent conductivity (Λ) of a solution or gel of polyelectrolytes is the product of the degree of dissociation of the charged species and the sum of the mobilities of the free ions in the electric field [73].

$$\Lambda = \kappa/C \qquad [\Omega^{-1}\ m^2\ equiv^{-1}] \tag{3.3}$$

This property is related to the specific conductance by equation (3.3), where κ is the specific conductance measured in our experiments and C is the concentration, in equivalents per liter, of charged groups.

CHAPTER 4. SYNTHESIS AND CHARACTERIZATION OF HMWSPS

A series of hydrophobically modified acrylamide-based copolymers, incorporating linear alkyl side chains containing 8-18 carbons at level of 0.75-7 mol%, hydrolysis level ranging from 0-65 mol%, have been prepared by two synthetic routes described in previous chapter. They are micellar copolymerization in aqueous solution, using sodium dodecyl sulfate as a surfactant and potassium persulphate as the initiator, and graft reaction of a precursor polymer in mixed organic solvent. The result of kinetic study of graft reaction also presented. The products of the two synthetic routes have been characterized by NMR for hydrophobe level, classical light scattering for molecular weight and elemental analysis for hydrolysis level. In this chapter, I also present a comparison of the two synthetic routes, including the products structure, the conversion of hydrophobic modifier and the procedure of the two routes.

4.1 Introduction

Three different type hydrophobically modified polyacrylamide-based polymer were synthesized in this study. They are RAMn/x, HRAMn/x-y and HRAM-AAn/x, where n, x and y are number of carbons in side chains, hydrophobe level and NaA level, respectively. RAMs and HRAMs are made from micellar copolymerization incorporating 0.75 and 1.5 mol% hydrophobic side chains containing 8 ~ 12 carbons, and 1.53 ~ 24.1 mol% NaA for HRAMs. HRAM-AAs are made from the graft reaction grafting 1.2 ~ 7 mol% hydrophobic side chains. Micellar copolymerization is a simpler procedure of two synthetic routes, since the graft reaction requires both a polymerization and grafting step. However, micellar copolymerization is not suitable to synthesize the HMWSPs possessing high molecular weight ($\sim 10^6$) and high hydrophobe level (>1.5 mol%), due to the gelation at the end of the reaction that makes purification of the product impossible. Therefore, in this study the graft reaction was used to make high (1.2~7 mol%) $C_{12} \sim C_{18}$ modified polymers. This new reaction scheme was investigated to enable us to make the product with high hydrophobe level that is suitable to make hydrogels. HRAM-AAs having a M_w 3.1×10^6, with 5 mol% NaA, 53 ~ 58.8 carboxyl acid and 1.2 ~ 7.0 mol% linear alkyl side chains containing 12 to 18 carbons were made by a graft reaction.

This chapter will be organized as follows, micellar copolymerization to produce RAMs, graft reaction to make HRAM-AA and comparison of two synthesis routes.

4.2. Micellar Copolymerization to Produce RAMs

Starting from the synthesis of hydrophobic monomers, RAMs with linear alkyl side chains containing 8-12 carbons at feed level of 0.75 and 1.5 mol% were made by a micellar copolymerization [27]. Among them, the synthesis of RAM10/1.5 is reported here for the first time. In order to improve the aqueous solubility of RAMs, electrolytes were introduced on the RAM backbone by a hydrolysis reaction. This section will discuss the synthesis and characterization of linear alkylacrylamide monomers, RAMs and HRAMs made from micellar copolymerization. The characterization of the polymer is focused on hydrophobe level and molecular weight, as well as hydrolysis level for HRAMs.

4.2.1 Synthesis of Linear Alkylacrylamide

The hydrophobic monomers used in micellar copolymerization were made by an amidation of N-alkylamine containing 8 ~ 12 carbons and acryloyl chloride in the presence of triethylamine. Yield of N-alkylacrylamide monomers and melting points measured by DSC are shown in Table 4.1. Some product was lost during purification, especially for octylacrylamide because forming a crystal is difficult due to the relatively low melting point. The products were analyzed by FTIR and NMR instrument. The FTIR, and ^{1}H and ^{13}C NMR spectra of our monomer products are the same as those published in reference [24].

4.2.2 Synthesis of RAMs

RAMs were prepared from acrylamide (AM) and N-alkylacrylamide (R). The AM monomer has a high k_p^2/k_t and is the hydrophilic component. N-alkylacrylamide has the hydrophobic character. Copolymerizations were conducted under micellar reaction

conditions in SDS/H_2O using potassium persulfate as the initiator. The hydrophobic monomer and the acrylamide were dissolved in the micellar aqueous solution and the resulting polymer, RAM, was also soluble in the solution. After 18 hours reaction, a clear and viscous solution was obtained for low hydrophobe level, 0.75 mol%, RAMs. The copolymers were recovered by adding the viscous aqueous solution into a large amount of acetone under stirring to precipitate the products. For high hydrophobe level RAMs (1.5 mol%), the final products were viscoelastic hydrogels that can't be dissolved in water. The hydrogels were dissolved in an EtOH/H_2O (30:70) mixed solvent. Then, the polymer was precipitated out from acetone. When the hydrophobic monomer feed ratio is higher than 1.5 mol%, the solution gels before the reaction is complete and the products of the copolymerization are very difficult to purify. The conversion for both monomers determined by weight of resulting polymer relative to starting monomer was close to 100%.

4.2.3 Synthesis and Hydrolysis Level Determination of HRAMs

In order to improve the aqueous solution solubility of RAMs, the polymers were hydrolyzed in NaOH aqueous solution using the procedure described in [25]. The hydrolysis level can be controlled by the adjusting concentration of NaOH and the reaction time. In this study, the hydrolysis level was controlled by the concentration of NaOH. All reactions were run at 50 $\pm$ 1°C for 1 hour. The feed compositions are shown in Table 4.2. The compositions of the HRAMs were determined by an elementary analysis. The mole fraction of sodium acrylate in hydrolyzed polymers was calculated according to following equation [25]:

$$m_{AA} = \frac{x_{Na}[(MW_H - MW_{AM})m_H + MW_{AM}]}{AW_{Na} + x_{Na}(MW_{AM} - MW_{AA})} \quad (4.1)$$

AW_{Na}: atomic weight of sodium

m_{aa}: mole fraction of sodium acrylate

m_H: mole fraction of hydrophobic group

MW_{AA}: molecular weight of sodium acrylate monomer unit in hydrolyzed polymer

MW_{AM}: molecular weight of acrylamide monomer

MW_H: molecular weight of hydrophobic group

x_{Na}: weight fraction of sodium in hydrolyzed polymer

Varying amounts of base were used to regulate the level of sodium acrylate groups, as shown in Table 4.2. The feed ratio in the table is the molar ratio of NaOH to amide group in backbones. The data confirm that the level of hydrolysis is markedly increased by increasing the level of added base, i.e., sodium hydroxide, however, it is far from the theoretical value. Perhaps, the reaction can be made to go to higher conversion by increasing the reaction time.

4.2.4 Characterization of RAMs

Hydrophobe Level Results by NMR

The composition of RAMs was determined by NMR. The ^{1}H NMR spectra of RAMs are shown in Figure 4.1. The peak assignments are labeled in the figure. The assignments of backbone peaks are analogous to those in the spectra of PAM [74]; the upfield resonances

(1.53, 1.60, 1.71, 1.90) are assigned to the β-protons of the backbone, and the downfield resonances (2.22, 2.38) are assigned to the α-proton of the backbone. The other peak assignments are based on a comparison of the unknown peaks with the spectra of the hydrophobic monomers. The resonance of 0.91 ppm is assigned to the methyl protons in the side chain, the resonance of 3.19 ppm is assigned to the methylene protons that are close to the amide group and the resonance of 1.34 ppm is assigned to the other methylene protons. It is clear that the resonance peak of the methyl proton in the side chain is well separated from the resonance peaks of the other protons. Therefore, the peak at 0.91 ppm may be used for estimating the hydrophobe level in RAMs. The hydrophobe level, m_H, defined as the ratio of the number of side chains to the number of repeat units in the backbone, was determined from

$$m_H = M/(N - 2nM/3) \qquad (4.2)$$

where M is the area under the peak corresponding to methyl protons in the side chain (0.91 ppm) and N is the total peak area of methylene and methine protons in the side chain and the backbones (1.34, 1.53, 1.60, 1.71, 1.90, 2.22, 2.38, 3.19). The other parameter, n, is the number of methylene carbons in each side chain.

The results of NMR analysis on the hydrophobe content of RAMs are reported in Table 4.3. The amount of hydrophobe in the copolymers is close to that in feed. This means that all hydrophobic monomers have been polymerized with the hydrophilic monomers during micellar copolymerization, as expected, because the similarity in the structure of the

hydrophobe and acrylamide may also lead to very similar values of their reaction rate.

Molecular Weight Measurement by Light Scattering

Zimm plots for RAM8/0.75 in formamide are shown in Figure 4.2 and 4.3 from Brookhaven instrument and DAWN DSP-F laser photometer, respectively. The reason for this distortion in figure 4.3 might be the aggregation of side chains [75], since the sample solution was filtered carefully and should be dust free. Thus, the molecular weight result by light scattering from the polymer formamide solution is not reliable, although the distortion of Zimm plot is not as significant as in Figure 4.2, because higher angles were used compared with Figure 4.3.

In summary, micellar copolymerization has been used successfully to synthesize RAMs with C_8, C_{10} and C_{12} side chains at hydrophobe level not higher than 1.5 mol%. All hydrophobic monomers were incorporated in the final product. When the hydrophobe level is higher than 1.5 mol%, it becomes difficult to purify the product of micellar copolymerization owing to gelation during the reaction.

4.3 Graft Reaction to Make HRAM-AA

A series of HRAM-AAs, MW 3.1×10^6, with 5 mol% NaA, 53~58.8 mol% carboxyl acid and 1.2 ~ 7.0 mol% linear alkyl side chains containing 12 to 18 carbons were synthesized by the graft reaction. This graft reaction was adapted from the synthetic route used to produce hydrophobically modified polyacrylic acid containing 1 ~ 10 mol% $C_{12} \sim C_{18}$ linear

alkyl groups with a molecular weight of 150,000 reported elsewhere [21]. Considering our objectives to make two phase hydrogel, those lower charge density and higher molecular weight HMWSPs compared with the reference are required. Thus, a partially hydrolyzed polyacrylamide with a molecular weight of order 10^6 was chosen as the precursor polymer to run the graft reaction. This polymer is insoluble in NMP, the solvent used in the earlier report. Therefore, we conducted several experiments to select the solvent for our graft reaction. The criterion of the solvent selection is that the reactants should have reasonable solubility and the reaction rate should be reasonably high in the solvent as well. In this section, we present the results of synthesis and characterization of HRAM-AAs.

4.3.1 Synthesis of HRAM-AAs

The starting material for the graft reaction is PAM. It was hydrolyzed first so that some amide groups were changed to carboxyl groups that reacted with the amine group of the hydrophobic modifiers in the graft reaction. This section will be divided into three parts, as follows, preparation of the control polymer-HPAM, solvent selection for the graft reaction and graft reaction of HPAM.

Preparation and Analysis of Precursor Polymer-HPAM

The control polymer HPAM for this study was prepared from PAM in alkali solution and then, the sodium acrylate groups produced from the reaction were converted to the acrylic acid form using concentrated HCl. We chose this method instead of directly using acid to make HPAM, because imidization occurs in the hydrolysis reaction if a strong acid is used

[66]. If a weak acid is used in the hydrolysis reaction, the reaction rate is too low for practical purposes [76]. The reaction conditions and procedure were adapted from Higuchi and Truohg [77-78]. The acrylic acid (AA) concentration per unit polymer sample was determined by titration with standard NaOH solution. Elemental analysis of nitrogen and sodium was used to determine the amount of acrylamide (AM) and sodium acrylate (NaA), respectively. The mole fractions of the three repeat units in the final product were determined by the following equations using the elemental analysis and titration results.

$$MW_{AA}m_{AA} + MW_{AM}m_{AM} + MW_{Na}\, m_{Na} = M_{app} \quad (4.3)$$

$$M_{app} \times N_{Na}/W = m_{AA} \quad (4.4)$$

$$AW_N \times m_{AM}/M_{app} = N\% \quad (4.5)$$

$$1-m_{AA}-m_{AM} = m_{Na} \quad (4.6)$$

AW_N: atomic weight of nitrogen

m_{AA}: mole fraction of acrylic acid

m_{Am}: mole fraction of acrylamide

M_{app}: apparent molecular weight of repeat unit in HPAM

m_{Na}: mole fraction of sodium acrylate

MW_{AA}: molecular weight of acrylic acid unit

MW_{AM}: molecular weight of acrylamide monomer unit

MW_{Na}: molecular weight of sodium acrylate monomer unit

N %: weight percentage of nitrogen in HPAM obtained from elemental analysis

N_{na}: Normal number of NaOH that is consumed in titration

W: weight of polymer samples used in titration

Mole fractions AA, AM and NaA are 60 ± 1 mol%, 35 ± 1.5 mol% and 5 ± 1.5 mol% respectively.

Note that the calculated value for m_{Na} was used rather than the measured value obtained from elemental analysis because the latter value fell within the error region of the measurement. The atomic absorption of sodium in our polymer gives values between 0.15 wt% to 0.84 wt%, but the error of this analysis method is ±0.3 wt%.

Solvent Selection for Graft Reaction

Solvent selection is very important for our graft reaction system. There are two factors that limit our choice. One is the solubility of the reactants in the solvent and the other is the reaction rate. Amidation of carboxyl group in the presence of DCC for small molecules is usually conducted in nonpolar or low polarity solvents, such as THF, dioxane and methylene chloride. Unfortunately, our starting material, HPAM is insoluble in these solvents. It is expected that the reaction rate will be relatively fast in nonpolar solvents considering the mechanism of the reaction, described below.

The accepted mechanism for amidation of HPAM with amines in the presence of

DCC, as deduced from studies on the reaction of carboxylic acid and amino acid ester [79], is shown in scheme 1 (page 68). The first step is protonation of the carbodiimide to yield the intermediate (I), which is attacked by a carboxylate anion to produce the O-acylurea (II). This, in turn, can (a) form the N-acylurea (III) by intramolecular rearrangement, (b) react with the amine to form the amide (IV), or © react with another carboxylic acid to yield the urea and the anhydride (V) that later participates in further amidation. No kinetic data have been reported for any of these. However, we can assume that a nonpolar solvent is preferred by step 2 and 4 because the nonpolar solvent stabilizes the products (II, III and V) more than the reactants in these steps. The polarity of solvent may not affect the reaction rate of the step 3 much due to the structure of reactants and products. The protonation of the carbodiimide is the only step which is preferred polar solvent. Based on the kinetics, protonation of the carbodiimide is a fast reaction that should not be a rate controlling step in this reaction. Thus, the amidation of carboxyl group with amine in the presence of DCC is favored by a nonpolar solvent.

In order to study the effect of solvent polarity on the reaction rate, a reaction of small molecules was used in model reactions. Three organic solvents that have the potential to dissolve HPAM based on the solubility data of PAA and PAM were used [67]. They are dioxane, NMP and formamide. Reactants used here are lauric acid and octylamine and their molar ratio to DCC is 1:1:1. The reaction conditions and results are listed in Table 4.4. The polarity of the solvents listed in Table 4.4 increases from top to bottom. The yield of amide given in the table was determined by a comparison of the weight of amide formed from the

reaction with the theoretical value. Table 4.4 shows that the reaction rate decreases significantly as solvent polarity increases. This conclusion is consistent with what we expected based on the foregoing discussion.

Binary mixtures of dioxane, NMP or formamide were tried to run the graft reaction of HPAM based on the solubility of HPAM in these solvents and the effect of solvent polarity on the reaction rate. Of these three solvents, formamide is the only one in which HPAM has reasonable solubility. However, the reaction rate is very slow in it. In order to obtain a reasonable solubility and reaction rate, we evaluated mixed solvents of formamide combined with one of the other solvents for the reaction. The ratio of formamide to the other solvent was chosen to be low enough just to solubilize the desired amount of HPAM in the solvent because of the reaction rate consideration. Information on the reaction yield can be obtained from the viscosity data because the viscosity of HRAM-AA in aqueous solution increases with the hydrophobe level of HRAM-AA within our study region. We used the viscosity of 0.5 wt% HRAM-AA solutions as a measurement to determine the level of hydrophobe incorporation. Results are given in Table 4.5. The viscosity of the control polymer aqueous solution is 80 cp. The hydrophobe used in this study is 1.5 mol% C_{12} amine (feed ratio) and reaction time is 72 hours.

Table 4.5 shows that the aqueous solution viscosity of the product formed from a (50/30) formamide/dioxane mixture is similar to that of the unmodified polymer. Thus, almost no reaction occurred in this system. On the other hand, the aqueous solution viscosity

of HRAM-AA made in a NMP/formamide mixture (70/20 v/v) is higher than that of the precursor. It can be concluded that a 70/20 NMP/formamide mixture is the best solvent of the three listed in Table 4.5.

Synthesis of HRAM-AAs

HPAM was modified by C_{12}, C_{14} and C_{18} amines in a 70/20 v/v mixture of NMP and formamide. Based on a similar graft reaction of polyacrylic acid and alkylamine [21], as well as the kinetic data given in Table 4.4, the reaction was run 24 hours at 60°C. The feed ratio of hydrophobe to repeat units in the HPAM was varied from 3 to 10 mol%. Such high hydrophobe level and long side chain length were chosen since it is expected that would give a strong hydrophobic aggregate leading to a good hydrogel.

4.3.2 Characterization of HRAM-AA

Hydrophobe Level Results by NMR

The hydrophobe incorporation level of HRAM-AA was measured by ^{1}H NMR. The spectrum is shown in Figure 4.4, for the 3 mol% C_{12} modified HRAM-AA. Results are given in Table 4.6. Based on the hydrophobe level data of C_{12} HRAM-AA given in Table 4.6, the kinetics of the graft reaction was studied. Different reaction models were tested for fitting the experimental data and it was found that the second order reaction model was the best one. The reaction rate is only a function of the concentration of amine and DCC (see chemical equation in page ?****) because the carboxyl group in HPAM is in excess. Thus, the concentration of acid can be treated as a constant. The kinetics equation is given below:

$$dc/dt = -k[amine][DCC] \quad (4.7)$$

The feed ratio of alkylamine and DCC is 1:1, thus, we have:

$$dc/dt = -kc^2 \quad (4.8)$$

$$1/C(t) - 1/C(0) = kt \quad (4.9)$$

C(0) is the concentration of alkylamine at the beginning of the reaction and C(t) is that in the end of the reaction. We kept the same reaction time for the different hydrophobe contents and side chain length graft reactions. Therefore, the right side of the Equation 4.9, kt, can be treated as a constant, K. Thus the Equation 4.9 changes to

$$1/C(t) - 1/C(0) = K \quad (4.10)$$

The experiment data presented by Figure 4.5 are well fitted with the Equation 4.10 except one point. The reaction rate constant, k, which was determined from the intercept of the line divided by the reaction time, is 1.17×10^{-2} mL/mol S. The slope of the line is 1.3 and the theoretical value is 1.

Figure 4.6 shows that the incorporation of hydrophobic modifier increases with side chain length at constant feed hydrophobe concentration, 4 mol%. This means that the reaction rate increases with side chain length. The explanation of this requires further study.

One possibility might be as follows. The reaction medium is formamide which is polar solvent. Thus the hydrophobic modifiers are not so compatible with formamide, resulting in the hydrophobic modifiers adsorbing on polymer chains. The driven force for adsorption increases with side chain length. The hydrophobe adsorption renders a higher local reactant concentration near the polymer chain. Therefore, the reaction rate increases.

Molecular Weight Results by Light Scattering

Light scattering was attempted using several solvents to determine the molecular weight of HRAM-AAs produced by the graft reaction. The HRAM-AAs are ionic HMWSPs. The light scattering measurement requires a solvent that can eliminate the intermolecular hydrophobic interaction and the charge-charge interaction, because these two interactions influence the intensity of light scattering directly. So far, we found that the HRAM-AAs can only be dissolved in formamide and water or water/alcohol mixture. We tried to make HRAM-AA solution in a mixture of 40/60 (v/v) EtOH/H_2O and NaCl, from 6 mM to 80 mM. EtOH was used to break hydrophobic aggregation and salt was used to shield charge-charge repulsion. However, it was problematic in that polymer precipitated out from solution when salt was added to the solution. This means that the solubility of the HRAM-AAs in the mixture of 40/60 (v/v) EtOH/H_2O and NaCl had dropped too much to measure refractive index increment (dn/dc) values and molecular weight by light scattering before charge-charge repulsion had been shielded by salt. Formamide cannot be used as a light scattering solvent either, because accurate dn/dc values for the hydrophobically modified polyelectrolytes cannot be obtained in formamide solution [38].

In an attempt to establish the baseline molecular weight of HRAM-AA, control polymers, PAM and HPAM were studied in deionized water and 80 mM brine, respectively, by classical light scattering. We decided use 80 mM brine as a solvent for HPAM study, because the intrinsic viscosity result indicated that charge-charge interaction are shielded in 80 mM brine solution. The intrinsic viscosity result of HPAM in different salt concentration solution is plotted in Figure 4.7. It is clear that [η] decreases with NaCl concentration until 80 mM and then remains unchanged. This indicates that polyelectrolyte effect on the solution has been eliminated in 80 mM brine. We subjected some samples for molecular weight analysis to identical shear condition in the absence of hydrophobe prior to conducting our light scattering experiments, because both PAM and HPAM are susceptible to shear degradation. The refractive index Increment (dn/dc) for PAM in water that is found from the literature [67] is 1.83 and dn/dc for HPAM in 80 mM brine water that was measured ourselves is 1.63. We found that the weight average molecular weight M_w of the starting material, PAM, is around 4.0×10^6 (Figure 4.8). The M_w of HPAM treated under identical shear condition is around 3.1×10^6. It indicates that shear degradation cannot be ignored for the graft modification reaction.

4.4 Comparison of theTwo Synthetic Routes

Micellar copolymerization has a different procedure and different products from chemical modification graft reaction. Therefore, both have theirown advantages and disadvantages. Considering the procedure of the two synthesis routes, we can conclude that micellar copolymerization is easier to conduct than the graft reaction. Micellar

copolymerization relies on the complete solubilization of the water insoluble monomers in aqueous solution by means of a dilute surfactant solution. The monomers are changed to copolymers in one step and the conversion of hydrophobes reaches 100% after 24 hour. Two or more steps are required for the graft reaction method from monomer to the HMWSPs. The first step is polymerization of precursor polymers and then, the precursor polymer is modified by hydrophobic modifier. The graft reaction requires a suitable solvent in which the precursor polymer and hydrophobic modifier can be dissolved. In addition, the reaction should have a reasonable rate in the solvent. Generally, solvent selection is difficult and the dissolution of precursor polymer requires an additional 24 hours due to high MW. The conversion of hydrophobic modifier is around 40 ~ 60% after 24 hour reaction in our study. Thus, the micellar copolymerization is a simple method to make HMWSPs.

Considering the product structure of the two synthesis routes, we learn that the graft reaction can produce HMWSPs possessing high hydrophobe level and high MW. Based our knowledge, there is no hydrophobe level limitation on the final product in graft reaction. It was reported that a 70% 4-butylaniline modified copolymer of maleic acid-ethyl vinyl ether has been made by graft reaction [33]. On the other hand, HMWSPs with high MW and high hydrophobe level can not be obtained in micellar copolymerization owing to the gelation at the end of the reaction that makes purification of product impossible.

Table 4.1 Yield and melting points of alkylacrylamides

hydrophobic monomer	yield (%)	melting point (°C.)
octyl acrylamide	37.6	34
decyl acrylamide	56	42
dodecyl acrylamide	62	56

Table 4.2 NaA level of HRAMs determined by elemental analysis

feed ratio (mol%)	1 %	2 %	5%	10%	20%	30%	100 %
	NaA level on the polymer backbone						
HRAM8/1.5			1.53 %		3.58%	4.81%	24.1%
HRAM10/1.5	0.26%	0.48%		2.28%			23.8%

Table 4.3 Hydrophobe level of RAMs determined by ^1H NMR

side chain length	feed hydrophobe level mol%	real hydrophobe level mol%	hydrophobic monomer conversion %
C_8	0.75	0.71	95
	1.50	1.49	99
C_{10}	0.75	0.75	100
	1.50	1.43	95
C_{12}	0.75	0.78	104

Table 4.4 Effect of solvent polarity on monitor reaction rate

solvents	reaction temperature	reaction time	yield of amide
Dioxane	60°C	8 h	96%
NMP	60°C	21 h	44%
Formamide	60°C	73 h	24.4%

Table 4.5 Solvent effect on solubility of HPAM and graft reaction rate

solvents	solubility of HPAM in different solvents (g/dl)	HRAM-AA aqueous solution viscosity (cp)
Formamide/dioxane 50/50 v	< 0.6	
Formamide/ dioxane 50/30	> 0.6	76
NMP/formamide 70/20	> 0.6	424

Table 4.6 Effect of feed hydrophobe level on incorporation level in HRAM-AAs

side chain length	feed hydrophobe level mol%	real hydrophobe level mol%	conversion rate of hydrophobes%
C_{12}	3.0	1.3	0.43
	4.0	1.8	0.45
	5.0	2.9	0.58
	6.0	3.1	0.52
	7.0	3.8	0.54
	10.5	7.0	0.67
C_{14}	4.0	2.8	0.70
C_{18}	4.0	3.0	0.75

Mechnism of The Graft Reaction

$$R\text{-}N{=}C{=}N\text{-}R + H^{+} \qquad (1)$$

(DCC)

$$RNH^{+}{=}C{=}NR + P\text{-}COO^{-} \xrightarrow{} \underset{\text{II}}{RNH\text{-}C(OCOP){=}NR} \xrightarrow{a} \underset{\text{III}}{RNHCN(COP)R} \qquad (2)$$

I (HPAM)

$$\text{II or III} + NH_2R' \xrightarrow{b} \underset{\text{IV}}{P\text{-}CONHR'} + \underset{\text{(DCU)}}{RNHCONHR} \qquad (3)$$

(HRAM-AA)

$$\text{II} + H^{+} \xrightarrow{c} RNH\text{-}C(OCOP){=}NHR \xrightarrow{+P\text{-}COO^{-}} \underset{\text{V}}{P\text{-}COOCO\text{-}P} + DCU \qquad (4)$$

$$\text{V} \xrightarrow{+\,NH_2R'} P\text{-}CONHR' + P\text{-}COO^{-}$$

(HRAM-AA)

R = cyclohexyl

P = HPAM

R' = n-$C_{12}H_{25}$, $C_{14}H_{29}$, $C_{18}H_{37}$

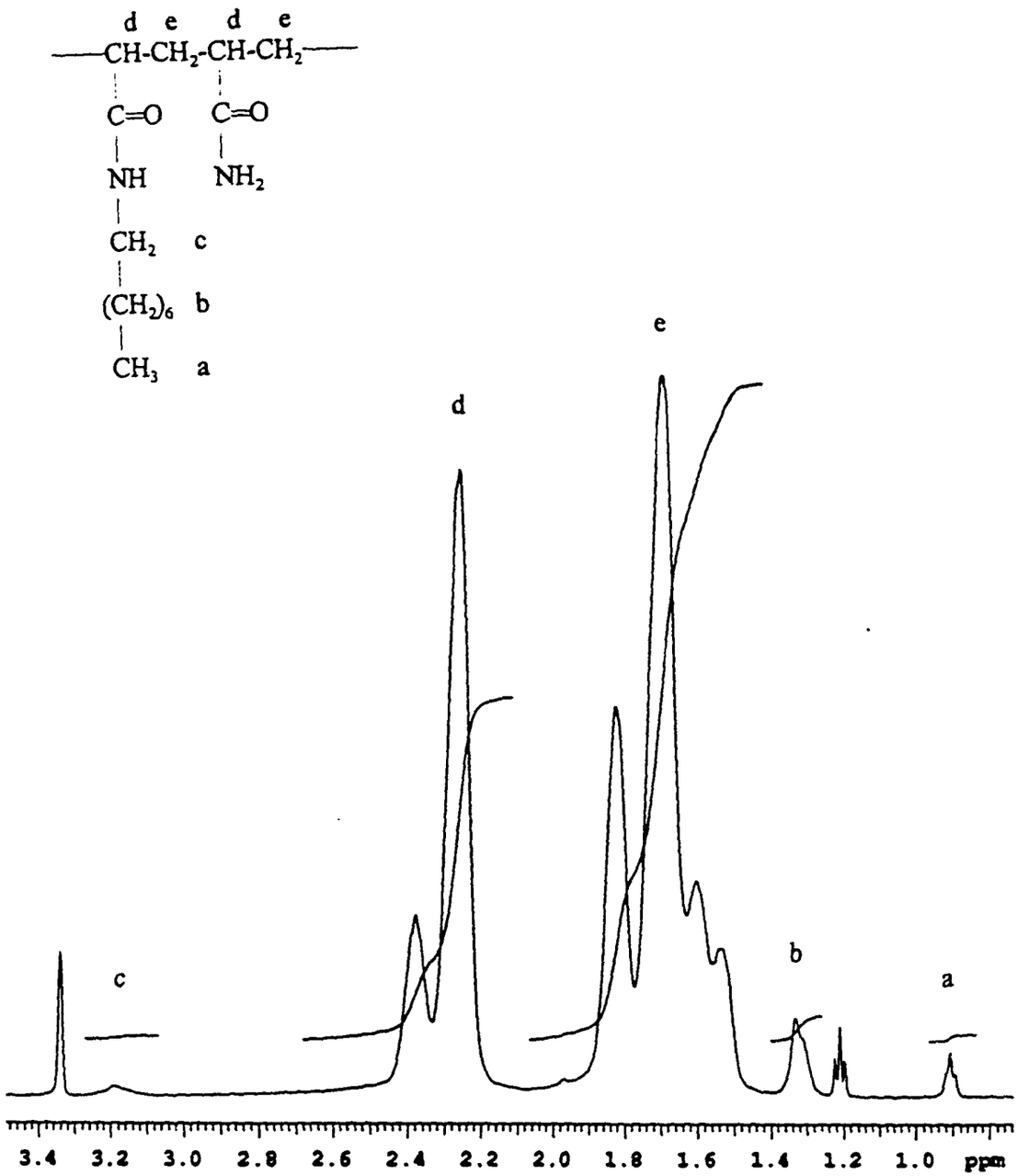


Figure 4.1 ^{1}H NMR spectrum of RAM8/0.75

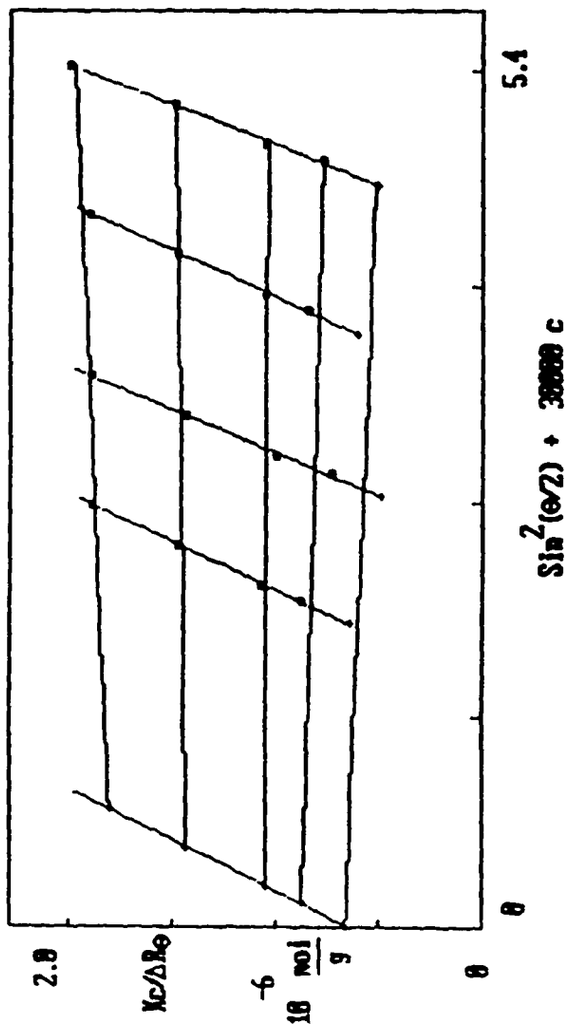


Figure 4.2 Zimm plot of RAM8/0.75 (by Brookhaven Instrument)

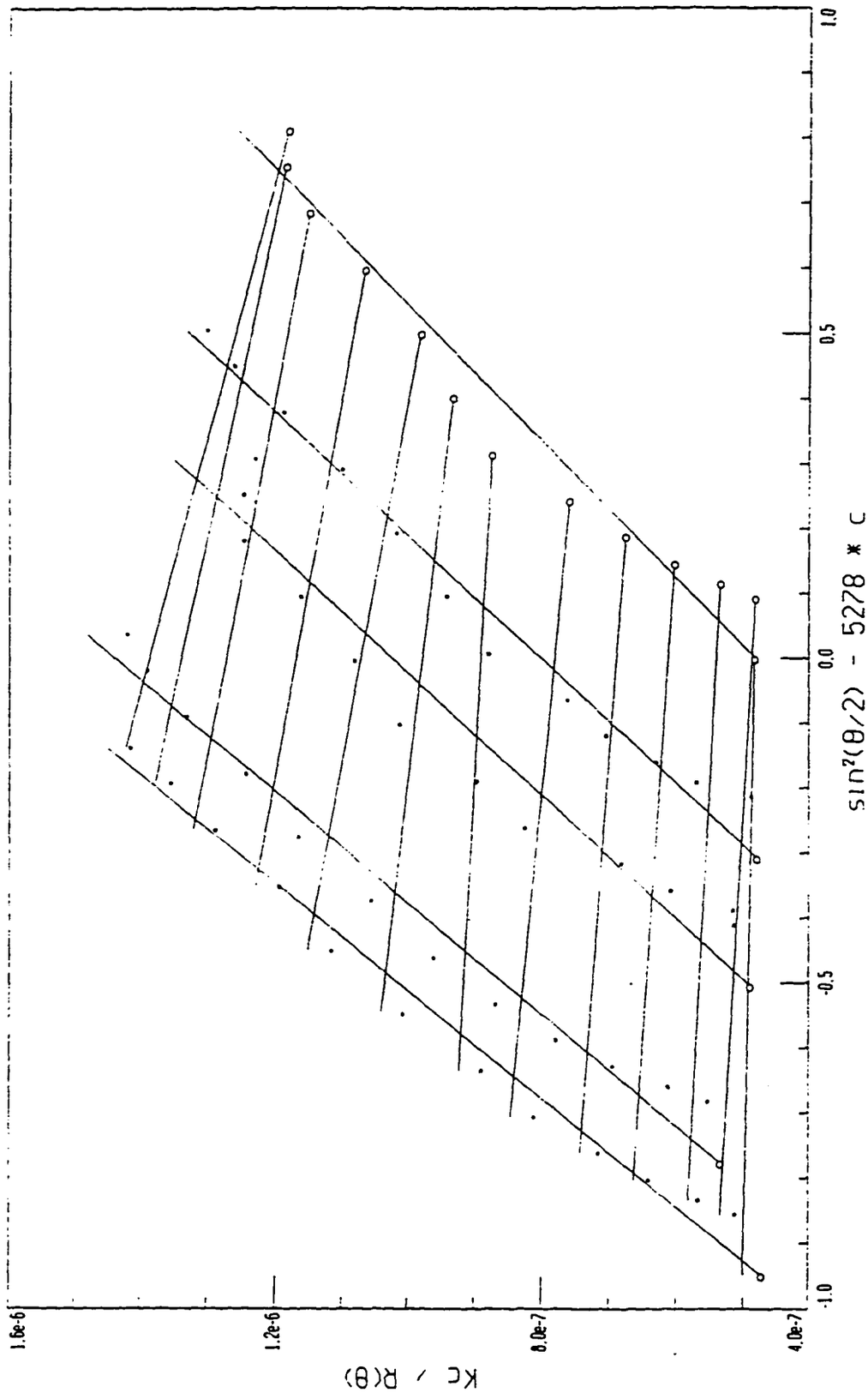
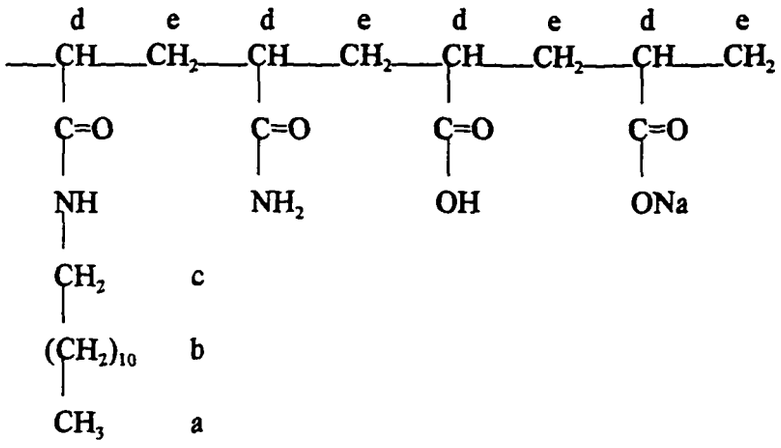


Figure 4.3 Zimm plot of RAM8/0.75 (by DAWN DSP-F)



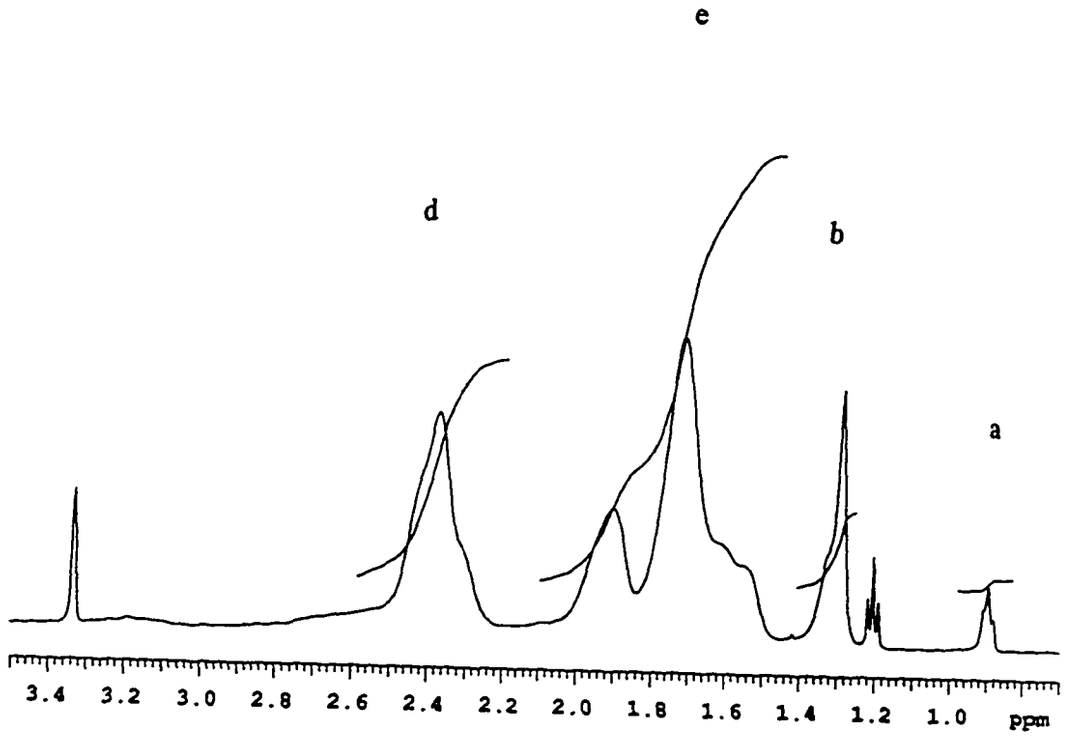


Figure 4.4 ^{1}H NMR spectrum of HRAM-AA12/3

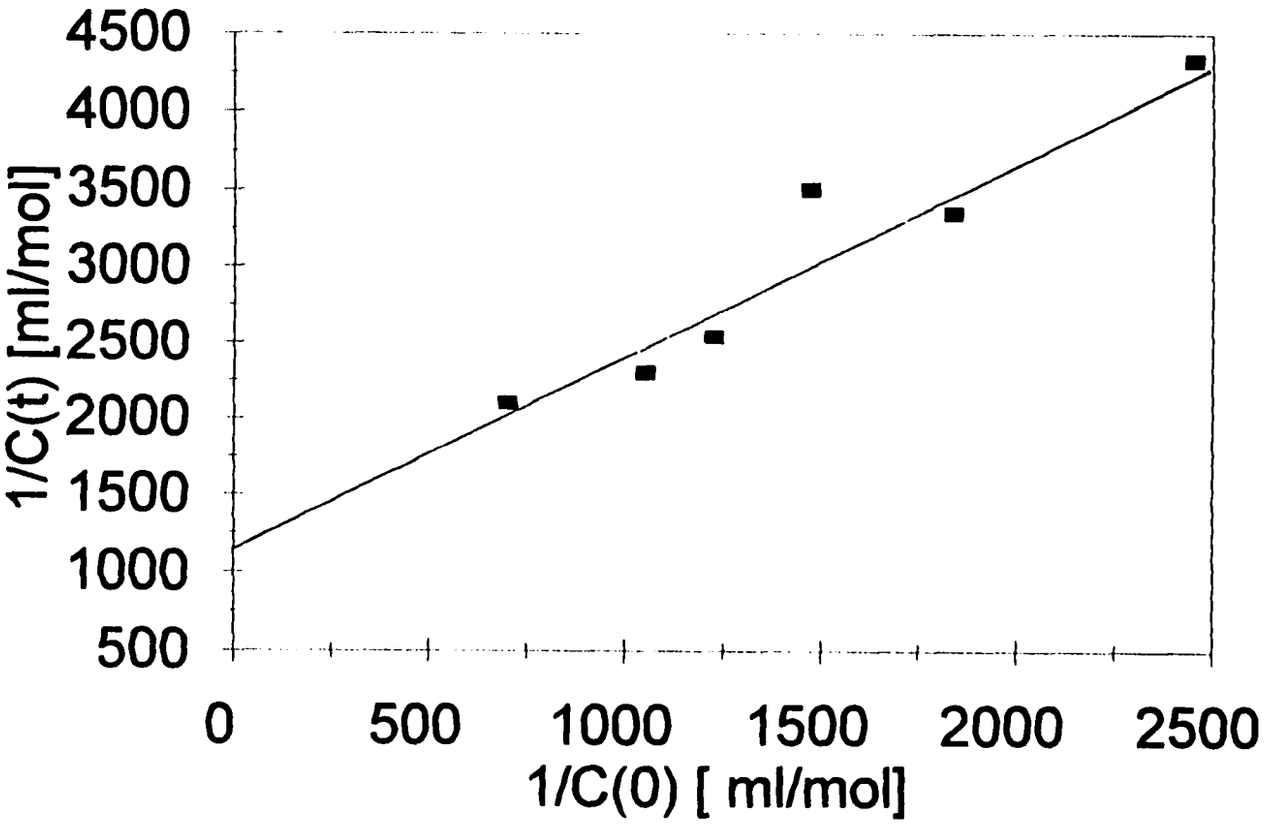


Figure 4.5 Kinetic study of graft reaction using dodecylamine as modifier

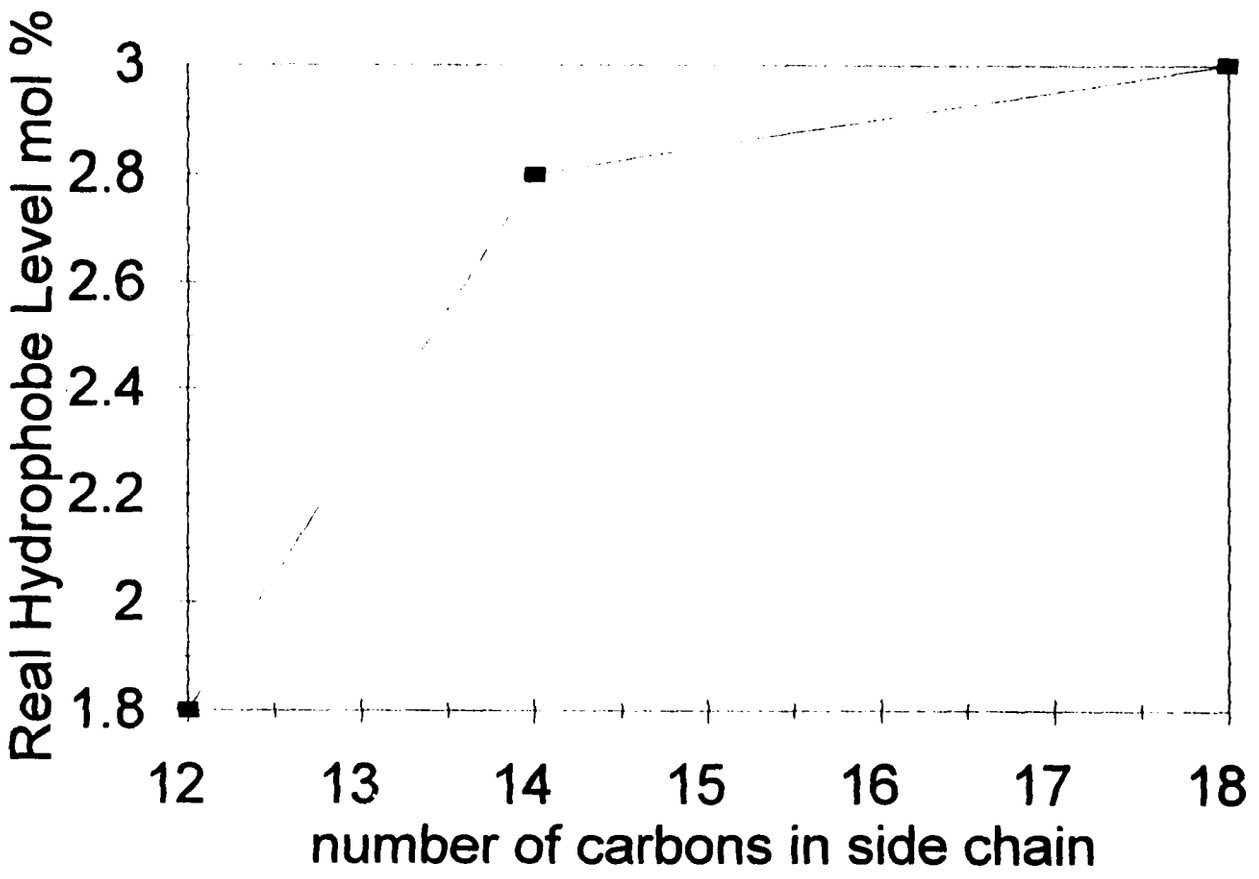


Figure 4.6 Chain length effect on graft reaction rate at constant feed hydrophobe level

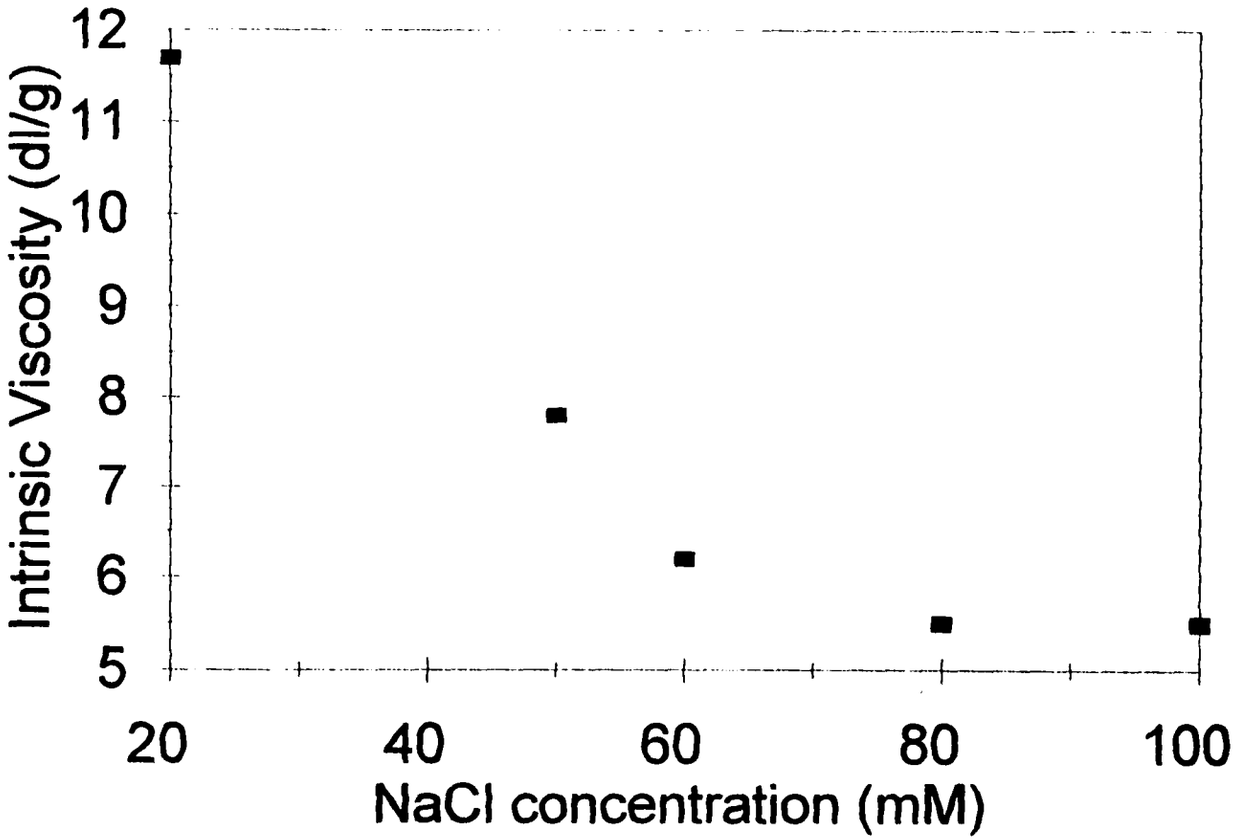


Figure 4.7 Effect of salt concentration on intrinsic viscosity of the precursor polymer for graft reaction

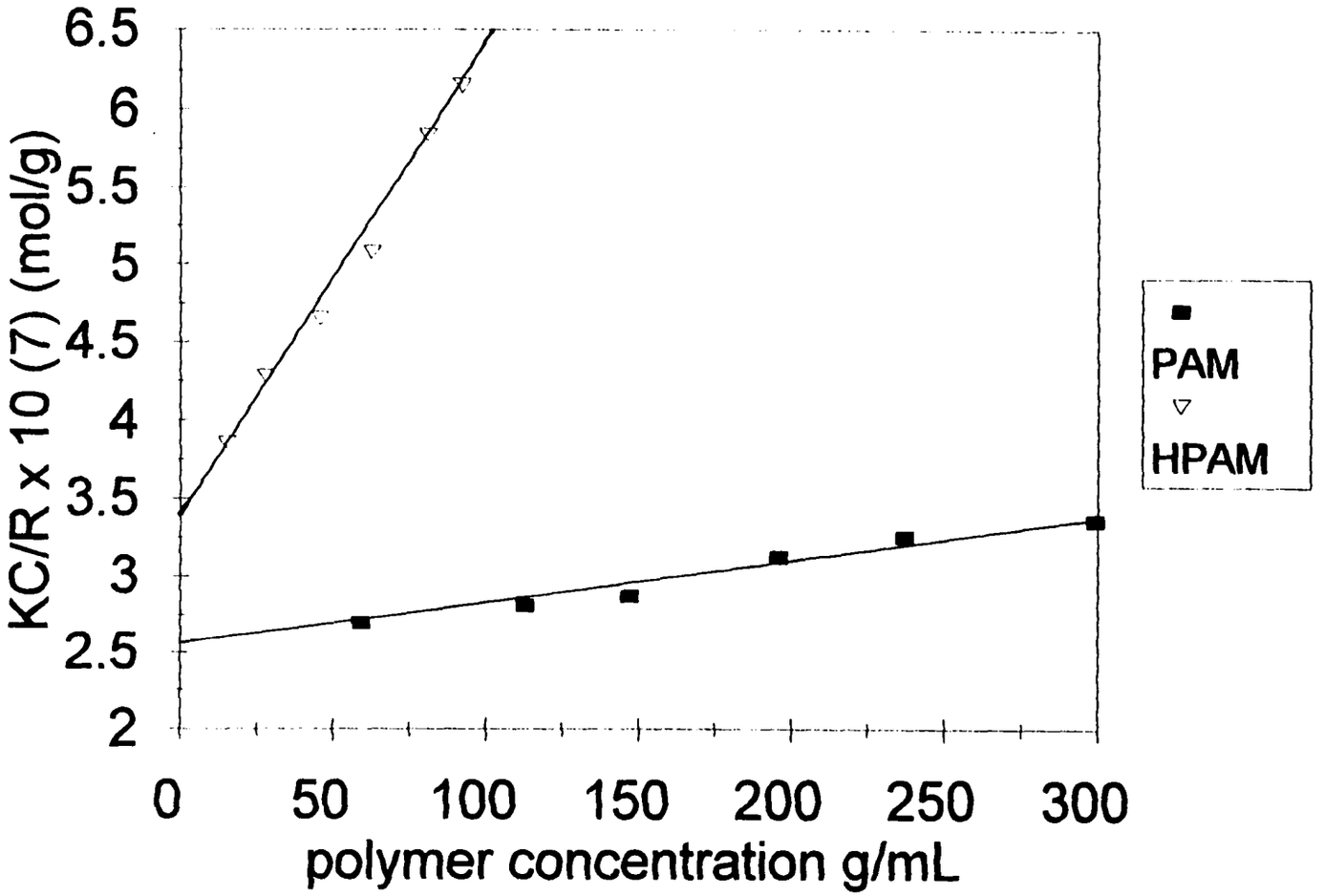


Figure 4.8 Low angle light scattering (KMX-6) measurement of molecular weight of the precursor polymers

CHAPTER 5. HMWSP PROPERTIES IN AQUEOUS SOLVENTS

Viscoelastic amphiphilic gels have been made from both HRAMs and HRAM-AAs. This chapter focuses on bulk and microscopic properties of hydrogels made from HRAMs. HRAM-AA gels were prepared and characterized by a fellow student [81]. Specifically, this chapter details the results of solubility, viscometry, dynamic rheometry, fluorescence spectroscopy and conductimetry of HMWSP aqueous solutions and gels. Based on these results, a relationship between polymer structure and resulting gel property has been established quantitatively. The following nomination, for HRAMs: HRAMn/x-y, where n, x and y are the number of carbons in the side chain, hydrophobe level, and NaA level, respectively, is used in this chapter.

5.1 Introduction

Many reports have appeared in the literature on the properties of solutions made from HMWSPs, as summarized in Chapter 2. The work presented here is the first systematic study on the effects of HMWSP structure on viscoelastic gel properties. Hydrophobically modified water-soluble polymers are less compatible with water than their unmodified backbones because of the tendency for the side chains to be driven out of solution. This may cause the macromolecular chains to collapse, rendering them insoluble, or it may result in the formation of intermolecular hydrophobic interactions, producing a non-Newtonian solution or a viscoelastic network. The present of charge in the polymer backbone will enhance the the solubility of HMWSPs in water, due to the associated increase in the polarity of the backbone and also to intramolecular charge-charge repulsion. This will drive more side chains into the solution. However, the charge will inhibit the formation of intermolecular hydrophobic aggregates in two ways. First, mutual electrostatic repulsion among the backbones will prevent close approach of the macromolecules required for hydrophobic aggregates to form [50-51]. Second, a high charge density on the backbone will render it relatively rigid, reducing its configurational entropy and preventing rearrangement of the chains necessary for the formation of stable intermolecular hydrophobic clusters. Hence we expect to see an optimum backbone charge level at which the extent of intermolecular hydrophobic interaction is maximized.

In the present study the relationship between polymer structure, including hydrophobe level, side chain length and NaA level, and properties of gels or solutions made from HRAMs

and HRAM-AAs were investigated. The NaA level is an important structural parameter because it determine the radius of gyration of the backbone, which, in ture, affects the number of side chains available for aggregation. It is expected that by adjusting the radius of gyration of the polymer, the relative concentrations of unassociated, intramolecularly associated, and intermolecularly associated side chains should change as well. Besides the polymer structure, the solvent composition also has a significant effect on the gel or solution properties, therefore, the effects of salt and surfactant (SDS) concentration on HMWSP solution or gel properties were investigated.

The present study on the effects of polymer structure on hydrogel properties focuses on two aspects: the bulk properties including mechanical integrity, mechanical stability and viscoelasticity, and the polarity of the hydrophobic microdomain. The specific conductance of the solutions or gels estimates the degree of dissociation of the backbones. G'_0, provides the extent of intermolecular hydrophobic association in the viscoelastic systems. Fluorescence spectra of pyrene in these systems are used to establish the presence of hydrophobic aggregates and to infer information about their composition.

5.2 Solution Properties

5.2.1 Solubility of HMWSPs

The solubility was defined as the highest concentration of polymer that produced a clear solution or gel (based on visual inspection) in water after stirring at room temperature for 48 hours. Above this concentration the solutions appeared cloudy or were characterized

by suspended polymer particles. For polymers that were insoluble in water, the minimum concentration of ethanol required to solubilize the polymer at a level of 0.1 g/dl in ethanol/water mixed solvents were also determined

The solubility of the micellar copolymerization products in water decreases with hydrophobe length and hydrophobe level and increases with NaA level, as expected. Results are shown in Table 5.1, giving the solubility and gel point, where applicable, of PAM, HPAM, RAMs, and HRAMs in aqueous solvents. Unmodified PAM and HPAM are soluble in water at levels ≥ 1.5 g/dl. Uncharged polymers (RAMs) with C_{10} and C_{12} hydrophobes are insoluble in water even at very low concentration (<0.02 g/dl). However the incorporation of even low levels of charge on the backbones renders them water soluble, indicating that in these systems intramolecular charge-charge repulsion prevents the chains from collapsing fully.

The water-insoluble RAMs may be solubilized in ethanol/water solutions, as shown in Table 5.1. The minimum ethanol concentration required to solubilize 0.1 g/dl RAM10 and RAM12 increases with both the hydrophobe length and the hydrophobe level on the polymer (Table 5.1). These trends are reasonable, since ethanol solubilizes the hydrocarbon side chains, and will also disrupt intramolecular hydrophobic interactions if they presented [5, 37, 39].

The solubility of the graft reaction products is reported in Table 5.2. Two solvents were used in this study. They are pure water and the EtOH/water mixture (50:50 v/v). The

solubility of HRAM-AAs in aqueous solvent decreases with both hydrophobe level and side chain length. However, the table shows that hydrophobically modified polyelectrolytes possessing high molecular weight (~10^6) and a relative high hydrophobe level (>1.5 mol%) are insoluble in these two solvents, although the polymers have a high hydrolysis level (~55 mol% Acrylic acid and ~5 mol% NaA). Thus, charge-charge repulsion is not able to prevent these chains from collapsing, when the feed hydrophobe content is higher than 7 mol%. Therefore, only these HRAM-AAs with feed hydrophobe level less than 7 mol% are suitable to fabricate hydrogels.

5.2.2 Viscosity of HRAM in Dilute Solution

The viscosity of 0.1% (w/w) solutions of HRAM8s and unmodified polymer PAM and HPAM in water is shown in Figure 5.1 as a function of shear rate. This concentration is below the gel point for all of the polymers. For hydrolysis levels >1.53 all of the solutions exhibit shear-thinning behavior in the shear rate range 5.76 to 115 s^{-1}, reflecting the effects of polymer-polymer interactions. HRAM8/1.5-1.53 is not shear-thinning in this frequency range, reflected a low R_g by the relative low viscosity. The viscosity at constant shear rate increases with increasing hydrolysis level, as expected due to the associated increase in the radius of gyration of the polymer. In addition, at high hydrolysis level the presence of hydrophobes does not affect the solution viscosity, reflecting the fact that charge-charge repulsion inhibits association of the hydrophobic side chains. The viscosity of PAM, HPAM and the two highest NaA level HRAMs at constant shear rate is shown in Figure 5.2 for solutions below the gel point. The solution viscosity of these polymers increases steadily with

concentration.

5.3 Gel Properties

This section will focus on structure/property relationships of gels made from HRAMs. Gels were also made successfully from HRAM-AA. Above the gel point, the HRAM-AA gels precipitated out from the solution to form stiff viscoelatic material. This study focuses on the gels made from HRAMs. They are one phase, clear and homogeneous in macroscopy. Their macroscopic and microstructural properties are discussed in detail in this section, which is ordered as follows: 1) gel point, 2) dynamic rheological properties, 3) conductivity, and 4) pyrene fluorescence.

5.3.1 Gel Point

We define the gel point of a particular polymer as the lowest concentration of that polymer at which G'=G" over the frequency range $\omega \geq 6.28\ s^{-1}$ (Figure 5.3). This frequency range was selected because it encompassed the plateau region in the rheological spectra of all of our gels. Gel points are shown on Table 5.1. Neither of the control polymers formed gels up to a concentration of at least 1.5 g/dl. No networks formed with RAMs or low NaA level HRAMs, whose solubility was very low (~0.1-0.2 g/dl). However, all of the HRAMs with NaA levels ≥ 1.53 mole % formed viscoelastic hydrogels in water, and were soluble up to concentrations well above the gel point. The gel point of HRAM decreases with side chain length at constant NaA level and increases with NaA level at constant side chain length.

The tendency for gels to form in these systems will depend on the balance between the forces driving the side chains into aggregates and those opposing the aggregation process. The driving force for aggregation is directly related to the concentration of available (aqueous phase) side chains in the solution, the energy of interaction binding the side chains in stable aggregates, and the configurational entropy of the backbone. It is inversely related to the solubility of the side chains in the aqueous phase and the magnitude of the intermolecular electrostatic repulsion arising due to the charge on the backbones. Thus the dependence of the gel properties on various aspects of polymer architecture is very complex. For example, longer side chains will be relatively insoluble in the aqueous phase and more tightly bound in the aggregates; however these groups will reduce the configurational entropy of the backbones due to steric hindrance. The proportion of side chains solubilized in the aqueous phase may be increased by increasing the charge on the backbone, but this will render the polymer relatively inflexible and also resistant to aggregation due to intermolecular electrostatic repulsion. Our results show that reduced configurational entropy due to increased side chain length is relatively unimportant in our systems. Also, intermolecular electrostatic repulsion dominates over increased side chain availability in the formation of gels from HRAMs.

5.3.2 Dynamic Rheological Properties of HRAM Gels

Polymers in Pure Water

The factors governing gel formation in HRAMs will have an impact on the dynamic rheological properties of the gels as well. The dynamic storage modules is a measure of both

the number of network linkage points and the resistance of these linkage points to shear. The number of linkage points is a function of the concentration of available side chains, the aggregation number of the most favored aggregates, the flexibility of the backbones, and the magnitude of the intermolecular electrostatic repulsion. The mechanical stability of the aggregates depends on the extent to which they exclude water. At low (0.1 g/dl) polymer concentration all of HRAMs form non-Newtonian solutions in water, as shown in Figure 5.1, thus the hydrophobic aggregates in these systems are not mechanically stable. Only those aggregates formed at concentrations above the gel point are sufficiently resistant to shear to serve as network linkage points. These aggregates will resist shear in proportion to their thermodynamic stability, i.e. the energy of interaction binding the hydrophobes together and the ability of the aggregates to oppose the infringement of water from the surroundings. This in turn depends on the number of pairwise interactions among -CH_2- groups in the cluster, i.e. the side chain length, the packing density, and the aggregation number. The configurational entropy of the backbone segments between aggregates plays a role as well.

The dynamic rheological properties of solutions of PAM, HPAM, and 1.5% C_n HRAMs were measured as a function of polymer concentration to determine the effects of polymer structure on the network properties. The polymer concentration was varied in increments of 0.1 g/dl beginning at 0.1 g/dl. Neither of the control polymers exhibited viscoelastic behavior in water up to polymer concentration of 1.5 g/dl as evidenced by the fact that D" > G' for all of these solutions (e.g. Figure 5.4 and 5.5 for 1.5 g/dl PAM and HPAM, respectively). In contrast, the hydrophobically modified polymers HRAMs except

HRAM8/1.5-24.1, which gel point is higher than 1.5 g/dl, exhibit viscoelastic behavior above gel point, as evidenced by the presence of a rubbery plateau where G'>G". Typical spectra of a viscoelastic polymer gel are shown in Figure 5.6 for a system containing 0.5 wt% HRAM8/1.5-1.53. For purposes of comparison we used the parameter G'_0, defined as the average G' at $\omega \geq 6.28\ s^{-1}$ (7 frequencies total). All of the viscoelastic systems were characterized by G' > G" in this frequency range. Results are shown in Figures 5.7 and 5.8 for the C_8 and C_{10} polymers, respectively. G'_0 of all the gels goes up with polymer concentration. This is reasonable since the total concentration of hydrophobe in the system goes up as well, while electrostatic repulsion decreases with polyelectrolyte concentration [82] due to the concomitant decrease in the degree of dissociation of the macromolecules. G'_0 exhibits a more complex dependence on the NaA level of the polymer backbone. For both the C_8 and C_{10} HRAMs G'_0 at the gel point increases with NaA level of the polymer. However, from Figure 5.7 we see that at constant C_8-HRAM concentration G'_0 exhibits a peak with NaA level occurring at between 1.53 and 4.81% NaA. An analogous peak probably exists in the C_{10} polymers as well (see Figure 5.8). Thus there exists an optimum NaA level at which the strength of the network is maximized for a given side chain length and polymer concentration, as expected. Note that the dynamic storage modules of the C_{10} gels is an order of magnitude higher than that of the C_8 gels for constant polymer concentration and hydrolysis level. Thus the C_{10} aggregates are more resistant to shear and to intermolecular electrostatic repulsion than the C_8 aggregates. This reflects the fact that the activation energy for disengagement of hydrophobic clusters increases with increasing side chain length [83]. In addition, since the longer side chains are more driven to aggregate in

solution, there may be a higher total number of aggregates in the C_{10} system. This will only be the case if the process of aggregation is not opposed by limits on the configurational entropy of the backbone.

Polymers in Brine

Salt affects the backbones and side chains of HM-polyelectrolytes in aqueous solutions in different ways. The effect of salt on the backbones is to screen electrostatic repulsion. Screening of intramolecular repulsion will result in a relatively low R_g which has an adverse effect on G'_0. However the absence of intermolecular repulsion permits close approach of the macromolecules, which may result in the formation intermolecular hydrophobic aggregates giving rise to a high G'_0. Salt also renders the aqueous solvent more polar, driving the hydrocarbon groups into aggregates, by analogy to "salting out" of nonionic surfactants. These aggregates can be intermolecular aggregates that will result in a high G'_0, or intramolecular aggregates that will result in a low G'_0. The net effect of salt on the rheological properties of our systems will reflect a combination of these effects, and will depend on structural properties such as NaA level, backbone rigidity, and side chain length on the polymer. Recall that the polymer was added directly to brine, so the resulting gel properties reflect the equilibrium dimensions of the polymer chain in brine, and do not reflect any transition from a highly extended (as in water) to relatively collapsed one.

The effect of 10 mM NaCl on the rheological properties of 0.5 /dl HRAM gels is shown in Figure 5.9 and Figure 5.10 or C_8 and C_{10} HRAMs respectively. Different factors

dominate in each case. For HRAM8/1.5-1.53 and HRAM8/1.5-3.58, G' is insensitive to 10 mM salt. On the other hand, 0.5 g/dl HRAM8/1.5-4.81, which is just at its gel point in water, forms a strong gel in 10 mM NaCl. HRAM8/1.5-24.1 does not gel in either medium. Thus apparently the HRAM8/1.5-1.53 and HRAM8/1.5-3.58, with 1.06 and 2.49 mM NaA, respectively, in solution, do not exhibit sufficient intermolecular electrostatic repulsion in water to oppose network formation. Intermolecular repulsion in 0.5 g/dl HRAM8/1.5-4.81 ([NaA] = 3.34 mM) is strong but may be quenched by 10 mM NaCl, while in 0.5 g/dl HRAM8/1.5-24.1 ([NaA] = 16.7 mM) 10 mM NaCl is not sufficient to shield the repulsion and allow a gel to form. The C_{10} polymers present a different picture. G'_0 of HRAM10/1.5-2.28 systems in 10 mM NaCl is equal to 35.4 [Pa], which is only ~22% of its value in water. Since the NaA level ([NaA] = 1.58 mM in 0.5 g/dl solutions) of this polymer is intermediate between those of the two C_8 polymers that were unaffected by 10 mM salt, we can assume that the effect of salt on both inter- and intramolecular electrostatic interactions is not significant. Thus the relatively low G'_0 in the HRAM10/1.5-2.28 NaCl gels may be attributed to the fact that the C_{10} side chains are relatively insoluble in this system, so the radius of gyration of the polymer is lower than in water and fewer intermolecular hydrophobic aggregates can form. Note that G'_0 of the HRAM10/1.5-2.28 salt gel is still a factor of 2-3 higher than that of any of the HRAM8 salt gels, reflecting the relatively high tendency of the C_{10} groups to associate (for example, the cmc of sodium decyl sulfate is 3.2×10^{-2} M while the cmc of sodium octyl sulfate is 1.3×10^{-1} [84]).

We conclude that the rheological properties of HRAM gels may be manipulated to

some extent by the addition of NaCl, but that the polymer architecture is the most significant factor determining gel properties in water and saline solutions up to 10 mM NaCl.

Polymers in Surfactant Solution

Samples for this study were prepared by stirring 0.5 g/dl polymer in SDS solutions containing 0.5 mM to 10 mM surfactant (critical micelle concentration (cmc) for SDS in pure water = 8 mM [84]). The rheological properties of (watery) HPAM solutions were unaffected by SDS, as expected since the surfactant and polymer are both negatively charged and are therefore unlikely to associate. However, all of the HRAMs, including HRAM8/1.5-24.1 and HRAM10/1.5-23.7 (for which 0.5 g/dl is below the gel point), formed viscoelastic gels in > 0.5 mM SDS. Thus even in the face of electrostatic repulsion by the backbone, the anionic surfactant molecules are driven to associate with the side chains on the polymer to form hydrophobic aggregates. Moreover, the energy binding these aggregates together is sufficient to overcome mutual electrostatic repulsion among the backbones, even those with high levels of charge. Recall that HRAM8/1.5-24.1 did not gel in 10 mM NaCl.

The dynamic storage modules of HRAM gels exhibits a maximum with SDS concentration, as shown in Figures 5.11 and 5.12 for the C_8 and C_{10} HRAMs, respectively, and drops to near control (water) values above the cmc. The SDS serves to solubilize the side chains, thereby influencing the radius of gyration of the polymer backbones. At the same time, the concentration of SDS also influences the extent of intermolecular interaction in the system. At very low [SDS], the polymer chains are relatively collapsed, with relatively few

side chains exposed to the solution. The hydrophobic aggregates will contain few SDS molecules and a relatively high proportion of side chains [3, 58], and a viscoelastic network will result. As [SDS] is increased, the number of available side chains goes up as well and more intermolecular aggregates form, as seen from the increase in G'_0 leading up to the peak. Above the peak, the polymer is fully extended and the SDS redistributes itself among the hydrophobic sites in the system. The number of hydrophobic aggregates goes up as the number of side chains per aggregate goes down, and the network opens up.

The position and magnitude of the peak in G'_0 vs [SDS] depend on the NaA level on the polymer. This reflects the fact that the level of charge on the backbone governs both the R_g of the polymer, hence the number of side chains available to aggregate, and the magnitude of the intermolecular electrostatic repulsion inhibiting aggregate formation. For both the C_8 and C_{10} polymers (Figures 5.11 and 5.12) the SDS concentration at the peak increases with NaA level. Thus R_g of the polymer when it is fully extended increases with NaA level, as expected, and once the chain reaches this size the effect of additional surfactant is to disrupt the intermolecular hydrophobic interactions and reduce G'_0. The magnitude of G'_0 at the peak follows essentially the same trend with NaA level as G'_0 in water, indicating that there is an optimum backbone charge at which the energy driving intermolecular hydrophobic association exceeds intermolecular electrostatic repulsion.

It is interesting to compare the effects of 10 mM SDS and 10 mM NaCl on each of the HRAM gels, as given in Table 5.3 for gels containing 0.5 g/dl polymer. G'_0 is nearly the

same in both salt and surfactant for all of the polymers. This indicates that the Na+ on the SDS probably plays the same role as the Na+ on the NaCl in governing gel properties in these materials.

5.3.3 Conductivity of HRAMs' Aqueous System

The equivalent conductivity, (Λ [Ω^{-1} m^2 $equiv^{-1}$]), of a solution of electrolytes is defined as the product of the degree of dissociation (α) of the charged species and the sum of the mobilities (μ [m^2 s^{-1} V^{-1}]) of the free ions in the electric field

$$\Lambda = \alpha F(\mu_c + \mu_a) \qquad (5.1)$$

where F is faraday constant. Λ is related to the specific conductance by $\Lambda = \kappa/C$, where κ is the specific conductance measured directly in our experiments and C is the concentration, in equivalents per liter, of charged groups [73]. The degree of dissociation of polyelectrolytes is known to decrease with polymer concentration [82]. In our systems the mobility of the polymer backbones is small compared with that of the Na+ counterions and may be neglected. The mobility of the free ions goes down with increasing viscosity, hence polymer concentration, (see Figure 5.2) and with increasing static charge. Thus we expect the Λ of our solutions to decrease steadily with polymer concentration as well.

The effect of polymer concentration on Λ for HPAM and HRAMs is given in Figure 5.13. Here Λ was obtained by dividing the measured specific conductance, κ, by both NaA

level and polymer concentration, giving the conductivity per unit sodium acrylate in each solution. The high (23.8-24.1 mole %) NaA level polymers, both modified and unmodified, behave as expected, with an average slope of -0.73 $\pm$ 0.03 for the three polymers at concentration >0.1 g/dl. This is accompanied by an increase in the measured specific conductance, κ. Note that the curves for these three polymers coincide, even though the low-shear viscosities of their solutions differ by as much as 50-80% at constant polymer concentration (Figure 5.2). We conclude that Λ is insensitive to the viscosity of the solution in these systems, and that the degree of dissociation of the high NaA level polymers goes down steadily with polymer concentration, even as the total free ion concentration in the solution increases. The degree of dissociation of a polyelectrolyte goes down with total charge present in the solution, hence with increasing NaA level at constant HRAM concentration in our systems. Moreover, the viscosity of our HRAM solutions goes up with NaA level at constant polymer concentration (Figure 5.1). Thus the decrease in Λ seen with NaA level seen at low (<0.1 g/dl) polymer concentration is expected.

The most interesting feature of Figure 5.13 is the fact that all of the low (1.53-4.81) NaA level HRAMs exhibit a local maximum in Λ vs. polymer concentration at or near the gel point. At low polymer concentration the degree of dissociation of the polymer is relatively high, and the polymer coils are highly expanded. The coils collapse with increasing polymer concentration as the degree of dissociation, hence intramolecular electrostatic repulsion, goes down. This process is interrupted at the gel point, however. At this concentration stable intermolecular hydrophobic aggregates form, binding the

macromolecules in a rigid network. Our results suggest that the aggregates constrain the backbones in a relatively extended conformation, permitting a higher degree of dissociation than would be expected from the unperturbed dimensions of the polyelectrolyte. Above the gel point the degree of dissociation of the polymers continues to decrease with polymer concentration, as seen from the decline in Λ. In addition, G' of the gels increases with polymer concentration, reducing the mobility of the free ions and contributing to the drop in Λ.

5.3.4 Hydrophobicity of HRAMs' Aqueous System

Pyrene is a fluorescence probe whose spectrum provides a polarity measurement of its microenvironment. The emission spectrum of the pyrene molecule exhibits five vibronic peaks in the range of 350-450 nm. The ratio of the intensities of the third (λ_3 = 382 nm) and first (λ_1 = 372 nm) peaks increases with increasing average hydrophobicity of the pyrene's environment, weighted according to the partition coefficient. In our systems pyrene may be solubilized in free water, in the vicinity of the polymer backbone, or in the interior of the hydrohpobic microdomains; however since pyrene is only sparingly soluble in water (solubility = 6×10^{-7} M at 25 °C [69]), it will partition preferentially into the hydrophobic regions.

The hydrophobicity of PAM and HPAM solutions increases with polymer concentration in the range 0.05-1.5 g/dl polymer, with HPAM being uniformly more hydrophobic than PAM (Figure 5.14). Thus the hydropobicity of pyrene's environment in aqueous solutions of water-soluble polymers is a function of the segment density, and the

pyrene resides predominantly in the vicinity of the polymer segments. That I_3/I_1 is greater for HPAM than for PAM is probably due to the fact that the former chains are more extended (refer to the viscosity results), presenting more polymer surface with which the pyrene may associate. This conclusion is based on our control studies showing that solutions of NaCl in water exhibit the same I_3/I_1 as water alone and solutions of PAM with NaCl exhibited I_3/I_1 values comparable to those of PAM, and much lower than those of HPAM. Thus we will assume that pyrene is insensitive to the free sodium in these systems.

The hydrophobicity of solutions of HRAMs is a complex function of both polymer concentration and NaA level on the polymer (Figure 5.14). Solutions of HRAM8/1.5-24.1 behave like the control HPAM, showing no evidence of hydrophobic microdomains up to at least 1.5 g/dl polymer, as expected from the rheology and conductivity results. On the other hand, solutions and gels of all three low NaA level HRAMs are more hydrophobic than the control polymers at the same polymer concentration, as expected based on the rheological properties of these systems. I_3/I_1 in these systems ranges from 0.67 at 0.05 g/dl polymer to 1.1 at 0.8 g/dl polymer, depending on polymer structure and concentration. These numbers are comparable to I_3/I_1 in surfactant micelles [69]. We conclude that low NaA HRAMs form hydrophobic microdomains in solution. Furthermore, for all three low NaA level HRAMs I_3/I_1 exhibits a short plateau with concentration, beginning at or near the gel point, then continues to rise. The plateau spans the same concentration range as the peak in conductance vs. polymer concentration. The magnitude of I_3/I_1 is a measure of the average porosity of the microdomains, i.e. the extent of water penetration into these assemblies and hence the

micropolarity of the pyrene's environment. Thus the hydrohpobic microdomains detected below the gel point, which are mechanically unstable and do not give rise to a viscoelastic network, are relatively porous. The domains formed at the gel point are mechanically stable and can exclude water; it is reasonable that their size and packing density should be insensitive to polymer concentration over some finite range. Even at the gel point, however, some of the porous aggregates remain, and their presence is reflected in I_3/I_1. Thereafter, the degree of dissociation of the backbone charges drops to its lowest level (Figure 5.13), imparting a high configurational entropy to the backbone segments between aggregates. The system responds by forming additional thermodynamically stable (i.e. highly hydrophobic) aggregates (as reflected in the increasing G'_0), and the average hydrophobicity of the domains increases as well.

The average hydrophobicity of the low NaA systems increases with NaA level on the backbone. Thus there is not a direct correlation between the strength of the network and its average hydrophobicity. While G'_0 is a measure of the number of mechanically stable aggregates per unit volume in the gel, I_3/I_1 reflects the presence of hydrophobic aggregates and also the dimensions of the polymer backbone, as discussed above.

Figure 5.15 shows the effect of hydrolysis level on I_3/I_1 for C_{10} modified HRAMs at polymer concentrations 0.05-1.5 g/dl. For HRAM10/1.5-2.28, the increase of I_3/I_1 vs. polymer concentration is rapid at low concentration, then curve flattens out beginning near the gel point, much like the low NaA level C_8 HRAMs. As with the C_8 polymers, formation

of hydrophobic aggregates is more favored at lower NaA level than at 23.7 mole % NaA. HRAM10/1.5-23.7, which has the same NaA level as the control HPAM, shows evidence of hydrophobic association above 0.3 g/dl. Note that in contrast to the high NaA C_8 HRAM, the high NaA C_{10} HRAM forms a viscoelastic gel in the concentration range shown on Figure 5.15 (see Table 5.1). Thus the driving force for the formation of hydrophobic aggregates is stronger with C_{10} side chains than with C_8 side chains, as expected, and is sufficient to overcome even the high degree of electrostatic repulsion present with NaA level of 23.7 mole%.

Table 5.1 Solubility of RAM and HRAM in aqueous solvents

polymer code	solubility (ppm)	solvents	gel point (g/dl)
PAM	>15000	H_2O	
RAM8/0.75	>2000	H_2O	
RAM8/1.5	1000~1500	H_2O	
RAM10/0.75	1000	12 wt% EtOH	
RAM10/1.5	1000	20 wt% EtOH	
RAM12/0.75	1000	20 wt% EtOH	
HRAM8/1.5-1.53	>8000	H_2O	0.2-0.3
HRAM8/1.5-3.58	>8000	H_2O	0.2-0.3
HRAM8/1.5-4.81	>8000	H_2O	0.5
HRAM8/1.5-24.1	>15000	H_2O	1.5-3
HRAM10/1.5-0.26	<500	H_2O	
HRAM10/1.5-0.48	500~1000	H_2O	
HRAM10/1.5-2.28	>8000	H_2O	0.05
HRAM10/1.5-23.7	>15000	H_2O	0.6-0.7

Table 5.2 Solubility of HRAM-AAs in the aqueous solvents

polymer code	real hydrophobe level mol %	solubility of HRAM-AA in water	solubility of HRAM-AA in EtOH/H_2O
HRAM-AA12/3	1.3	>1 wt%	>1 wt%
HRAM-AA12/4	1.8	>1 wt%	>1 wt%
HRAM-AA12/5	2.9	<0.5 wt%	>1 wt%
HRAM-AA12/6	3.1	insoluble	swellable
HRAM-AA12/7	3.8	insoluble	insoluble
HRAM-AA12/10	7.0	insoluble	insoluble
HRAM-AA14/4	2.8	<0.5wt%	>1 wt%
HRAM-AA18/4	3.0	insoluble	>0.5 wt%

Table 5.3 G'_0 of HRAMs' gels in different solvents

solvents	HRAM8-1.53	HRAM8-3.58	HRAM8-4.81	HRAM10-2.28
water	7.2	10.65	1.4	158
10 mM NaCl	5.8	10.3	3.3	35.4
10 mM SDS	5.5	16	5.6	49.3

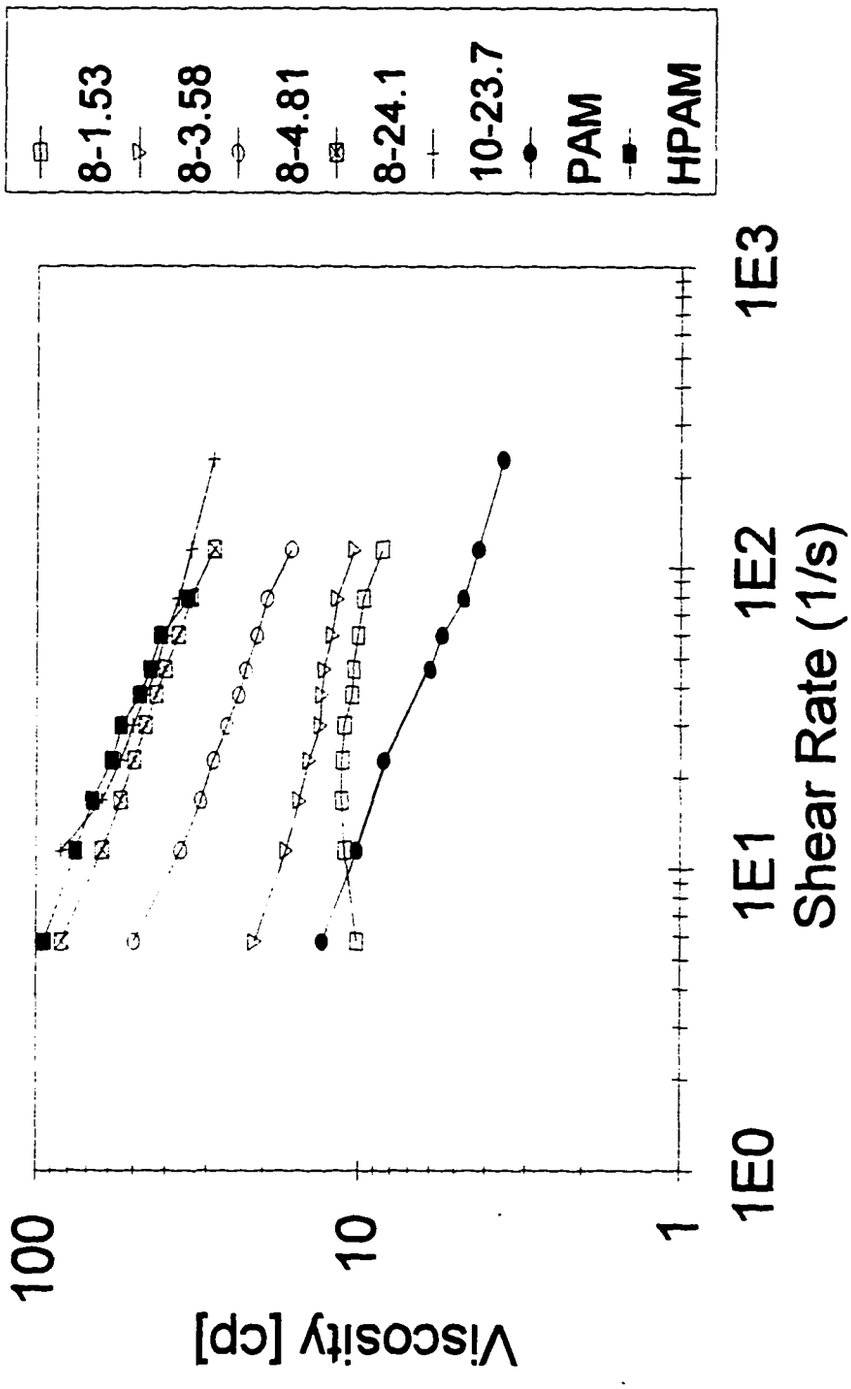


Figure 5.1 Hydrolysis level effect on aqueous solution Viscosity for HRAM8/1.5 and unmodified polymers

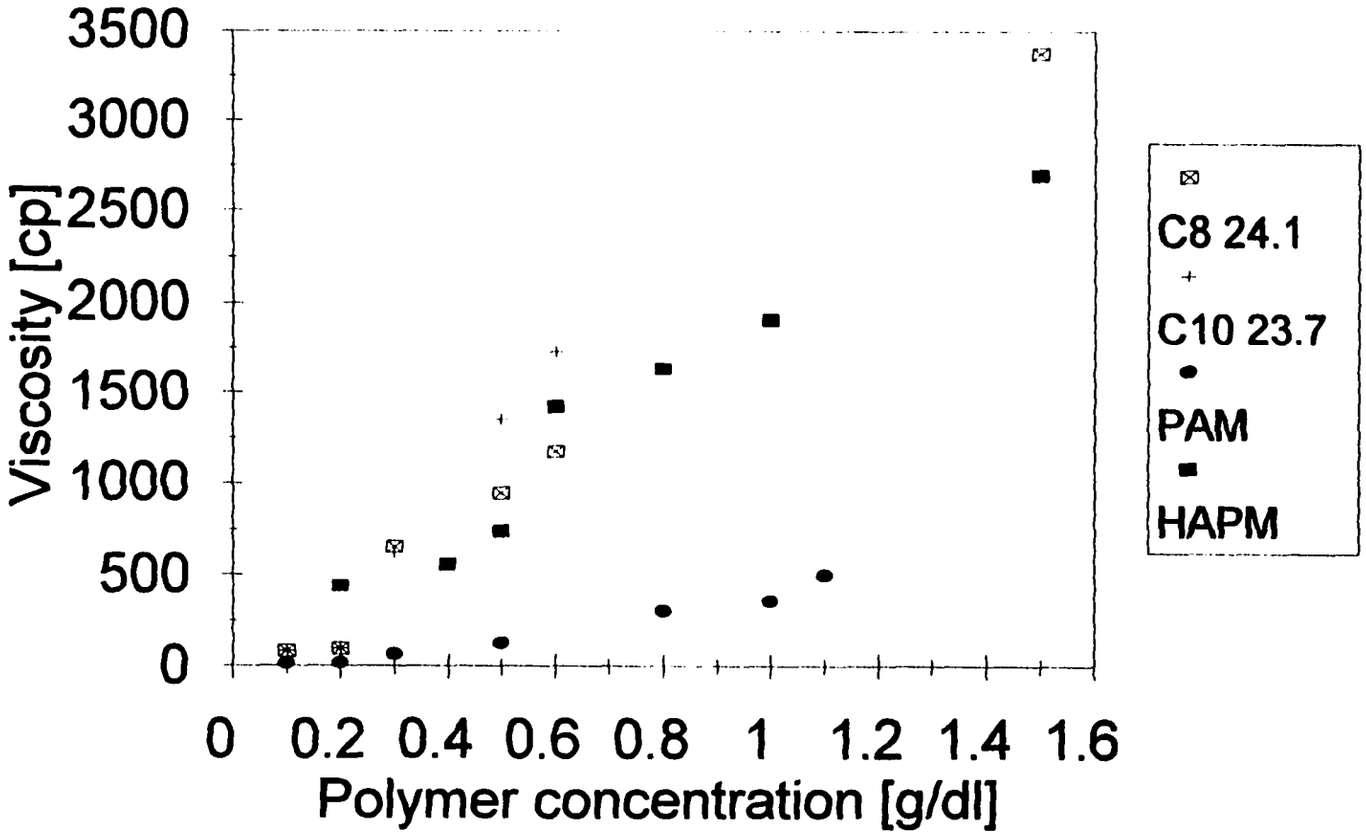


Figure 5.2 Aqueous solution viscosity vs. polymer concentration at shear rate of 5.76 1/s for HRAM8/1.5-24.1, HRAM10/1.5-23.7 and unmodified polymers

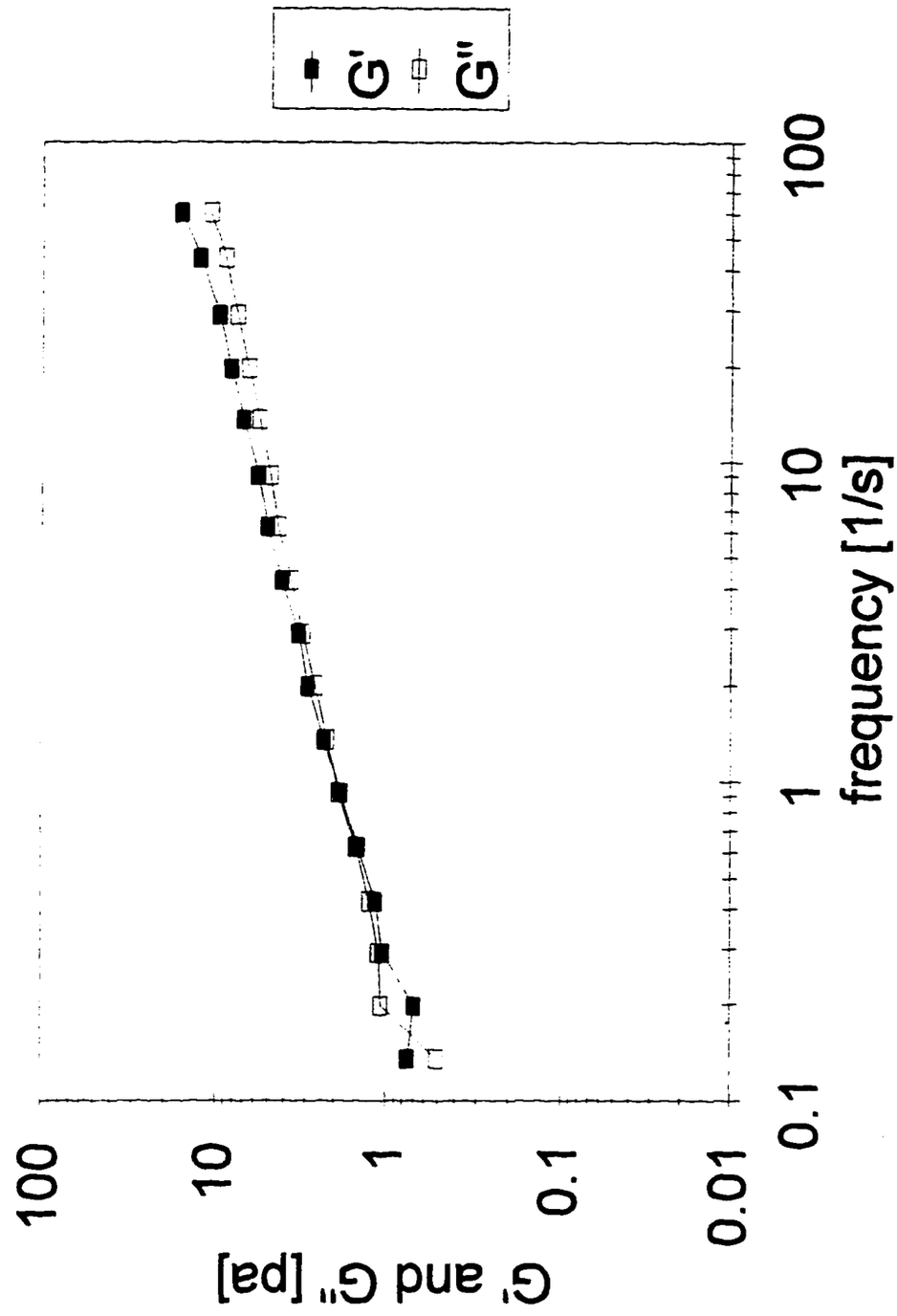


Figure 5.3 Typical dynamic rheological spectrum at gel point

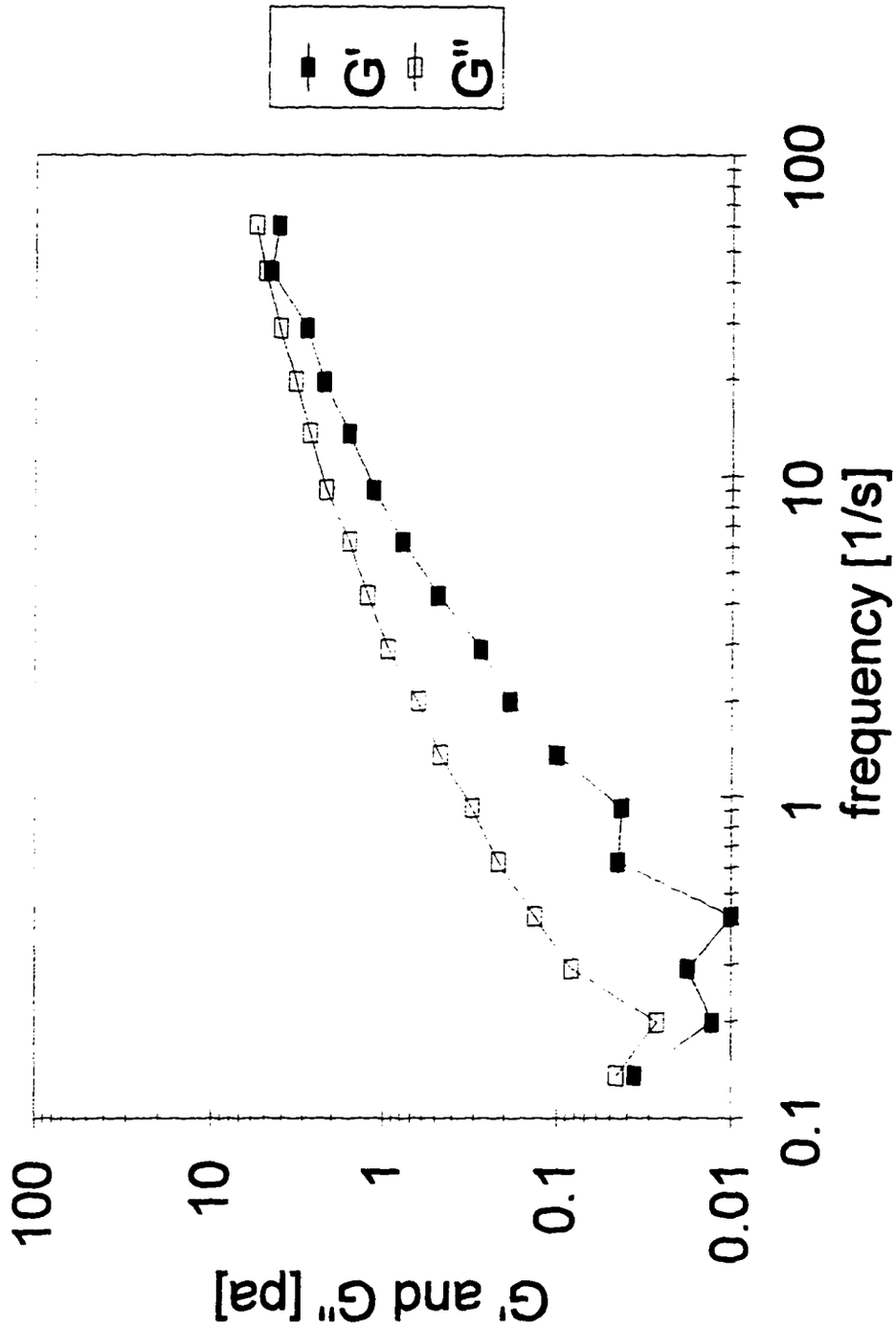


Figure 5.4 Dynamic rheological spectrum of PAM aqueous solution at the concentration of 1.5 g/dl

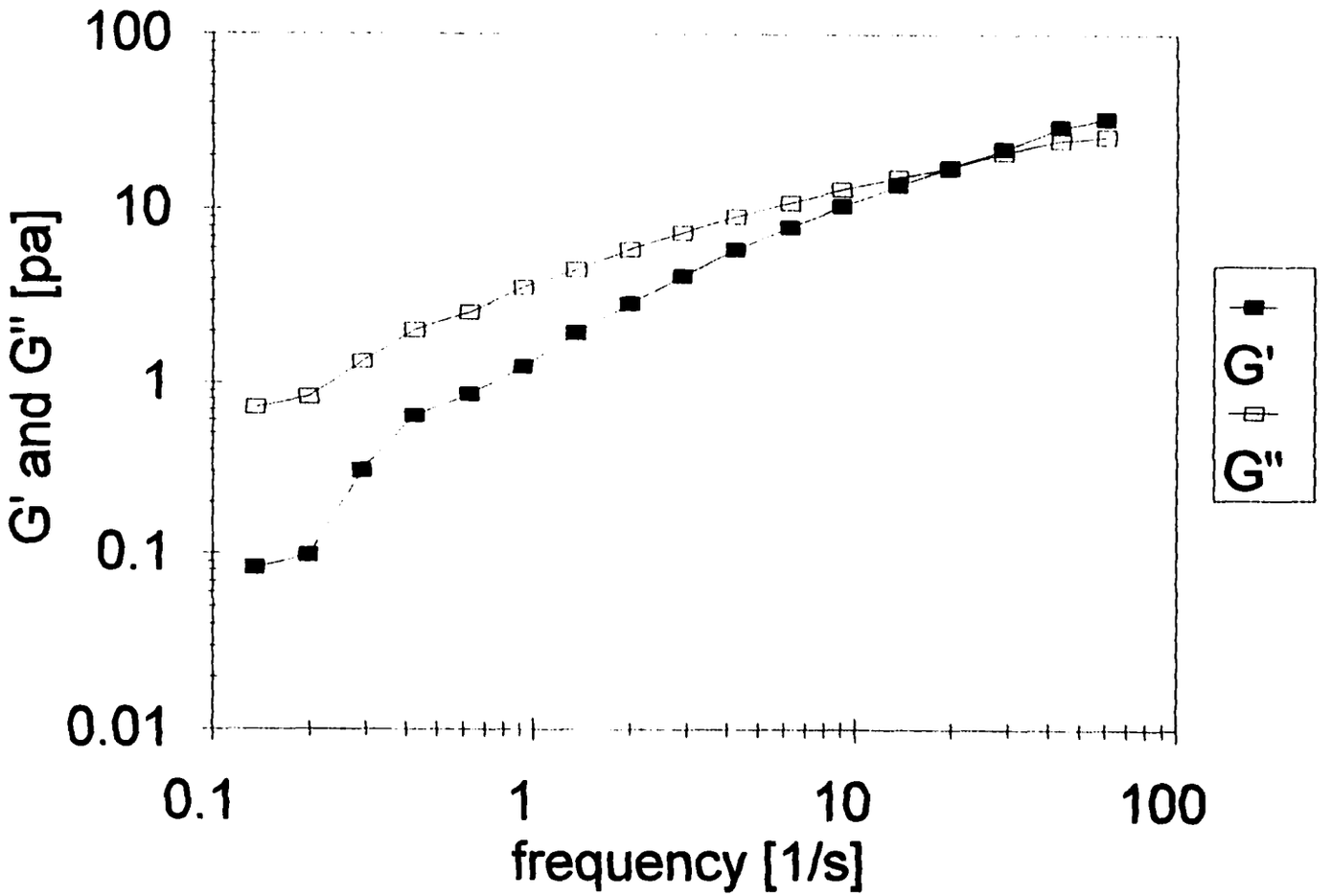


Figure 5.5 Dynamic rheological spectrum of HPAM aqueous solution at the concentration of 1.5 g/dl

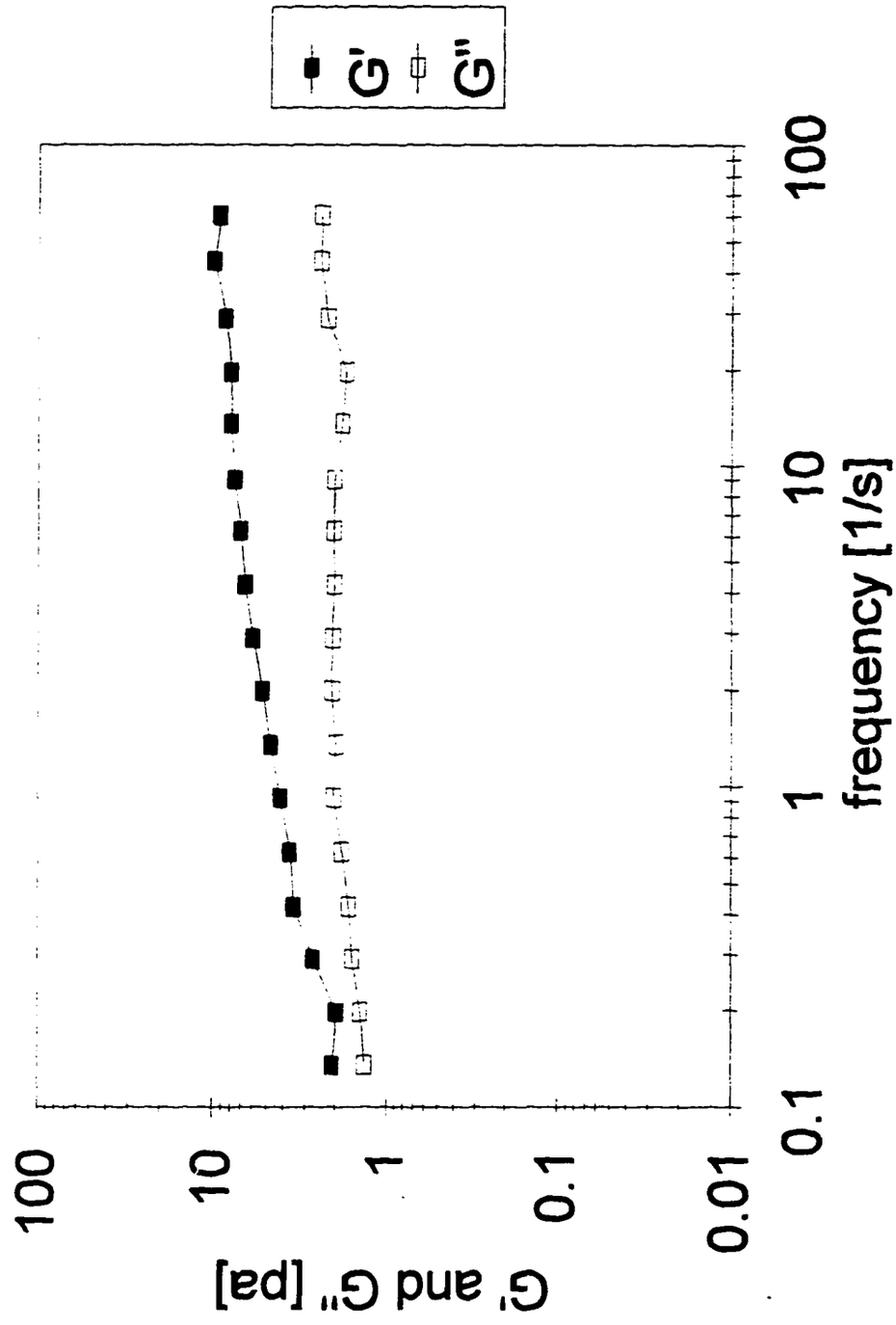


Figure 5.6 Dynamic rheological spectrum of HRAM8/1.5-1.53 water gel at the concentration of 0.5 g/dl

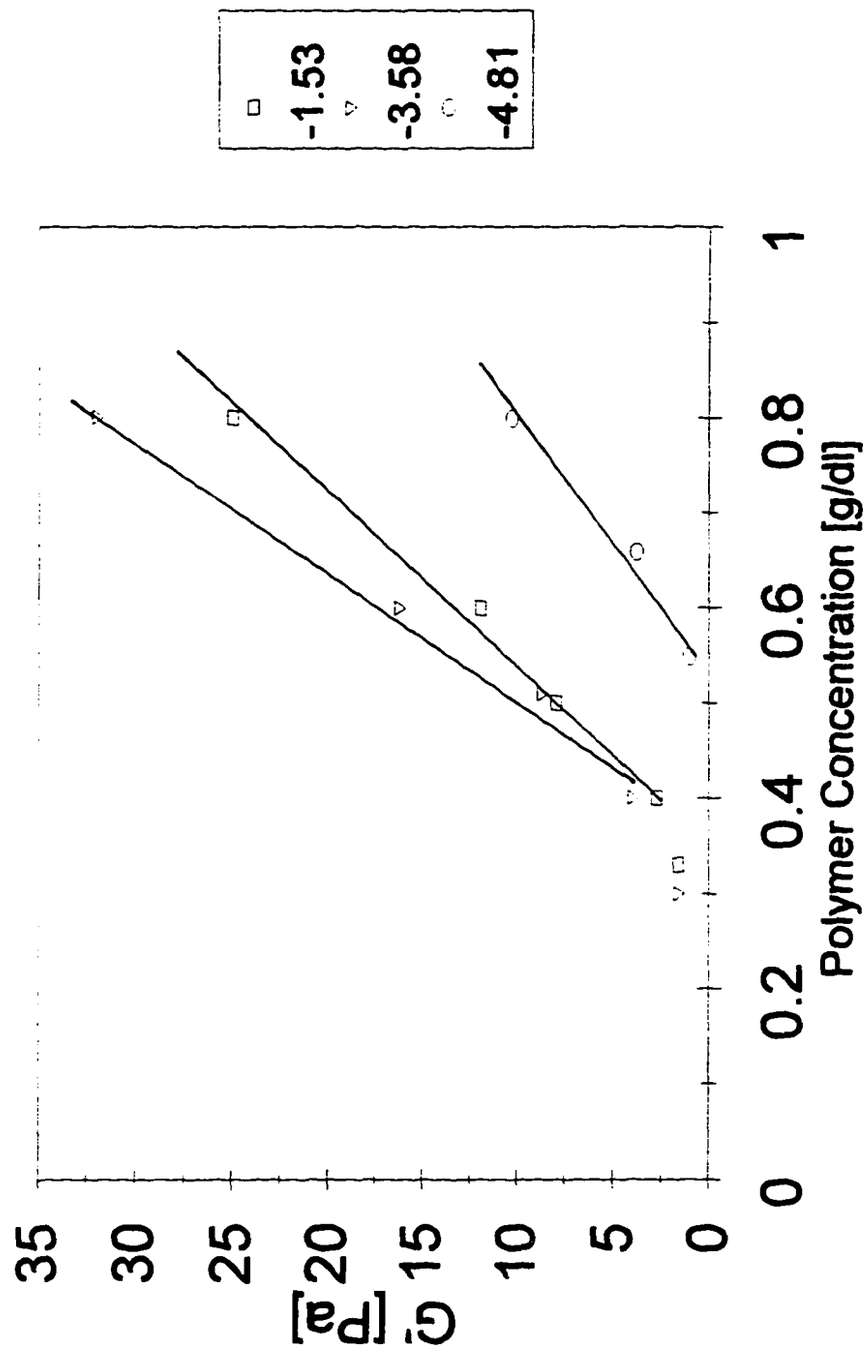


Figure 5.7 Effect of hydrolysis level on G' for HRAM8/1.5 water gels at varied polymer concentration

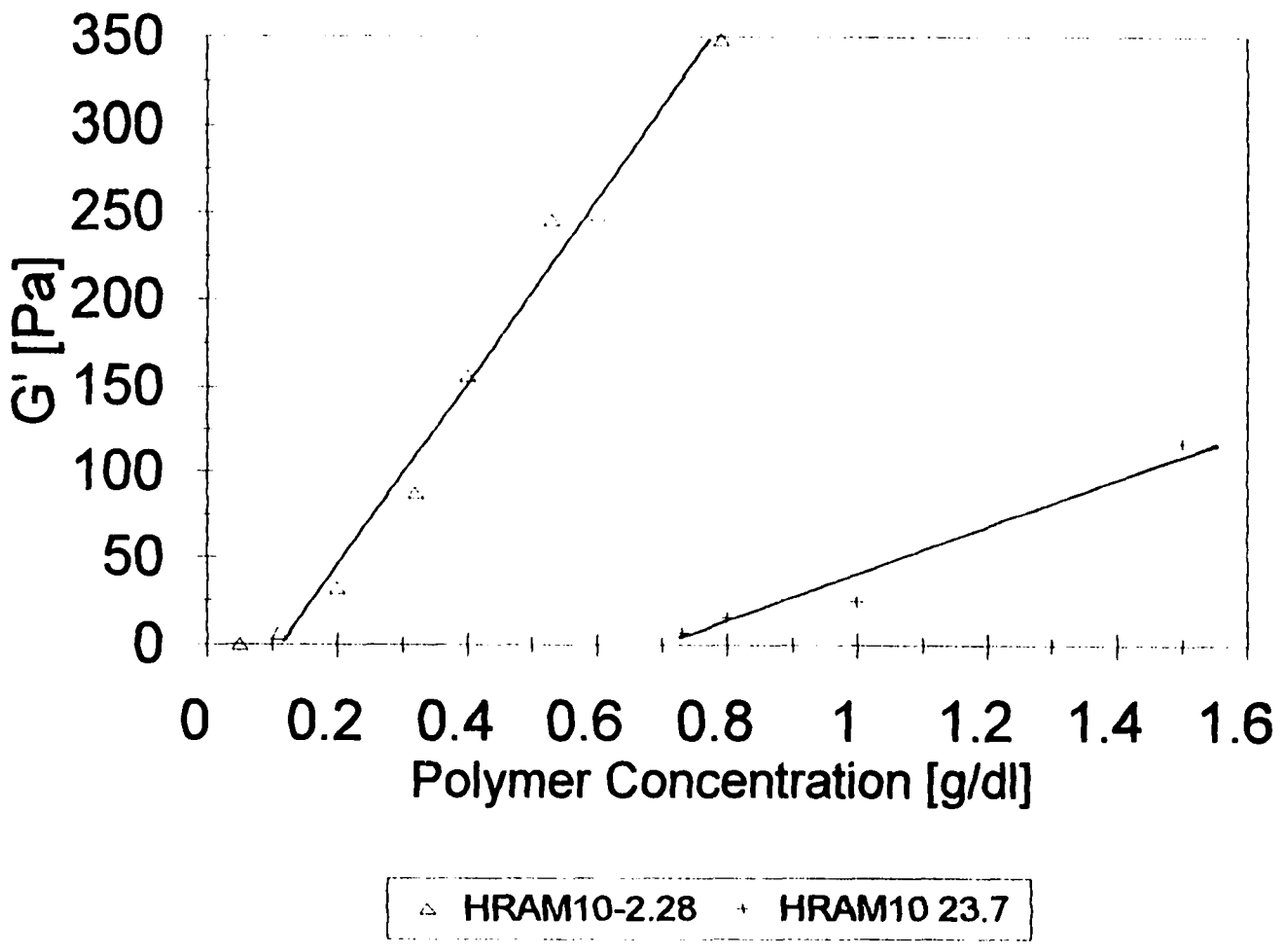


Figure 5.8 Effect of hydrolysis level on G' for HRAM10/1.5 water gels at varied polymer concentration

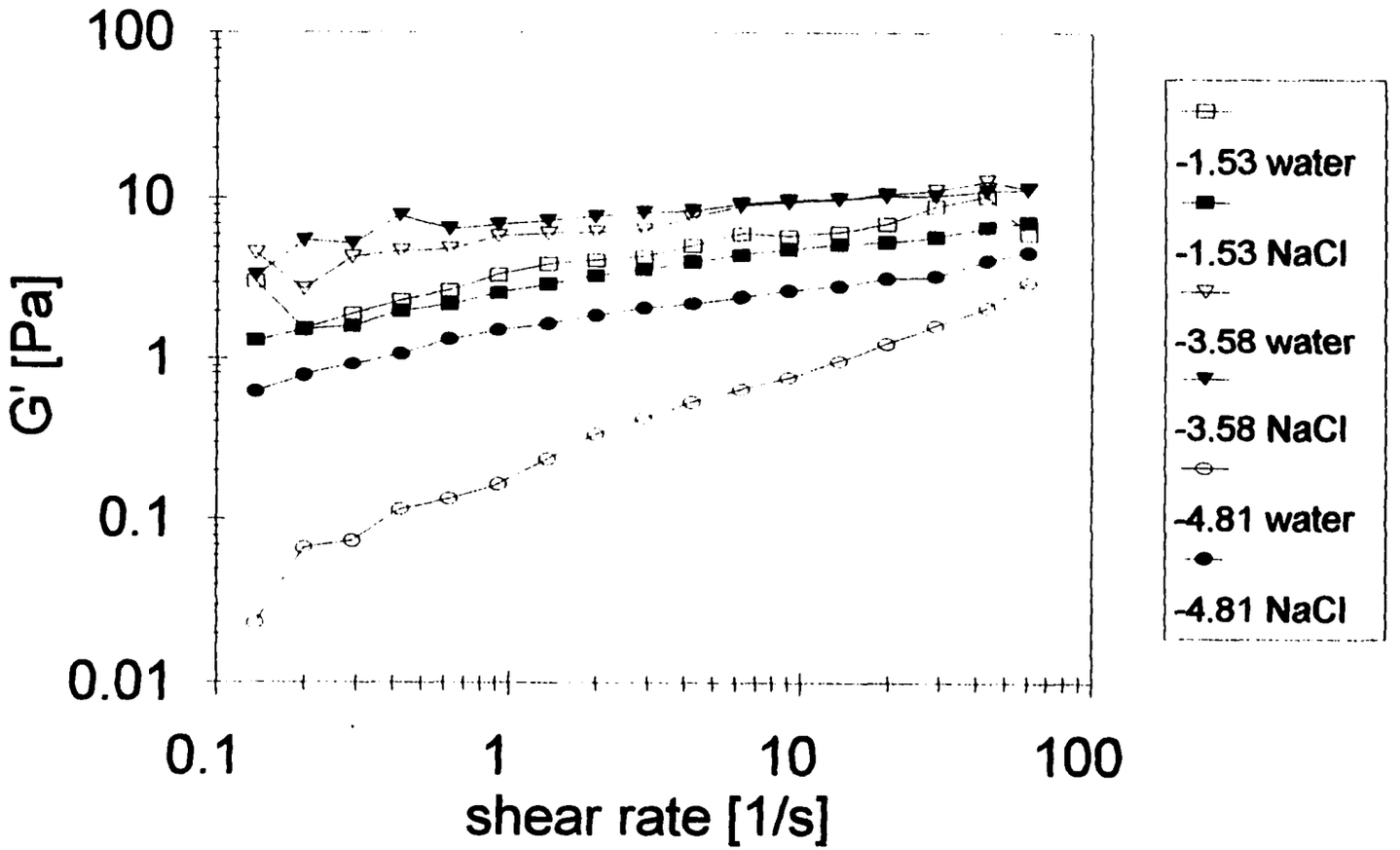


Figure 5.9 Comparison of G' between HRAM8/1.5 brine gels and water gels

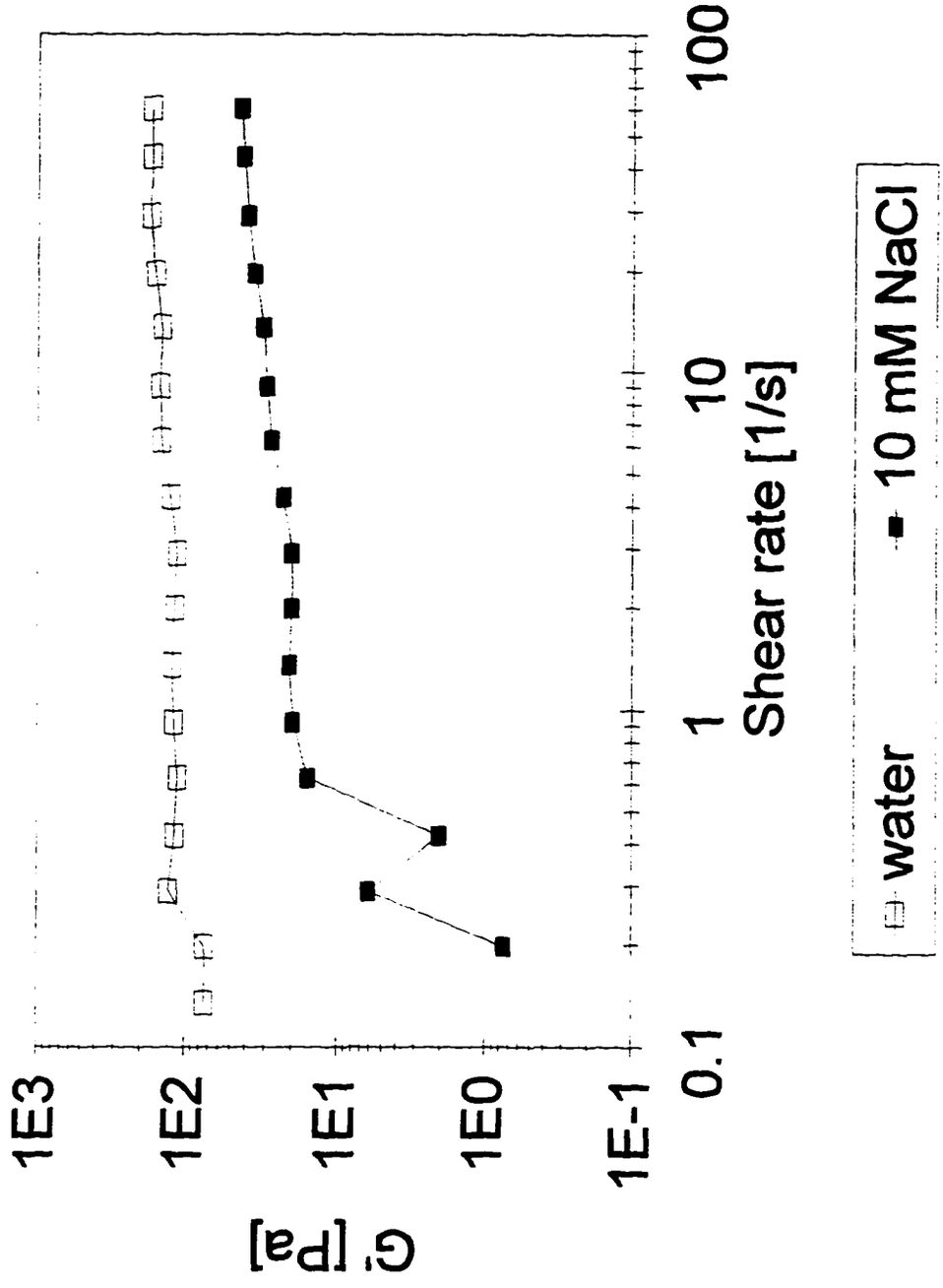


Figure 5.10 Comparison of G' between HRAM10/1.5-2.28 brine gel and water gel

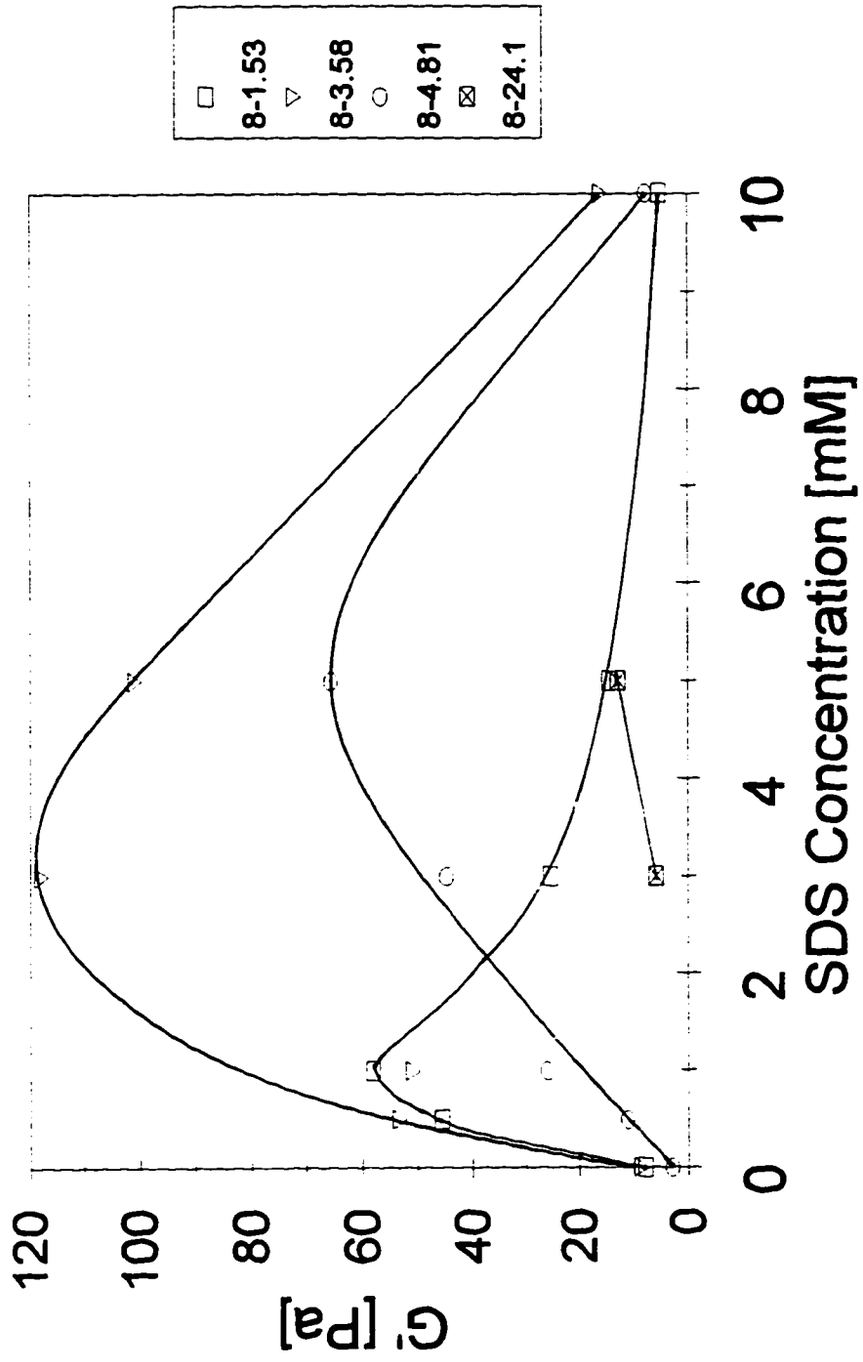


Figure 5.11 SDS concentration effect on G' for HRAM8/1.5 surfactant gels

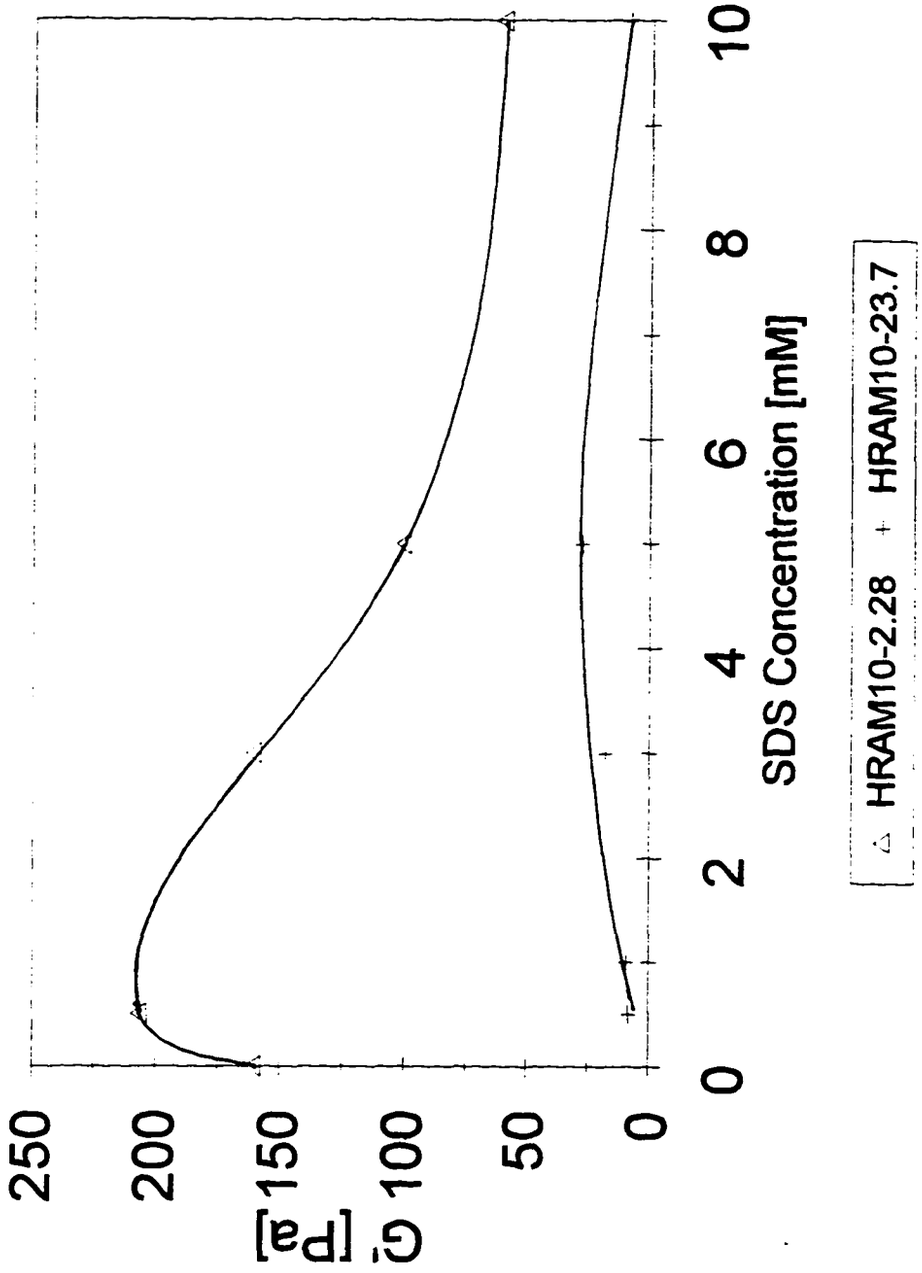


Figure 5.12 SDS concentration effect on G' for HRAM10/1.5 surfactant gels

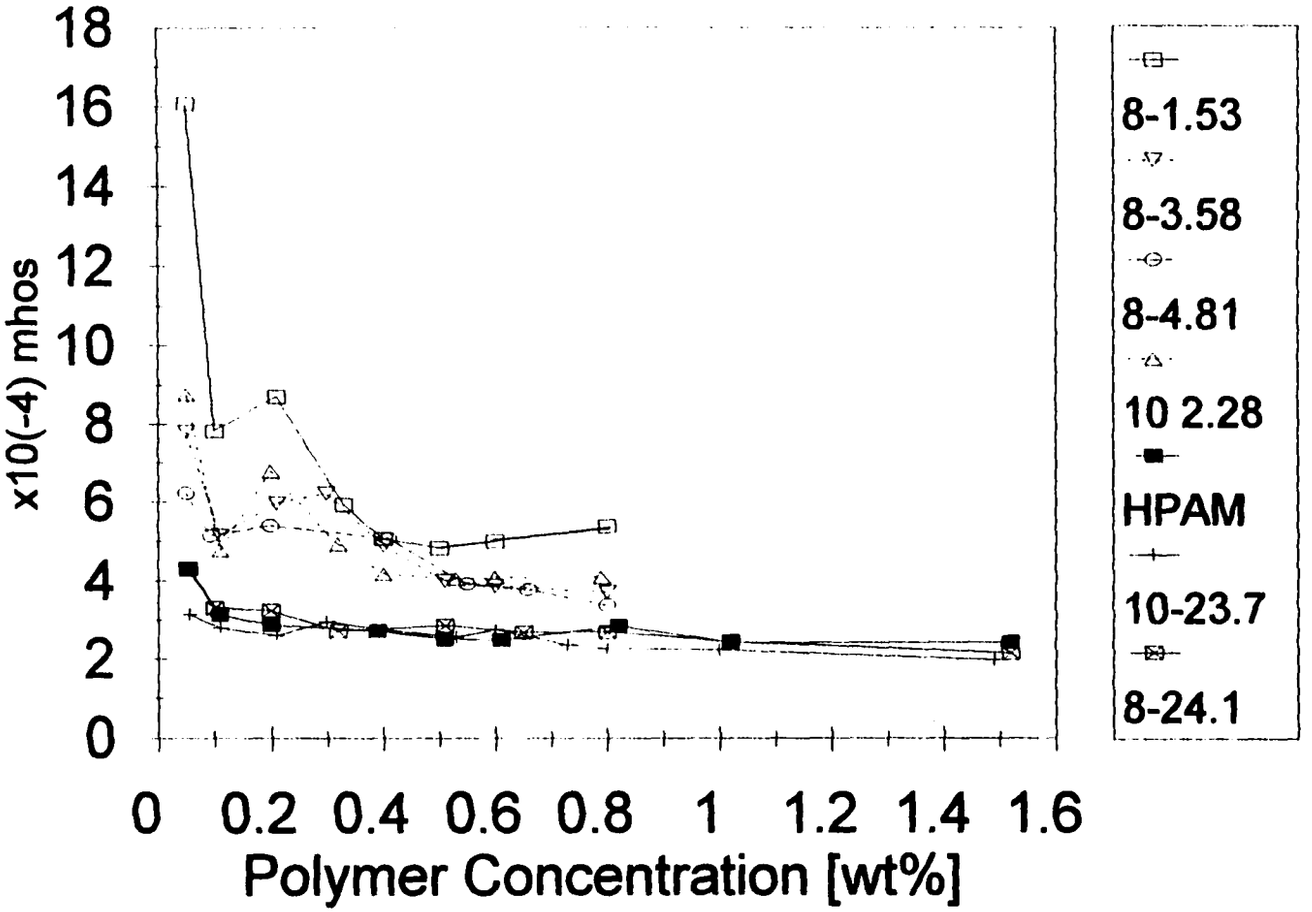


Figure 5.13 Effect of polymer concentration on conductance of HRAM aqueous systems

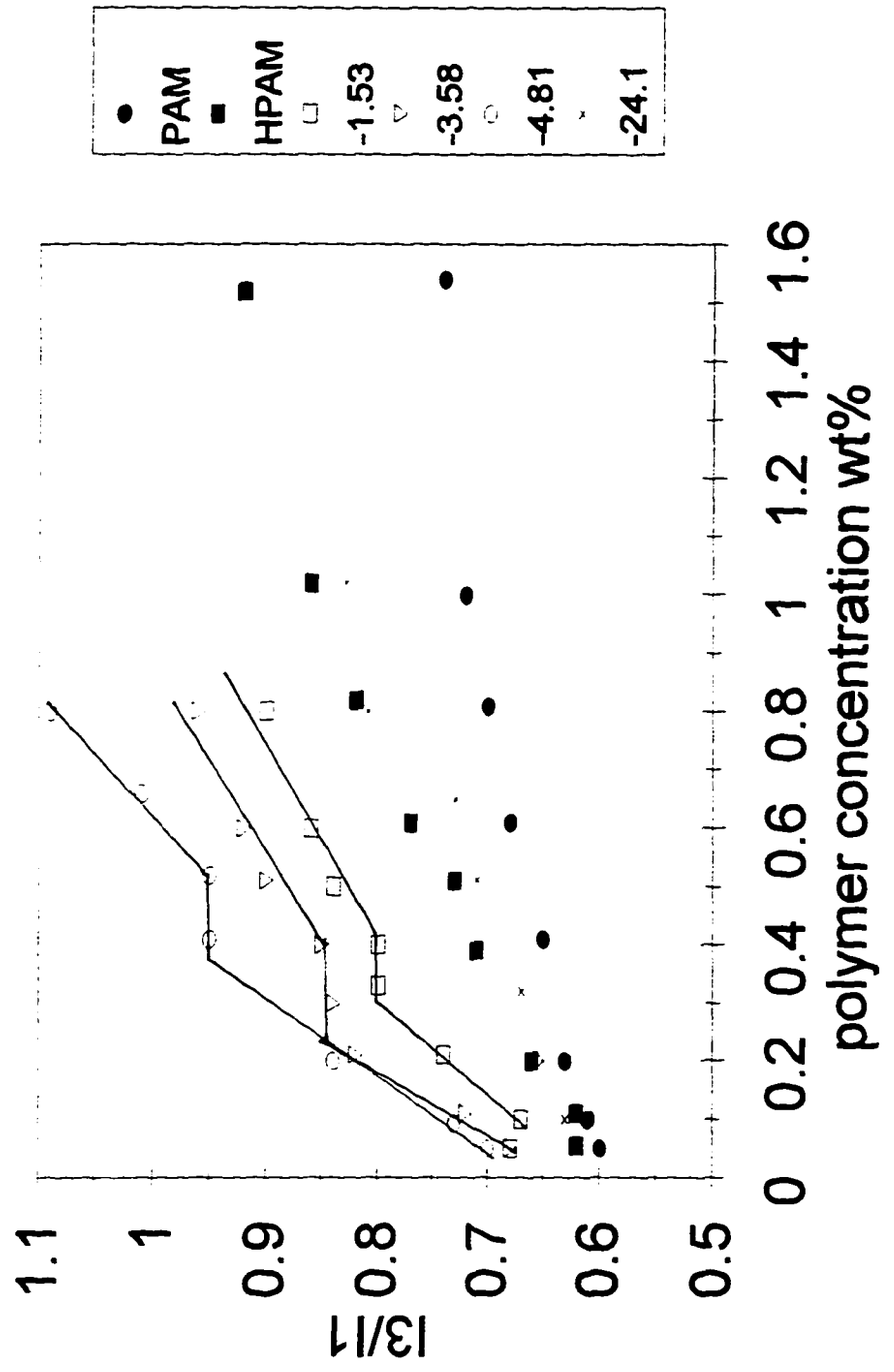


Figure 5.14 Hydrolysis level effect on hydrophobicity for HRAM8/1.5 and unmodified polymer aqueous systems

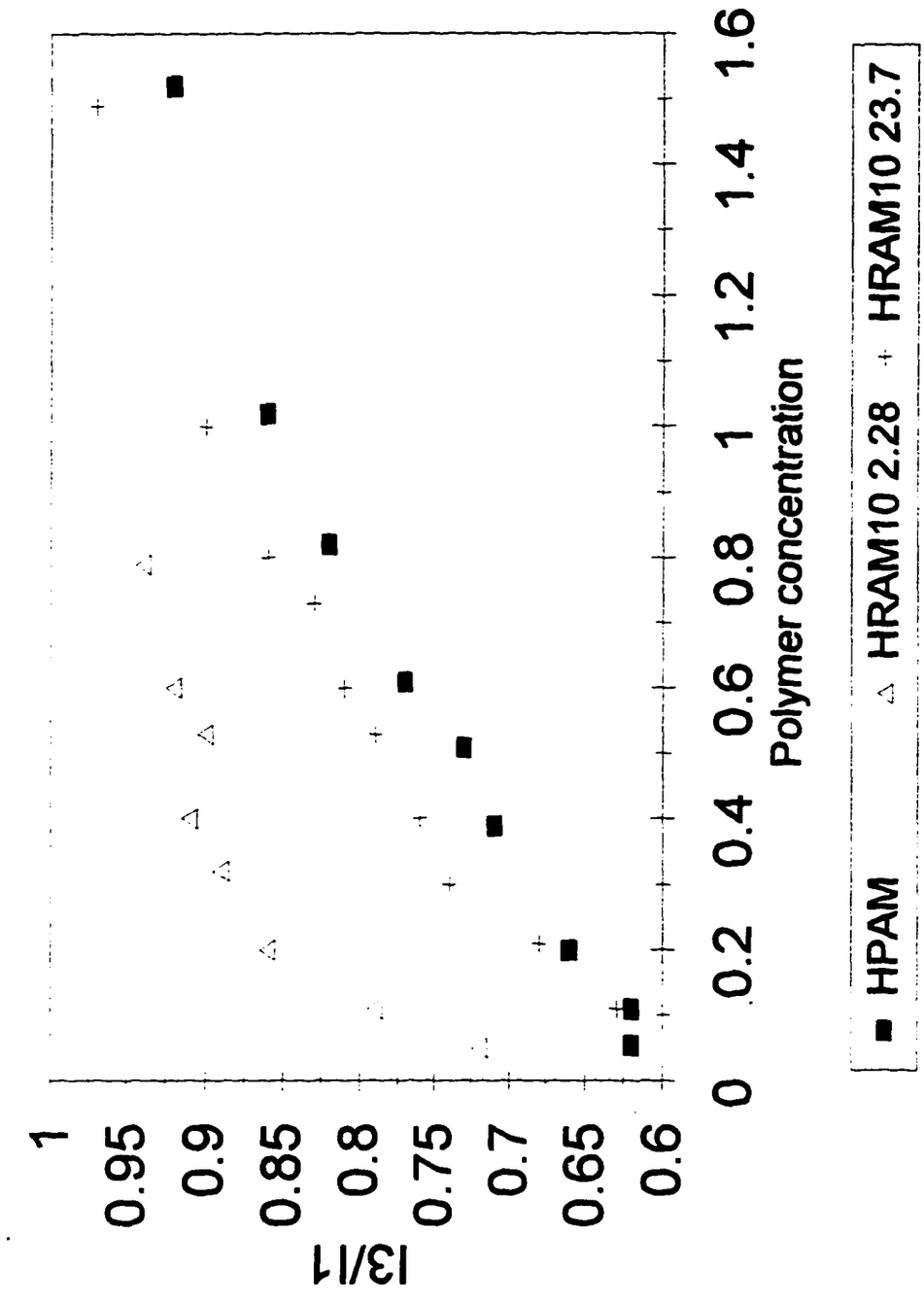


Figure 5.15 Hydrolysis level effect on hydrophobicity for HRAM10/1.5 aqueous systems

CHAPTER 6. SUMMARY, CONCLUSIONS AND FUTURE WORK

6.1 Summary and Conclusions

In summary, I have synthesized several polymers for the first time. The RAM10/1.5 and HRAM10/1.5 are the highest hydrophobe levels RAMs and HRAMs reported to date. They were synthesized via micellar copolymerization with a conversion of 100% of both the hydrophobic and hydrophilic monomers. The HRAM-AAs, synthesized by the graft reaction, are the first reported hydrophobically modified partially hydrolyzed terpolymers produced by grafting. They differ from those reported elsewhere [21] in the different polymer backbones. They were produced with 1.3-7 mol% incorporation of feed hydrophobe. I also report here the first successful use of NMR to characterize the molecular composition of HMWSPs with linear alkyl side chains at incorporation level less than 1 mol %. I attribute this success to two factors. First, I was able to obtain sharp peaks in my spectra by using a binary D_2O/deuterated methanol solvent, which gives a low viscosity solution characterized by the narrow peaks. Second, I used a higher power NMR than those used by other workers, giving better spectral resolution.

I also report for the first time the fabrication of novel dispersed-phase hydrogels made from hydrophobically modified polyacrylamides. Both the dynamic storage modulus of the gels and the hydrophobicity of the microdomains increase with the side chain length. In addition, these gel properties both exhibit maxima with NaA level on the polymer, reflecting

the importance of backbone charge on the number and packing density, respectively, of the microdomains. The maxima in these two functions occur at relatively low values of NaA level.

I also studied the effects of salt and sodium dodecyl sulfate (SDS) on hydrogel properties made from different HRAMs. The dynamic storage modulus of 0.5 g/dl hydrogels made from C_8 substituted HRAMs with NaA level $\leq$ 3.58 is not sensitive to the presence of salt at a level of 10 mM. However, the dynamic storage modulus of 0.5 g/dl gels made from higher NaA level HRAMs is higher in 10 mM NaCl than in water. This was attributed to the screening of intermolecular electrostatic repulsion by salt, which permits close approach of the backbones and the formation of intermolecular hydrohpobic aggregates. In contrast, the dynamic storage modulus of C_{10} substituted HRAMs in NaCl solutions is limited by the relatively low solubility of the side chains in these systems, which inhibits complete solubilization of the polymer molecules. All of the HRAMs exhibited a maximum in the dynamic storage modulus with surfactant concentration. This is analogous to the behavior of viscous surfactant solutions of hydrophobically modified water soluble polymers.

In conclusion, the bulk and microstructural properties of dispersed-phase hydrogels made from HRAMs depend on both the side chain length and the backbone charge on the polymer. I have identified several important structure/property relationships for these systems. This work is the first systematic study of the effects of backbone charge and side chain length on the properties of these novel hydrogels.

6.2 Recommendations for future work

Since it is desirable to know the MW and Rg of these polymers quantitatively, it is important to refine the light scattering experiment accurately so we can determine the values of these important parameters. I recommend using different solvents, such as, a mixture of NMP and formamide, to disrupt the hydrophobic aggregates.

The NaA levels investigated in this study spanned a wide range with wide gaps. HRAMs with NaA levels 7, 12 and 17 mol % should be synthesized by micellar copolymerization to obtain a more finely tuned picture of the polymer backbone response in aqueous HRAM gels.

Small angle neutron scattering is a technique which allows us to probe the size, shape. and number density of microscopic structures within a gel. This method could be used with our hydrogels to investigate the properties of the microdomains direclty. This information is important in the design of gels for applications such as controlled release, where the solubility of solutes in the domains and the interfacial mass transfer resistance will determine the efficacy of the gel. This technique requires the use of deuterated polymr. I have found a synthetic route to alkylamine from alkyl bromide, which may be used in future research in this area.

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