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Quarterly Technical
Progress Report
for

Responsive Copolymers for Enhanced Petroleum Recovery

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by

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A. Task 1. Hydrophobically Modified Acrylamide/Acrylic Acid Copolymer Synthesis

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 care.[1-4] Such amphiphilic systems may be tailored to yield associative thickeners that 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 that 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 laboratories[6-9] as well as in others.[10-14] Furthermore, study of the micellar polymerization process has become increasingly important due to the unique microstructure that results.[7-9,14-16]

In this study 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 1. This work complements the studies using fluorescently labeled 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 terpolymers.[9] The purpose of this study is twofold. First we wish to extend the concepts of the micellar polymerization to more complex systems, including those that utilize ionizable monomers. Second, we wish explore the electrolyte-responsive nature of these hydrophobically-modified polyelectrolytes by tailoring of the microstructure through manipulation 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.

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 and Polymer Synthesis

The synthesis of **3**, N-[(4-decyl)phenyl]acrylamide (DPAm) was accomplished by a procedure adapted from previous methods.[18,25]

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 dodecyl sulfate (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 $[K_2S_2O_8]/[\text{monomer}]$ 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 7-8 and the polymers were dialyzed against deionized water in SpectraPor® No. 4 dialysis tubing (MW cut-off 10-14 × 10^3 g/mol) for at least one week. The samples were then lyophilized to a constant weight.

A. Task 2. Characterization of Molecular Structure and Solution Behavior

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 (λ_{Ex} = 335nm, I_1 = 372nm, I_3 = 384nm). Viscosity measurements were conducted on a Contraves LS-30 low shear rheometer at 25 °C and a shear rate of 6.0 s^{-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 (d*n*/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.

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 μL) 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 d*n*/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 μm Millipore filters.

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 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]acrylamide[18]. This monomer has both the hydrophobic character and chromophore desired. The DPAm model compound N-[(4-decyl)phenylamido]proprionic acid (DPAPA, not depicted) was synthesized by a procedure similar to that previously reported for N-[(4-butyl)phenylamido]proprionic acid[18]. The molar absorptivity, ε of this model compound in water was determined to be 10,700 $M^{-1}cm^{-1}$ at 250nm. Polymerization was carried out under micellar reaction conditions in SDS/H_2O 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 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 1) in this study were determined by a combination of elemental analysis (EA) and UV spectroscopy by the previously published methods[18]. The amount of acrylic acid in the polymers is slightly greater than the feed composition, consistent with reactivity ratio predictions[21]. 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%).

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 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 polymerization.[7-9] Decreasing SMR results in an intially 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/micelle.[14]

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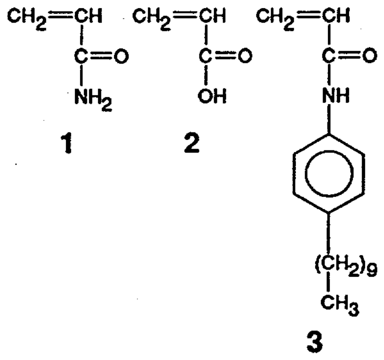

Figure 1. Monomers for micellar polymerizations: acrylamide (Am) **1**, acrylic acid (AA) **2**, and N-[(4-decyl)phenyl]acrylamide (DPAm) **3**.

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

SAMPLE	SMR*	FEED RATIO Am:AA	MOLE% Am	MOLE% AA	MOLE% DPAm	%Conv.
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.

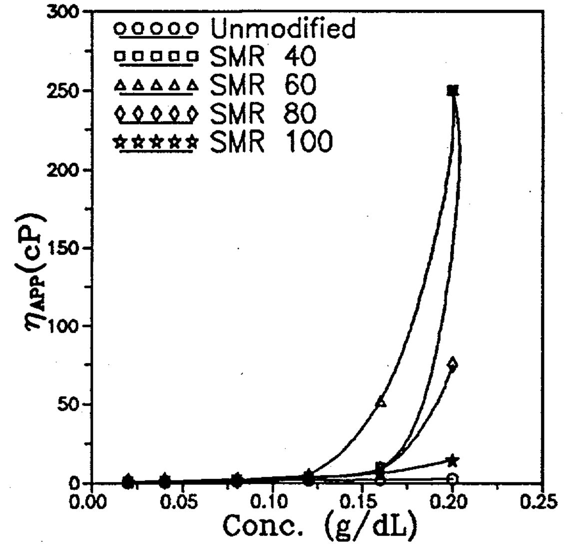

Figure 2. Apparent viscosities as a function of polymer concentration in 0.5M NaCl at 25 °C and a shear rate of $6s^{-1}$.

B. Task 1. Acrylamide/Acrylic Acid/Sulfobetaine Terpolymer Synthesis

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 that 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 polyampholytes.[22-34]

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 reported.[19] 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.

B. Task 2. Characterization of Molecular Structure and Solution Behavior

Copolymer Characterization

^{13}C n.m.r spectra of the polymers were obtained at 50.3 MHz on a Bruker AC 200 spectrometer using 10-15 wt% aqueous (D_2O) 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.

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 Figure 3. 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.

Figure 4 examines the effect of increasing NaCl concentration on the intrinsic viscosities of the AADAPS, AAAM, and DAPSAM terpolymer polymer series. In Figure 9, 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 previously discussedA_2 values.[35]

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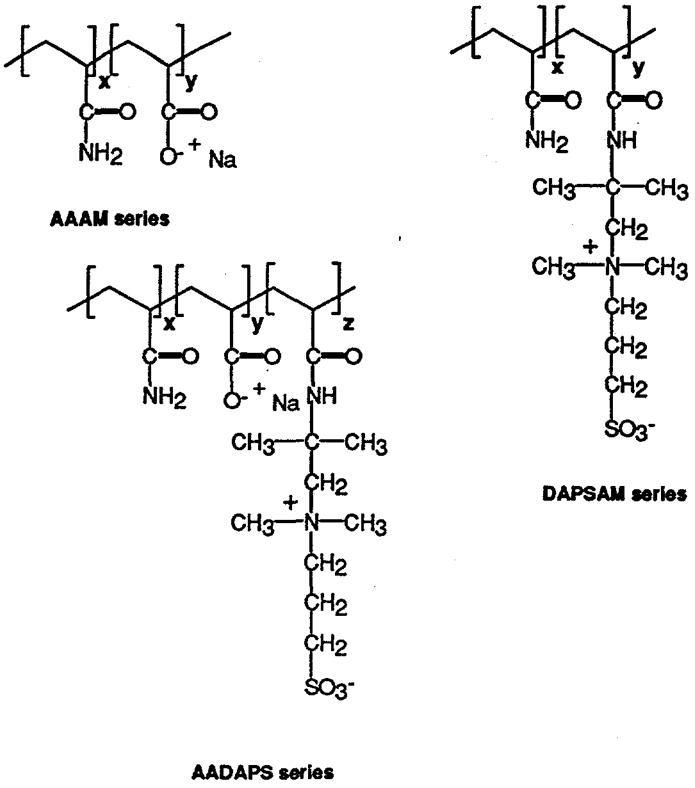

AAAM series

DAPSAM series

AADAPS series

Figure 3. Acrylamide co- and terpolymer structures

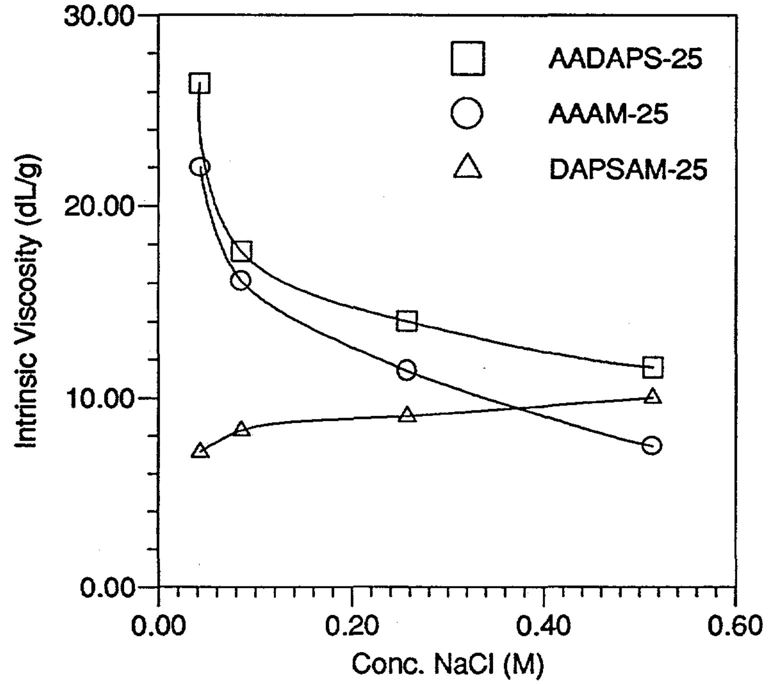

Figure 4. Dependence of intrinsic viscosity as a function of NaCl concentration (determined at a shear rate of 6 sec^{-1} and pH 8).

C. Solution Flow Characterization in Porous Media

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 Durst[1], 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 the reduction he observed 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 those in the experiments performed by Durst. The dilute solution flow properties of several high molecular weight acrylamide based copolymers[2] 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 1.

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 parallel[3]. 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.

Secondly, the fluid flow field extensional stresses imposed upon a polymer coil are cyclic. 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. 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 cycle frequency 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 law[4]. It is a function of bed porosity, ϕ , solvent viscosity, μ_o , and polymer density, ρ , and intrinsic viscosity, η_{intr}.

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

Using the above concepts the coil extensional strain, γ , or response to the fluid extensional flow field developed in the porus media can the 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

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

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

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

The total work per coil cycle is twice the work 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 dimension or 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, $z = 1/(\eta_{intc}\rho)$.

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

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 volummetric 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. The pressure drop not due to coil deformation which is approximated as $\Delta P_o(1 + c\eta_{intr})$ where ΔP_o 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

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

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 .

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

In the above relationships ψ is the tortuosity of the packed bed which is the average coil path length to column length and κ d 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 3/4 and 2, respectively[5].

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

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

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

$$\frac{\eta_{intr} c}{\Delta P_s - \Delta P_o (1 + \eta_{intr} c)} = \frac{G}{\alpha Q^2} + \frac{\zeta \eta^2}{G} \quad \text{where} \quad \zeta = \frac{16 \pi \psi}{\alpha \phi \kappa d D_{bed}^2}$$

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

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

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

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

With a knowledge of the α and ζ parameters and the experimentally determined slope, b, and intercept, a, taken from a plot of $\eta_{intr} c / [\Delta P_s - \Delta P_o (1 + \eta_{intr} c)]$ 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.

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

Figure 2 shows a typical plot of $\eta_{intr} c / [\Delta P_s - \Delta P_o (1 + \eta_{intr} c)]$ versus $1 / Q^2$ for a 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 9.4 dyne sec / cm^2 and coil modulus of 7700 dyne / cm^2.

The fit of the model to experimental data using the normalized solution flow resistance versus Deborah number plotting technique of Durst is shown in Figure 1. The model is consistent with the data and provides a maximum for the NSFR. Coil strain depends upon the Deborah number and ranges from 10 at low Deborah numbers to a maximum of 43 at a Deborah number of 0.15. These strain values are much less than that for a fully extended macromolecule but are larger than expected. Future work will center on understanding the physical meaning of the coil viscosity and modulus and their relationship to macromolecular and solvent properties.

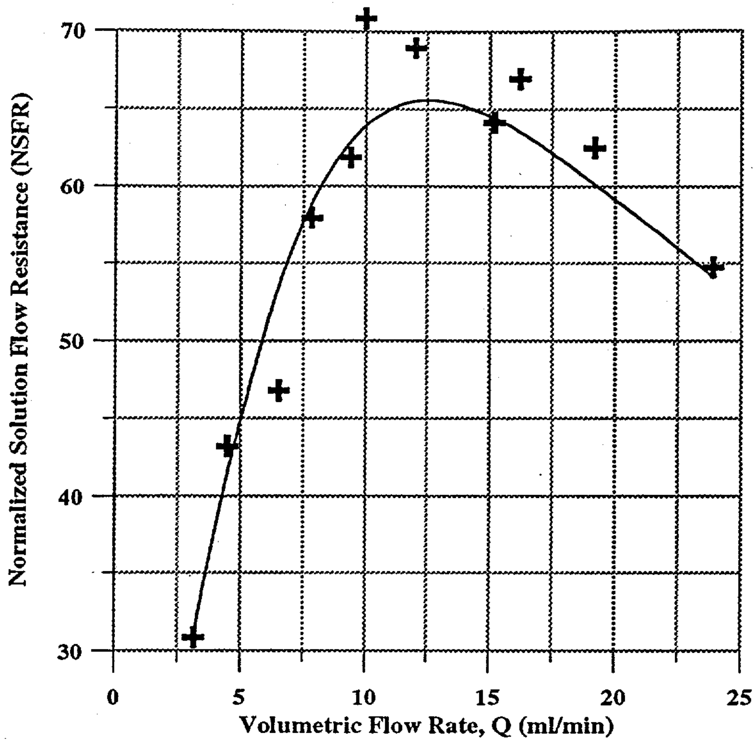

Figure 1 : Normalized solution flow resistance versus volumetric flow rate through a bed packed with uniform size solid spheres. Data shown as + and model fit to the data shown as a solid line. See Table I.

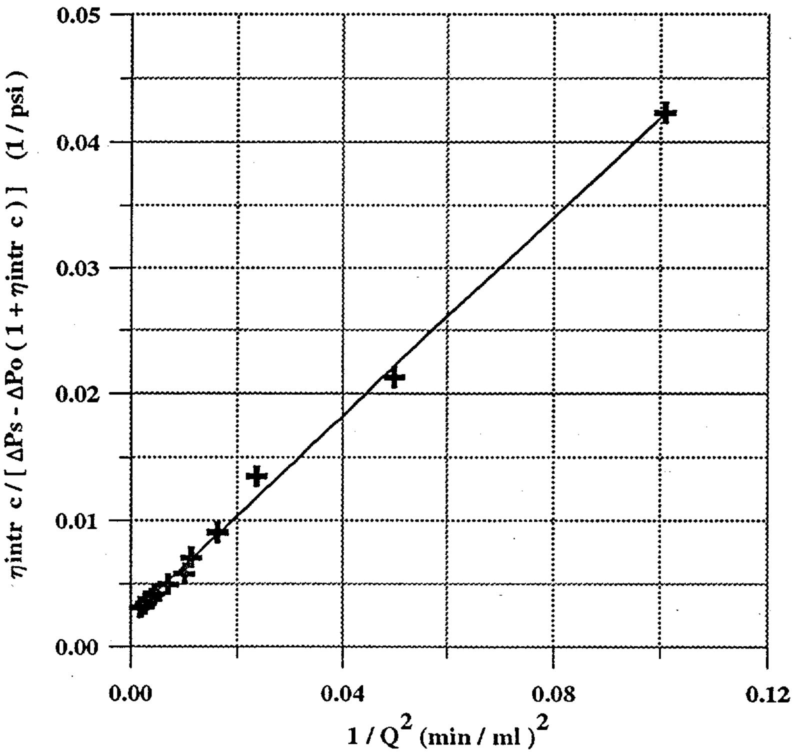

Figure 2 : Model fit to the experimental data. See Table I.

NOMENCLATURE

Table I
Symbol Descriptions

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	polymer coil hydrodynamic diameter	5.9×10^{-5} cm
d	packing spherical diameter	0.015 cm
G	polymer coil modulus	calculated as 7700 dyne / cm^2
L	length of the packed bed	10.0 cm
M	polymer molecular weight	1.4×10^7 g / mole
N	total number of cycles experienced by a coil	
N_A	Avogadro`s Number	6.02×10^{23} / mole
NSFR	$\Delta P_s - \Delta P_o(1+\eta_{intr}c)/[\Delta P_o(1+\eta_{intr}c)\eta_{intr}c]$	Normalized Solution Flow Resistance
Q	fluid volummetric Flow Rate	
T	temperature	297 K
t	time	
W	work per coil cycle	
z	volume fraction of polymer within a coil	$1/(\eta_{intr}\rho)$
α	collection of known parameters	
ΔP_o	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 9.4 dyne sec / cm^2
η_{intr}	polymer intrinsic viscosity	4600 ml / g
κ	factor used to relate coil path length to d	3 / 4
λ	coil response time	calculated as 0.0012 sec
μ_o	solvent shear viscosity	0.01 dyne sec / cm^2
θ	average residence time of a coil in a bed	
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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