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Responsive Copolymers for Enhanced
Petroleum Recovery

Final Report

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CHAPTER ONE: BACKGROUND, OBJECTIVES, AND OVERVIEW OF RESEARCH DURING FY 1995

I. Introduction

During the period FY 1993- FY 1995 a research program involving synthesis, characterization, and rheology has been conducted to develop *advanced polymer systems* which are more efficient than conventional macromolecules in enhanced oil recovery. In this third and final report on the DOE-sponsored project "Responsive Copolymers for EOR" we describe new synthetic polymers, their solution behavior, and rheological properties as well as new techniques for measuring extensional flow behavior under controlled conditions in packed bed geometries. Details of work in FY 1993 and FY 1994 are found in published annual reports DOE/BC/14882-5, August 1994 (184p) and DOE/BC/14882-10, May 1995 (190p).

Key features of the microstructurally tailored systems allow triggered response to environmental stimuli including pH, ionic strength, shear, and temperature. Ampholytic and hydrophobic interactions between polymer chains have been utilized for desired rheological response.

Since 1978, DOE-sponsored research projects in our laboratories have been directed toward establishing fundamental, unifying interrelationships among polymer microstructure, solution behavior, and flow through porous media under controlled conditions of pH, ionic strength, temperature, and polymer concentration. We have clearly demonstrated that polymer architecture and hydrodynamic volume influence the most important factors in mobility control including:

- critical polymer concentration
- viscosity in the presence of electrolytes
- phase stability as a function of ionic strength and temperature
- adsorption to porous media
- sweep efficiency and slug dispersion
- network pore clogging
- rheological behavior
- inter- and intra-molecular associations
- polymer/surfactant interactions

II. Research Goals

The *overall goal* of this research is to tailor advanced copolymers for use as mobility control agents in EOR that rely on *microheterogeneous associations* or *ampholytic associations* to produce shear-thinning, high viscosity, aqueous solutions. Desirable qualities include: (1) efficient viscosity enhancement at low concentration and moderate molecular weight, (2) maintenance or gain in viscosity in the presence of electrolytes, (3) increase or maintenance of viscosity at elevated temperatures, and (4) sufficient flow through relatively tight porous media for efficient sweep.

A second major goal is to investigate the feasibility of utilizing a *hydrophobically-modified polymer/surfactant* combination to both emulsify oil and serve as a viscosifying agent in mobility control.

Specific research objectives are:

- Synthesis of advanced copolymers which rely on hydrophobic or ampholytic associations at low concentration for rheological control. Such associations are responsive to changes in pH and ionic strength.
- Synthesis and characterization of hydrophobically modified copolymers which can serve as both surfactant and viscosifier in EOR.
- Determination of hydrodynamic volume utilizing viscometry, low angle laser light scattering (LALLS), dynamic light scattering (DLS), and size exclusion chromatography (SEC) techniques.
- Development of predictive models based on interrelationships of molecular structure and solution behavior under operational conditions of temperature, shearing stress, concentration, and ionic strength.
- Education and training of young scientists in innovative energy recovery research.
- Technology transfer to the private sector for scale-up and field testing.

III. Responsive Copolymer Structures, Characterization, and Behavior in Aqueous Media

A. Molecular Architecture

The copolymers and terpolymers synthesized in this research contract were prepared from the monomers shown in Scheme III-1. Acronyms are shown below

each structure and are combined to designate appropriate compositions of copolymers and terpolymers prepared from these precursors.

Scheme III-1. Representative Monomers for Synthetically tailored EOR Polymers.

Synthesis, characterization, and solution behavior of co- and terpolymers of AM/NaAMB, AM/NaAMB/RAM, AM/NaAMB/AMPDAC, AM/AMPDAPS, and AM/APS are described in our First Annual Report, DOE/BC/14882-5 (August 1994). Systems based on AM/NaAMB/AMPDAC, AM/AMPDAPS, MA/NVF, NVF/AM, NVF/NA, NVF/BA, DAMAB/AM, are described in detail in the Second Annual Report, DOE/BC/14882-10 (May 1995). Also detailed in the latter report are novel methods via C-13 NMR for structural determination of viscous samples and for the use of factorial design in static and light scattering characterization of high molecular weight water-soluble polymers.

In this Third Annual and Final Report we discuss the remaining copolymer systems based on AA/AM/RAM, AM/APS, and AA/AM/AMPDAPS in chapters 2-4. Chapters 5-6 detail binding studies of calcium, magnesium, sodium, and potassium counterions to AM/AA, AM/NaA, AM/NaAMB, AM/NaAMPS utilizing Na-23 NMR methods. Chapter 7 and 8 discuss development of extensional flow models and experimental data on selected copolymers.

B. Amphiphilic Terpolymers of AM/AA/RAM

Associative terpolymers of acrylamide (AM), acrylic acid (AA), and N-[4-decyl)phenyl]acrylamide (RAM) synthesized by a micellar technique are discussed in Chapter 2. The ratio of surfactant, sodium dodecyl sulfate (SDS), to RAM in the polymerization was found to drastically alter viscosity. Those polymers prepared at low SDS/monomer ratios showed associative thickening behavior with the lowest critical overlap concentration of 0.13 g/dl. These polymers are believed to have microblocky structures which are responsible for long range intermolecular interactions at concentrations above critical overlap.

C. Polyelectrolyte Copolymers Labeled with APS

Chapter 3 describes investigation of the Micellar polymerization mechanism for preparation of associative copolymers utilizing the fluorescent, hydrophobic monomer N-[1-pyrenylsulfonamido)ethyl]-acrylamide (APS) and comonomers acrylamide (AM) and acrylic acid (AA). The fluorescence intensity ratios of excimer-to-monomer were found to scale with the number of APS monomers per micelle. Previously, we reported (Chapter 5 and 6 on the First Annual Report, DOE BC/14882-5) that blocky microstructures were responsible for associative properties. We now can combine the results from Chapter 2 and from Chapter 3 to conclude that not only can we prepare polymers with associative properties, but that we can also control the viscosity by introducing pH- or salt-responsive functionality-in this case acrylic acid. These terpolymers have potential utility as viscosifiers, channel blocking agents, fracturing fluids, and for altering mobility and conformance. Of particular interest is the reversible rheological behavior *in situ*.

D. Terpolymers of AA/AM/AMPDAPS

Chapter 4 reports synthesis of a novel sulfobetaine monomer, 3-[2-acrylamido-2-methylpropyl]dimethylamonio]-1-propanesulfonate (AMPDAPS), and terpolymers with acrylic acid (AA) and acrylamide (AM). The relative molar concentrations of the monomers were varied over a wide range and the properties of the resulting terpolymers studied in aqueous solutions at varying ionic strength and pH values. By controlling the AMDAPS content and the pH, viscosity at high salt concentration can be easily controlled. Again, these polymers are good candidates for *insitu* rheology control.

E. Study of the Effects of Added Monovalent and Divalent Salts on Ion-binding Behavior

In previous work in our laboratories, we have shown that copolymers of acrylamide (AM) with sodium 3-acrylamido-3-methylbutanoate (NaAMB) are exceptionally suited for mobility control in EOR due to high salt and temperature stability. For example unlike partially hydrolyzed acrylamides, this copolymer does not phase separate up to 130°C in saturated calcium chloride solutions. Reasonable viscosity is attainable even at high ionic strength. In Chapter 5 we report studies of competitive ion binding of Ca^{++} and Mg^{++} for these copolymers and for AA/AM copolymers. Significant differences in the Na-23 NMR relaxation times with added divalent cation for these systems have been attributed to differential ion-binding and polymer solvation. We believe conformational differences may be related to extensional viscosity behavior observed (Chapters 7 & 8) for these systems.

F. The Effects of Hydrophobic Modification of AA Copolymers on Ionization

In Chapter 6, we have studied the effects of ionization of hydrophobically modified polyacrylic acid on viscosity and conformation as studied by Na-23 NMR. Longitudinal and transverse relaxation rates were determined for copolymers of AA with varying degrees of hydrophobic comonomer incorporation. Sharp transitions as a function of extent of ionization were observed which conformational changes, likely long range ones in aqueous media. These data are consistent with previous photophysical data on the same systems and with results discussed in Chapter 5.

G. Extensional Rheology of Dilute Polymer Solutions

In Chapter 7 a model of dilute polymer solution extensional flow behavior is developed using an energy balance technique. Single high molecular weight molecules were considered as deformable coils that undergo both extension and recovery when placed in porous media containing converging and diverging fluid flow fields. Polymer coil deformation transforms fluid kinetic energy into heat and is the mechanism by which the mobility of polymer solutions is reduced when

flowing through oil reservoirs. The model mathematically defines a polymer coil as a dashpot and spring connected in parallel. In Chapter 8 laboratory data from several polymer solution flow through controlled porous media studies was fit to the model to determine each polymer coil dashpot viscosity and spring modulus. These parameters were then compared with polymer structure to establish which polymer types have the lowest mobility and thus are the better candidates for polymer flooding. The AM/AMBA 80/20 copolymers were superior to acrylamide homopolymer or hydrolyzed acrylamide.

RELATED DISSERTATIONS - Ph.D Theses which were supported by the EOR program of the Department of Energy in our Polymer Science Laboratories are listed below.

"Synthesis and Characterization of Hydrophobically Modified Polyelectrolytes Exhibiting pH and Electrolyte Responsive Intermolecular Associations," Kelly Branham, 1995.

"Synthesis, Characterization, and Controlled Release Behavior of Acrylic Acid Copolymers with Pendently Attached Allelopathic Compounds," Chase Boudreaux, 1995.

"Rheological and Photophysical Studies of Environmentally Responsive Associations in Aqueous Solutions of Water-Soluble Polyelectrolytes," Michael C. Kramer, 1995.

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"Effects of Polymer Parameters on Drag Reduction," Abbas M. Safieddine, 1990.

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"Synthesis, Characterization, and Rheological Studies of Model Graft Copolymers of Dextran," L. S. Park - May 1982.

"Synthesis, Characterization, and Dilute Solution Studies of Random Copolymers of Acrylamide," G. S. Chen - August 1982.

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1995

"Fluorescence Studies of Pyrene-Labeled, Water-Soluble Polymeric Surfactants," Michael C. Kramer, Jamie R. Steger, and Charles L. McCormick, *American Chemical Society Symposium Series*, January 1995.

"Photophysical and Rheological Studies of Amphiphilic Polyelectrolytes: Correlation of Polymer Microstructure with Associative-Thickening Behavior," Kelly D. Branham and Charles L. McCormick, *American Chemical Society Symposium Series*, January 1995.

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CHAPTER TWO. ASSOCIATIVE AMPHIPHILIC TERPOLYMERS OF ACRYLAMIDE, ACRYLIC ACID AND N-[(4-DECYL)PHENYL] ACRYLAMIDE

Abstract

Water-soluble terpolymers of acrylamide, acrylic acid, and N-[(4-decyl)phenyl]acrylamide have been synthesized by a micellar polymerization technique. Neutralization of the acid groups after polymerization yields hydrophobically-modified polyelectrolytes. The ratio of the surfactant to the hydrophobic comonomer (SMR) was varied in successive polymerizations to yield a series of terpolymers with varied amphiphilic microstructures. Although each terpolymer in the series was identical in overall composition and molecular dimensions, profound differences in associative behavior were observed. Terpolymers synthesized at low SMR exhibit large enhancements in viscosity due to hydrophobic associations in 0.5M NaCl. Those synthesized at high SMR behave in a similar fashion to a control acrylamide/acrylic acid copolymer. While viscometric studies indicate associative thickening behavior, pyrene probe fluorescence studies fail to indicate the presence of well organized hydrophobic microdomains.

Introduction

Hydrophobically modified water-soluble polymers are of increasing interest as aqueous thickening agents in areas such as enhanced oil recovery, formulation of water based coatings and in personal care¹⁻⁴. Such amphiphilic systems may be tailored to yield associative thickeners which rely on intermolecular hydrophobic associations above a critical overlap concentration (C^*). In aqueous solution C^* often appears well below the critical entanglement concentration of the unmodified or parent polymer of equivalent molecular weight. One particularly useful synthetic method for preparing co- and terpolymers which possess these properties is the micellar polymerization method of Turner *et. al.*⁵. Copolymers of acrylamide (Am) and hydrophobic acrylamido or acrylate monomers prepared by this method have been the subject of study in our laboratories⁶⁻⁹ as well as in others¹⁰⁻¹⁴. Furthermore, study of the micellar polymerization process has become increasingly important due to the unique microstructure which results^{7-9,14-16,24}.

Elucidation of the mechanism of micellar polymerization has proven difficult for a number of reasons. A major limitation of earlier studies with n-alkylacrylamides as the hydrophobic comonomer^{5,6,17} was the difficulty in accurately determining the number of hydrophobic groups incorporated into the polymer. Insufficient concentration of hydrophobic monomer was present for analysis by traditional methods such as NMR or elemental analysis. Incorporation of a hydrophobic comonomer, which contains a chromophore, allows detection by ultraviolet spectroscopy^{11,12,14,18}. However, microstructural placement of the hydrophobic units is not easily ascertained from these systems.

For a number of years academic and industrial researchers postulated the existence of "microblocky" segmental structure; however, only recently has strong evidence been gained with fluorescent labels linking viscosity enhancement with microstructure. In our laboratories, for example, we have utilized fluorescent monomers which serve as the sole hydrophobic entity to prepare associative copolymers. Copolymers of acrylamide and a pyrene-sulfonamide containing comonomer (APS) prepared by the micellar polymerization method have a "blocky" microstructure relative to a random distribution in polymers synthesized by solution polymerization^{7,8}. High values of excimer to monomer intensity, I_E/I_M , in the former indicate a higher local chromophore concentration and, therefore, a more "blocky" microstructure. Also, rheological studies indicate that such arrangement is responsible for viscosity enhancement (intermolecular associations above C^*)⁷.

In a similar system with a hydrophobic monomer bearing a naphthalene chromophore, the surfactant-to-hydrophobic monomer molar ratio (SMR) was varied⁹. I_E/I_M for the naphthyl groups decreased with increasing SMR, indicating that sequence of the hydrophobic mers could be controlled by adjusting the initial number of hydrophobic monomers per micelle. While the naphthyl groups did not impart sufficient hydrophobicity to the copolymers for marked associative behavior, an increase in bulk solution viscosity was noted for copolymers synthesized at lower SMR values.

Although the nonionic copolymer systems described above provide useful properties, they possess distinct disadvantages. Dissolution from the dry state is difficult, often requiring weeks for rehydration. This practical limitation has resulted in a refocusing on hydrophobically-modified polyelectrolytes^{17,18}. These terpolymers consist of Am and various amounts of one of several anionic comonomers and small amounts of N-n-decylacrylamide¹⁷ or the N-aryl substituted acrylamide, N-(4-butyl)phenylacrylamide¹⁸. These low-to-moderate charge density polyelectrolytes offer increased solubilities over nonionic thickening agents and provide pH or electrolyte-responsive properties. However, due to electronic interferences between the anionic groups and the negatively charged SDS micelles during polymerization, much lower levels of hydrophobe incorporation are achieved¹⁸. For significant control of rheological properties, it is necessary to further elucidate the mechanism of the micellar polymerization process.

In this paper we report the synthesis and solution properties of terpolymers of Am, acrylic acid (AA), and N-[(4-decyl)-phenyl]acrylamide (DPAm) polymerized in the presence of specified concentrations of sodium dodecylsulfate (SDS). The structures of these monomers are shown in Figure 2-1. This work complements the studies using fluorescent-labelled hydrophobic monomers in which we originally identified the surfactant-to-hydrophobe molar ratio as the defining parameter for the control microstructural architecture of hydrophobically-modified water soluble co- and terpolymers⁹. The purpose of this study is twofold. First we wish to extend

the concepts of the micellar polymerization to more complex systems, including those which utilize ionizable monomers. Second, we wish to explore the electrolyte-responsive nature of these hydrophobically-modified polyelectrolytes by tailoring of the microstructure through manipulating the SMR during polymerization. In this study we present further evidence that the "initial polymerization conditions" dictated by the SMR have profound effects on the associative behavior of the resulting microblocky terpolymers.

Experimental

Instrumentation and Analysis

Elemental analysis was performed by M-H-W Laboratories, Phoenix Az.. HPLC was performed with a Hewlett-Packard Model 1050 equipped with a photodiode-array detector. A Waters C18 column was employed with methanol as the mobile phase. UV spectra were obtained with a Hewlett-Packard Model 8452A Photodiode-Array Spectrophotometer. IR spectra were obtained with a Mattson Model 2020 FT-IR spectrophotometer. ^{13}C NMR spectra were obtained with a Bruker AC 200 spectrometer. Steady-state pyrene fluorescence studies were performed with a Spex Fluorolog 2 Fluorescence Spectrophotometer equipped with a DM3000F data system ($\lambda_{\text{EX}} = 335\text{nm}$, $I_1 = 372\text{nm}$, $I_3 = 384\text{nm}$). Viscosity measurements were conducted on a Contraves LS-30 low shear rheometer at 25 °C and a shear rate of 6s^{-1} unless otherwise noted. An upper limit of 250 centipoise may be obtained on the Contraves LS-30 at this shear rate. This value was arbitrarily assigned to samples which exceeded this upper limit for means of comparison. Surface tension measurements were performed with a Kruss K12 Processor Tensiometer using the Wilhemy Plate method. Refractive index increments (dn/dc) were obtained with a KMX-16 Laser Differential Refractometer. Light scattering studies were conducted with a Spectra-Physics 127 laser operating at 632.8 nm. Data points for classical scattering were taken at multiple angles with a Brookhaven Instruments model BI-200SM automatic goniometer interfaced with a personal computer and Zimm plots were constructed using the software provided by the manufacturer. Dynamic light scattering studies were performed at 90° and the signals were processed with a Brookhaven BI-2030AT autocorrelator. Effective hydrodynamic diameters were calculated using the algorithm CONTIN and associated software provided by the manufacturer. Multiple analyses were performed to insure reproducibility.

Materials

Acrylamide (Am)(electrophoresis grade), 4-decylaniline (DA), triethylamine (TEA), succinic anhydride (SA), and sodium dodecyl sulfate (SDS) were purchased from Aldrich and used as received. Acrylic acid (AA) and acryloyl chloride (AC)

were purchased from Aldrich and distilled under vacuum prior to use. Potassium persulfate was purchased from Aldrich and recrystallized from water. Pyrene was purchased from Aldrich and recrystallized three times from ethanol. HPLC indicated a purity of >99.9%.

Monomer Synthesis. The synthesis of 3, N-[(4-decyl)phenyl]acrylamide (DPAm) was accomplished by a procedure adapted from previous methods¹⁸. DA (0.021 mole) and TEA (0.027 mole) were dissolved in 100mL diethyl ether and cooled to 2 °C in an ice/water bath. AC (0.027 mole) was placed in an addition funnel and added drop-wise with stirring over a period of approximately 40 minutes. A precipitate (TEA·HCl) formed as the AC was added. The reaction mixture was allowed to stir in the ice bath for 45 minutes after addition of AC was complete, then allowed to warm to room temperature, with stirring, overnight. The precipitate was collected by filtration, washed with 100mL ether and discarded. The filtrate was extracted three times with 10%HCl, once with 10%NaHCO₃ and the ether layer was dried over MgSO₄. The ether layer was filtered and the solution volume was reduced by evaporation at reduced pressure to 70-80mL. This solution was then placed at -25 °C for approximately four hours. White to off-white crystals were isolated by vacuum filtration and dried overnight under vacuum at room temperature (2.4g, 40% yield). HPLC analysis indicated this material to be 99.7% pure. Analysis- EA calc. for C₁₉H₂₉NO (MW 287.44): %C, 79.39; %H, 10.17; %N, 4.89; %O, 5.57. Found: %C, 79.26; %H, 10.07; %N, 4.89; %O (not anal.), 5.78. M.P. 97-98 °C. IR (KBr pellet): N-H 3285, vinyl and aromatic C-H 3133 and 3082, aliphatic CH₃ and CH₂ 2920 and 2949, carbonyl 1665. ¹³C NMR (d₆DMSO): aliphatic CH₃, 13.8; aliphatic CH₂, 22.1-34.6 (8 peaks resolved); vinyl carbons, 126.1 and 132.0; aromatic carbons, 119.3, 128.3, 136.7, 137.3; carbonyl, 162.8.

Model Compound Synthesis. The synthesis of N-[(4-decyl)phenylamido] propionic acid (DPAPA, not depicted) and its water soluble potassium salt were synthesized as previously described¹⁸. Succinic Anhydride (SA) (0.01 mole) was slurried in 100mL diethyl ether. Decylaniline (DA) (0.01 mole) was dissolved in 20mL diethyl ether and placed in an addition funnel and added drop-wise at room temperature over a period of approximately 15 minutes. As the DA solution was added, the SA dissolved, followed by formation of a white precipitate. White crystals were isolated by vacuum filtration. The filtrate was chilled in an ice bath and more crystals were isolated. The product was dried under vacuum at room temperature (2.2g, 70% yield). HPLC analysis show that this material was approximately 99.5% pure. Analysis- EA Calc. for C₂₀H₃₀NO₂·H₂O (MW 334.46): %C, 71.81; %H, 9.04; %N 4.19; %O, 14.96. Found: %C, 71.58; %H, 9.05; %N, 4.15; %O (not anal.), 14.96. M.P.: 153-154 °C. IR (KBr pellet): 3320, 3185, 3115, 3044, 2922, 2850, 1697, 1661, 1597, 1531, 1412, 1325, 1188. ¹³C NMR (d₆ DMSO): aliphatic CH₃, 13.9, aliphatic CH₂, 22.1-34.6 (8 peaks resolved), aromatic carbons 118.9, 128.3, 136.8, 137.0, carbonyls 169.7 (amide) and 173.8 (acid).

The potassium salt of DPAPA was made by dissolving approximately 4 × 10⁻⁵ mole in 100mL deionized water containing an equivalent amount of KOH.

Dilutions of this stock solution were made with deionized water and the molar absorptivity, ϵ , was determined to be $10,666 \text{ M}^{-1}\text{cm}^{-1}$ at 250nm.

Polymer Synthesis and Purification. Polymer synthesis was accomplished using the micellar polymerization method of Turner *et. al.*⁵ Total monomer concentration was 0.44 M, with the following feed ratios: Am, 0.695; AA, 0.30; DPAm, 0.005. Sodium dodecylsulfate (SDS) was used as the surfactant to solubilize the hydrophobic comonomer and potassium persulfate was used as a free radical initiator. The surfactant/hydrophobic monomer molar ratio or SMR, was varied from 40 to 100 and $[\text{K}_2\text{S}_2\text{O}_8]/[\text{monomer}]$ was kept constant at 1/3000. The method previously published from our laboratories^{17,18} was followed except as noted. The acrylic acid monomer was reacted in its acidic form and neutralized after polymerization. Polymerization was conducted at pH 4-5 for 3 to 3.5 hours at 50 °C. Polymers were isolated by precipitation into acetone, followed by drying, and redissolution into water. After one week of dissolution, the pH was adjusted to between 7-8 and the polymers were dialyzed against deionized water in SpectraPor No.4 dialysis tubing (MW cut-off 10-14K) for at least one week. The samples were then lyophilized to a constant weight.

Sample Preparation

Samples for viscosity measurements were made by preparing stock solutions of 0.20g/dL of polymer in deionized H_2O and adjusting the pH to approximately 7.5-7.7 using microliter amounts of NaOH and HCl solutions. The solutions were shaken on an orbital shaker for at least one week before dilutions were made. For samples containing added salt, the dry NaCl was added to the polymer solutions. Samples were equilibrated a minimum of 24 hours.

Samples for pyrene probe experiments were prepared by adding microliter amounts (typically 1-2 microliters) of a stock solution (pyrene in methanol) necessary to give a final pyrene concentration of 10^{-6} M to polymer solutions of the desired concentration and ionic strength. These solutions were allowed to equilibrate for a minimum of 24 hours.

Samples for dn/dc and light scattering measurements were prepared by dissolving the appropriate amount of polymer in the desired solvent. After a minimum of one week, the pH of the solution was adjusted to between 7.1 - 7.5 using microliter amounts of NaOH and HCl solutions. Solutions were filtered through 0.2 or 0.45 micron Millipore filters.

Results and Discussion

Terpolymer Synthesis and Composition

The amphiphilic polyelectrolytes of this study were prepared from 1, acrylamide (Am), 2, acrylic acid (AA), and 3, N-[(4-decyl)phenyl]acrylamide (DPAm) (Figure 2-1). The Am monomer has a high k_p^2/k_t and is the hydrophilic component along with the pH and electrolyte responsive AA units. DPAm was synthesized by the procedure similar to that reported previously for N-[(4-

butyl)phenyl]acrylamide¹⁸. This monomer has both the hydrophobic character and chromophore desired. The DPAm model compound N-[(4-decyl)phenylamido]propionic acid (DPAPA, not depicted) was synthesized by a procedure similar to that previously reported for N-[(4-butyl)phenylamido]propionic acid¹⁸. The molar absorptivity, ϵ , of this model compound in water was determined to be $10,666 \text{ M}^{-1}\text{cm}^{-1}$ at 250nm. Polymerizations were carried out under micellar reaction conditions in SDS/H₂O utilizing potassium persulfate as the initiator. A control copolymer of Am/AA, 4, was synthesized in the presence of surfactant. The feed compositions are shown in Table 2-1. Identical feed ratios were used for the terpolymers 5 - 8 and the terpolymer microstructure was varied by changing the surfactant concentration as discussed below. Compositions of the terpolymers 5 - 8 and copolymer, 4, (Table 2-1) in this study were determined by a combination of elemental analysis (EA) and UV spectroscopy by the previously published methods¹⁸. The amount of acrylic acid in the polymers is slightly greater than the feed composition, consistent with reactivity ratio predictions²¹. Polymerization at low pH eliminates ionic interferences between the charges on the growing polymer radical and the negatively charged SDS micelles. In the case of the terpolymers, percent conversions were approximately the same (52-57%).

The statistical distribution of hydrophobic groups in micellar systems can be accurately described using the Poisson distribution²⁰, provided that the critical micelle concentration, CMC, and aggregation number, N , of the surfactant is known. In our systems, the CMC of SDS (at 50 °C) was determined to be $6.5 \times 10^{-3} \text{ M}$ in deionized water containing 0.306M Am and 0.132M AA. These conditions closely approximate the polymerization conditions in this study. An aggregation number of 60 was assumed for SDS in this study.

From the above values, the number of DPAm molecules per micelle can be calculated using the equation:

$$n = \frac{N [\text{DPAM}]}{[\text{SDS}] - \text{CMC}} \quad (1)$$

Table 2-2 shows the surfactant concentrations and the calculated average number of DPAm molecules per micelle for the terpolymers 5 - 8 in this series. Surfactant to monomer ratios of 40, 60, 80 and 100 were used in the polymerizations. A molar ratio of SDS to DPAm approximately 60/1 corresponds to a 1:1 hydrophobe-to-micelle ratio or a statistical distribution of one hydrophobic monomer per micelle; at lower SMR there would be more than one hydrophobic monomer per micelle on the average. The surfactant to hydrophobe ratios in this study are well below the ones used by Peer¹⁵ and in the low range of the values indicated by Biggs, et. al.¹⁴

Light Scattering Studies

Attempts were made at determination of molecular weight in several solvents. Candau and coworkers¹⁴ indicated that formamide was a suitable solvent for hydrophobically-modified polyacrylamides. However, we were unable to obtain accurate differential refractive index (dn/dc) values for the hydrophobically-modified polyelectrolytes in our study, likely complicated by osmotic effects in the low ionic strength medium. Also light scattering experiments were attempted in 0.5M NaCl and 50/50 (v/v) water/methanol solutions; however, retention of the terpolymers by the filter membranes proved to be problematic. Addition of 1.0% SDS, however, lowered the solution viscosities and sufficiently stabilized the terpolymers for dynamic scattering studies.

In an attempt to establish the baseline molecular weight and scale of molecular size for this polymer series, classical light scattering studies were performed on the unmodified copolymer 4 in 0.5M NaCl ($dn/dc = 0.2296$); dynamic light scattering studies were conducted on the copolymer and the terpolymers 5 - 8 in 1.0% SDS.

Classical light scattering indicates a weight-average molecular weight (M_w) of 7.2×10^5 g/mole, a second virial coefficient (A_2) of 7.0×10^{-3} cm³ mole/g² and an estimated radius of gyration (R_G) of 68 nm for the unmodified copolymer in 0.5M NaCl. Dynamic light scattering data for the polymers in 1.0% SDS are presented in Table 2-3. Average hydrodynamic diameters range from approximately 200 to 250 nm with a standard error of ± 31 nm. Diameter distributions are broad; the unmodified copolymer 4 and terpolymer 7 (SMR 80) exhibit bimodal (but continuous) distributions. These data indicate that the molecular dimensions of the co- and terpolymers are quite similar in solution. The source of the bimodal distributions is currently under investigation.

Viscometric Studies

As noted in the preceding sections, the compositions of the terpolymers in this study are virtually identical and the molecular dimensions in solution are similar. Therefore differences in terpolymer aggregation may be attributed to variation of polymer microstructure based on the SMR during the respective polymerizations⁷⁻⁹.

Viscometric studies were first carried out in deionized water at specified terpolymer concentrations. Plots of apparent and reduced viscosities as a function of polymer concentration (Figures 2-2 and 2-3) indicate that the terpolymers, as well as the unmodified Am/AA copolymer, behave as typical polyelectrolytes in deionized water. Figure 2-2 indicates that the apparent viscosity increases in a linear fashion; curvature generally associated with intermolecular hydrophobic associations is not evident. The polymers exhibit high viscosities in deionized water due to the large hydrodynamic volume typical of polyelectrolytes. Plots of reduced viscosity vs. polymer concentration (Figure 2-2) illustrates that hydrophobic

modification does not inhibit the classical polyelectrolyte behavior; expanded hydrodynamic size results upon dilution.

The same general trends for each terpolymer in this study are observed in both Figures 2-2 and 2-3. Terpolymer 7 (SMR 80) has the highest hydrodynamic volume in water, followed by 5 (SMR 40). Terpolymers 6 (SMR 60) and 8 (SMR 100) have hydrodynamic volumes approximately equal to the unmodified copolymer 4. Also, as indicated by dynamic light scattering, similar hydrodynamic diameters for the control copolymer and the terpolymers in 1.0% SDS are found.

Addition of NaCl to hydrophobically-modified polyelectrolytes would be expected to result in: 1) the loss of hydrodynamic volume of the individual polymer coils by shielding of intra-coil ionic repulsions, and 2) the enhancement of hydrophobic associations. Figure 2-4 shows plots of apparent viscosity vs. polymer concentration in 0.5 M NaCl. At low polymer concentration, all the polymers exhibit very low viscosities and thus hydrodynamic volumes, indicative of collapse of the individual polymer coils. Under these conditions, the terpolymers behave identically to the unmodified polymer at low concentration. At sufficient polymer concentration, three of the four terpolymers exhibit sharp increases in apparent viscosity due to hydrophobic associations of individual polymer coils. At this ionic strength, a correlation between SMR of the polymerization and the associative properties of the resulting terpolymers is noted. Terpolymers 5 and 6 with SMR values of 40 and 60 appear to be the most strongly aggregated, with the latter having the lowest C^* (ca. 0.13g/dL). Terpolymer 5 and 7 (SMR 80) appear to have approximately the same C^* (ca. 0.16g/dL), but 5 appears to be more strongly aggregated. It is important to note that 5 and 6 have higher viscosities than 7 above C^* , even though the latter has the highest hydrodynamic volume in water below C^* . Terpolymer 8 (SMR 100) exhibits the lowest viscosity; rheological properties are similar to that of the unmodified copolymer 4.

The different viscometric responses of the terpolymers result from differences in apparent microstructures formed during polymerization⁷⁻⁹. Decreasing SMR results in an initially larger number of DPAm molecules per micelle. This should theoretically increase the length of the runs of hydrophobic mers in the resulting polymers. In this system where the number of hydrophobes per micelle initially present is approximately 2 or less, some hydrophobe migration or aggregate coalescence process would be necessary in order to obtain "blocks" of a sufficient length. Large differences in association are exhibited by the terpolymers in this series, indicating that hydrophobe migration might occur to build blocks of larger than predicted size. Also the differences in associative properties, and thus hydrophobe migration, appear to be augmented at lower SMR. These observations are in agreement with other studies which indicate that polymer heterogeneity is greatest at higher numbers of hydrophobes/micelle¹⁴.

To further study the response of the Am/AA/DPAm terpolymers 5 - 8 to changes in ionic strength, viscometric studies at selected NaCl concentrations were performed at a constant terpolymer concentration of 0.20 g/dL (above C^*). Figure 2-5 relates apparent viscosity to NaCl concentration. Several features are notable.

First, **5** and **6** do not exhibit large increases in viscosity below a NaCl concentration of approximately 0.2 M. Thereafter, the viscosity gains are significant. Terpolymer **7** exhibits a rapid increase in viscosity in the range of 0.01M to 0.1M NaCl. Viscosity remains high up to 0.3M NaCl, after which it drops significantly. The viscosity of **8** has very little dependence on NaCl concentration and remains relatively low over the entire range of NaCl concentration. Above C^* and a critical salt concentration, the terpolymers synthesized at low SMR exhibit the highest viscosities. These results are in agreement with the studies in 0.5 M NaCl. However, the unusual behavior of terpolymer **7** (SMR 80) as a function of ionic strength has yet to be explained.

The effects of shear on solution viscosity were also studied for terpolymers **5** and **6** in 0.5M NaCl and above C^* (0.16 g/dL). Plots of apparent viscosity versus shear rate appear in Figure 2-6. This study was conducted by first increasing the shear rate at three minute intervals and then decreasing the shear at the same rate following the 94.5 s⁻¹ measurement. Apparent viscosities for terpolymer **6** are higher due to stronger aggregation in 0.5M NaCl, but the same trends are noted for both terpolymers. Solution viscosities for both terpolymers are greater along the decreasing portion of the shear cycle, indicating that more intermolecular contacts are induced with the application of shear. The original viscosity was recovered on standing (approximately one day), and the curves were reproducible within experimental error. These data are in agreement with earlier findings for hydrophobically modified acrylamide copolymers⁶, implying that associations recover from shear very quickly and that increases in viscosity with the application of shear are due to participation of a greater number of hydrophobic groups in hydrophobic associations in solution.

Pyrene Fluorescence Studies

In an attempt to gain insight into the nature of aggregation, pyrene probe experiments were preformed. The ratio of the fluorescence intensity of the first band to that of the third band (I_1/I_3) has been related to the polarity of the local environment experienced by the pyrene probe. The third vibronic band in the fine structure of pyrene fluorescence is relatively insensitive to solvent polarity, while the first vibronic band shows a marked increase with increasing solvent polarity²². Typical values of I_1/I_3 are approximately 1.9 for water, 1.6-1.8 for polar organic solvents such as acetone or DMF, 1.2-1.3 for solvents such as THF and chloroform, and 0.6 for hydrocarbons such as hexane and cyclohexane. Values in common surfactant micelles are typically 1.1-1.2.

Plots of I_1/I_3 as a function of polymer concentration in 0.5M NaCl are shown in Figure 2-7 for the terpolymers **5** - **8** and the unmodified Am/AA copolymer **4**. Values (1.85-1.90) at low polymer concentration indicate that the probe is solvated in an aqueous environment. As polymer concentration is increased to 0.20g/dL, I_1/I_3 values for the unmodified copolymer **4** and the terpolymer **8** are quite similar, decreasing to approximately 1.73. The I_1/I_3 values for the remaining terpolymers

decrease with concentration to slightly lower values, the lowest value being for terpolymer 5 of 1.65. This value approaches that of pyrene in acetone. These data indicate some change in probe environment with increasing polymer concentration, but the absolute value of I_1/I_3 indicates a relatively polar environment. These results are in contrast to previous studies on non-ionic hydrophobically associating polymers^{13,23} in which values of 1.1-1.2 (similar to common surfactant micelles) were obtained. No dramatic changes in the curves are evident as the polymers approach C^* . Associations may be open and somewhat hydrated; this is consistent with fluorescence studies on labelled polyacrylamides which have been previously published⁸. Also, studies with other probes on partially hydrolyzed copolymers of acrylamide and a hydrophobic comonomer have indicated that the presence of ionic groups may lead to microdomains which are more polar than their nonionic counterparts²⁴. While it appears that some correlation between I_1/I_3 and SMR and thus the microstructure of the terpolymers may exist, the differences in values are slight. This observation leads us to conclude that pyrene probe fluorescence is not sufficiently sensitive to allow elucidation of the nature of associations present in these systems.

Conclusions

A series of Am/AA/DPAm terpolymers 5 - 8, as well as an unmodified Am/AA copolymer 4, have been synthesized varying the [SDS]/[DPAm] ratio, or SMR. These have similar compositions with the Am content being 60-65 mole%, the AA content being 35-40 mole%, and a DPAm content of approximately 0.4 to 0.5 mole%. Classical light scattering studies on the Am/AA copolymer 4 in 0.5M NaCl indicate a molecular weight of 720,000 and dynamic light scattering studies in 1.0% SDS indicate that the hydrodynamic diameters of the terpolymers are similar, ranging from 200 to 250 nm. The terpolymers show similar viscosity behavior to that of the unmodified polymer in the dilute concentration regime in 0.5M NaCl. Differences in the solution properties at higher concentrations are attributed to microstructural differences arising from variation of the surfactant concentration in the micellar polymerization process. The terpolymers synthesized at low SMR show the strongest associative behavior above C^* in 0.5M NaCl. Those synthesized at high SMR behave much like the unmodified polymer. Terpolymers 5 and 6 exhibit the best associative behavior. Terpolymer 7 has moderate associations, while 8 has viscometric behavior similar to that of the unmodified Am/AA copolymer 4. It is expected that at lower SMR, there are a larger number of DPAm molecules per micelle, resulting in a more "blocky" polymer microstructure. However, the lack of significant changes in probe solubilization lead us to conclude that pyrene probe fluorescence studies are not sufficiently sensitive to indicate differences in local polarity for the terpolymers above C^* . While this study neither provides direct evidence of microstructural placement nor an estimate of hydrophobe block length, it clearly demonstrates that manipulation of the synthetic parameters in micellar polymerization allows one to tailor the associative properties of hydrophobically-modified polyelectrolytes. Studies on polyelectrolytes prepared by micellar

polymerization containing fluorescent labels to more effectively probe the microstructure of hydrophobically-modified polyelectrolytes will be reported in a forthcoming paper.

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Table 2-1
Compositional Data for the Am/AA copolymer, 4, and Am/AA/DPAm
terpolymers, 5-8.

Sample	SMR*	FEED	MOLE%	MOLE%	MOLE%	%Conv.
		RATIO Am:AA				
4	Unmodified	70:30	60.4	39.6	0	25
5	40	69.5:30	62.2	37.4	0.4	53
6	60	69.5:30	63.6	35.9	0.5	53
7	80	69.5:30	64.9	34.7	0.4	57
8	100	69.5:30	64.8	35.9	0.5	52

* Surfactant to hydrophobic monomer (DPAm) ratio.

Table 2-2
DPAm molecules/micelle as a function of SMR and [SDS] for terpolymers 5-
8. [DPAm] = 0.0022, CMC = 6.5×10^{-3} and N = 60.

SAMPLE	SMR*	[SDS]	DPAm
			Molecules/Micelle
5	40	0.088	1.62
6	60	0.132	1.05
7	80	0.176	0.78
8	100	0.220	0.62

* Surfactant to hydrophobic monomer (DPAm) ratio.

Table 2-3
Dynamic Light Scattering for copolymer, 4 and terpolymers 5-8 in 1.0%
SDS.

SAMPLE	SMR*	D_0 (cm ² /sec x 10 ⁸)	d_H (nm)
4	Unmodified	1.89	256 [†]
5	40	2.38	203
6	60	1.94	249
7	80	1.88	257 [†]
8	100	2.26	214

* Surfactant to hydrophobic monomer (DPAm) ratio.

[†] Diameter distribution was bimodal.

Figure 2-1. Monomers used for micellar polymerizations: acrylamide (Am) **1**; acrylic acid (AA) **2**; N-[(4-decyl)phenyl]acrylamide (DPAM) **3**.

Figure 2-2. Apparent viscosities as a function of polymer concentration in deionized water at 25 °C and a shear rate of 6 s⁻¹.

Figure 2-3. Reduced viscosities as a function of polymer concentration in deionized water at 25 °C and a shear rate of 6 s⁻¹.

Figure 2-4. Apparent viscosities as a function of polymer concentration in 0.5M NaCl at 25 °C and a shear rate of 6 s^{-1} .

Figure 2-5. Apparent viscosities as a function of NaCl concentration at 25 °C and a shear rate of 6 s^{-1} .

Figure 2-6. Apparent viscosities as a function of shear rate in 0.5M NaCl at 25 °C and 0.16 g/dL polymer.

Figure 2-7. I_1/I_3 values as a function of polymer concentration in 0.5 M NaCl.

CHAPTER THREE. PYRENESULFONAMIDE-LABELED COPOLYMERS OF ACRYLIC ACID AND ACRYLAMIDE

Abstract

Synthesis of a series of pyrenesulfonamide-labeled polyelectrolytes with varied label proximities has been accomplished by a micellar polymerization technique. The solution properties of these terpolymers consisting of acrylamide (AM), acrylic acid (AA) and N-[(1-pyrenyl-sulfonamido)ethyl] acrylamide (APS) are examined using viscometry, light scattering and fluorescence spectroscopy. Classical light scattering indicates high molecular weights ($> 10^6$ g/mole) and very good polymer solvation even at high NaCl concentrations ($A_2 \sim 10^4$ cm³mole/g²). Viscometry and dynamic light scattering studies indicate no interpolymer aggregation of the hydrophobic APS labels. Also, no intermolecular associations are evident through measurement of I_E/I_M as a function of terpolymer concentration in 0.5M NaCl or at pH 3 and 7. Further photophysical results are interpreted on the basis of intramolecular excimer formation. Steady-state fluorescence emission studies indicate that I_E/I_M scales with the surfactant to APS ratio (SMR) in polymerizations. Also, I_E/I_M is a linear function of n , the initial number of APS monomer molecules per micelle. Steady-state excitation and time-resolved fluorescence emission studies have been utilized to probe the microenvironment surrounding the APS labels at varying polymer concentration, electrolyte concentration, and pH values.

Introduction

Copolymers exhibiting associative thickening behavior in aqueous media have become increasingly important in the formulation of pharmaceuticals, cosmetics, agricultural chemicals, and coatings.¹⁻³ Not only are the rheological properties desirable, but also the opportunity for phase transfer of hydrophobic ingredients into microheterogeneous domains is intriguing. The commercial development of such systems is currently hindered by a lack of fundamental understanding of the parameters which control domain organization.

Of special interest to our group have been 1) the elucidation of the mechanism of associative thickening and 2) the tailoring of thickeners with reversible associations responsive to changes in pH, ionic strength, temperature, or shear stress. An especially attractive polymerization technique, termed "micellar" polymerization, first reported independently by Evani⁴ and by Turner, et. al.,⁵ utilizes a surfactant to solubilize a relatively low mole percent of a hydrophobic monomer in water for copolymerization with a hydrophilic monomer.

Among the attractive features of micellar polymerization, is the relatively small concentration of hydrophobic monomer required for an

efficient, thickening copolymer. For example, in copolymerization of n-alkyl acrylamides in SDS/water with acrylamide (AM), concentrations as low as 0.5 mole % hydrophobic comonomer yield effective copolymers⁶. While attractive from a cost standpoint, analytical determination of the extent of comonomer conversion and incorporation into the copolymer is difficult for such low concentrations. These problems were solved by Valint, et al.,⁷ who utilized chromophore-containing acrylamido comonomers such as N-(4-butyl)phenylacrylamide (BPAM), which may be examined analytically by UV spectroscopy. However, direct evidence of specific microstructural placement is not available in these systems.

Recently we have conducted experiments with chromophore-labeled hydrophobic monomers to further study the relationship between the copolymer microstructure and solution behavior utilizing pyrenesulfonamide-labeled monomers, in which the monomer served as both the hydrophobe and fluorescent reporter molecule.^{8,9} Micellar polymerization resulted in a microblocky structure consisting of short runs of hydrophobic monomer randomly spaced between long runs of hydrophilic monomer. The excimer-to-monomer ratio (I_E/I_M) and apparent viscosity increased with copolymer concentration. No associative effects were observed for copolymers of identical composition with random placement of hydrophobic monomer units prepared by solution polymerization.

We have considered the difficulty of dissolution of the uncharged associative copolymers and have, therefore, introduced functionality responsive to changes in pH or ionic strength.^{10,11,12} For example, we recently reported associative terpolymers of AM with non-charged hydrophobic comonomers and sodium acrylate (NaA), sodium 3-acrylamido-3-methyl butanoate (NaAMB), or sodium 2-acrylamido-2-methyl propanesulfonate (NaAMPS). In the group of terpolymers containing carboxylate functionality, viscosity in water was shown to be dependent on composition, microstructure, molecular weight, polymer concentration, ionic strength, temperature, and pH.^{10,11} Also, we demonstrated the degree of associative thickening behavior of AM/NaA-based terpolymers to be a function of the surfactant to monomer ratio (SMR) in micellar polymerization.¹²

In this report, we examine the role of surfactant-to-monomer ratio (SMR) in the reaction medium on microstructure utilizing the N-[(1-pyrenyl-sulfonamido)ethyl] acrylamide (APS) monomer as a fluorescent label. Comparison is made with previously reported terpolymers of identical AM/AA compositions with N-(4-decyl)-phenylacrylamide as the hydrophobic monomer. Unlike the uncharged copolymer of AM/APS, however, the AM/AA/APS terpolymers of this study do not show intermolecular associative thickening, apparently due to insufficient liaisons of hydrophobic microdomains even at high concentrations of terpolymer.

Experimental Section

Materials

The following materials were purchased from Aldrich and used as received unless otherwise noted: acrylamide, sodium dodecyl sulfate (SDS) and acrylic acid (vacuum distilled before use), $K_2S_2O_8$ (recrystallized from water). All other materials we purchased commercially and used as received.

Monomer and Model Compound Synthesis. The syntheses of N-[(1-pyrenylsulfonamido)ethyl]acrylamide (APS,) and the water soluble model compound, 2,4-dimethyl-N-[(1-pyrenylsulfonamido)ethyl]gluconamide (PSGL), have been reported previously.⁸

Co- and Terpolymer Synthesis and Purification. The general procedures for terpolymer synthesis by micellar polymerization have been described earlier.^{10,11,12} Polymerizations were conducted at 50 °C for 3.5 hr in deionized water. A total monomer concentration of 0.44M was used and [monomer] : [$K_2S_2O_8$] was 3000:1. Feed ratios for the terpolymers were as follows: AM, 0.695; AA, 0.300; APS, 0.005. The surfactant (SDS) to APS molar ratio, SMR, was varied in successive polymerizations at 40, 60, 80 and 100. A control polymer of AM and AA was also synthesized in the presence of SDS (0.132M) with an AM:AA ratio of 0.70:0.30. The AA monomer was used in its acidic form (below pH 4 during polymerization) and neutralized during purification. Polymers were isolated by precipitation into acetone followed by drying and redissolution in water. After one week, the pH was adjusted to 7-8 and the polymers were dialyzed against deionized water using SpectraPor No.4 dialysis tubing (MW cut-off 12-14K) for an additional week. The samples were then lyophilized to a constant weight.

Solution Preparation

Stock solutions of the copolymer and terpolymers were prepared at 0.2-0.5 g/dL in deionized water. After dissolution, the pH of the polymer solutions was adjusted to 7.1- 7.5 using μ L amounts of concentrated HCl or NaOH solutions unless otherwise noted. Dilutions were made with deionized water. For 0.5M NaCl solutions, dry NaCl was added to solutions identical to the ones described above. Dilutions were made with 0.5M NaCl.

Co- and Terpolymer Composition

Copolymer composition was determined by elemental analysis (M-H-W Laboratories, Phoenix, AZ). A previously published method using a combination of elemental analysis and UV spectroscopy was employed to determine terpolymer compositions.^{11,12} UV spectra of dilute solutions (0.02g/dL) of terpolymers in water were obtained and the amount of APS incorporation was determined at 352 nm ($\epsilon = 24000 \text{ M}^{-1}\text{cm}^{-1}$).⁸

UV/VIS Spectroscopy

UV/VIS spectra were obtained on a Hewlett-Packard Model 8452A Photodiode-Array Spectrophotometer. Polymer concentrations were 0.02g/dL in water ($[APS] \approx 4 \times 10^{-6}$ mole/L).

Steady-State Fluorescence Spectroscopy

Steady-state fluorescence spectra were obtained with a Spex Fluorolog 2 Fluorescence Spectrophotometer equipped with a DM3000F data system. Slit widths were maintained at 1-2 mm. Emission spectra were obtained by excitation at 340 nm while monitoring the emission from 350 to 600 nm. Monomer intensities were recorded at 400 nm and excimer intensities were recorded at 519 nm. Spectra were normalized at 400 nm. Excitation spectra were obtained by exciting from 250 to 400 nm while monitoring the emission intensity at either 400 nm (monomer emission) or 519 nm (excimer emission). Due to lower emission intensities for the excimer species, excimer excitation spectra were normalized to monomer excitation at 350 nm. All spectra were corrected for photomultiplier response by an internal correction provided by the manufacturer.

Time-Resolved Fluorescence Spectroscopy

Time-resolved fluorescence data were obtained with a Edinburgh Analytical Instruments FL900CDT single photon counting instrument equipped with an H₂ filled nanosecond flashlamp. 10^4 counts in the maximum channel were taken. Fluorescence lifetimes were obtained from fits of the decay profiles utilizing software provided by the manufacturer, which employs the standard iterative deconvolution method.

Viscometry

Viscosity measurements were conducted on a Contraves LS-30 low shear rheometer at 25 °C and a shear rate of 6 s⁻¹.

Classical and Dynamic Light Scattering

Refractive index increments for classical studies were obtained on a Chromatix KMX-16 Laser Differential Refractometer at 25 °C. A Spectra - Physics 127 laser operating at 632.8 nm was used for all light scattering studies. Data points for classical studies were taken at multiple angles at 25°C using a Brookhaven Instruments model BI-200SM automatic goniometer interfaced with a Brookhaven Instruments personal computer. Zimm plots were constructed using software provided by the manufacturer. Polymer solutions of 2.0×10^{-4} g/mL at pH 7.3-7.5 in 0.5M NaCl were filtered through Millipore 0.45µm filters to remove dust and diluted with filtered 0.5M NaCl. Dynamic light scattering studies were performed at 90 ° and the signals were processed with a Brookhaven Instruments model BI-2030AT autocorrelator. Data were analyzed using the algorithm CONTIN and associated software provided by the manufacturer. Polymer solutions of 2.0×10^{-4} g/mL at pH 7.3-7.5 in 0.5M NaCl were filtered through tygon tubing filter loops using Millipore 0.45µm filters to remove dust. Typical filtration

times were 14 - 48 hours. Multiple analyses were performed to insure reproducibility.

Results and Discussion

Terpolymer Synthesis. The fluorescently labeled polyelectrolytes of this study, **P2-P5**, were prepared from acrylamide (AM), acrylic acid (AA), and N-[(1-pyrenylsulfonamido)ethyl]acrylamide (APS). The structures of these monomers and the resulting terpolymers are shown in Figure 3-2. The synthesis of APS and the water-soluble model compound 2,4-dimethyl-N-[(1-pyrenylsulfonamido)ethyl]glutaramide (PSGL) (Figure 3-1), have been reported in an earlier study.⁸ The polymerization procedure has also been detailed previously.¹² In this study AM is utilized as the major hydrophilic component since it is readily polymerized to high molecular weight in aqueous media. AA copolymerizes readily with AM and provides ionizable groups along the polymer backbone. The composition of AM:AA:APS in the feed was 69.5:30.0:0.5. Potassium persulfate $K_2S_2O_8$, a water soluble initiator, was used in a ratio of 3000:1, [total monomer]:[initiator]. These feed ratios provided a series of high molecular weight, moderate charge-density polyelectrolytes which contain small numbers (~35) of hydrophobic APS units per chain. Terpolymerizations were carried out in deionized water at 50 °C under micellar reaction conditions utilizing sodium dodecylsulfate (SDS) as the surfactant to solubilize the hydrophobic APS comonomers. The SMR or surfactant to monomer ratio is defined by Equation 1 below:

$$SMR = \frac{[SDS]}{[APS]} \quad (1)$$

[SDS] is the molar concentration of surfactant and [APS] is the hydrophobic APS comonomer molar concentration. The SMR may be varied to control the average number of hydrophobic monomers per micelle, n , as predicted from the Poisson distribution by:

$$n = \frac{N [H]}{[SDS] - CMC} \quad (2)$$

where CMC is the critical micelle concentration of SDS in this system and N is the aggregation number of SDS.^{13,14} At the polymerization temperature and monomer concentrations of this study, a CMC value of 6.5×10^{-3} mole/L was obtained for SDS.¹² An aggregation number of approximately 60 is

generally accepted for SDS. Equation 2 is appropriate if the aggregation number of the micelle is not significantly altered by the presence of the hydrophobic monomers. This assumption should be quite valid at low values of n .

By setting the SMR values in successive polymerizations at 40, 60, 80 and 100, the initial number of hydrophobic molecules per micelle can be adjusted as indicated in Table 3-1. At SDS concentrations well above the CMC, Equation 2 may be approximated by $n = N(\text{SMR})^{-1}$. The relationship between n and SMR is shown in Figure 3-3. Decreasing SMR results in a higher number of hydrophobic comonomers per micelle. Note that an SMR of 60 predicts approximately 1 hydrophobe per micelle initially; below 60 there is an average of less than one hydrophobe/micelle. Persistent turbidity in polymerization feeds with an SMR of slightly below 40 (approximately 2 monomers per micelle) precludes the use of lower SMR values for the APS system. As indicated in Table 3-1, the range of n in this study is therefore limited to values of hydrophobic monomer per micelle of 0.62 to 1.62. Although this range of n is quite narrow, the data show that slight variation of the synthetic conditions can effect differences in terpolymer microstructure as evidenced by the photophysical properties of the terpolymers.

A copolymer of AM and AA, **P1**, was synthesized in the presence of SDS (0.132 M SDS and AM:AA feed ratio of 70:30) as a control. Comparison of the bulk and molecular properties of the terpolymers with this copolymer are made before considering the microstructural properties of the terpolymers.

Terpolymer Composition

The compositions of terpolymers, **P2-P5**, as well as the control AM/AA copolymer, **P1**, are shown in Table 3-2. Terpolymers **P2-P5** are very similar in AM and AA composition, with approximately 60-62% AM and 38-40% AA in the resulting terpolymers. The AM:AA ratio of copolymer **P1** is 57:43. For **P2-P5** the degree of APS incorporation is less than half that expected from the feed concentrations. Decreased hydrophobe incorporation in micellar polymerizations with carboxylate monomers has been attributed to charge repulsions during polymerization.¹¹ Conducting the polymerization below the pK_a of the ionizable group can alleviate such problems.¹² Decreased APS incorporation has, however, also been noted in nonionic copolymers prepared by micellar polymerization⁸ as well, and may result from the location of APS monomer in SDS micelles.

Polymerizations were terminated at low conversion to limit compositional drift in the terpolymers. Also, mole% APS in the terpolymers appear to be unaffected by increasing SMR. This is in contrast to studies utilizing smaller hydrophobic monomers which indicate enhanced hydrophobe incorporation at low surfactant levels.^{7,15}

Viscometric Studies

Bulk or macroscopic solution properties of the copolymer **P1** and the terpolymers **P2-P5** were examined at neutral pH using viscometry. Apparent viscosities in deionized water (Figure 3-4) and 0.5M NaCl (Figure 3-5) were measured as a function of polymer concentration.

Copolymer **P1** exhibits a linear increase in apparent viscosity with concentration in deionized water (Figure 3-4). Also the values of the viscosity are very high, typical of high molecular weight polyelectrolytes in low ionic strength media. Terpolymers **P2-P5** exhibit similar behaviors in deionized water at pH 7 (Figure 3-4), but the values are lower than **P1** over the concentration range investigated. Lower viscosities for the terpolymers are most likely due to both lower molecular weights and reduced hydrodynamic volume due to intramolecular associations of the hydrophobic APS units.

Little difference in viscosity is evident when comparing terpolymers **P2-P5** and copolymer **P1** in 0.5M NaCl (Figure 3-5). Apparent viscosities are an order of magnitude lower when compared to those in water, attributed to shielding of the charge-charge repulsions of carboxylate anions along the polymer chain. Viscosities for **P1-P5** essentially lie on the same line and increase in a linear fashion with concentration. No break in the curves or rapid increase in viscosity is evident; therefore, intermolecular associations are not apparent at the macroscopic level.

This behavior differs from that observed for uncharged AM/APS copolymers of similar label content^{8,9} in which significant intermolecular aggregation was observed. At neutral pH, the high charge densities (≈ 40 mole% carboxyl groups) of **P2-P5** would not be expected to promote intermolecular association, especially in deionized water. Studies on hydrophobically-modified polyelectrolytes from our laboratories have correlated decreased intermolecular associations with high polyelectrolyte charge density^{11,12}, particularly at low ionic strength. These observations are consistent with light scattering and fluorescence studies to be presented in subsequent sections.

Light Scattering Studies

Light scattering experiments were carried out in 0.5M NaCl at 25 °C. The pH values of these solutions were 7.3-7.5. Refractive index increments (dn/dc values) were also obtained under these conditions. Values for dn/dc were found to be very similar for the five polymers, and an average value of 0.1703 ± 0.0124 was used for all calculations since the polymers differ very little in composition.

Classical light scattering with the standard Zimm analysis was used to determine the weight average molecular weights (M_w), the second virial coefficients (A_2) and the mean radii of gyration (R_g) for **P1-P5** (Table 3-3). Weight average degrees of polymerization (DP_w), calculated from M_w values

using an average molecular weight per repeat unit of 71.5 g/mole (60:40, AM:AA) are also displayed in Table 3-3.

The molecular weight of copolymer **P1** is the highest with a value of 1.7×10^6 g/mole ($DP_w = 2.4 \times 10^4$). Terpolymers **P2-P5** are of slightly lower molecular weight with values of $1.2- 1.3 \times 10^6$ g/mole ($DP_w = 1.7-1.8 \times 10^4$). Candau and coworkers¹⁵ have noted that surfactants such as SDS contain alcohols capable of chain transfer reactions as impurities. Since the labeled polymers are more hydrophobic and interact more effectively with the SDS micelles during polymerization, chain transfer reactions are more likely and molecular weights are lower. A_2 values ($7-14 \times 10^{-4}$ cm³ mole/g²) indicate that **P1-P5** are very well solvated even in 0.5M NaCl due to the high degree of ionization of the polymer chain at neutral pH. R_g values are consistent with M_w and A_2 data, with values for hydrophobically modified **P2-P5** lower than that of **P1**, ranging from 82-89 nm. These lower values of R_g may be attributed to the lower molecular weights of the terpolymers as well as a slightly more collapsed state due to hydrophobic interactions of the APS groups.

Dynamic light scattering by the standard autocorrelation method allowed determination of diffusion coefficients (D_0) for **P1-P5**. The hydrodynamic diameter (d_H) of the polymer coil can be determined from D_0 by the Stokes-Einstein equation:

$$D_0 = \frac{kT}{3\pi\eta_0 d_H} \quad (3)$$

in which k is Boltzman's constant, T is temperature and η_0 is the viscosity of the medium. Diffusion coefficients and hydrodynamic diameters are shown in Table 3-4. Values for D_0 ($6.5- 7.4 \times 10^{-8}$ cm²/s) and d_H (63-72 nm) are very similar for the copolymer and the four terpolymers. Values of d_H are reproducible with a standard deviation of ± 5 nm. The magnitude of the diffusion coefficients and hydrodynamic diameters corroborate the classical light scattering data, indicating that **P1-P5** occupy large dimensions in 0.5M NaCl. In all cases the distributions in 0.5M NaCl solutions are broad, unimodal, and approximately symmetrical. Distributions of copolymer **P1** and terpolymer **P2** are shown in Figure 3-6. Also, the similarity of the distributions of **P2-P5** (not shown) to **P1** indicate that the presence of interpolymer aggregates is minimal, consistent with the viscosity data.

Photophysical Studies

The studies discussed above indicate that terpolymers **P2-P5** behave as unimolecular coils at neutral pH even at high NaCl concentration. On both the macroscopic and molecular level **P2-P5** behave much like copolymer **P1** which contains no APS label.

Steady-State Fluorescence Emission Studies

Steady-state fluorescence emission spectra for **P2-P5** are shown in Figures 3-7 and 3-8 (concentration of 0.02g/dL and a pH of 7.1-7.5). Emission spectra in water (Figure 3-7) and in 0.5M NaCl (Figure 3-8) are qualitatively identical and exhibit both normal, or "monomer" fluorescence, from approximately 360 to 450 nm as well as excimer fluorescence from 450 to 600 nm (see figure insets). These data are summarized in plots of I_E/I_M in deionized water (○) and 0.5M NaCl (●) vs. SMR (Figure 3-9). The dilute solution spectra in Figures 3-7 and 3-8 support the existence of "blocky" microstructures in terpolymers **P2-P5** at ≤ 0.2 mole% of the APS chromophore.

Excimer formation in labeled polymer systems may occur through either intermolecular or intramolecular fluorescent label interactions. Measurement of I_E/I_M as a function of terpolymer concentration in water at various pH values and in 0.5M NaCl were also conducted to confirm the absence of interpolymer aggregates. I_E/I_M values were measured in deionized water at pH 3.0 and 7.0 and in 0.5M NaCl (pH 7.0). Only modest increases were noted over a ten-fold increase in concentration for **P2-P5** under these conditions. This contrasts with studies on uncharged AM/APS copolymers prepared by micellar^{8,9} polymerization in which an increase in I_E/I_M with concentration due to intermolecular hydrophobic associations of the APS labels was observed.

At pH 7, nearly all the acrylic acid groups of **P2-P5** are in the carboxylate ion form. Under these conditions, the high density of charged groups reduces hydrophobic intermolecular associations. Urry¹⁶ has proposed a mechanism involving water structuring around charged and hydrophobic groups to explained conformational transitions in synthetic proteins. He suggests that water may not simultaneously participate in the hydration of hydrophobic and charged groups. In the present case, the water structure which drives interpolymer hydrophobic associations in the AM/APS copolymers appears to have been disrupted by the high local concentration of charged groups. Even with the addition of NaCl, which shields the carboxylate charges and enhances the structure of water, no significant increase in I_E/I_M is noted with terpolymer concentration.

Under acidic conditions, the properties of the terpolymers may be expected to be more like the nonionic AM/APS copolymer. However, previous studies of AM/AA copolymers^{17,18} indicate that hydrogen bonding between AA and AM groups plays a crucial role in the solution properties of these systems over a wide range of pH. Light scattering studies by Kulicke and Horl¹⁷ support increases in chain stiffness and excluded volumes effects due to intramolecular hydrogen bonding between adjacent amide and carboxylate groups. These effects were dependent on composition reaching a maximum at approximately 65 mole% acid groups. Also, Klenina and Lebedeva¹⁸ reported that hydrogen bonding effects in AM/AA copolymers are enhanced at

low pH. They reported precipitation due to strong hydrogen bonding between acid and amide groups for copolymers containing more than 30 mole% AA in 0.05M HCl. Accordingly, precipitation of **P1-P5** (cf. Figure 3-10) is observed at or below pH 2.8 depending on polymer concentration. Strong intra-coil hydrogen bonding is likely responsible for the monotonic increase in I_E/I_M with terpolymer concentration at a pH of 3.0.

Intramolecular label interactions in these systems should be related to polymer conformation (long range label interactions) or neighboring group interactions. Differentiation of these two types of interactions has been accomplished by monitoring changes in I_E/I_M in solvents or solutions where the macromolecular dimensions are significantly altered. The dependence of I_E/I_M on the thermodynamic quality of the solvent¹⁹, for example, is an indication of long range label interactions. Steady-state emission spectra and I_E/I_M values of **P2-P5** in deionized water, 0.5M NaCl and at various pH values is expected to yield valuable information about the extent of interactions present in aqueous terpolymer solutions.

Fluorescence spectra in deionized water at neutral pH (Figure 3-7) indicate significant values of I_E/I_M for terpolymers **P2-P5**. At a pH of 7 in deionized water , the degree of ionization of the carboxylate groups along the polymer backbone is high and the polymer chains are in an extended conformation. Intramolecular interactions of APS labels or "blocks" of labels from distant parts of the molecule are unfavorable due to the rigidity of the polymer backbone. However addition of electrolytes to the system results in charge shielding allowing a more random coil conformation. The emission spectra of **P2-P5** in deionized water (Figure 3-7) and in 0.5M NaCl (Figure 3-8) reveal qualitative similarity even though the polymer coils experience a large decrease in hydrodynamic volume in 0.5M NaCl (as evidenced by large decreases in apparent viscosities shown in Figures 3-4 and 3-5). Figure 3-9 also illustrates the effects of NaCl addition. For terpolymers synthesized at each respective SMR, I_E/I_M is only slightly higher for the terpolymers in 0.5M NaCl, even though the bulk viscosity is an order of magnitude lower. Apparently, the polymer can adopt multiple conformations in solution and APS interactions within the blocky microstructure (which were spatially inaccessible in deionized water) may occur in 0.5M NaCl.

The fact that APS chromophore interactions occur on the local level even in 0.5M NaCl is apparent when the I_E/I_M ratio for these systems is examined as a function of pH. An example of the pH dependent behavior is shown in Figure 3-10 (0.05g/dL). These data indicate a collapse of the polymer coil below pH 6 until phase separation occurs below pH 2.8 (solid symbol). This classical behavior for labeled polyacids as a function of pH^{20,21} is indicative of long range chromophore interactions in the compact polymer coil at low pH.

Since it is evident that excimer formation at neutral pH in these terpolymer systems arises from a unique microstructure, we may now

compare the microstructure and relative label proximity within this series of terpolymers. Examination of the excimer peaks in the fluorescence spectra of **P2-P5** (inset, Figures 3-7 and 3-8) reveals that excimer formation scales with the micellar parameters in the polymerization feed. **P2** (SMR 40) has the largest excimer peak followed by **P3** (SMR 60), **P4** (SMR 80) and **P5** (SMR 100), respectively. The I_E/I_M vs. SMR curves in Figure 3-9 show a striking resemblance to the curve for micellar occupancy number, n , versus SMR (Figure 3-3). I_E/I_M plots as a function n (for **P2-P5**) in deionized water (○) and in 0.5M NaCl (●) are shown in Figure 3-11. The plot of I_E/I_M as a function n in Figure 3-11 indicates that label proximity is directly related to the initial number of hydrophobic monomers per micelle.

Reid and Soutar^{22,23} have noted that a linear dependence of I_E/I_M with local chromophore composition can be predicted from kinetic models according to equation 4,

$$\frac{I_E}{I_M} = k_c k_{em} [M] \quad (4)$$

where k_c is a composite of rate constants for internal conversion, intersystem crossing, fluorescence and dimer deactivation processes and k_{em} is the rate constant for excimer formation. The term $[M]$ is a concentration term indicative of the local chromophore concentration and the number of potential excimer sites in the polymer. Equation 4 is a general expression and should be applicable to a variety of systems. For example, random copolymer systems utilizing labels such as vinyl naphthalene, $[M]$ is a function of the number of adjacent chromophore pairs and it is anticipated that I_E/I_M is a linear function of the number of potential excimer sites at constant temperature if the proper corrections for energy migration are included.^{19,22,23} However, in the present system, a linear fit (Figure 3-11) is obtained without consideration of energy migration according to equation 5,

$$\frac{I_E}{I_M} = Kn \quad (4)$$

where K is a constant encompassing the rate constants for the photoprocesses considered in equation 4, as well as those necessary to describe the kinetics for dimer formation and deactivation. As noted below, the photophysics of these terpolymer systems are complex and no relationship to a specific kinetic scheme can be made at this time. However, the use of a single term to describe the extent of excimer formation clearly indicates that the initial number of APS monomers per micelle, n , in micellar polymerizations can be used to control local chromophore microcomposition. Although a blocky microstructure is present, other forces play crucial roles in

determining the associative behavior of P2-P5 in solution. In the next section the nature and environment of these "microblocky" polymer segments is addressed.

Steady-State Fluorescence Excitation Studies

Steady-state fluorescence excitation spectra were obtained for terpolymers P2-P5 in both deionized water and 0.5M NaCl at neutral pH. Spectra were measured by exciting from 250 to 400 nm and measuring the emission at both 400 nm (monomer) and 519 nm. The excitation spectra for all terpolymers in water were essentially identical, as expected. Furthermore, addition of NaCl had little effect on the characteristics of the excitation spectrum regardless of the wavelength at which the emission was monitored. A representative example is shown for P2 (SMR 40) in deionized water (Figure 3-12). A slight red shift is noted for the long wavelength-emitting species (top line, dotted) as compared to that of the monomer (bottom line, solid). Further excitation studies²⁴ at a lower bandpass (< 1 nm) utilizing a more sensitive instrument have indicated a red-shift of 2-3 nm in these systems at pH values from 3 to 7. It was noted for AM/APS copolymer systems that the "excimer" excitation exhibited a 4 nm red shift⁹ indicating chromophore pairs existed in the ground state. Perturbation of the ground state energy levels yielded species of lower energy for the dimers in that system. Although the long wavelength emitting species in P2-P5 appears to be similar in nature to that in the previous system,⁹ the existence of dynamically formed excimers can not be ruled out.

Also, we found it possible to excite the ground-state dimers exclusively by employing an excitation wavelength of 410 nm. The emission spectra from 450 to 650 nm showed a broad, symmetrical, but structureless peak centered around 510 nm. This result is consistent with previous studies⁹ employing an excitation wavelength of 395 nm.

Time-Resolved Fluorescence Emission Studies

Time-resolved fluorescence emission studies for APS model compounds have been published previously.⁹ In this work, fluorescence lifetimes of PSGL (Figure 3-1) in deionized water (pH 3 and 7) and 0.5M NaCl (pH 7) were measured. PSGL (0.5 μ mole/L) exhibited only monomer fluorescence at the specified conditions and the decays were exponential yielding lifetimes of approximately 12-13 nanoseconds. These values are consistent with previous fluorescence decays of PSGL in aqueous solution⁹ indicating that the addition of NaCl or aqueous acid does not decrease the lifetime of the pyrene-sulfonamide chromophore.

The emission decay curves at short (419 nm) and long (519 nm) were complex and not resolvable into a complementary set of sum (monomer-419 nm) and difference (excimer-519 nm) of exponential terms as is dictated by a classical excimer equilibrium kinetic analysis.²⁵ It is possible that multiple excimer geometries, energy migration within block sequences of APS groups to excimer forming sites, a microheterogeneous environment for the emitting

species, and even emission from excited ground-state dimers can contribute to the complex, multi-exponential decay curves recorded for terpolymers P2-P5. Due to the number of processes which may be involved, no physical significance should be attached to individual components.

Also, we attempted to measure fluorescence decay times of the ground state dimers by direct excitation at 410 nm. Under all solution conditions (pH, NaCl conc., etc.), these decays were complex, and the sum of three to four exponentials was necessary to satisfactorily fit these decays. Due to their complexity, no interpretation of these decays is possible.

Conclusions

A series of AM/AA/APS terpolymers have been synthesized by micellar polymerization varying the surfactant to APS ratio (SMR) in the polymerization. The terpolymers were found to be of essentially of identical composition and molecular weight. Their solution properties were investigated by viscometry, light scattering and fluorescence spectroscopy, and compared with a control AM/AA copolymer.

Solution viscosity profiles, dynamic light scattering studies, and measurements of I_E/I_M as a function of terpolymer concentration indicate the absence of intermolecular hydrophobic association of the APS labels. The lack of intermolecular associations is an interesting result since interpolymer APS interactions were noted in uncharged AM/APS copolymers of similar label content. This is likely due to two effects. At high pH the presence of a large number of carboxylate groups may sufficiently perturb the water structure, removing the driving force responsible for intermolecular hydrophobic associations. At low pH it is likely that intramolecular hydrogen bonding is responsible for stabilizing intramolecular chromophore interactions to the exclusion of intermolecular interactions.

Since the above studies did not indicate interpolymer association, photophysical studies comparing terpolymers synthesized in the presence of varying amounts of surfactant could be interpreted by considering intramolecular interactions of the APS chromophores only. Measurement of I_E/I_M as a function of solution pH indicates that chromophore interactions are on the local level (i. e. through "near" neighbors) even in the presence of 0.5M NaCl.

Values of I_E/I_M for the terpolymers scale with the initial SDS to APS molar ratio (SMR) in their respective polymerization feeds. The resulting terpolymers exhibit variably blocky microstructures evidenced by decreasing I_E/I_M , and thus APS label proximity with increasing SMR. Also I_E/I_M scales linearly with n , the initial number of APS molecules per SDS micelle. While the issue of hydrophobic comonomer migration during polymerization was not specifically addressed, the linearity of I_E/I_M with n implies that if APS migration occurs on the time scale of free-radical propagation, it is uniform over the surfactant-to-APS ratios in this study.

Also steady-state excitation and time-resolved emission studies indicate the presence of ground-state dimers in aqueous solutions of the terpolymers.

This assessment of the terpolymer microstructures accessible through micellar polymerization is extremely important in light of complementary studies on AM/AA/decylphenylacrylamide terpolymers.¹² The critical aggregation concentration and extent of hydrophobic associations are extremely dependent on the SMR in micellar polymerization, in these studies. Also, these studies indicate that composition and charge density of hydrophobically modified AM/AA copolymers may play critical roles in determining associative properties in solution.

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Table 3-1
Initial Micellar Parameters in Polymerizations.

Sample	SMR ^a	[SDS] ^b	n ^c
P2	40	0.088	1.62
P3	60	0.132	1.05
P4	80	0.176	0.78
P5	100	0.220	0.62

^a Calculated from Equation (1)

^b Molar concentration of surfactant

^c APS molecules/micelle calculated from Equation (2)

Table 3-2
Co- and Terpolymer Composition and Conversion Data.

Sample	SMR ^a	Feed Ratio AM:AA:APS	Mole% AM ^b	Mole% AA ^b	Mole% APS ^c	%Conv. ^d
P1	-	70:30:0.0	57.3	43.7	0.00	36
P2	40	69.5:30.0:0.5	60.3	39.5	0.20	23
P3	60	69.5:30.0:0.5	61.0	38.8	0.17	24
P4	80	69.5:30.0:0.5	61.7	38.1	0.16	27
P5	100	69.5:30.0:0.5	60.6	39.2	0.16	28

^a Calculated from Equation (1)

^b Determined from elemental analysis

^c Determined from UV spectroscopy

^d Percent conversion, determined gravimetrically

Table 3-3
Classical light scattering data in 0.5M NaCl for P1-P5 at 25 °C.

SAMPLE	SMR ^a	$M_w \times 10^{-6}$ (g/mole) ^b	$DP_w \times 10^{-4}$ ^c	$A_2 \times 10^4$ (cm ³ mole/g ²) ^d	R_g (nm) ^e
P1	-	1.7	2.4	10.0	100
P2	40	1.3	1.8	11.5	82
P3	60	1.2	1.7	14.1	89
P4	80	1.3	1.8	12.1	84
P5	100	1.2	1.7	6.7	82

^a Calculated from Equation (1)

^b Weight-average molecular weight

^c Weight-average degree of polymerization

^d Second virial coefficient

^e Radius of gyration

Table 3-4
Dynamic light scattering data in 0.5M NaCl for P1-P5 at 25 °C.

SAMPLE	SMR ^a	$D_0 \times 10^8$ (cm²/sec)^b	d_H (nm) ^c	R_H/R_G
P1	-	6.8	68	0.340
P2	40	6.5	72	0.439
P3	60	6.5	72	0.404
P4	80	7.4	63	0.375
P5	100	6.8	69	0.421

^a Calculated from Equation (1)

^b Translational diffusion coefficient

^c Hydrodynamic diameter calculated from Equation (3)

Figure 3-1. Structures of the fluorescent monomer, APS, and its water soluble model compound, PSGL.

Figure 3-2. Synthesis of AM/AA/APS Terpolymers **P2 -P5**.

Figure 3-3. APS molecules/micelle (n) as a function of SMR (Equation 1) calculated from the Poisson distribution.

Figure 3-4. Apparent viscosity as a function of polymer concentration in deionized water for copolymer **P1** and terpolymers **P2-P5** at 25 °C and 6 s⁻¹.

Figure 3-5. Apparent viscosity as function of polymer concentration in 0.5M NaCl for copolymer P1 and terpolymers P2-P5 at 25 °C and 6 s⁻¹.

Figure 3-6. Examples of diameter distributions (in nm) of P1 (left) and P2 (right) from dynamic light scattering studies in 0.5M NaCl at 25°C.

Figure 3-7. Fluorescence Spectra of terpolymers **P2-P5** in water. Inset: Excimer region from 450 to 600 nm for **P2 (SMR 40)**, **P3 (SMR 60)**, **P4 (SMR 80)**, and **P5 (SMR 100)**.

Figure 3-8. Fluorescence Spectra of terpolymers **P2-P5** in 0.5M NaCl. Inset: Excimer region from 450 to 600 nm for **P2** (SMR 40), **P3** (SMR 60), **P4** (SMR 80), and **P5** (SMR 100).

Figure 3-9. I_E/I_M as a function of the SMR (Equation 1) used in polymerization for terpolymers **P2-P5** in water and 0.5M NaCl.

Figure 3-10. I_E/I_M as a function of solution pH for **P2** in deionized water at 0.05g/dL. The filled symbol indicates the onset of phase separation.

Figure 3-11. I_E/I_M versus n (Equation 2) for P2-P5 measured in deionized water and 0.5M NaCl.

Figure 3-12. Fluorescence Excitation Spectra of P2 (SMR 40) in water 0.02g/dL:
 Top line, (dotted): $\lambda_{em} = 519\text{nm}$, bottom line (solid): $\lambda_{em} = 400\text{nm}$.

CHAPTER FOUR. TERPOLYMERS OF ACRYLIC ACID, ACRYLAMIDE, AND A NOVEL SULFOBETAINE MONOMER

Abstract

Terpolymers of acrylic acid (AA), acrylamide (AM), and the zwitterionic monomer 3-(2-acrylamido-2-methylpropane-dimethylammonio)-1-propanesulfonate (AMPDAPS) have been prepared by the free-radical polymerization in 0.5M NaCl aqueous solution using potassium persulfate as the initiator. The feed ratio of AMPDAPS:AA:AM was varied from 5:5:90 to 40:40:20 mol% with the total monomer concentration held constant at 0.45M. Terpolymer compositions were obtained by ^{13}C NMR. Low angle laser light scattering provided molecular weights and second virial coefficients which varied from 3.0×10^6 to $7.9 \times 10^6 \text{ g mol}^{-1}$ and 2.23 to $2.95 \text{ ml mol g}^{-2}$, respectively. The solubilities of the resulting terpolymers are dependent on pH as well as the amount of AMPDAPS and AA present in the feed. At pH 4 and for higher incorporation of AA and AMPDAPS in the feed (>25 mol%), the terpolymers are insoluble in deionized water and 0.25 M NaCl. At pH 8, all terpolymers are soluble in deionized water and salt solutions. The dilute and semi-dilute solution behavior of the terpolymers were studied as a function of composition and added electrolytes. Polyelectrolyte behavior was observed for all terpolymers at pH 8 as evidenced by a viscosity decrease in the presence of added electrolytes. The terpolymers exhibit higher viscosities in the presence of NaSCN versus NaCl. Comparison of the solution behavior of the terpolymers to copolymers of AM and AA as well as copolymers of AMPDAPS and AM have been made.

Introduction

The synthesis of electrolyte tolerant water-soluble polymers that contain ionic pendent groups has been the subject of study in our laboratories for the past several years.¹⁻⁸ Polyelectrolytes display high viscosities in deionized water at low concentrations and thus are commercially used as viscosifying agents in numerous applications. However, in the presence of added electrolytes, charge-charge repulsions are shielded resulting in a considerable decrease in viscosity and, in some cases, phase separation. In striving to synthesize polymers that show tolerance in the presence of added electrolytes, we have recently focused our attention on polyampholytes, polymers which possess both cationic and anionic pendent groups. Polyampholytes have shown an enhancement in viscosity in the presence of added electrolytes as intramolecular columbic attractions are shielded.⁹⁻²¹ In our laboratories, high charge density copolymers of cationic and anionic monomers have been synthesized. The rheological behavior of these polymers is dictated by the charge ratio of the cationic and anionic groups. If there is a charge imbalance, the polymers behave as a polyelectrolytes and display a decrease in viscosity in the presence of added electrolytes. However,

when there are equimolar anionic and cationic monomers, polyampholytic behavior is observed and viscosity increases as the ionic strength of the medium is increased. Low charge density polyampholytes have also been synthesized in which a neutral monomer such as acrylamide has been terpolymerized with cationic and anionic monomers. These polymers intermolecularly associate in deionized water and can form gels that may be used as "superabsorbers"¹⁷.

Polyampholytes have also been synthesized from zwitterionic monomers in which the cationic charge is provided by a quaternary ammonium functionality and the anionic charge provided by a carboxylate or sulfonate group. These monomers are unique in that they exhibit a net charge of zero at appropriate pH. A number of investigations have focused on the unusual solution behavior of zwitterionic polyampholytes²²⁻³⁴.

The goals of this research are to synthesize polymers that will display either polyampholytic or polyelectrolytic behavior depending on the pH of the environment. Special attention has been focused on monomers that contain the carboxylate group. Thus, the synthesis and solution behavior of terpolymers of acrylic acid, acrylamide, and a sulfobetaine monomer will be discussed.

Experimental

Materials

Acrylamide (AM) from Aldrich was recrystallized twice from acetone and vacuum-dried at room temperature. Acrylic Acid (AA) from Aldrich was distilled prior to use. 3-(2-Acrylamido-2-methylpropanedimethylammonio)-1-propanesulfonate (AMPDAPS) was synthesized by the ring opening reaction of 1,3-cyclopropanesultone with 2-acrylamido-2-methylpropanedimethylamine as previously reported¹⁹. Potassium persulfate from J.T. Baker was recrystallized twice from deionized water. All other materials were used as received.

Synthesis of Terpolymers of 3-(2-acrylamido-2-methylpropane dimethylammonio)-1-propanesulfonate, Acrylamide, and Acrylic Acid. The terpolymers of AMPDAPS, AM, and AA (the AADAPS series) were synthesized by free radical polymerization in a 0.5M NaCl aqueous solution under nitrogen at 30 °C using 0.1 mol % potassium persulfate as the initiator at a pH of 8. The feed ratio of AMPDAPS:AA:AM was varied from 5:5:90 to 40:40:20 mol % with the total monomer concentration held constant at 0.45M.

In a typical synthesis, specified quantities of each monomer were dissolved in small volumes of 0.5M NaCl solution. The separate solutions were then combined and diluted to a 0.45M monomer concentration with 0.5M NaCl solution. One equivalent of sodium hydroxide per equivalent of acrylic acid was then added and the pH adjusted to 8. The reaction mixture was sparged with nitrogen then initiated with 0.1 mol % potassium persulfate. The reaction was usually terminated at <55% conversion due to the high viscosity of the reaction medium and as a precaution against copolymer drift. The polymers were

precipitated in acetone, redissolved in deionized water, then dialyzed using Spectra/Por 4 dialysis bags with molecular weight cutoffs of 12,000 to 14,000 g/mol. Half of the samples were dialyzed against deionized water adjusted to pH 4 while the other half were dialyzed against deionized water adjusted to pH 8. Polymers containing 25 mol% or more of AMPDAPS and AA in the feed (AADAPS-25 and AADAPS-40) precipitated during dialysis against deionized water adjusted to pH 4. After dialyzing for two weeks, the polymers were isolated by lyophilization. Conversions were determined gravimetrically. I.R.: AADAPS-40 copolymer isolated at pH 4 (KBr pellet): O-H 3600-2600 cm^{-1} (bd); N-H 3280 cm^{-1} (s); C-H 3050 cm^{-1} (m) and 2980 cm^{-1} (m); C=O 1700, 1655, 1637 cm^{-1} ; N-H 1560 cm^{-1} (m); C-O-H 1460 cm^{-1} (m); C-O 1208 cm^{-1} (s); S-O 1189, 1042 cm^{-1} (s).

Synthesis of Copolymers of 3-(2-acrylamido-2-methylpropane dimethylammonio)-1-propanesulfonate with Acrylamide and Acrylic Acid with Acrylamide. The polymerization procedures for copolymers of AMPDAPS with AM have been previously reported by Salazar and McCormick.¹⁹ Copolymers of AM and AA were prepared using similar techniques for the terpolymer synthesis.

Copolymer Characterization

¹³C n.m.r spectra of the polymers were obtained at 50.3 MHz on a Bruker AC 200 spectrometer using 10-15 wt% aqueous (D₂O) polymer solutions with DSS as a reference. A recycle delay of 6 s, 90° pulse length, and gated decoupling to remove all NOE were used for quantitative spectral analysis. F.T.I.R. spectra were obtained using a Mattson Galaxy 2020 series spectrometer. Molecular weight studies were performed on a Chromatix KMX-6 low angle laser light scattering instrument. Refractive index increments were obtained using a Chromatix KMX-16 laser differential refractometer. For quasielastic light scattering a Langley-Ford Model LF1-64 channel digital correlator was used in conjunction with the KMX-6. All measurements were conducted at 25 °C in 1M NaCl at a pH of 8.

Viscosity Measurements

Stock solutions of sodium chloride were prepared by dissolving the appropriate amount of salt in deionized water adjusted to either pH 4 or pH 8 in volumetric flasks. Polymer stock solutions were made by dissolving designated amounts of polymer in the salt solutions. The solutions were then diluted to appropriate concentrations and allowed to age for seven to ten days before being analyzed with a Contraves LS-30 rheometer. Intrinsic viscosities were evaluated using the Huggins equation.

Results and Discussion

Compositional Analysis

The terpolymers of AMPDAPS, AM, and AA (the AADAPS series) were synthesized by varying the feed ratios of AMPDAPS:AA:AM from 5:5:90 to 40:40:20 mol%. Copolymers of AM and AA (the AAAM series) were synthesized by varying the feed ratio of AA:AM from 10:90 to 25:75 mol%. Copolymers of AMPDAPS and AM (the DAPSAM series) have been synthesized previously.¹⁹ All polymers reported in this paper are shown in Table 4-1. The polymer compositions were determined by integration of the carbonyl resonances and agree favorably with past results. AMPDAPS and AM incorporation in both the AADAPS and DAPSAM series approximates the feed composition indicating little preference for addition of either monomer. AA incorporation in both the AADAPS and AAAM series was found to be approximately half the feed composition denoting a partiality towards the addition of the acrylamido-type monomers. The reaction parameters and the resulting copolymers compositions are given in Table 4-1.

Low angle laser light scattering

Table 4-2 shows the weight-average molecular weights determined by low-angle laser light scattering at 25 °C in 1M NaCl. The molecular weight for the AADAPS series varies from 3.0 to $7.9 \times 10^6 \text{ g mol}^{-1}$. The second virial coefficients (A_2) for the AADAPS series have values between the DAPSAM series and the AAAM series. This is expected due to the presence of the strongly hydrated carboxylate functionalities in the AADAPS terpolymers.

Quasi-elastic light scattering was used to obtain the mean diffusion coefficients (D_0) and diameters (d_0) shown in Table 4-2. As molecular weight and degree of polymerization increase, D_0 decreases and d_0 increases on an average although solvent quality (A_2 values) as well as steric factors must also be considered. AADAPS-25 and DAPSAM-25, both having similar molecular weights, demonstrate enhanced solvation of AADAPS-25 due to the presence of carboxylate functionalities resulting in a larger hydrodynamic volume.

Dilute Solution behavior

Effects of Copolymer Composition and pH. To study the effects of pH on the terpolymers, 0.25 g/dL stock solutions were prepared from the terpolymer samples dialyzed at pH 4 and pH 8. Of the samples dialyzed against pH 4, only two of the samples were soluble in deionized water; AADAPS-5 and AADAPS-10. AADAPS-25 was insoluble in deionized water and 0.25M NaCl; however, the copolymer was soluble in 1M urea. AADAPS-40 was insoluble in all of the above solvents.

The solubility behavior is a culmination of two effects: (1) charge-charge interaction between the AMPDAPS mer units and (2) hydrogen bonding between the amide and carboxylic acid units. The insolubility of polyampholytes in deionized water has been observed numerous times and is clearly due to strong columbic attractions. In our group, copolymers of AM and AMPDAPS have been studied¹⁹. Those copolymers containing 60 mol% or more of AMPDAPS were insoluble in water and required the addition of a critical concentration of NaCl before solubility could be achieved. In the case of AADAPS terpolymers, the solubility is greatly reduced by substituting acrylamide units with acrylic acid units during synthesis.

The behavior of acrylamide/acrylic acid copolymers has been studied by numerous group³⁵⁻⁴¹. Precipitation has been observed for polymers containing more than 30 mol% acrylic acid in 0.05M HCl due to strong hydrogen bonding between the acid and amide groups³⁸. Similar behavior has been observed in AADAPS terpolymers and is further supported by the solubilization of AADAPS-25 which requires 1M urea. The presence of urea may disrupt hydrogen bonding between the carboxylic acid and amide groups and allows solubilization of the terpolymer.

Although polymer samples AADAPS-5 and AADAPS-10 were soluble in deionized water as well as salt solutions, viscosity data yielded little information due to the extremely low values that were obtained ($\eta_{red} < 0.5$). Extremely compact conformations are indicated in both deionized water and 0.514m NaCl. As for the samples dialyzed against pH 8, all were soluble in both deionized water and salt solutions.

Effects of Added Electrolytes on the AADAPS series

The effects of added salts on the viscosities of the AADAPS terpolymers were observed at a shear rate of 5.96 sec⁻¹. The apparent viscosities of the AADAPS terpolymers in deionized water at pH 8 are shown in Figure 4-1. As expected, the terpolymers display high viscosities due to a net negative charge on the chain which causes the polymer to behave as a polyelectrolyte. Viscosity tends to increase with increasing sodium acrylate mer units except for the discrepancy between AADAPS-40 and AADAPS-25, perhaps due to molecular weight differences or increased rigidity from cyclic interactions between amide and carboxylate groups. Our group and others have found that the highest intrinsic viscosities for copolymers of acrylamide and sodium acrylate occur when there is roughly an equal ratio of acrylamide to sodium acrylate units due to the cyclization mechanism noted above.^{35,36} This nearest neighbor effect may be broken up by the AMPDAPS mer units in AADAPS-40 which contains 50 mol% AMPDAPS.

The AADAPS terpolymers act as anionic polyelectrolytes with a reduction in the intrinsic viscosity as a function of increasing ionic strength as shown in Figure 4-2. As the concentration of NaCl increases, the anionic repulsions are shielded and the hydrodynamic volume decreases as the polymer chain relaxes

into a more compact configuration. AADAPS-40 displays a lower intrinsic viscosity than AADAPS-10 at higher ionic strengths, probably indicative of a lower molecular weight. Polyelectrolyte behavior was further illustrated by plotting intrinsic viscosity as a function of the reciprocal square-root of the ionic strength (Figure 4-3). All samples display linear dependence which is typical of polyelectrolytes. AADAPS-25 exhibits the highest slope and is, therefore, the most sensitive to changes in the ionic strength of the solution.

Figure 4-4 shows the reduced viscosity versus NaCl concentration at a polymer concentration of 0.25 g/dL. Once again typical polyelectrolyte behavior is observed even up to 3M NaCl. Polyampholytes normally display an enhancement in viscosity as the ionic strength of the medium increases due to the shielding of intramolecular coulombic attractions. As the ionic strength of the medium is increased, the electrostatic energy term plays a smaller and smaller role in the conformational stability of the chain while the rotational and hydrophobic terms as well as polymer solvation become the dominant factors in dictating the conformation of the polymer chain. The AADAPS terpolymers show no polyampholytic behavior at higher ionic strengths and the hydrodynamic volumes of the polymers appear to remain fairly constant between 0.5M to 3M NaCl.

The reduced viscosities were also examined as a function of the structure of the anion in the added electrolytes. Figures 4-5 and 4-6 display the differences in the reduced viscosity in NaCl and NaSCN solutions for AADAPS-10, AAAM-10 and AADAPS-25, AAAM-25. In agreement with the Hoffmeister series predictions, all polymers studied show an enhancement of reduced viscosity in NaSCN solutions compared to NaCl solutions; however, the effect is much less dramatic for AAAM copolymers. As noted by others³¹⁻³³ and in accord with the "hard-soft" acid-base theory, the SCN⁻ ion is a 'softer' ion than the Cl⁻ ion and is thus able to bind tighter to the 'soft' ammonium group. Salamone et. al.³¹ have proposed that tighter binding between the small anion and the ammonium group in sulphobetaine polymers reduces the draining ability of individual chains and thus an increase in viscosity is observed. It is further stated that as the concentration of salt is increased, the viscosity rises rapidly at first due to site binding then increases slowly as atmospheric binding becomes the only mode available for ionic interaction. Liaw et al.³³ suggest that if the small anion binds tighter to the ammonium group than the small cation does to the sulfonate group in sulphobetaine polymers, a partial negative charge may develop along the polymer chain and thus lead to an increase in viscosity.

Our systems show that at the lower ionic strengths, the differences in reduced viscosity between the NaSCN and NaCl solution are quite high. However, at higher salt concentrations the differences begin to narrow. This behavior is in agreement with the propositions put forth by Salamone and Liaw.^{31,33} At lower concentrations of salt, the SCN⁻ anion binds tighter to the ammonium group than does the Cl⁻ anion leading to an enhancement of the reduced viscosity. This 'tighter' binding not only reduces the draining ability of the polymer chain, but also leads to an amplification of the net negative charge

that is already present along the polymer chain due to the sodium acrylate mer units. At higher concentrations of salt, electrostatic repulsive forces are greatly diminished and the differences in viscosity between the NaCl and the NaSCN solutions are probably due to draining differences of the polymer in the different solutions as well as the enhanced 'salting-in' of the polymer chain by NaSCN.

Comparison of the Effect of Added Electrolytes on the AADAPS, DAPSAM, and the AAAM series. Figures 4-7 and 4-8 examine the effect of increasing NaCl concentration on the intrinsic viscosities of all the polymer series. In Figure 4-7, a structural comparison between AADAPS-10 and AAAM-10 may tentatively be drawn since both have similar molecular weights and degrees of polymerization. It can be seen that at low ionic strength, the pure polyelectrolyte has a higher intrinsic viscosity due to Donnan effects that have not been overcome. AADAPS-10 has a lower intrinsic viscosity because of columbic attractions between the cationic and anionic groups present along the polymer chain. When the ionic strength increases, the columbic attractions in AADAPS-10 are shielded sufficiently enough for the copolymer to adopt a more random configuration; however, there is still a decrease in the intrinsic viscosity due to the charge imbalance of the polymer. At higher ionic strengths there is a cross-over of intrinsic viscosity values of the AADAPS-10 and AAAM-10 polymers, with AADAPS-10 maintaining a higher intrinsic viscosity. This behavior is probably a result of the inherent bulkiness of the AMDPAPS mer unit restricting the rotational freedom of the polymer chain rather than a solvation effect. DAPSAM-10 displays typical polyampholyte behavior with the intrinsic viscosity increasing in the presence of added salt. DAPSAM-10 has the highest intrinsic viscosity in 0.5M NaCl, likely due to the higher molecular weight compared to the other polymers. In Figure 4-8, a structural comparison between AADAPS-25 and DAPSAM-25 may tentatively be drawn since molecular weights and degree of polymerization are similar. At low ionic strengths, AADAPS-25 has a higher intrinsic viscosity due to the charge imbalance of the polymer chain. At higher ionic strengths, AADAPS-25 still maintains a higher intrinsic viscosity than DAPSAM-25 due to the presence of the carboxylate functionalities which enhance the solvation of the polymer chain. This is in accord with the A_2 values discussed earlier.

Effects of Shear Rate. The effects of shear rate on the apparent viscosity of AADAPS-10 and AADAPS-25 were investigated in deionized water at both high and low polymer concentrations. The shear rates ranged from 0.94 to 127.47 s⁻¹. In Figure 4-9, the behavior of the terpolymers is shown at two different concentrations. Both terpolymers display pseudoplastic behavior as evidenced by the reduction in apparent viscosity as shear rates increase. In 0.514M NaCl, the terpolymers no longer display pseudoplastic behavior and viscosity is fairly constant over the range of shear rates studied.

Conclusions

Terpolymers of AA, AM, and AMPDAPS have been synthesized by free-radical polymerization in 0.5M NaCl. In deionized water at pH 4, the solubility of the polymers is greatly reduced due to ionic interactions as well as hydrogen bonding interactions. At pH 8, the polymers behave as typical polyelectrolytes displaying high apparent viscosities. As the ionic strength of the medium is increased, the intrinsic viscosity decreases due to shielding effects between like charges. The reduced viscosities are higher in NaSCN solutions compared to NaCl solutions due to the higher binding ability between the SCN⁻ anion and the ammonium group on the AMPDAPS mer unit. AADAPS-10 displays a higher intrinsic viscosity than AAAM-10 in 0.5M NaCl probably due to steric factors. AADAPS-25 displays a higher intrinsic viscosity due to solvation effects.

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AADAPS series

AAAM series

DAPSAM series

Table 4-1
Reaction Parameters for AADAPS terpolymers

Sample	Feed Ratio (mol %) (X/Y/Z)	Reaction Time (hrs.)	AMPDAPS found ^a (mol %)	AA found ^a (mol %)	AM found ^a (mol %)
AADAPS- 5	90/5/5	4.0	5.0	3.2	91.8
AADAPS- 10	80/10/10	4.0	10.2	4.6	85.2
AADAPS- 25	50/25/25	4.0	31.1	13.3	55.6
AADAPS- 40	20/40/40	5.5	50.4	25.4	24.2

^a Determined from ¹³C N.M.R.

Table 4-2
Reaction Parameters for AAAM and DAPSAM copolymers

Sample	Feed Ratio (mol %) (X/Y)	Reaction Time (hrs.)	AMPDAPS found ^a (mol %)	AA found ^a (mol %)	AM found ^a (mol %)
AAAM-10	90/10	4.0	-----	5.8	94.2
AAAM-25	75/25	6.0	-----	12.2	87.8
DAPSAM- 10 ^b	90/10	4.5	9.6	-----	90.4
DAPSAM- 25 ^b	75/25	23.0	27.7	-----	72.3

^a Determined from ¹³C N.M.R.

^b Ref. 19

Table 4-2
Classical and Quasielastic Light Scattering Data for AADAPS, AAAM,
and DAPSAM polymers

Sample Number	dn/dc	M_w ($\times 10^{-6}$ g/mol)	A_2 ($\times 10^4$ ml.mol/g ²)	$Do \times 10^8$ (cm ² /s)	do (Å)	DP $\times 10^{-4}$
AADAPS -5	0.186	3.0	2.77	4.07	1150	3.61
AADAPS -10	0.175	5.4	2.95	4.10	1150	5.69
AADAPS -25	0.193	7.9	2.23	3.91	1370	5.55
AADAPS -40	0.181	4.7	2.23	4.00	1180	2.50
AAAM -10	0.172	4.0	5.76	4.09	1180	5.49
AAAM -25	0.189	1.9	9.49	4.12	1060	2.53
DAPSAM -10	0.138	7.0	1.49	4.01	1380	7.50
DAPSAM -25	0.139	8.2	1.33	3.97	1180	6.35

Figure 4-1. Apparent viscosity of AADAPS terpolymers in deionized water. (Determined at 25 °C at a shear rate of 5.96 s⁻¹ and pH 8)

Figure 4-2. Dependence of intrinsic viscosity of AADAPS terpolymers as a function of NaCl concentration. (Determined at 25 °C at a shear rate of 5.96 s⁻¹ and pH 8).

Figure 4-3. Intrinsic viscosities of AADAPS terpolymers as a function of the inverse square root of ionic strength. (Determined at 25 °C at a shear rate of 5.96 s⁻¹ and pH 8)

Figure 4-4. Reduced viscosity of AADAPS terpolymers versus NaCl concentration with a polymer concentration of 0.25 g/dL. (Determined at 25 °C at a shear rate of 5.96 s⁻¹ and pH 8).

Figure 4-5. Reduced viscosity as a function of increasing ionic strength of various salts with a polymer concentration of 0.25 g/dL. (Determined at 25 °C at a shear rate of 5.96 s^{-1} and pH 8)

Figure 4-6. Reduced viscosity as a function of increasing ionic strength of various salts with a polymer concentration of 0.25 g/dL. (Determined at 25 °C at a shear rate of 5.96 s^{-1} and pH 8).

Figure 4-7. Dependence of intrinsic viscosity as a function of NaCl concentration. (Determined at 25 °C at a shear rate of 5.96 s⁻¹ and pH 8)

Figure 4-8. Dependence of intrinsic viscosity as a function of NaCl concentration. (Determined at 25 °C at a shear rate of 5.96 s⁻¹ and pH 8).

Figure 4-9. Effect of shear rate on the apparent viscosity of AADAPS-10 and AADAPS-25 in deionized water and different concentrations. (Determined at 25 °C and pH 8).

CHAPTER 5. SODIUM-23 NMR STUDIES OF ION-BINDING TO ANIONIC POLELECTROLYTES. EFFECTS OF MOLECULAR STRUCTURE AND ADDED CALCIUM AND MAGNESIUM SALTS IN AQUEOUS MEDIA

Abstract

^{23}Na NMR measurements of the longitudinal (R_1) and transverse (R_2) relaxation rates of copolymers of 1% and 10% 2-(1-naphthylacetamido)ethylacrylamide (NAEAM) with acrylic acid (NAA-1 and NAA-10) and methacrylic acid (NMA-1 and NMA-10) have been performed as a function of the degree of ionization. The transverse relaxation was sufficiently biexponential at low α to extract R_{2s} and R_{2f} for NAA-10, NMA-1, and NMA-10. The correlations times, τ_c , and values for $P_b\chi^2$, the product of the fraction of bound ions and the quadrupolar coupling constant were determined and indicated conformational transitions in NAA-10, NMA-1, and NMA-10. The incorporation of increasing concentration of hydrophobic NAEAM into the polyacids increases χ at low degrees of ionization. The results of the relaxation studies are shown to be consistent with previous viscosity and fluorescence studies on the same systems.

Introduction

Hydrophobic modification of polyelectrolytes can impart desirable properties to copolymers in aqueous solution. For example, hydrophobic substituents of properly-tailored systems can associate in aqueous solution to form microheterogenous domains. "Closed" or intramolecular associations may induce surface active qualities while "open" or intermolecular associations may lead to viscosification in aqueous media. The organization of the microheterogenous associates and responsiveness to changes in pH and ionic strength dictate the usefulness of such systems in applications ranging from phase transfer to rheology modification. An external probe such as naphthalene or pyrene can be solubilized within these microheterogenous zones and dynamic information about the environment may be obtained from fluorescence studies. Incorporation of the chromophore as a hydrophobic label allows examination of the internal dynamics of hydrophobically-modified polyelectrolyte systems.¹⁻⁵

Poly(methacrylic acid) (PMA) exhibits conformational reordering as the degree of ionization, α , along the polymer backbone reaches a critical value.⁶ The methyl groups associate at low pH, forming a compact coil (hypercoil) with hydrophobic domains. As the degree of ionization increases, coulombic repulsions overcome weak associations of the methyl groups, expanding the coil. This conformational transition has been observed by fluorescence techniques^{6,7} as well as classical methods⁸. Hydrophobically-modified poly(methacrylic acid) has been reported to adopt a "hypercoiled" structure in which the hydrophobes form an inner hydrophobic domain surrounded by ionized carboxylate units.^{9,10} These hypercoils

may persist even at high degrees of ionization if the pendent hydrophobes have flexible spacers.^{1,2,10,11}

The major objective of this work was to investigate via ^{23}Na NMR the behavior of sodium hydroxide-neutralized acrylic and methacrylic acid copolymers which have been prepared with one and ten mole % 2-(1-naphthylacetamido)ethylacrylamide (NAEAM) comonomer (Figure 5-1). The NAEAM comonomer serves a dual purpose of acting as a "hydrophobe" and a fluorescence label. A further objective of this work was to ascertain whether or not the ^{23}Na NMR method might be useful in probing the pH-responsive domain organization deduced from previous photophysical and viscometric studies.^{1,2}

Our approach was guided largely by ^{23}Na NMR relaxation rate studies designed to observe conformational changes in polymethacrylic acid (PMA)¹¹ and poly (2-hydroxyethyl methacrylate-co-methacrylic acid).¹² Major contributions to the development of the ^{23}Na NMR method, including the key expressions utilized in data analysis, are detailed in the introduction of the previous chapter. Hereafter, to avoid redundancy, appropriate expressions will be cited. In this approach longitudinal and transverse relaxation rates for sodium counterions have been measured as a function of α (degree of ionization) for the modified copolymers shown in Figure 5-1. The corresponding correlation times, τ_c , values for $P_b\chi^2$, the product of the fraction of bound ions, and the quadrupolar coupling constant for the Na^+ nuclei are calculated using R_1 and R_2 values as well as the biexponential transverse relaxation rates of the copolymers. These data strongly suggest that a conformational transition induced by the presence of sufficient hydrophobic label occurs at low charge density for both PAA and PMA. These conclusions are supported by previously reported viscosity and fluorescence measurements on these or related systems.^{1,2} The correlation time, τ_c , can be determined by employing a theoretical estimate for P_b ¹¹⁻¹⁴ or by assuming P_F (the fraction of free ions) $\gg P_b$ ¹⁵. Once τ_c is known, $P_b\chi^2$, and χ may be determined. χ is a measure of quadrupolar interactions and is proportional to the magnitude of the electric field gradient experienced by counterion nuclei. In this work, we employ an experimental measure for P_b of Na^+ determined for PAA and PMA using an electrophoretic technique¹⁶

Previous studies on PMA have shown that $P_b\chi^2$ and χ vary substantially with increasing degree of ionization, α , in PMA when using theoretical estimates for P_b . These studies demonstrated that the changes observed in $P_b\chi^2$ could not be solely accounted for by changes in P_b ; thus, χ must change with α . Similar variations in both χ and τ_c were observed when determined from the $\Delta(R_1/R_2)$ and $\Delta(R_{2f}/R_{2s})$.¹¹ (See equations 9-11 in the preceding chapter).

Experimental

Sodium NMR measurements were conducted at 25°C on a Bruker MSL-400 operating at 105.8 MHz for ^{23}Na nuclei. The glass cylinders supporting the transmitter/receiver coils were replaced with Teflon[®] counterparts to minimize signal interference from sodium borosilicate glass. Teflon[®] NMR tube liners from Wilmad Glass Company were used in place of glass NMR tubes. Longitudinal relaxation rates (R_1) were measured using the inversion-recovery method. All curves were observed to be single exponential decays and were fit to Equation 5 (see Introduction of previous chapter) using the Bruker SIMFIT program. Transverse relaxation rates (R_2) were measured (non-spinning) using the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence and were fit to Equations 5 and 6. Since no previous criteria have been established for the determination of the onset of biexponential relaxation behavior, we have arbitrarily chosen a cutoff for the onset of biexponentiality as being the point where the error of the fit of Equation 5 exceeded that of Equation 6 by 10%. Error bars on the plots are given at the 95% confidence level.

The synthesis of the copolymers (Figure 5-1) has been previously² described with the mole percent of NAEAM incorporated as follows: 0.9% NAEAM in PAA (NAA-1), 9.3% NAEAM in PAA (NAA-10), 1.02% NAEAM in PMA (NMA-1), and 11.8% NAEAM in PMA (NMA-10). Poly(acrylic acid) (PAA, MW = 250,000 g/mole) and poly(methacrylic acid) (PMA, MW=15,000 g/mol) were obtained from Polysciences, Inc. Polymer solutions were prepared to 0.1 g/dL concentration with 5% D₂O to provide a frequency lock. The polymer concentration for these studies was selected to provide a good signal-to-noise ratio with a reasonable number of scans and to fall within the dilute regime in order to minimize possible associative interactions between isolated polymers. The polymers were initially prepared at pH 9 and titrated with 1M HCl to the desired pH values. Attempts to titrate from an acidic polymer solution using NaOH were unsuccessful due to the insolubility of the 10% NAEAM-labelled polymers at low pH. The degree of ionization was determined from the amount of added acid.

Results and Discussion

In the following discussion, the longitudinal and transverse relaxation rates of PAA, PMA, and the labelled, hydrophobically-modified NAA and NMA series (Figure 5-1) will be presented.² The slow and fast transverse relaxation rates, R_{2s} and R_{2f} , respectively, are included when the relaxation decays displayed biexponential character at low α . At α values above 0.8, biexponential rate behavior was observed; however, these data are not presented since the region of interest for this study are α values less than approximately 0.8. Correlation times, τ_c , are calculated from $\Delta(R_1/R_2)$ since $\omega\tau_c > 0.25$ over the range of all α values. For

the NMA series, the biexponential relaxation rates observed at low α were also employed to calculate $P_b\chi^2$.

In Figure 5-2, the transverse and longitudinal relaxation rates for NAA-1 are plotted as a function of the degree of ionization. R_1 and R_2 values are nearly identical for NAA-1 and PAA. Also the values for the latter are consistent with those from previous studies.¹³ In Reference 13, R_2 has slightly higher values than R_1 indicating that $\omega\tau_c > 0.25$.¹¹ The data presented in our work also demonstrate that $\omega\tau_c > 0.25$ as evidenced by the inequality of R_1 and R_2 over the range of pH values studied. Both relaxation rates increase smoothly towards $\alpha = 1$. The similarity in the relaxation rates for PAA and NAA-1 demonstrates that incorporation of 1% NAEAM has no observable effect on the ^{23}Na NMR behavior.

Figure 5-3 illustrates the dependence of R_1 and R_2 on α for NAA-10. The behavior is quite different from that observed in PAA and NAA-1. Below $\alpha = 0.5$, R_2 can be resolved into slow and fast (R_{2s} and R_{2f}) components. It is interesting to note that a substantial decrease in R_2 and R_{2f} is matched by a marked increase in I_E/I_M (the fluorescence intensity ratio of excimer to monomer designated by the stars in Figure 5-3) as α approaches 0.5. These superimposed data are from previous studies² on this polymer by our group. This behavior is consistent with the adoption of a pseudomicellar conformation with high values of I_E/I_M . This pseudomicellar conformation has been termed a "hypercoil" in which the hydrophobic groups form a center core surrounded by a sheath of carboxylate moieties. The decreases in the relaxation rates are consistent with this conformation since a lowering of the rates would be expected if the relative hydrophobicity of the domains in which the Na^+ are bound decreases.

In Figure 5-4, τ_c is plotted as a function of α for NAA-1 and NAA-10. The data for PAA (not included) are virtually identical to that for NAA-1. The correlation times were determined using Equation 8 (preceding chapter) and the P_b values for PAA provided by Ander et. al.¹⁶ The slope of the τ_c vs. α for NAA-10 is greater than that of NAA-1 indicating that the local motions of the Na^+ counterions are slowed in the NAA-10 copolymer. The P_b values determined by Ander¹⁶ are from an electrophoretic technique and may arguably not reflect the same fraction of ions bound on the NMR time scale. However, rather than employing theoretical estimates for P_b ¹¹⁻¹⁴, we have chosen this experimental measure for P_b . As shown by Lindman and coworkers¹⁵, the precise values of P_b may not be important for an unambiguous interpretation of the relaxation data.

The values of $P_b\chi^2$ (Figure 5-5) and χ (Figure 5-6) were determined from the derived τ_c values using Equation 7 (preceding chapter). Higher values of $P_b\chi^2$ and χ at $\alpha < 0.3$ are observed for the NAA-10 copolymer compared to NAA-1. This increase in $P_b\chi^2$ for NAA-10 can be largely attributed to changes in χ as clearly established by considering the extreme limits of $P_b\chi^2$ from Equation 7 assuming that all of the ions are bound ($P_b = \alpha$) or that none of the ions are bound ($P_b = 0$). This behavior might be projected from a decrease in the local dielectric constant

within the hydrophobic domain affecting the bound sodium ions and is consistent with the I_E/I_M data in Figure 5-3. This will be discussed further in the section to follow on the NMA copolymers.

In Figures 5-7, 5-8, and 5-9, the relaxation rates for PMA, NMA-1, and NMA-10, respectively, are presented with increasing α . In Figure 5-9, the dependence of I_E/I_M on α for NMA-10 is also shown. There are maxima in both R_1 and R_2 at low α for each of the polymers (PMA, NMA-1, and NMA-10). Similar maxima are observed in the behavior of R_{2s} and R_{2f} . This behavior is analogous to that observed for PMA by other researchers.¹¹ As with NAA-1, the incorporation of 1% NAEAM into the copolymer has no observable effect on the relaxation rates compared to the PMA homopolymer.

Biexponential relaxation rates are observed at low α and become exponential with increasing degree of ionization. The magnitude of the relaxation rates is somewhat lower than that observed by Lindman et al.¹¹ and may be due to the differences in the neutralization procedures employed or the polymer concentration. For both NMA polymers, a decrease in R_2 (and R_{2f}) occurs between $\alpha = 0.45$ and 0.60 coinciding with an increase in I_E/I_M observed for these systems.² Again, as with the NAA polymers, this decrease is consistent with the formation of hypercoils as it relates to the hydrophobic environment that the Na^+ ions experience.

In Figures 5-10 and 5-11, the correlation times, τ_c , are plotted as a function of the degree of ionization for NMA-1 and NMA-10. τ_c was determined as before, using Equation 7 (preceding chapter) and the values for P_b from Ander.¹⁶ A decrease in τ_c is observed with increasing α , as previously reported for PMA¹¹ (only the data for NMA-1 are presented in Figure 10, due to the similarity of the calculated τ_c values to those determined for PMA). In Figure 11, τ_c for NMA-10 is observed to increase for α values between 0.3 and 0.55. This, in turn, is manifested as an increase in $P_b\chi^2$ for NMA-10 vs. NMA-1 (Figure 5-12). Values for $P_b\chi^2$ calculated from Equations 10 and 11 (preceding chapter) are also shown in Figure 5-12. These values are somewhat higher than those calculated from Equations 7 and 8, consistent with previous investigations.¹¹

The variation in $P_b\chi^2$ with α for many polymer systems is often rationalized by assuming χ to be constant. Therefore, as α increases, changes in $P_b\chi^2$ would be due only to changes in P_b .^{14,17} This assumption appears to be consistent with experimental data as long as a conformational change does not occur over the range of α values studied. For PMA, however, for which conformational changes have been demonstrated by a number of classical techniques, variations in $P_b\chi^2$ must be due to significant changes in χ as a function of α . As discussed by Lindman et al.¹¹ for PMA, an increase in P_b alone is not sufficient to account for the increase in $P_b\chi^2$ with increasing α . A similar argument is applied to the differences in $P_b\chi^2$ for NMA-10 compared to NMA-1. At $\alpha \approx 0.3$, $P_b\chi^2$ ranges from 0.347 to $0.768 \times 10^{10} \text{ Hz}^2$ (for values of $P_b = 0$ and $P_b = \alpha$, respectively) for NMA-1 and 0.61 to 0.971×10^{10}

Hz² for NMA-10. Thus, if χ were constant for NMA-1 and NMA-10, a near doubling of P_b for NMA-10 compared to NMA-1 would be necessary to account for the increase in $P_b\chi^2$; obviously this is not likely.

Using the values for P_b provided by Ander for PAA¹⁶, a more reasonable dependence of χ on α is shown in Figure 5-13. A significant increase in χ for NMA-10 compared to NMA-1 at low values of α is observed. It has been independently established for the NAA and NMA series that the hydrophobicity of the domains that form at low values for α increases with an increasing amount of NAEAM in the NMA copolymer.² An increase in the hydrophobicity of the domains should result in lowering the local dielectric constant, increasing the strength of the ionic bond between Na⁺ and the carboxylate moieties, and concomitantly increasing χ . Thus, an increase in χ at low α to account for the increases in $P_b\chi^2$ is consistent with results from previous fluorescence studies.² The $P_b\chi^2$ values derived from $\Delta(R_{2f}/R_{2s})$ show the same trend as those from $\Delta(R_1/R_2)$, although the relative error is much larger.

As α increases beyond 0.5, $P_b\chi^2$ increases substantially. Some researchers have demonstrated that this increase is consistent with changes in P_b only.^{14,17} As shown in Figures 5-6 and 5-13, χ increases only slightly for both NAA and NMA at $\alpha > 0.5$ when using experimental P_b values.¹⁴ In this region of α , the increases in $P_b\chi^2$ (Figures 5-5 and 5-12) cannot, at least for these copolymers, be attributed specifically to one parameter (P_b or χ). It is interesting that the increase in $P_b\chi^2$ for both polymer systems is significant in the region of α between 0.5 and 0.6, near Manning's theoretical prediction of $\alpha = 0.65$ for the onset of counterion condensation. This may be coincidental considering that the local dielectric constant values in microphase domains must surely be different from those in bulk solution. However, further study of this observation should be attempted. Also warranting study is Manning's suggestion that the onset of global polymer transitions may be related to the presence of locally folded structures that become extended as the linear charge density parameter, ξ , exceeds one.¹⁸

Conclusions

The data from this study demonstrate that sufficiently large concentrations of hydrophobic groups in PAA and PMA copolymers can cause pH-dependent associations affecting relaxation rates of the Na⁺ counterions. The increase in $P_b\chi^2$ for NAA-10 over that in NAA-1 implies a stronger binding of Na⁺ to the carboxylate sites, consistent with a decreased dielectric constant in the hydrophobic domains. Similar behavior is observed for the NMA-1 and NMA-10 copolyelectrolytes. An increase in the amount of NAEAM in the NMA polymer is reflected in the calculated values of τ_c and $P_b\chi^2$. The $P_b\chi^2$ values of NMA-10 pass through a maximum as α increases, suggesting that an increase in χ is responsible for the

observed behavior. These results are consistent with those previously obtained from fluorescence studies.²

Interpretation of the $P_b\chi^2$ vs. α behavior for the NAA and NMA copolymers should be approached with some caution for the following reasons. Theoretical models (such as Manning's theory or the Poisson-Boltzmann "cell" model) can be used for the estimation of P_b values. However, these models predict different P_b values and do not address local dielectric constant changes. In our study, an experimental measure of P_b for PAA and PMA was used for the determination of τ_c , $P_b\chi^2$, and χ . It has been pointed out that an electrophoretic technique was employed to measure these values of P_b . Furthermore, it has yet to be established that such measured values of P_b would be accurately accommodated by the two-site model used in interpretation of ^{23}Na NMR since the respective time and distance scales of the measurements are significantly different.

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R = -H: NAA-1, 10

R = -CH₃: NMA-1, 10

3772.

Figure 5-1. Structures for NAA and NMA copolymers.

Figure 5-2. Transverse (R_2) and longitudinal (R_1) relaxation rates of PAA and NAA-1 with increasing α . Polymer concentration is 01.g/dL.

Figure 5-3. Transverse (R_2) and longitudinal (R_1) relaxation rates of NAA-10 with increasing α along with the biexponential transverse relaxation rates (R_{2s} and R_{2f}). The ratio of the excimer to monomer fluorescence emission, I_E/I_M , is also shown as a function of α . Polymer concentration is 01.g/dL.

Figure 5-4. Correlation times, τ_c , with increasing degree of ionization, α , for NAA-1 and NAA-10. These data were derived from Equation 8 using the P_b from Anders et.al.¹⁶

Figure 5-5. Values of $P_b\chi^2$ for NAA-1 and NAA-10 derived from Equation 7 using τ_c from Figure 5-4 and P_b from Anders. et. al.¹⁶

Figure 5-6. Values of χ for NAA-1 and NAA-10 derived from Equation 7 using τ_c from Figure 5-5 and the values of P_b from Anders et. al.¹⁶

Figure 5-7. Transverse (R_2) and longitudinal (R_1) relaxation rates for PMA (NMA-0) with increasing α along with the biexponential transverse relaxation rates (R_{2s} and R_{2f}). Polymer concentration is 0.1 g/dL.

Figure 5-8. Transverse (R_2) and longitudinal (R_1) relaxation rates for NMA-1 with increasing α along with the biexponential transverse relaxation rates (R_{2s} and R_{2f}). Polymer concentration is 0.1 g/dL.

Figure 5-9. Transverse (R_2) and longitudinal (R_1) relaxation rates for NMA-10 with increasing α along with the biexponential transverse relaxation rates (R_{2s} and R_{2f}). The ratio of the excimer to monomer fluorescence emission, I_E/I_M , is also shown as a function of α . Polymer concentration is 01.g/dL.

Figure 5-10: Correlation times, τ_C , with increasing degree of ionization, α , for NMA-1. These data were derived from Equation 8 using P_b from Anders.¹⁶

Figure 5-11. Correlation times, τ_c , with increasing degree of ionization, α , for NMA-10. These data were derived from Equation 8 using P_b from Anders et al.¹⁶

Figure 5-12. Values for $P_b \chi^2$ for NMA-1 and NMA-10 derived from Equations 6 and 7 using τ_c from Figures 5-10 and 5-11 and P_b from Anders.¹⁶

Figure 5-13. Quadrupolar coupling constants, χ , for NMA-1 derived from Equations 6 and 7 using τ_c from Figure 5-8 and P_b from Anders.¹⁶

CHAPTER 6. ION-BINDING STUDIES OF HYDROPHOBICALLY-MODIFIED COPOLYMERS OF 2-(1-NAPHTHYLACETAMIDO)ETHYLACRYLAMIDE WITH ACRYLIC ACID AND METHACRYLIC ACID

Abstract

^{23}Na NMR studies of counterion relaxation behavior in the presence of added electrolytes have been performed to determine the relative binding affinities of Na^+ , K^+ , Mg^{++} , and Ca^{++} ions to the homopolymers of poly(sodium acrylate) (NaAA), poly(sodium 2-acrylamido-2-methylpropanesulfonate) (NaAMPS), and poly(sodium 3-acrylamido-3-methylbutanoate) (NaAMB). The addition of Mg^{++} and Ca^{++} to the biopolymer poly(sodium galacturonate) (NaGAL) was also investigated. Addition of salts yielded the order of binding $\text{Ca}^{++} > \text{Mg}^{++} > \text{K}^+ \approx \text{Na}^+$ for NaAA and NaAMB, $\text{Ca}^{++} \approx \text{Mg}^{++} > \text{K}^+ > \text{Na}^+$ for NaAMPS. Significant differences in the ^{23}Na NMR behavior for NaAA are observed for added Mg^{++} and Ca^{++} and were interpreted in terms of hydration of the polyelectrolyte near phase separation, although a conformational change cannot absolutely be ruled out. Differences observed upon addition of Mg^{++} and Ca^{++} in the NaGAL system are discussed in relation to the "egg-box" model of Ca^{++} binding to NaGAL. Viscosity profiles for each of the polymers with the above cations are related to the NMR data. Phase separation studies on NaAMB demonstrate increased hydrophobicity of the polymer in the presence of excess Ca^{++} .

Introduction

The behavior of uncharged polymers and polyelectrolytes in the presence of simple electrolytes is a subject of continuing research in our laboratory. The large viscosity losses and, ultimately, phase separation of anionic polyelectrolytes by a divalent cation are due to the strong chelating effect that reduces hydrodynamic volume and solvation. Sufficient inter- and intramolecular binding occurs to reduce the hydration of the polymer to a critical point at which phase separation occurs. The maintenance of viscosity in high concentrations of electrolytes is critical for application of polymers in areas such as enhanced oil recovery, drag reduction, and controlled release. Synthetic efforts have resulted in polymer systems that maintain viscosity in the presence of both monovalent and divalent ions and do not phase separate readily.¹⁻⁵ An increased understanding of the ion-binding and phase separation phenomena of these polymers is necessary for tailoring polymer systems for use in areas where high salt concentrations adversely affect performance.

The viscosity behavior and phase stability of polyelectrolytes in the presence of excess salts have been extensively studied.¹⁻¹⁴ Poly(acrylates)⁶⁻⁸ and hydrolyzed polyacrylamide (HPAM)^{1,9-11} exhibit large viscosity losses and may phase separate in the presence of divalent counterions such as Mg^{++} , Ca^{++} , and Ba^{++} . Poly(sodium acrylate) (NaAA) precipitates from solution when the concentration of divalent counterion (Mg^{++} , Ca^{++} , Ba^{++}) reaches a critical value relative to the number of anionic sites available (approximately 0.8 on an equivalent basis).⁶ Macroscopic

solution properties (viscosity, phase separation) of poly(vinylsulfonate) (PVS) are dependent on the nature of the counterion species.^{13,14}

Copolymers of acrylamide with sodium 2-acrylamido-2-propanesulfonate (NaAMPS)^{1,3,4} and 3-acrylamido-3-methylbutanoic acid (NaAMB) maintain viscosity in high concentrations of divalent salts and do not phase separate in the presence of Ca^{++} at temperatures up to 100°C (polymer structures are shown in Figure 6-1).^{3,4} However, unlike NaAMPS, the NaAMB homopolymer will phase separate at temperatures above 70°C in high concentrations of CaCl_2 .³ The amount of Ca^{++} necessary to precipitate NaAMB far exceeds the stoichiometric concentration required to bind to all of the anionic sites. This difference has been attributed to a weaker binding of the divalent ion to the sulfonate moiety in NaAMPS and the possibility of intramolecular ion complexation of the divalent ion to the pendent NaAMB side-chain, preventing formation of insoluble ionic bonds.⁴

The subject of this work was to investigate homopolymers of NaAA, NaAMB, and NaAMPS to determine the relative binding characteristics of cations, Na^+ , K^+ , Mg^{++} , and Ca^{++} , and to elucidate structural influence on macroscopic solution behavior (i.e., viscosity and phase separation). In particular, we wished to ascertain differences in binding characteristics of carboxylate or sulfonate functional groups near to or removed from the polymer backbone. Comparison of the behavior between homopolymers of NaAA, NaAMB, and NaAMPS have thus been made. ^{23}Na nuclear magnetic resonance (NMR) relaxation rate studies have been performed on these polymers both with and without added electrolytes. ^{23}Na NMR measurements of poly(sodium galacturonate) (NaGAL) with added Mg^{++} and Ca^{++} are also included since specific differences in the binding of ions are known to occur. Viscosity profiles of NaAMB and NaAMPS in the presence of each of the salts are presented as well as phase behavior studies on NaAA and NaAMB.

The ^{23}Na relaxation rates for the polyion systems studied in this work have been employed to yield correlation times, τ_c , by employing a theoretical estimate for the fraction of bound monovalent ions, P_b , in the presence of excess divalent ions. Correlation times were then utilized to obtain values for the quadrupolar coupling constant, χ . Values for P_b for Na^+ in the presence of excess divalent ions were determined using the Manning two-variable theory,¹⁵ which has been demonstrated to be qualitatively descriptive of the fraction of ions bound in the presence of divalent ions.¹⁹⁻²¹

Background

Manning's treatment of polyelectrolyte behavior is based on the reduction of the dimensionless linear charge density, ξ , to $\xi_{\text{crit}}=1$ by "condensation" of sufficient numbers of counterions according to (1)

$$\xi = \frac{\alpha e^2}{\epsilon k T l} \quad (1)$$

where ϵ is the dielectric of the medium (78.54 for water), α is the degree of ionization, and l is the charge separation along the backbone. For polyelectrolytes prepared from vinyl monomers, $l = 0.25$ nm leading to the value of 2.85 for ξ . The fraction of counterions bound to a poly(sodium acrylate) solution (NaAA) is predicted to be 65%.¹⁵ For a divalent ion ($z = 2$) such as Ca^{++} , the fraction of bound ions is predicted to be much higher (82% on an equivalent basis). However, this approach cannot account for differences in the residence times of Na^+ ions at the polyion surface and treatment of the dielectric constant at the polyion surface has been questioned.¹⁶ Although Manning's approach has been very successful in many respects, ^{23}Na NMR studies have observed counterion-polymer interactions inconsistent with the theory.¹⁷ In some cases, changes in counterion relaxation behavior as a function of the degree of ionization and concentration are better modelled using the Poisson-Boltzmann "cell" model.¹⁸ However, for cases of added salt, solutions to the Poisson-Boltzmann equation require numerical analysis. Again, the treatment of dielectric constant is likely insufficient.

Kwak and coworkers¹⁹⁻²¹ have used Manning's two-variable theory as a theoretical basis for predicting the binding of divalent ions to biopolymers such as dextran sulfate¹⁹ and heparin²⁰, and the synthetic polymers, carboxymethylcellulose²¹ and poly(styrenesulfonate)²¹ in mixed electrolyte systems. The activity coefficients of Mg^{++} and Ca^{++} were determined by a dye-fluorescence technique and their binding behavior studied as a function of ionic strength. The ion-binding effects for dextran sulfate indicated that, in general, Ca^{++} ions had a greater affinity for the polymer and their behavior was better described by the model than Mg^{++} ions under similar conditions.¹⁹ This work also revealed that the ionic strength dependence of the degree of binding was determined by the nature of the added monovalent ion, Na^+ or K^+ . In a similar study²¹, the binding of Ca^{++} to polygalacturonate (pectin) was found to be much stronger than that predicted on the basis of Manning's theory. In contrast, the theory was very successful for binding of Mg^{++} and Ca^{++} to poly(styrenesulfonate) where no specificity between the ions was observed.²¹

Ion-association and changes in water structure surrounding the polyelectrolyte upon binding have been investigated by dilatometry^{13,22,23}, refractive index studies,²⁴ sound-velocity measurements^{25,26}, and determination of activity coefficients.^{19-21,28-30} Specific ion effects have been observed in viscosity¹⁴ and volume changes for different ions.^{13,22,23,27} The dehydration of Mg^{++} and Ca^{++} ions upon binding to NaAA indicates that Ca^{++} ion forms intimate ion pairs with NaAA, while Mg^{++} does not.^{25,26}

The gelling behavior of several naturally-occurring polysaccharides in the presence of Ca^{++} has been extensively studied.³¹⁻³⁵ The so-called "egg-box" model of binding has been reported for the carrageenans, alginates, and pectins.³¹ In this model, the gelation of certain polysaccharides in the presence of Ca^{++} initially proceeds through the formation of dimers in which Ca^{++} ions are sandwiched between the helical polysaccharide chains.³²⁻³⁴ The Ca^{++} ions are tightly bound and

cannot be removed even during extensive dialysis against high concentrations of monovalent salts.^{32,33} A number of studies have shown that the amount of Ca^{++} bound to the dimers is approximately 50% of the stoichiometric amount of carboxylate groups present.^{32,33} As the amount of Ca^{++} is increased, the ions bind to the exposed carboxylate groups on the dimers until nearly 100% of the stoichiometric requirement of carboxylate groups is fulfilled; at this point an extensive gel network forms.³² The gelation occurs with a number of divalent ions including Ca^{++} , Ba^{++} , Sr^{++} , Cu^{++} , Cd^{++} and Ca^{++} , but not with Mg^{++} . This is reportedly due to the small size of Mg^{++} and its inability to fit within the interstices of the polysaccharide chains.³⁵

²³Na NMR and Polyelectrolytes. ²³Na nuclei are well suited for the study of cation binding behavior to electrolytes due to a 100% natural abundance and a high magnetogyric ratio that allow observation by NMR. The sodium ion has a spin 3/2 nucleus in which relaxation is dominated by quadrupolar effects in solution. The relaxation rates, R_1 and R_2 , are sensitive to changes that affect the overall motion in solution and to electric field gradients (efg) about the nuclei. ²³Na relaxation rate measurements and chemical shift values thus provide a means for investigation of cation binding to polyelectrolytes^{17,36-45} and observation of conformational changes that may occur as the degree of ionization along the polymer backbone increases.^{41,43,46,47}

The results for ²³Na NMR relaxation studies have generally been interpreted using a two-site model for the observed linewidths or relaxation rates.^{17,36,41,43} The two-site model is justified when the exchange rate for the Na^+ nuclei between the polyanion and bulk solution is faster than the NMR observation time, usually the case for the sodium salts of polyanions. The observed relaxation rates are, therefore, an average of the relaxation rates for the unbound fraction (P_F) or free sodium nuclei and the fraction of ions bound (P_b) to the polymer,

$$R_{1,\text{obs}} = P_F R_{1,F} + P_b R_{1,b} \quad (2)$$

$$R_{2,\text{obs}} = P_F R_{2,F} + P_b R_{2,b} \quad (3)$$

The magnitude of the relaxation rate depends on the strength of the efg experienced by the sodium nuclei at the polyion surface, the lifetime of the Na^+ at the site, and the number of the sodium nuclei that are bound.⁴² The longitudinal and transverse relaxation rates generally display single exponential behavior of the intensity of the NMR signal (M_{obs}) as a function of t , the relaxation delay.

$$M_{L,\text{obs}}(t) - M_{L,0} = (M_L(0) - M_{L,0}) \exp(-R_1 t) \quad (4)$$

$$M_{T,\text{obs}}(t) = M_t(0) \exp(-R_2 t) \quad (5)$$

This is a result of the rapid motion and reorientation of the sodium nuclei such that $\omega\tau_c < 0.25$ and consequently, $R_1=R_2$. Under conditions of fast exchange and $\omega\tau_c > 1.5^{42}$, R_1 is no longer equal to R_2 , and the relaxation rates become biexponential decays of the intensity of the NMR transition and the relaxation delay, t .⁴⁸

$$M_{L,obs}(t) = M_L(0) 0.6 \exp(-R_{2f}t) + M_L(0) 0.4 \exp(-R_{2s}t) \quad (6)$$

Here R_{2f} and R_{2s} refer to the fast and slow components of the relaxation decay. In practice, only the transverse relaxation has been observed to display significant biexponential decay with the longitudinal relaxation having single exponential behavior.^{44,47} When $0.25 < \omega\tau_c < 1.5$, the biexponential behavior is diminished but the relaxation rates are approximately exponential with $R_1 \neq R_2$. Under these conditions, τ_c can be obtained from the ratio of R_1 to R_2 .^{36,47}

$$R_1 = (1-P_b)R_{1,F} + \frac{2P_b\pi^2\chi^2\tau_c}{5} \left(\frac{0.2}{1 + \omega^2\tau_c^2} + \frac{0.8}{1 + 4\omega^2\tau_c^2} \right) \quad (7)$$

$$R_2 = (1-P_b)R_{2,F} + \frac{P_b\pi^2\chi^2\tau_c}{5} \left(0.6 + \frac{1}{1 + \omega^2\tau_c^2} + \frac{0.4}{1 + 4\omega^2\tau_c^2} \right) \quad (8)$$

$$\Delta\left(\frac{R_1}{R_2}\right) = \frac{R_1 - P_F R_{1,F}}{R_2 - P_F R_{2,F}} = \frac{\frac{1.6}{1 + 4\omega^2\tau_c^2} + \frac{0.4}{1 + \omega^2\tau_c^2}}{0.6 + \frac{0.4}{1 + 4\omega^2\tau_c^2} + \frac{1}{1 + \omega^2\tau_c^2}} \quad (9)$$

As τ_c becomes larger and $\omega\tau_c$ exceeds 1.5, the biexponential relaxation is pronounced and τ_c may be found from the ratio of R_{2s} to R_{2f} .⁴⁷

$$R_{2f} = (1-P_b)R_{2,F} + \frac{P_b\pi^2\chi^2\tau_c}{5} \left(1 + \frac{1}{1 + \omega^2\tau_c^2} \right) \quad (10)$$

$$R_{2s} = (1-P_b)R_{2,F} + \frac{P_b\pi^2\chi^2\tau_c}{5} \left(\frac{1}{1 + \omega^2\tau_c^2} + \frac{1}{1 + 4\omega^2\tau_c^2} \right) \quad (11)$$

$$\Delta\left(\frac{R_{2f}}{R_{2s}}\right) = \frac{R_{2f} - P_F R_{2,F}}{R_{2s} - P_F R_{2,F}} = \frac{1 + \frac{1}{1 + \omega^2 \tau_c^2}}{\frac{1}{1 + \omega^2 \tau_c^2} + \frac{1}{1 + 4\omega^2 \tau_c^2}} \quad (12)$$

The correlation time, τ_c , is determined by employing a theoretical estimate for P_b ⁴⁷ or by assuming $P_F \gg P_b$ ⁴¹. Once τ_c is known, $P_b \chi^2$, the product of P_b and χ , the quadrupolar coupling constant, may be determined. χ is a measure of quadrupolar interactions and is proportional to the magnitude of the efg experienced by the counterion nuclei. The determination of χ requires independent knowledge of P_b . Using theoretical estimates for P_b , χ has been found to range from 35 - 700 kHz^{36,37}, although some researchers have reported higher values.⁴⁹ The value of the quadrupolar coupling constant is expected to increase as the strength of binding increases³⁶ and higher values (1.2 MHz) have been attributed to site binding of the sodium counterion to anionic sites on heparin.⁴⁹ Grasdalen and Kvam reported χ values of 440 and 770 kHz for polymannuronate and polyguluronate, respectively, although these higher values could not be absolutely ascribed to site binding.³⁶

Lindman and coworkers⁴¹ used ²³Na NMR to identify an increased affinity of potassium over sodium in solutions of multi-chain chondroitin sulfate (CS) at low pH. A more rapid decrease in the transverse relaxation rate of sodium ions upon addition of a particular competing cation is interpreted as an increased affinity compared to Na⁺. This behavior has been employed to rank relative binding affinities of Na⁺ and K⁺ to solutions of CS. However, addition of calcium to a multichain CS caused a sharp increase in R_2 which has been interpreted either as a change in the polymer conformation or an aggregation of individual polymer chains.⁴¹ Similar behavior has been observed for addition of Mg⁺⁺ to vascular connective tissue and is ascribed to a conformational change in the polyelectrolyte in the presence of Mg⁺⁺.⁴³ The concentration dependence of R_2 in PMA⁴⁷ and increases in the sodium counterion linewidth upon storage of polyguluronate³⁶ solutions have been attributed to aggregation phenomena.

Recently, Spencer *et al.* have conducted several studies employing ²³Na NMR to determine relative binding strengths of various ions with a number of polymer systems.^{17,38-40} Solutions of PVS³⁹ and PSS¹⁷ were found to bind the counterions in order of preference of Cs⁺ > Rb⁺ > K⁺ > Na⁺ > Li⁺. However, polyelectrolytes, such as NaGAL and NaAA, containing carboxylate moieties indicated no preference for any of the monovalent ions studied. The Poisson-Boltzmann "cell" model was found to be predictive of the binding behavior of Mg⁺⁺ in NaGAL, NaAA, and sodium malonate solutions.^{17,38-40}

Experimental Section

Materials. 2-Acrylamido-2-methylpropanesulfonate (AMPS) was washed repeatedly with 2-propanol to remove impurities and vacuum dried at 30 °C before use. All salts (KCl, NaCl, CaCl₂, MgCl₂, Mg(NO₃)₂, and Ca(NO₃)₂) were 99.98% purity or greater and were purchased from Aldrich Chemical Company. Potassium persulfate was obtained from Aldrich Chemical Co. and was recrystallized in water prior to use. 3-Acrylamido-3-methylbutanoic acid (AMB) was synthesized via a Ritter reaction using acrylonitrile and 3,3-dimethylacrylic acid in the presence of water and excess sulfuric acid.⁵⁰ Polygalacturonic acid (MW between 25 - 50,000 g/mol) was purchased from Fluka.

Polymer Synthesis. Polymers of NaAA, NaAMB, or NaAMPS were prepared at a concentration of 0.45 M by free radical initiation in water at 30 °C using potassium persulfate. After dissolution of the monomer, the pH of the solution was adjusted to 9 by addition of NaOH to insure that the monomer was present in the ionized form (NaAMB and NaAMPS). Excess NaOH was used in the polymerization of NaAA to minimize chain end repulsion to yield a higher MW. The mixture was purged with nitrogen for 20 minutes before initiation with an appropriate amount of potassium persulfate (0.1 mole percent). After 4-6 hours, the reaction mixture was diluted with 2-4 volumes of H₂O followed by precipitation of the polymer in reagent grade acetone while stirring. The polymer was washed repeatedly with excess acetone and vacuum dried at 40 °C before dissolution into H₂O. The aqueous polymer solution was dialyzed in water for one week before freeze-drying. The polymer was vacuum dried at 40°C overnight and stored under desiccant. Polymer conversions were approximately 50%. The molecular weights of NaAMB and NaAMPS homopolymers were approximately 3×10^6 g/mole.⁵¹ The viscosity average MW of the NaAA homopolymer was estimated from the Mark-Houwink parameters to be approximately 6×10^5 g/mole.

Poly(sodium galacturonate) (NaGAL) was prepared by neutralization with NaOH to pH 7.7. Dialysis was performed to remove excess salt.³⁵ Given the temporal nature of gel formation³⁴, Ca⁺⁺/NaGAL solutions were allowed at least 30 minutes to reach equilibrium and were checked at regular intervals over the course of 24 hrs for changes in the ²³Na relaxation rates.

NMR, Viscosity, and Phase Separation Measurements. Sodium NMR measurements were conducted at 25 °C with a Bruker MSL-400 operating at 105.6 MHz for ²³Na nuclei.

All polymers were vacuum-dried overnight at 40°C prior to use. Salts were vacuum-dried at 80°C and 5 Torr pressure before use. Polymer solutions were prepared at 0.1 g/dL concentration with 5% D₂O to provide a frequency lock. The polymer concentration was chosen for these studies to provide a good signal-to-noise with a reasonable number of scans and a reasonably low solution viscosity. Solution volumes for the NMR measurements were 4 mL. Salt solutions were prepared at concentrations between 0.25 and 1M to cover a range of cation/polymer

ratios on an equivalent basis. The maximum volume addition to a polymer solution was 200 μL . Addition of an equivalent amount of H_2O to a control polymer solution resulted in no change in the relaxation rate of the Na^+ ions due to dilution effects. R_1 and R_2 measurements on similar concentrations of NaCl solutions were found to have values of 17.3 and 30.3 sec^{-1} , respectively, and were employed in all calculations involving R_1 and R_2 . The relaxation rates for the monomers, NaAA, NaAMB, and NaAMPS, were also measured and were close to those values for sodium chloride. The natural linewidth of a sodium counterion is 16.7 sec^{-1} and this value is used in all calculations involving R_{2s} and R_{2f} .⁴⁷ All calculations and curve fitting were performed with the commercial software program Mathcad®. The experimental errors on the plots are the errors about the mean at the 95% confidence level.

Viscosity measurements were conducted on a Cannon-Fenske capillary viscometer at 25°C and a polymer concentration of 0.1g/dl. Polymer solutions were aged for at least one month prior to measurement. Phase separation studies were performed on a Brinkmann PC-800 colorimeter using solutions identical to those employed in the viscosity measurements.

Results and Discussion

²³Na NMR. Interpretation of the ²³Na NMR measurements require the condition of fast exchange such that the observed relaxation rates are an average of the bound and unbound Na^+ ions (two-site model). This was verified as an increase in R_{2s} with reciprocal of temperature (Figure 6-2), as described by Grasdalen and Kvam³⁶ and has been reported for a number of polyelectrolytes.^{36,37,44,47} The relaxation data are plotted versus the ratio of the number of equivalents of added salt to the number of charged polymer sites.

Biexponential relaxation rates were observed to be time-dependent in solutions of NaAA, NaAMB, and NaAMPS, with R_{2f} decreasing slightly to a constant value over the course of approximately one month. This behavior is reminiscent of the time-dependency in the viscosity of NaAMB² and is consistent with initial clustering of polymer chains upon dissolution that slowly deaggregate. Polymer solutions, stored in polypropylene containers to eliminate the possibility of Na^+ ions diffusing into the solutions from glass, behaved the same as those stored in glass containers. The increase in biexponential relaxation ($\Delta R_2 = R_{2f} - R_{2s}$) with decreasing polymer concentration for NaAA correlated with that predicted by Halle et al.³⁷ ΔR_2 with no added salt is approximately 140 Hz for the polymer concentration (0.011M) employed in this work.³⁷

The behavior of R_2 for sodium counterions with NaAA in the presence of added Na^+ and K^+ is shown in Figure 6-3. The effect of added Na^+ on R_1 is also shown. The R_1 data for K^+ and the single exponential fits to the transverse relaxation are not presented to avoid further confusion on the plots. The R_1 data for K^+ are nearly identical to those for Na^+ . The experiments by Leyte and coworkers demonstrated that the biexponential behavior of sodium poly (styrene sulfonate),

NaPSS, diminished as the concentration of added NaCl increased to approximately twice the polymer concentration.^{37,44} In Figure 6-3, R_{2f} and R_{2s} reach similar values at $C_{\text{salt}}/C_p \approx 3$. Biexponential relaxation of NaAA with added Na^+ and K^+ is nearly identical, indicating similar binding of the ions to NaAA.

In Figure 6-4, the relaxation rates are plotted as the concentration of Mg^{++} ion increases. R_{2s} and R_{2f} decrease gradually to the values corresponding to those obtained ($C_{\text{Mg}^{++}}/C_p \approx 0.8$) where a slight increase in the relaxation rates is observed and the polymer precipitates from solution. In Figure 6-5, both relaxation rates initially decrease with added Ca^{++} as observed with Mg^{++} . However, at $C_{\text{Ca}^{++}}/C_p \approx 0.8$, a sharp rise in R_{2f} occurs. This increase in R_{2f} occurs just prior to the Ca^{++} concentration that causes phase separation of the polymer from solution, as measured from turbidimetry (see Table 6-I). There is also a small increase in R_{2s} prior to phase separation. If the increase in the biexponential relaxation behavior were due solely to aggregation, the R_2 behavior would be similar for Mg^{++} and Ca^{++} . These data suggest that a conformational transition or rearrangement of the polymer chains occurs upon binding of Ca^{++} ; such an event is not observed with Mg^{++} . The biexponential relaxation persists at phase separation for both divalent ions, indicating that a significant amount of Na^+ is bound to the chain in the presence of excess divalent salt.

The changes in R_{2s} and R_{2f} with added salt for the individual polymers NaAMB and NaAMPS are shown in Figures 6-6 thru 6-9. Again, as in Figure 6-3, the R_1 data for K^+ and the single exponential fits to the transverse relaxation data are not presented. In Figure 6-6, R_{2f} exhibits a more negative slope in the presence of K^+ than Na^+ for NaAMPS. This behavior demonstrates that K^+ is binding tighter to NaAMPS than Na^+ . Literature precedent for this has been reported for sulfonated polyelectrolytes such as PSS¹⁷ and PVS.³⁹ In Figure 6-7, Mg^{++} and Ca^{++} behave similarly upon binding to NaAMPS, indicating a lack of specificity.

The binding of Na^+ and K^+ to NaAMB is presented in Figure 6-8. The behavior of R_{2s} and R_{2f} is nearly identical for these ions. Figure 6-9 depicts the effect of addition of Mg^{++} and Ca^{++} on the transverse relaxation rate behavior of NaAMB. The decrease in R_{2f} is greater for Ca^{++} than for Mg^{++} indicating a slight preference for Ca^{++} binding to NaAMB. At the higher C_{Salt}/C_p ratios, R_2 values are slightly smaller in the presence of Ca^{++} as compared to Mg^{++} .

In Figure 6-10, $P_b \chi^2$ for NaAA is plotted as a function of C_{Salt}/C_p for Mg^{++} and Ca^{++} . Values of $P_b \chi^2$ have been calculated using Equation 12 with a theoretical estimate for P_b to determine τ_c ; equation 11 is used to determine χ . Manning's two variable theory¹⁵ has been employed for estimation of the fraction of bound sodium ions with increasing concentration of divalent ions. Although Manning theory is reported to be inconsistent in regard to the concentration dependence of the ^{23}Na relaxation rates for polyelectrolytes³⁶, the two-variable theory has been successfully employed for predicting P_b in some polyelectrolytes, based on activity coefficients.²¹ Also included in Figure 6-10 are estimates for the upper and lower limits for the fraction of sodium ions bound assuming P_b is, for a lower limit, $0.2 - C_{\text{Salt}}/C_p$ with the lowest possible value of $P_b = 0.01$. The upper limit of binding is chosen to be $P_b =$

0.8 - C_{Salt}/C_p with the lowest value of $P_b = 0.1$. These limits are independent of any theories and represent reasonable estimates for the upper and lower values of P_b over the course of this experiment.

An increase in $P_b\chi^2$ is observed with increasing Ca^{++} near phase separation, suggesting either a sudden increase in P_b or χ . In Figure 6-11, $P_b\chi^2$ values for NaAA with Mg^{++} and Ca^{++} are shown using the Manning prediction for P_b . An increase in $P_b\chi^2$ is not observed in the presence of Mg^{++} below $C_{\text{Ca}^{++}}/C_p \approx 0.8$. The maximum limits of $P_b\chi^2$ for Mg^{++} range from 0.68 ($P_b = 1$) to $1.44 \times 10^{10} \text{ Hz}^2$ ($P_b = 0$) for $C_{\text{Mg}^{++}}/C_p = 0.8$. The experimentally observed value of $P_b\chi^2$ for Ca^{++} of approximately $2 \times 10^{10} \text{ Hz}^2$ cannot be accounted for by changes in P_b alone since the P_b value for Na^+ at $C_{\text{Ca}^{++}}/C_p$ of 0.8 would have to nearly triple to yield the observed values of $P_b\chi^2$. Even at the unreasonable limits of $P_b = 0$ and $P_b = 1$, the magnitude of $P_b\chi^2$ observed for Ca^{++} cannot be attained using Equation 12, without significant changes in χ over $C_{\text{Ca}^{++}}/C_p$ values of 0.6 to 0.8 in the NaAA/ Ca^{++} system.

Previous literature studies have shown that Mg^{++} does not bind as strongly as Ca^{++} to NaAA and that the hydration sphere of Mg^{++} is less perturbed on binding.^{6,25,26} A less hydrated coil in the presence of Ca^{++} would result in a lower local dielectric constant and a concomitant increase in χ for the sodium ions that remain bound within the polymer domain. However, a conformational change of NaAA in the presence of Ca^{++} near phase separation that affects the τ_c values cannot be ruled out.

Measured values of the quadrupolar coupling constant, χ , as function of $C_{\text{Ca}^{++}}/C_p$ yield some insight into solution behavior. As shown in Figure 6-1, NaAMB and NaAMPS have identical structural components except for the carboxylate and sulfonate moieties, respectively. For NaAA, the carboxylate moiety is located closer to the backbone. For Manning's two-variable theory, values for P_b for each of these polymers would be identical for a given $C_{\text{Ca}^{++}}/C_p$ value. Using such an assumption, Figure 6-12 was constructed from Equation 8 for NaAMB and NaAMPS and Equation 11 for NaAA.

Several features of this plot should be addressed. First of all, only slight differences in χ are exhibited by NaAMB and NaAMPS. χ values above $C_{\text{Ca}^{++}}/C_p > 0.4$ diverge to a small but significant degree. This is consistent with a slightly stronger binding of Ca^{++} to the carboxylate units on NaAMB as compared to the sulfonate units on NaAMPS. However, experiments with Ca^{++} selective electrodes at $C_{\text{Ca}^{++}}/C_p = 1$, yielded P_b values for Ca^{++} of 0.71 and 0.66 in 0.36M KCl for NaAMB and NaAMPS, respectively.^{4,52} Since values of χ in Figure 6-12 were constructed from $P_b\chi^2$ data, differences in behavior of NaAMB and NaAMPS may actually reflect differences in P_b .

A second striking feature in Figure 6-12 is the rapid increase in χ for $C_{\text{Ca}^{++}}/C_p$ values of 0.6 to 0.8 for NaAA. As discussed previously, the magnitude of this increase cannot be accounted for by changes only in P_b and must be due to changes in χ . A third feature is the lack of change in χ over the range of $C_{\text{Ca}^{++}}/C_p$ values for both NaAMB and NaAMPS as compared to NaAA. In the former cases, it is likely

that little conformational change occurs, while in the latter, dramatic molecular structural changes probably ensue with a maximum in χ at $C_{Ca^{++}}/C_p = 0.8$ at phase separation. Note that no such increase is observed for Mg^{++} (Figure 6-11). The increased magnitude of χ for NaAA compared to NaAMB and NaAMPS is consistent with an increased local dielectric constant with ionic sites tethered away from the more hydrophobic backbone. In addition, χ values calculated from biexponential relaxation rates (Equations 11 and 12) have been previously reported to yield higher values for χ compared to those obtained from R_1 and R_2 (Equations 8 and 6-9).⁴⁷

In Figure 6-13, the relaxation rates for NaGAL are plotted as a function of increasing Mg^{++} . Both R_{2s} and R_{2f} follow a smooth decrease that levels out at higher $C_{Mg^{++}}/C_p$ values. This is similar to the behavior observed for NaAA. The decrease in both relaxation rates is due to a smaller fraction of Na^+ ions binding to the polyelectrolyte as the concentration of the divalent ion increases. The relaxation rates reach a constant value as the bound Na^+ ions are replaced by Mg^{++} . However, the biexponential relaxation behavior would be expected to diminish if all of the Na^+ ions were no longer associated with the NaGAL chain. Thus, a significant number of the Na^+ ions appear to be associated in some fashion with the chain even though sufficient numbers of Mg^{++} ions are present to bind all of the carboxylate sites.

In Figure 6-14, the transverse relaxation rates of the Na^+ counterions are plotted as a function of increasing Ca^{++} concentration. The behavior is markedly different from that observed for added Mg^{++} ions. R_{2f} increases while R_{2s} decreases up to $C_{Ca^{++}}/C_p \approx 0.4-0.5$, at which point R_{2f} begins to decrease in similar fashion to R_{2s} . At $C_{Ca^{++}}/C_p > 1$, both relaxation rates drop precipitously, indicating a sharp decrease in the amount of Na^+ that is bound to NaGAL. This behavior can be rationalized in terms of the "egg-box" model proposed by Rees and coworkers for poly(galacturonic acid).³⁷ As the concentration of Ca^{++} ions increases up to $C_{Ca^{++}}/C_p \approx 0.5$, bound Na^+ ions are replaced and R_{2s} decreases. The increase in R_{2f} is probably due to the dimerization of the NaGAL chains which effectively dilutes the polyelectrolyte in the solution. The decrease in concentration from 0.0046 M to 0.0023 M has been predicted to increase ΔR_2 by approximately 210 Hz.³⁷ Assuming the two site model with $R_{2,obs} = R_{2f}$ and using $P_b = 0.26$ ⁴⁷ to find $R_{2b} = 2245$ Hz (Equation 3), the decrease in R_{2f} due to displacement of half of the bound Na^+ ions ($P_b = 0.13$) is approximately 320 Hz. The decrease in R_{2f} due to a lower fraction of bound Na^+ would be nearly offset by the increase in ΔR_2 due to dimerization. When the concentration of Ca^{++} ions increases beyond $C_{Salt}/C_p \approx 0.5$, both relaxation rates should decrease; the bound Ca^{++} ions approach the stoichiometric number of carboxylate moieties, expelling Na^+ ions from the network thus causing a sharp drop in the relaxation rates. Consistent with experimental results from the Mg^{++} /NaGAL system, a significant fraction of Na^+ apparently remains bound (evidenced by the persistence of the biexponential relaxation at $C_{Salt}/C_p \approx 1$).

Viscosity and Phase Separation. In Figures 6-15 and 6-16, the relative viscosities versus C_{Salt}/C_p (Na^+ and Ca^{++}) are presented for NaAMB and NaAMPS, respectively. The relative viscosities of the polymers differ due to a slightly higher molecular weight and a higher repeat unit concentration for the NaAMB homopolymer. In both figures, the viscosity is reduced dramatically with increasing C_{Salt}/C_p and nearly level above $C_{\text{Salt}}/C_p \approx 1$ for added Mg^{++} and Ca^{++} . This behavior parallels the NMR results which indicate that, at higher C_{Salt}/C_p ratios, the divalent ions replace most of the Na^+ ions. Since addition of more divalent ion does not reduce the viscosity beyond a residual relative value, the remaining hydrodynamic volume is likely due to hydration of polymer segments not involved in ion-binding. In contrast, NaAA precipitates from solution when a critical ratio of added divalent ion (Mg^{++} , Ca^{++} and Ba^{++}) to the number of anionic sites is reached.¹³

Phase separation studies of NaAMB in the presence of divalent salts were conducted in an effort to clarify the mechanism for phase separation of this polyelectrolyte. CaCl_2 causes precipitation of NaAMB homopolymer at high temperatures; MgCl_2 does not.⁵¹ Addition of $\text{Mg}(\text{NO}_3)_2$, MgSO_4 , and MgCl_2 to a 0.1 g/dL solution of NaAMB results in no precipitation of the polymer from solution. Addition of $\text{Ca}(\text{NO}_3)_2$ and CaCl_2 has different effects on the phase separation temperature (T_c) of NaAMB as shown in Figure 6-17. CaCl_2 depresses T_c to a larger degree (salting out) than $\text{Ca}(\text{NO}_3)_2$. This is the expected behavior when hydrophobic interactions influence the phase separation.⁵³⁻⁵⁵ The dependence of the T_c with added urea at constant CaCl_2 is also shown in Figure 6-17. Urea is a known water-structure breaking agent and causes a disruption of hydrophobic bonding in aqueous systems.⁵⁶ The increase in T_c with increasing urea concentration also suggests that hydrophobic effects play a role in the phase separation mechanism in NaAMB.

Conclusions

The differences in the phase separation behavior of NaAMB and NaAMPS in the presence of Ca^{++} have been previously attributed to a weaker binding of the ion to the polymer sites and is consistent with the ^{23}Na NMR results presented here. A faster decrease for R_{2f} and $P_b\chi^2$ values are observed for added Ca^{++} as compared to Mg^{++} in NaAA; thus, the relative ion affinity is $\text{Ca}^{++} > \text{Mg}^{++} > \text{Na}^+ \approx \text{K}^+$. An increase in χ is demonstrated for NaAA in the presence of Ca^{++} near phase separation. The ^{23}Na NMR relaxation measurements of NaGAL in the presence of Mg^{++} indicate simple exchange of Mg^{++} for Na^+ at the anionic sites. However, addition of Ca^{++} to NaGAL solutions results in complex relaxation rate behavior consistent with an interpretation based on the "egg-box" model. For NaAMB, the order is the same as that for NaAA with a slight preference for Ca^{++} over Mg^{++} . For NaAMPS, the order of binding is $\text{Ca}^{++} \approx \text{Mg}^{++} > \text{K}^+ > \text{Na}^+$.

The NMR studies performed here cannot distinguish between intra- and inter-mer complexation of divalent ions to the side chains of NaAMB. However, the estimated χ values suggest that the lack of phase separation of NaAMB and

NaAMPS as compared to NaAA is related to differences in affinities of ions for the respective polymers.

The turbidimetric studies illustrate the effects of hydrophobicity in phase separation. It appears that χ increases in a more hydrophobic environment (see following paper) and the relationships between the local dielectric constant and ion-binding are important in phase separation. In the studies performed on NaAA, the changing local environment experienced by the Na^+ ion may be observed by following changes in χ with added Ca^{++} . In NaAMB and NaAMPS, the anionic groups are decoupled from the backbone and may allow the bound Na^+ ions to experience a region of higher dielectric constant. No such dramatic changes in χ are observed with added divalent ions for these systems probably because spacing allows additional conformational freedom of the side chains.

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Table 6-1
Turbidimetry of NaAA , % Transmittance

C_{salt}/C_p	Mg^{++}	Ca^{++}
0	100	100
0.25	100	100
0.5	100	100
0.75	100	100
0.8	99.4	99.6
0.85 ^a	95.6	95.3

^a Solutions visibly cloudy.

Figure 6-1. Structure for NaAMB, NaAMPS, NaAA, and NaGAL.

Figure 6-2. The slow component of the relaxation rate, R_{2s} , of NaAA, NaGAL, NaAMB, and NaAMPS as a function of temperature at a polymer concentration of 0.1 g/dL.

Figure 6-3. Longitudinal (R_1) and transverse (R_{2s} and R_{2f}) relaxation rates of NaAA with increasing Na^+ and K^+ concentration. Polymer concentration is 0.1 g/dL.

Figure 6-4. Transverse (R_{2s} and R_{2f}) relaxation rates of NaAA with increasing Mg^{++} concentration. Polymer concentration is 0.1 g/dL.

Figure 6-6. Longitudinal (R_1) and transverse (R_{2s} and R_{2f}) relaxation rates of NaAMPS with increasing Na^+ and K^+ concentration. Polymer concentration is 0.1 g/dL.

Figure 6-7. Longitudinal (R_1) and transverse (R_{2s} and R_{2f}) relaxation rates of NaAMPS with increasing Mg^{++} and Ca^{++} concentration. Polymer concentration is 0.1 g/dL.

Figure 6-8. Longitudinal (R_1) and transverse (R_{2s} and R_{2f}) relaxation rates of NaAMB with increasing Na^+ and K^+ concentration. Polymer concentration is 0.1 g/dL.

Figure 6-9. Longitudinal (R_1) and transverse (R_{2s} and R_{2f}) relaxation rates of NaAMB with increasing Mg^{++} and Ca^{++} concentration. Polymer concentration is 0.1 g/dL.

Figure 6-10. $P_b \chi^2$ for NaAA with increasing Ca^{++} concentration. Reasonable limits for P_b are used to provide a boundary of solutions for $P_b \chi^2$. Manning's "two-variable" theory has been employed to provide specific values of P_b . Polymer concentration is 0.1 g/dL.

Figure 6-11. $P_b \chi^2$ for NaAA with increasing Mg^{++} and Ca^{++} concentrations using the Mannin prediction for the fraction of bound ions. Polymer concentration is 0.1 g/dL.

Figure 6-12. Values of χ for NaAA, NaAMB, and NaAMPS with increasing Ca^{++} concentration. The Manning prediction is employed for estimation of P_b . Polymer concentration is 0.1 g/dL.

Figure 6-13. Transverse (R_{2s} and R_{2f}) relaxation rates of NaGAL with increasing Mg^{++} concentration. Polymer concentration is 0.1 g/dL.

Figure 6-14. Transverse (R_{2s} and R_{2f}) relaxation rates of NaGAL with increasing Ca^{++} concentration. Polymer concentration is 0.1 g/dL.

Figure 6-15. Dependence of the relative viscosity of NaAMPS with increasing concentration of Na⁺, K⁺, Mg⁺⁺, and Ca⁺⁺. Polymer concentration is 0.1 g/dL.

Figure 6-16. Dependence of the relative viscosity of NaAMB with increasing concentration of Na⁺, K⁺, Mg⁺⁺, and Ca⁺⁺. Polymer concentration is 0.1 g/dL.

Figure 6-17. Dependence of the phase separation temperature, T_c , of NaAMB with CaCl_2 and $\text{Ca}(\text{NO}_3)_2$. The increase in T_c after addition of urea to the NaAMB/ CaCl_2 is also depicted. Polymer concentration is 0.1 g/dL.

CHAPTER SEVEN. MODEL DEVELOPMENT FOR DILUTE POLYMER SOLUTION EXTENSIONAL FLOW IN POROUS MEDIA

Introduction

Oil recovery during flooding of a reservoir is enhanced when the displacing fluid mobility is similar to that of the fluid being displaced. Aqueous polymer solutions are used for flooding because they have mobilities much lower than water even when the solutions are very dilute. The low mobility of a dilute polymer solution is due to macromolecular extension during flow through the reservoir. This paper proposes a mechanism for polymer extension in a porous medium and develops a laboratory method and data analysis technique to characterize polymer solutions for extensional flow properties.

The flow resistance of dilute polymer aqueous solutions through beds of uniform size spheres can be used to characterize the extensional viscosity of the solutions. As shown by Durst¹, the solution flow resistance or pressure drop across a bed of uniform solid spheres was strongly dependent upon flow rate, polymer molecular weight, number of macromolecules per unit volume of fluid and the size of the individual polymer coils. However, the theoretical explanations on polymer coil extension in packed beds given by Durst were not compatible with all the solution properties he observed. In particular, the Durst explanation does not address his observed reduction in normalized solution flow resistance (NSFR) at higher fluid flow rates through the bed.

In this laboratory solution flow through packed bed experiments were carried out at conditions similar to that performed by Durst. The dilute solution flow properties of several high molecular weight acrylamide based copolymers² were also found to have a maximum and then a reduction in NSFR at higher flow rates through the bed. An example of this behavior is shown in Figure 7-1.

Major Assumptions

In an effort to explain the above maximum in NSFR, a model of polymer coil response in a fluid extensional flow field has been proposed. Two major assumptions are used to develop this model. The first major assumption concerns the mechanical definition of a polymer coil in solution. The second assumption deals with the description of the packed bed extensional fluid flow field.

It is assumed that a single coil in a dilute solution responds to an extensional fluid flow field as a Kelvin mechanical model which is a spring and dashpot connected in parallel³. The spring is characterized by a modulus, G , and the dashpot by a viscosity, η . The spring represents the macromolecular forces which restore an extended polymer coil to its equilibrium shape. The dashpot represents the energy converted to heat when a coil is deformed.

Extensional Coil Stress

Secondly, it is assumed that the fluid flow field extensional stresses imposed upon a polymer coil are cyclic within a packed bed of uniform diameter spheres. A single stress cycle 1) extends the coil, 2) allow the extended coil to recover, 3) compress the coil, and 4) then allows the compressed coil to recover. See Figure 7-2. At a given fluid throughput, the fluid extensional stress, τ , placed on the coil can be approximated by the product of a factor, C , and a sin function.

$$\tau = C \sin(2\pi\omega t)$$

In the above equation ω is the frequency (cycles per unit time) in which the polymer coils are extended and t is the time that a coil has been in the packed bed. The factor C is the maximum stress and was estimated using a modification of Stoke's law⁴. It is a function of bed porosity, ϕ , solvent viscosity, μ_o , and polymer density, ρ , and intrinsic viscosity, η_{intr} and the coil shielding factor, S_h , which is set to unity.

$$C = 24 \pi S_h \rho \omega \mu_o \eta_{intr} (1 - \phi)$$

Extensional Coil Strain

Using the above concepts the coil extensional strain, γ , or response to the fluid extensional flow field developed in the porous media can be expressed by the following differential equation.

$$C \sin(2\pi\omega t) = G\gamma + \eta (d\gamma / dt)$$

Solving this equation for the coil strain, γ , using the initial condition that at time zero the extensional strain is zero, gives strain as a function of a Deborah number, $De = \omega \eta / G$.

$$\gamma = C[\sin(2\pi\omega t) - 2\pi De \cos(2\pi\omega t) + 2\pi De \exp(-Gt/\eta)] / [G(1 + 4\pi^2 De^2)]$$

The exp expression in the equation is an unsteady state term and will approach zero after the polymer coil is in the bed for a short time. Thus at steady state conditions the strain equation is

$$\gamma = C[\sin(2\pi\omega t) - 2\pi De \cos(2\pi\omega t)] / [G(1 + 4\pi^2 De^2)]$$

Coil Work

The extensional stress and strain expressions can be used to calculate the time averaged stress and strain experienced by a coil as it is taken through a half cycle.

$$\gamma_{avg} = 2C / [\pi G(1 + 4\pi^2 De^2)^{1/2}] \quad \tau_{avg} = 2C / [\pi(1 + 4\pi^2 De^2)^{1/2}]$$

The total work per cycle of deformation is twice the work done on the coil dashpot over a half cycle. This total work, W , can be calculated from the product of the average stress and the average cross-sectional area of polymer within the coil, A , times the product of the average coil strain and the unperturbed coil hydrodynamic diameter, D_h . The average area, A , can be estimated using unperturbed coil dimensions and the volume fraction of polymer within the coil, $z = 1/(\eta_{intc}\rho)$.

$$W = 2AD_h \tau_{avg} \gamma_{avg} \text{ with } A = \pi D_h^2 z / 4 \text{ gives } W = 2zD_h^3 C^2 / [\pi G(1 + 4\pi^2 De^2)]$$

Energy Balance

The total energy expended during extension and compression of all polymer coils as they travel through the packed bed is the product of the work of one coil cycle, the cycle frequency and the total number of polymer coils found within the packed bed. This energy is also equal to the product of the fluid volumetric flow rate through the bed, Q , and the pressure loss across the bed which is only due to the deformation of the polymer coils. This pressure loss is the measured solution pressure drop, ΔP_s , less the solution pressure drop not due to coil deformation which is approximated as $\Delta P_{so}(1 + c\eta_{intr})$ where ΔP_{so} is the solvent pressure drop at the same flow rate and c is the polymer mass concentration in the solution. Thus an energy balance gives

$$[\Delta P_s - \Delta P_{so}(1 + \eta_{intr}c)]Q = W\omega[\pi D_{bed}^2 L \phi c N_A / (4M)]$$

The total number of coils within a cylindrical bed of diameter D_{bed} , length L , porosity ϕ , and packed with solid spheres of diameter d is given by the expression in the right bracket where M is the polymer molecular weight and N_A is Avogadro's number. The coil cycle frequency, ω , is the total number of cycles experienced by a coil, N , as it passes through the bed divided by the average residence time that a coil is in the bed, θ .

$$N = \psi L / (\kappa d) \quad \theta = \pi \phi L D_{bed}^2 / (4Q) \quad \text{thus} \quad \omega = 4\psi Q / (\pi \kappa \phi d D_{bed}^2)$$

In the above relationships ψ is the tortuosity of the packed bed which is the average coil path length to column length and κd is the distance over which a single cycle occurs. For laminar flow in beds of uniform packed spheres κ and ψ have values of about 0.825 and 2, respectively⁵.

The coil hydrodynamic diameter, D_h , can be calculated by equating the volume of a polymer coil to the volume of a sphere.

$$\pi D_h^3 / 6 = \eta_{intr} M / N_A \text{ which gives } D_h = [6 \eta_{intr} M / (\pi N_A)]^{1/3}$$

Working Equation

Substitution for W , D_h , De and ω into the energy balance equation gives, after rearrangement, the following working equation.

$$\frac{\eta_{intr} c}{\Delta P_s - \Delta P_{so} (1 + \eta_{intr} c)} = \frac{G}{\alpha Q^2} + \frac{\zeta \eta^2}{G} \text{ where } \zeta = \frac{64 \pi \psi^2}{\alpha \phi^2 \kappa^2 d^2 D_{bed}^2}$$

$$\text{and } \alpha = \frac{12 \psi^3 96^2 \eta_{intr} c L S_h^2 \mu_o^2 (1 - \phi)^2}{\pi^2 d^3 \kappa^3 \phi^2 D_{bed}^4}$$

The above relationship indicates a linear relationship should exist between $1/Q^2$ and $\eta_{intr} c / [\Delta P_s - \Delta P_{so} (1 + \eta_{intr} c)]$ such that

$$\frac{\eta_{intr} c}{\Delta P_s - \Delta P_{so} (1 + \eta_{intr} c)} = a + b \frac{1}{Q^2}$$

$$\text{with intercept } a = \frac{\zeta \eta^2}{G} \text{ and slope } b = \frac{G}{\alpha}$$

The α and ζ parameters can be determined from experimental conditions. Thus with a knowledge of the α and ζ parameters and the experimentally determined slope, b , and intercept, a , taken from a plot of $\eta_{intr} c / [\Delta P_s - \Delta P_{so} (1 + \eta_{intr} c)]$ versus $1/Q^2$, the coil viscosity, η , and coil modulus, G , can be determined. The ratio of η/G is referred to as the coil response time, λ .

$$\eta = \sqrt{\frac{a b \alpha}{\zeta}} \text{ and } G = b \alpha$$

Plotting Experimental Data

Figure 7-3 shows a typical plot of $\eta_{intr} c / [\Delta P_s - \Delta P_{so} (1 + \eta_{intr} c)]$ versus $1/Q^2$ data. This data was taken from solutions made from a high molecular weight copolymer synthesized from acrylamide and 3-acrylamido-3-methylbutanoic acid monomers in the ratio of 80 to 20 as described by McCormick^{5,6}. The linear correlation is very good. The slope and intercept values predict a coil viscosity of 1.4 dyne sec / cm² and coil modulus of 1000 dyne / cm².

Model Expressed In Dimensionless Format

The extensional flow model can be expressed in a simpler format if dimensionless groups are defined and used in the function. Fluid resistance through a packed bed can be expressed as a normalized solution flow resistance, NSFR. The NSFR is

$$NSFR = \frac{\Delta P_s - \Delta P_{so}}{\Delta P_{so} \eta_{intr} c}$$

In the above relationship c is the polymer concentration and η_{intr} is the measured polymer intrinsic viscosity. The solution and solvent pressure drop across the packed bed are ΔP_s and ΔP_{so} , respectively. The polymer solution extensional flow conditions can be expressed in dimensionless format by using a Deborah number, $De = \omega \eta / G = [4\psi Q \eta] / [\pi (D_{bed})^2 \phi \kappa d G]$, a porous media dimensionless geometry, $P = [(\psi \phi) / \kappa]^2$, and a dimensionless coil viscosity, defined as $H = [\rho \mu_o \eta_{intr}] / \eta$. Using these grouped parameters, the model for dilute polymer solution flow through beds of spheres can be expressed in dimensionless format as

$$NSFR = 4 \pi^2 S_h^2 \frac{P H De}{1 + 4 \pi^2 De^2} + 1$$

The effects of the porous media geometry on NSFR are accounted for in the first term of the model and in the definition of the Deborah number. The ratio of macromolecular path length through the bed to bed length is ψ / κ and is approximately $4(2/9)^{1/3} = 2.42$. The polymer coil shielding factor, S_h , is taken as unity. The dimensionless Deborah Number is the ratio of polymer coil response time, $\lambda = \eta / G$ and $1/\omega$, the process extension time.

The above relationship shows that with a constant dimensionless coil viscosity the NSFR will be a maximum when the Deborah number, De , equals $1/2\pi$. Any increase in the dimensionless coil viscosity, H , will always increase the NSFR regardless of the Deborah number. Typical behavior of the model equation with respect to Deborah number and dimensionless coil viscosity is shown in Figure 7-4.

The fit of the flow data from the copolymer synthesized from acrylamide and 3-acrylamido-3-methylbutanoic acid solutions using the normalized solution flow resistance versus Deborah number plotting technique is shown in Figure 7-4.

The model is consistent with the data and provides a maximum for the NSFR versus Deborah number plot. Plots of this type can be used to determine a polymer solution's mobility under various fluid compositions and extensional flow conditions that are similar to those found in reservoir polymer flooding.

Summary

The extensional flow behavior of dilute polymer solutions through packed beds of solid spheres has been modeled by assuming that a single polymer molecule could be considered as a spring, with modulus G , and a dashpot, with viscosity η , connected in parallel. The polymer molecules are elongated and compressed as they pass through the bed and energy is converted to heat as the macromolecules are cyclically strained. This degradation of fluid kinetic energy to heat increases solution resistance to flow through the bed. This model is consistent with experimental bed pressure drop data collected using high molecular weight polymer solutions.

The model for extensional flow in a porous media suggests that for a polymer to be a good candidate as a mobility control agent in improved oil recovery (have a dilute solution that gives high resistance to flow within a reservoir) the polymer should:

- 1) Always have a high solution intrinsic viscosity. This increases H and thus fluid resistance to flow.
- 2) Usually have a coil viscosity that is low. A lower coil viscosity always increases H , which is desirable, but also lowers the coil response time, $\lambda = \eta / G$, which is undesirable because a greater fluid extensional strain rate is then required to have a Deborah number condition which would elongate the polymer. These high extensional strain rates are not usually present when flooding a reservoir.
- 3) Always have a coil modulus that is low. This enables polymer coil extension at the lower fluid extensional rates associated with lower fluid flow rates through a porous media.

Nomenclature

Symbol	Description	Example Value or Remarks
A	cross sectional area of polymer within a coil	
a	model working equation intercept	
b	model working equation slope	
C	maximum fluid extensional stress upon coil	
c	mass concentration of polymer in solution	0.054 g / liter
D_{bed}	diameter of the packed bed	1.0 cm
De	Deborah Number	$\omega \eta / G$
D_h	copolymer coil hydrodynamic diameter	5.9×10^{-5} cm
d	packing spherical diameter	0.015 cm
G	polymer coil modulus	calculated as 1000 dyne / cm ²
H	dimensionless coil viscosity	$[\rho \mu_o \eta_{intr}] / \eta$
L	length of the packed bed	10.0 cm
M	copolymer molecular weight	1.4×10^7 g / mole
N	number of cycles experienced by a polymer coil	$\psi L / (\kappa d)$
N_A	Avogadro's number	6.02×10^{23} / mole
NSFR	$[\Delta P_s - \Delta P_{so}] / [\Delta P_{so} c \eta_{intr}]$	Normalized Solution Flow Resistance
P	porous media dimensionless geometry	$[(\psi \phi) / \kappa]^2$
Q	fluid volumetric Flow Rate	
S_h	shielding factor	1.0
T	temperature	297 K
t	time	

W	work per coil cycle	
z	volume fraction of polymer in a coil	$1 / (\eta_{intr} \rho)$
α	collection of known parameters	
ΔP_{so}	solvent pressure drop across the bed	
ΔP_s	solution pressure drop across the bed	
ϕ	bed porosity	0.367
γ	coil strain	
γ_{avg}	average coil strain over a half cycle	
η	coil viscosity	calculated as 1.3 dyne sec / cm ²
η_{intr}	polymer intrinsic viscosity	4600 ml / g
θ	average time a coil is in a packed bed	
κ	factor used to relate coil path length to sphere diameter	0.825
λ	coil response time	calculated as 0.0012 sec
μ_o	solvent shear viscosity	0.01 dyne sec / cm ²
ρ	polymer monomer density	1.0 g / cm ³
τ	fluid extensional stress	
τ_{avg}	average fluid extensional stress	
ω	coil cycle frequency	
ψ	packed bed tortuosity	2.0
ζ	collection of known parameters	

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Figure 7-1. Normalized solution flow resistance versus fluid flow through the bed for 54 ppm AM/AMBA 80/20 copolymer solutions.

Figure 7-2. Macromolecular extensional behavior during flow through a packed bed of uniform spherical particles.

Figure 7-3. Model fit to experimental data.

Figure 7-4. Normalized solution flow resistance (NSFR) dependence upon Deborah number, De, and dimensionless coil viscosity, H. The porous media dimensionless geometry, P, is set for beds packed with uniform size spheres and is equal to 0.792.

CHAPTER EIGHT. EXPERIMENTAL RESULTS FOR DILUTE POLYMER SOLUTION EXTENSIONAL FLOW IN POROUS MEDIA

Introduction

When using a dilute polymer solution to flood an oil reservoir the displacing fluid should have a high resistance to flow within the porous medium. High flow resistance increases movement of residual oil to a producing well and thus enhances oil recovery. Fluid resistance results from polymer molecular distortions during flow through the small and tortuous channels of the porous medium. Polymer solution behavior in complex porous media can be simulated using packed beds of uniform solid spheres.

In dilute solution, each polymer molecule forms a coil having a hydrodynamic diameter, D_h . Each coil volume is mostly solvent weakly bonded together by the presence of the polymer molecule. The volume fraction of polymer molecule in a coil, z , is very small. The value of z is equal to $1/(\eta_{intr} \rho)$, where η_{intr} and ρ are the measurable intrinsic viscosity and polymer monomer density, respectively. Polymer solutions are dilute (no coil-coil interaction) when the product of the intrinsic viscosity and solution concentration, c , is less than one.

As explained in the previous chapter, when polymer coils in solution pass through a bed of packed spheres of diameter, d , they travel through a continuous and interconnected series of converging and diverging cavities. The fluid in this geometry will continually accelerate and decelerate as it passes from cavity to cavity. Fluid acceleration and deceleration forces will compel the polymer coils to extend and then recover after each extension. The frequency of coil extensions and recovery, ω , is proportional to the number of cavities passed through by the polymer in a given time.

Normalized Solution Flow Resistance

Each coil extension-recovery cycle will convert some fluid kinetic energy into heat. This energy conversion will be detected as a higher solution pressure drop across the bed, ΔP_s , as compared to the pressure drop of a solvent, ΔP_{so} , flowing through the bed at the same fluid volumetric flow rate, Q . This fluid pressure increase is expressed as a normalized solution flow resistance, NSFR. The NSFR is directly related to the amount of energy converted to heat by the polymer coils as they travel through the packed bed and are continually extended and contracted.

The normalized solution flow resistance is directly proportional to the difference between solution and solvent friction factors, $f_s - f_{so}$, and is also inversely proportional to the product of the dimensionless concentration of polymer coils in solution, and solvent friction factor. The dimensionless concentration of polymer coils is the product of the polymer's mass concentration and its intrinsic viscosity, $c \eta_{intr}$. Thus the NSFR is a measure of the increase in solution flow resistance as compared to solvent per dimensionless concentration of polymer coils in solution.

The NSFR measures solution flow resistance in a porous media under conditions specified by Reynolds and Deborah numbers. It is calculated from the friction factor of the solution, f_s , and the friction factor of the solvent, f_{so} , measured at the same bed Reynolds number. The Deborah Number, De , is the product of the polymer deformation frequency, ω , and the coil response time, λ , which is the ratio of coil viscosity, η , to coil modulus, G . The polymer deformation frequency depend upon average fluid velocity and the pore geometry. These dimensionless parameters are defined by the relationships given below.

$$\lambda = \frac{\eta}{G} \quad f \equiv \frac{d \phi^3}{v^2 (1 - \phi) \rho_{so}} \frac{\Delta P}{\Delta \ell}$$

$$\omega = \frac{4 \psi Q}{\pi D_{bed}^2 \phi d \kappa} \quad Re \equiv \frac{v d \rho_{so}}{\mu_o (1 - \phi)}$$

$$D_e = \lambda \omega \quad NSFR = \frac{f_s - f_{so}}{f_{so} \eta_{intr} c} = \frac{\Delta P_s - \Delta P_{so}}{\Delta P_{so} \eta_{intr} c}$$

As shown in the above equations, the nature of the porous medium is specified by the diameter of the spherical particles, d , forming a bed having porosity, ϕ , and diameter D_{bed} . For beds of uniform spheres the fluid path length is increased by ψ / κ which is equal to 2.42. The fluid flow resistance through the bed is measured by the pressure drop per unit length of bed, $\Delta P / \Delta \ell$. Flow conditions through the bed are defined by the average fluid velocity, v . This velocity is based on the cross sectional area of an empty bed, i.e., v equals $4 Q / (\pi D_{bed}^2)$. The fluid velocity within the pore channels in the bed would be the empty bed velocity divided by the bed porosity. Solvent properties of shear viscosity, μ_o , and density, ρ_{so} , are also used in the dimensionless groups.

Durst Plots

A Durst plot, which show the normalized solution flow resistance versus Deborah Number, show the efficiency that polymer coils convert fluid kinetic energy to heat as a function of flow conditions, porous media geometry, and polymer properties and concentration. Past experimental work has shown that as the Deborah number approaches unity a maximum in NSFR develops and then decreases slowly at higher Deborah Numbers^{3,4}. The maximum in the NSFR is a function of polymer molecular weight, macromolecular structure and the concentration of polymer coils in solution, c .

Experimental

Polymers

The high molecular weight random copolymers used in this study were synthesized from acrylamide (AM) and 3-acrylamido-3-methylbutanoic acid (AMBA) monomers in the ratios as described in previous publications ^{1,2}. Poly(ethylene oxide) was obtained from Polysciences, Inc. The aqueous solvent used to make all polymer solutions contained 0.514 M NaCl and had a viscosity of 0.934 cp at 25 ° C. Data for polyacrylamide and hydrolyzed polyacrylamide were taken from a paper by Durst³.

Solutions of AM/AMBA copolymers and poly(ethylene oxide) homopolymer were analyzed using static and dynamic light scattering techniques to find molecular weights. A low shear Contravis rheometer was used to estimate each solution intrinsic viscosity in the limit of zero shear rates. Table 8-I list each polymer properties.

Porous Media Rheometer

The porous media rheometer used for this study is shown in Figure 8-1⁴. Pressurized nitrogen gas forced polymer solution or solvent out of a 1000 ml sample reservoir through one of two porous media flow cells. The fluid flow rate was controlled by adjusting the nitrogen gas pressure with a Victor 0 to 200 psi, single stage, pressure regulator. Both flow cells were 1 cm diameter cylinders having a 12 cm length. The cells were packed with uniform diameter solid glass spheres manufactured by Cataphote Inc. Cell # 1 contained 297 micron diameter glass spheres. Cell # 2 contained 149 micron diameter glass spheres. Both packed beds had a porosity, ϕ , of 0.367. Fluid from a flow cell was directed into a flask that was placed upon a Mettler PM4000 balance. The fluid mass throughput was measure by recording the change in mass on the balance with respect to time.

The glass spheres were retained within the flow cells at each end by three polypropylene screens having mesh sizes of 149, 390, and 149. A threaded retaining plug, having 25 through holes, each having a diameter of 0.07 cm, was used at each flow cell end to compress the screens against the glass spheres. Each cell end was capped with a Swagelock SS-400-1-6ST fittings.

Pressure probes were position 10 cm apart in both packed beds. Each probe was a 0.159 cm diameter stainless steel tube that had two 0.09 mm wide by 4.2 mm long slit openings. The probes were position within the cells such that the slit centered the packed bed. The fluid pressure difference across the probes in each cell was measured using a Validyne DP15 differential pressure transducer with a number 48 diaphragm. The pressure transducers were previously calibrated by applying a hydraulic force across the transducers. The electrical signals from a pressure transducer (bed fluid pressure drop) and the balance (mass of fluid) were recorded each second by a Camile, model 2000, process controller. The controller graphically displayed both signals as a function of time.

After fluid is forced through the rheometer system by fixing a nitrogen gas pressure, steady state conditions were detected when the Camile real-time plots of flow rate and pressure drop versus time were constant. This usually required about one minute. After the system reached steady state, the pressure drop across the packed bed and the flow rate was averaged for 30 seconds. These averages were then recorded. Thereafter a new nitrogen gas pressure was then set to force fluid through the rheometer at a different mass throughput and the above procedure repeated.

Usually about 1000 ml of solvent was used to characterize the porous media flow properties of the solvent. Thereafter polymer solution was forced through the rheometer system over the same range of bed Reynolds numbers. Laminar fluid flow conditions were maintained in all bed flow test by always having a bed Reynolds numbers less than 10. Several solution flow rate and corresponding bed pressure drop data sets were collected.

After the polymer solution flow properties were measured, solvent was again forced through the rheometer. This was done to determine if any polymer has been retained in a packed bed. If the porous media flow properties of the second solvent were significantly greater than the first solvent then additional solvent was forced through the rheometer bed until the second solvent offered the same porous media flow resistance as the first solvent. This purging of a flow cell with solvent assured that the packed bed was free of polymer which, if present, could affect the rheometer measurements on subsequent polymer solutions. All data collected (solvent before polymer solution, polymer solution, and solvent after polymer solution), was imported into a Mathcad 5.0 document where calculations were performed to produce Durst plots of NSFR versus Deborah number.

Results

Table 8-I lists the polymer systems that have been studied using the solution extensional flow model and the parameters associated with each polymer system. The working equation developed for the polymer extension model explained in Chapter 7 was used to calculate the coil modulus and coil viscosity for each polymer system.

Recall that the extensional model for very dilute polymer solutions can be expressed in dimensionless format using the relationship

$$NSFR = 4 \pi^2 S_h^2 \frac{P H De}{1 + 4 \pi^2 De^2} + 1$$

The dimensionless geometry, $P = (\psi \phi / \kappa)^2$, for all porous media used in this study has a value of 0.792. The dimensionless coil viscosity, $H = (\rho \mu_o \eta_{intr}) / \eta$, will vary depending upon the polymer coil dashpot viscosity, η , solvent viscosity, μ_o , and monomer density, ρ . The coil shielding factor, S_h , is set equal to unity. The experimentally determined dimensionless coil viscosity, H , together with the maximum in the NSFR, are listed in Table 8-I for each polymer system studied.

Durst Plots

Figure 8-2 shows the Durst plots for the for three of the AM/AMBA polymer systems listed in Table 8-I. The lines shown on these plots are the model fits to the experimental data. As shown by Figure 8-2, the NSFR versus Deborah number curves elevate as the solution dimensionless concentration, $c \eta_{intr}$, decreases. This is due to a lowering of the coil dashpot viscosity at the lower solution concentrations where less polymer coil to coil interaction or entanglement is present (see Figure 8-3).

Note from Table 8-I that the solutions of the polyacrylamide (PAM), hydrolyzed polyacrylamide (HPAM) and polacrylamide copolymers (AM/AMBA) have coil parameters that are desirable for enhanced oil recovery. Each of these polymer systems have a large dimensionless coil viscosity, H , and this produces a large maximum in the NSFR. In contrast, all the poly(ethylene oxide) solutions have coil parameters that do not greatly increase the NSFR. These high molecular weight polymers are not suitable for polymer flooding an oil reservoir.

Model Application To Polymer Flooding a Sandstone Reservoir

As previously discussed⁵, the porosity, ϕ , and effective sand diameter, d , of Woodbrine sandstone can be approximated from a knowledge of the reservoir's permeability, k .

$$\phi = a + b \log(k) \quad d = \frac{1 - \phi}{\phi} \sqrt{\frac{180 k}{\phi}}$$

In the above relationship the permeability is expressed in cm^2 and a and b have values of 0.465 and 0.025, respectively.

The Deborah number used in the polymer extensional model can be determined from the average fluid velocity, v , and the sandstone parameters d and ϕ .

$$De = \frac{v \psi \eta}{G \phi \kappa d}$$

Usually at large distances away from the injection wellhead, fluid velocities in the reservoir are very low, about 1.0 ft/day. If we use this average fluid velocity, a typical sandstone permeability of 10 md (10^{-10} cm^2), and a polymer coil dashpot viscosity and spring modulus of 1.4 poise and 10^3 dyne / cm^2 , respectively, then the porosity, effective sand diameter, and Deborah number can be calculated to have values of 0.215, $1.1 \times 10^{-3} \text{ cm}$, and 5.3×10^{-3} , respectively. These fluid flow conditions are laminar (a bed Reynolds number of 3.8×10^{-5}).

Under these very low fluid flow conditions, $1 + 4 \pi^2 De^2 \simeq 1$, and the extensional model in dimensionless format simplifies to

$$NSFR = 1 + 4 \pi^2 S_h^2 P H De$$

We can use this relationship and the conditions given ($S_h = 1$, $P = 0.272$, $H = 33$, $De = 5.3 \times 10^{-5}$) to find a NSFR value of 2.9.

For a polymer flooding solution concentration, c , of $5.0 \times 10^{-5} \text{ g/ml}$ (50 ppm) and a polymer intrinsic viscosity of 4600 ml/g the dimensionless concentration, $c \eta_{intr}$, equals to 0.23. Therefore for this example

$$NSFR = \frac{\Delta P_s - \Delta P_{so}}{\Delta P_{so} \eta_{intr} c} = 2.9 \quad \text{or} \quad \frac{\Delta P_s}{\Delta P_{so}} = 1.67$$

Thus the solution is 67% more resistant to flow through the sandstone than the solvent alone. The polymer has reduced the mobility of the displacing fluid within the sandstone and would improve the flooding sweep efficiency.

The above example can be modified to determine the mobility of any polymer solutions in a sandstone reservoir if the polymer coil dashpot viscosity, spring modulus and intrinsic viscosity are determined from laboratory experiments. Figure 8-4 shows the model prediction of fluid resistance for three polymer systems that are listed in Table 8-I and three sandstone reservoirs having permeabilities of 0.1, 1.0 and 10 md. As expected the curves are linear at low average fluid velocities but curve upward at higher fluid velocities. Solution resistance is greatest for the AM/AMBA and PAM polymer systems with larger intrinsic and coil dashpot viscosities and a lower coil spring modulus. At 50 ppm concentration, the HPAM solution has low resistance to fluid flow and would not be an acceptable polymer for reservoir flooding.

General Flow Behavior of All Polymer Solutions

The Durst plots show the same general behavior regardless of polymer type. At Deborah numbers less than about 0.01, the normalized solution flow resistance is very low which indicates that a low degree of coil extension and recovery is occurring under these conditions. At Deborah numbers between 0.01 and 0.15, the normalized solution flow resistance increases to a maximum but then slowly decreases as the Deborah number increases to higher values. This suggests that the degree of polymer coil expansion and recovery is at first increasing under these conditions, then reaches a limit at a Deborah number of about 0.15. Above this Deborah number the polymer coils are probably not able to completely recover all of the large extensional strains developed during initial extension-recovery cycles. Thus they have less potential to extend in subsequent extension-recovery cycles. Therefore, at higher Deborah numbers the coils travel through the bed in a more extended state. They will have less and less recoverable extension as they travel from cavity to cavity. At very high Deborah Numbers the polymers travel through the bed in a highly extended state and therefore less fluid kinetic energy is converted to heat. Thus, if laminar conditions are maintained, the normalized solution flow resistance should eventually decrease to zero in the limit of very high Deborah numbers.

The NSFR reduction at higher Deborah numbers is due to the diminished ability of polymer coils to convert kinetic energy to heat as they are extended and recover at faster rates. At greater fluid flow conditions the polymer coils are not able to follow in concert with the rapidly changing local fluid velocities. At high flow rates insufficient time is available for coil extension during fluid acceleration and coil recovery during fluid deceleration. As a consequence, less total coil deformation is experienced each cycle and thus less energy is converted into heat by the macromolecules. Therefore the solution will have less resistance to flow through the porous medium at higher Deborah numbers.

Conclusions

Of all the polymer systems examined in this laboratory, the NaAMB/AM 20/80 copolymer solutions had the greatest porous media flow resistance. This is because the polymer coils of these macromolecular structures are greatly expanded (have large hydrodynamic diameters) and can elongate and recover in extensional flow fields having low average fluid velocities.

The use of high molecular weight, highly expanded copolymers versus lower molecular weight polymers that are not greatly expanded has a dual advantage in reservoir flooding. Solutions of larger molecular weight macromolecules with large polymer coils not only require less polymer mass for a given fluid flow resistance but this resistance is also experienced at lower flow rates through the porous media. Thus they are effective flooding agents even at low concentrations and have a significant economic advantage.

Nomenclature

Symbol	Description	Example Value or Remarks
a,b	parameters used to relate sandstone porosity to permeability	0.465, 0.025
c	mass concentration of polymer in solution	
D_{bed}	diameter of a packed bed	
De	Deborah Number	$\omega \eta / G$
D_h	copolymer coil hydrodynamic diameter	
d	packing spherical diameter	
fs	solution friction factor	
fso	solvent friction factor	
G	polymer coil modulus	
H	dimensionless coil viscosity	$[\rho \mu_o \eta_{intr}] / \eta$
k	permeability	
NSFR	$[\Delta P_s - \Delta P_{so}] / [\Delta P_{so} c \eta_{intr}]$	Normalized Solution Flow Resistance
P	porous media dimensionless geometry	$[(\psi \phi) / \kappa]^2$

Q	fluid volumetric flow rate	
Re	Reynolds number	
S _h	shielding factor	1.0
z	volume fraction of polymer within a coil	$1 / (\eta_{intr} \rho)$
ΔP_{so}	solvent pressure drop across the bed	
ΔP_s	solution pressure drop across the bed	
ϕ	bed porosity	
η	coil viscosity	
η_{intr}	polymer intrinsic viscosity	
κ	factor used to relate coil path length to sphere diameter	0.825
λ	coil response time	
μ_o	solvent shear viscosity	0.01 dyne sec / cm ²
ρ	polymer monomer density	1.0 g / cm ³
ρ_{so}	solvent density	
v	average fluid velocity	
ω	coil cycle frequency	
ψ	packed bed tortuosity	2.0

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Table 8-I . Packed bed extensional results for polymer solutions using 0.5 M NaCl solvent.

Polymer Type	Mol. Wt. g / mole $\times 10^{-6}$	Intrinsic Viscosity cm^3/g	Solution Conc. g / cm^3 $\times 10^{-6}$	Packing Sphere Size $\text{cm} \times 10^3$	Coil Dashpot Viscosity poise	Coil Spring Modulus $\text{dyne} / \text{cm}^2$ $\times 10^{-3}$	Coil Response Time msec	Dimen sionless Coil Viscosity	Dimen sionless Conc.	Maxium in NSFR
AM/AMBA ^a	14	4600	54	29	1.4	1.5	1.0	33	0.25	78
AM/AMBA ^a	14	4600	54	15	1.4	1.0	1.4	33	0.25	83
AM/AMBA ^a	14	4600	166	29	1.8	1.2	1.4	26	0.76	60
AM/AMBA ^a	14	4600	166	15	1.7	1.2	1.4	27	0.76	69
AM/AMBA ^a	14	4600	466	29	2.7	1.5	1.9	17	2.14	40
AM/AMBA ^a	14	4600	466	15	2.7	0.92	2.9	17	2.14	44
PAM ^b	19	2900	50	20	0.75	0.31	2.4	39	0.145	99
PAM ^b	19	2900	50	39	0.53	0.43	1.2	55	0.145	127
PAM ^b	19	2900	25	39	0.43	0.45	0.91	67	0.073	155
HPAM ^c	11	2200	50	39	0.53	0.95	0.56	42	0.11	95
HPAM ^c	11	2200	25	39	0.49	0.94	0.50	47	0.055	119
HPAM ^d	3.5	1200	50	39	0.51	2.3	0.22	24	0.060	55
PEO ^e	2.8	960	50	29	1.0	20.3	0.051	9.6	0.048	23
PEO ^e	2.8	960	100	29	1.3	14.9	0.088	7.4	0.096	18
PEO ^e	7.6	2100	50	29	4.5	113.0	0.039	4.7	0.105	12
PEO ^e	7.6	2100	100	29	5.9	41.9	0.14	3.6	0.21	9

a) Acrylamide and 3-acrylamido-3-methylbutanoic acid copolymers^{1,2} b) Polyacrylamide data³ c) Hydrolyzed polyacrylamide, 3 % hydrolysis³ d) Hydrolyzed polyacrylamide, 13 % hydrolysis³ e) Poly(ethylene oxide) from Polysciences, Inc.

Figure 8-2. Durst plots of 80/20 AM/AMBA copolymer solutions. See second (a), fourth (b) and sixth (c) listing in Table 8-I for solution properties and porous media information.

Figure 8-3. Variation of polymer coil properties with respect to dimensionless solution concentration for AM/AMB 80/20 copolymer.

Figure 8-4. Model prediction of solution flow resistance to solvent flow resistance for AM/AMBA copolymer (solid lines), polyacrylamide homopolymer (dotted lines) and 13% hydrolyzed polyacrylamide (dashed lines) in sandstone reservoirs. See the 2nd, 7th, and 12th listing in Table 8-1. All solutions have a polymer concentration of 50 ppm.