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Quarterly
Progress Report
for

Responsive Copolymers For Enhanced Petroleum Recovery

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by

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

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 Evani[4] 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.

In this report, we examine the role of surfactant-to-monomer ratio (SMR) in the reaction medium on microstructure utilizing the N-[(1-pyrenylsulfonamido)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.

Materials

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]glutaramide (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 μL 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.

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

Instrumentation and Analysis

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 ($\varepsilon = 24000\ M^{-1}cm^{-1}$)[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 H_2 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 x 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 x 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.

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 2. The synthesis of APS and the water-soluble model compound 2,4-dimethyl-N-[(1-pyrenylsulfonamido)-ethyl]gluconamide (PSGL) (Figure 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 of hydrophobic APS units. 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:

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

[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:

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

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.

Steady-state fluorescence emission spectra for **P2-P5** are shown in Figures 3 and 4 (concentration of 0.02g/dL and a pH of 7.1-7.5). Emission spectra in water (Figure 3) and in 0.5M NaCl (Figure 4) 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 5). The dilute solution spectra in Figures 3 and 4 support the existence of "blocky" microstructures in terpolymers **P2-P5** at ≤ 0.2 mole% of the APS chromophore.

References

1) *Water Soluble Polymers*, Shalaby, Butler and McCormick, Ed.s, **1991**, ACS Symposium Series #467, The American Chemical Society, Washington D. C.

2) *Polymers as Rheology Modifiers*, Schultz, D. N. and Glass, J. E., Ed.s, **1991**, ACS Symposium Series #462, American Chemical Society, Washington D. C.

3) *Polymers in Aqueous Media*, Glass, J. E., Ed., **1989**, Advances in Chemistry Series No. 223; American Chemical Society, Washington D.C.

4) Evani, S., US Patent 4 432 881, **1984**.

5) Turner, S. R.; Siano, D. B.; Bock, J., US Patent 4 520 187, **1985**.

6) McCormick, C. L.; Nonaka, T.; Johnson, C. B., *Macromolecules*, **1988**, *29*, 731.

7) Valint, P. L.; Bock, J.; Ogletree, J.; Zushuma, S.; Pace, S. J., *Polym. Prepr.*, **1990**, *31*, 67.

8) Ezzell, S. A. and McCormick, C. L., *Macromolecules* **1992**, *25*, 1881.

9) Ezzell, S. A.; Hoyle C. E.; Creed, D.; McCormick, C. L., *Macromolecules* **1992**, *25*, 1887.

10) McCormick, C. L.; Middleton, J. C.; Cummins, D. F., *Macromolecules*, **1992**, *25*, 1201.

11) McCormick, C. L.; Middleton, J. C.; Grady, C. E. , *Polymer*, **1992**, *33*, 4184.

12) Branham, K. D.; Davis, D. L.; Middleton, J. C.; McCormick, C. L., *Polymer*, **1994**, *35*, 4429.

13) Thomas, J. K., *The Chemistry of Excitation at Interfaces*, **1984**, The American Chemical Society, Washington D. C.

14) Kalyanasundarum, K., *Photochemistry in Microheterogeneous Systems*, **1987**, Academic Press, Orlando, Fla.

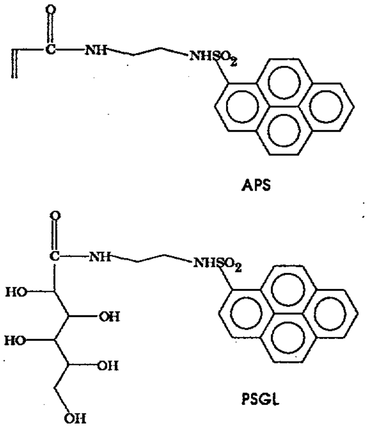

Figure 1. Structures of the fluorescent monomer, APS, and its water soluble model compound, PSGL.

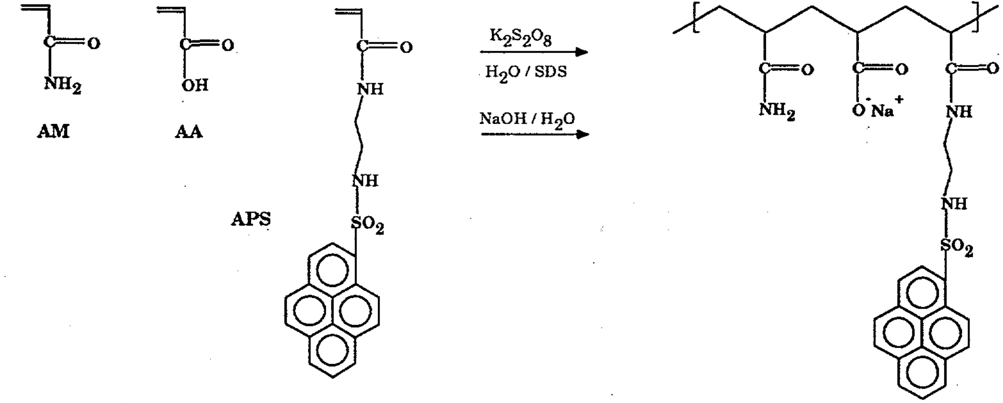

Figure 2. Synthesis of AM/AA/APS Terpolymers **P2 -P5**.

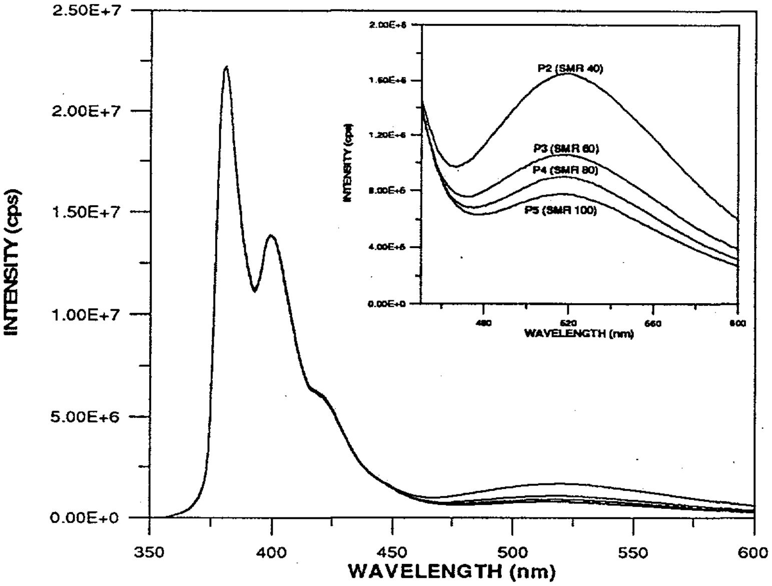

Figure 3. Fluorescence Spectra of terpolymers **P2-P5** in water. Inset: Excimer region from 450 to 600 nm for **P2** (SMR 40), **P3** (SMR 60), **P4** (SMR 80), and **P5** (SMR 100).

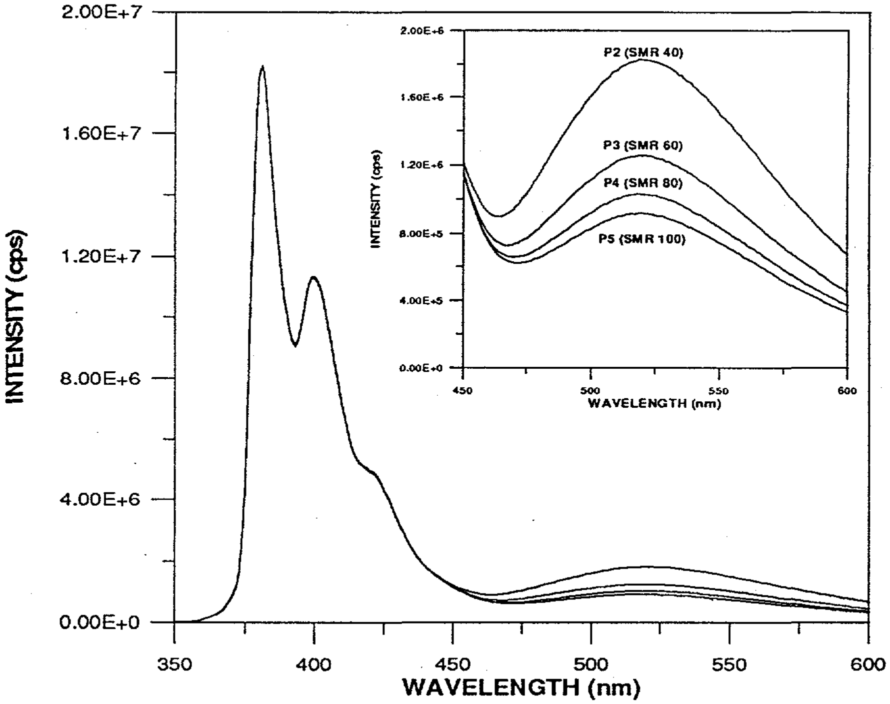

Figure 4. Fluorescence Spectra of terpolymers **P2-P5** in 0.5M NaCl. Inset: Excimer region from 450 to 600 nm for **P2** (SMR 40), **P3** (SMR 60), **P4** (SMR 80), and **P5** (SMR 100).

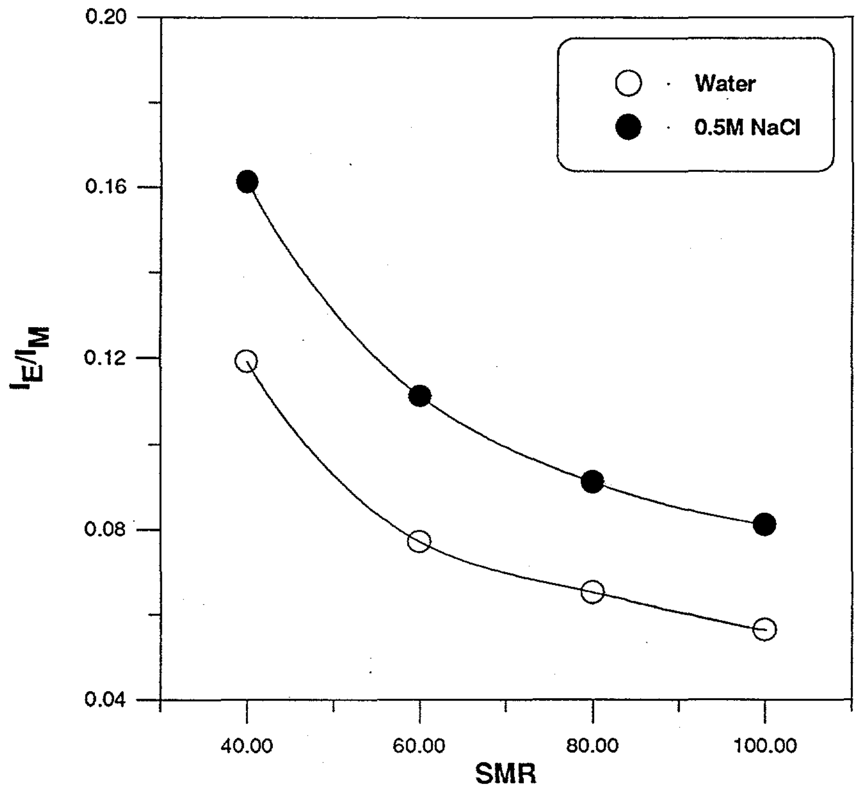

Figure 5. I_E/I_M as a function of the SMR (Equation 1) used in polymerization for terpolymers **P2-P5** in water and 0.5M NaCl.

B. Solution Flow Characterization in Porous Media

Background

As explained in the last report, the extensional flow behavior of dilute polymer solutions through packed beds of solid spheres was modeled by assuming that a single polymer molecules could be considered as a spring, with modules G, and a dashpot, with viscosity η, connected in parallel.

The polymer molecules are elongated and compressed as they passes through the bed and energy is converted to heat as the macromolecules are cyclically strained. This degradation of the fluid kinetic energy to heat increases solution resistance to flow through the bed.

Extensional Flow Model

Fluid resistance is usually expressed as a normalized solution flow resistance, NSFR . At very low polymer concentrations ($c\,\eta_{intr}$approaches zero) the NSFR is defined as

$$NSFR = \frac{\Delta P_s - \Delta P_o}{\Delta P_o\, \eta_{intr}\, c}$$

In the above relationship ΔP_s *and* ΔP_o are the solution and solvent pressure drop across the packed bed, respectively. The polymer solution extensional flow model can be expressed in a dimensionless formate by using a Deborah number, $De = [4\psi Q \eta] / [\pi (D_{bed})^2 \varphi \kappa d G]$, and a dimensionless coil viscosity, $H = [\rho \mu_o \eta_{intr}] / \eta$. See nomenclature for symbol descriptions.

$$NSFR = \frac{3(48)^2(\psi S_h)^2}{175} \frac{H\, De}{1 + 4\pi^2 De^2}$$

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 dimensionless Deborah Number is the ratio of polymer coil response time, $\lambda = \eta / G$ *and* $1/\omega$, the process extension time. As shown by the above relationship, 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 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 1.

Summary

The above model for extensional flow in a porous media indicates that for a polymer to be a good candidate as a mobility control agent in enhanced oil recovery the polymer should : 1) Have a high solution intrinsic viscosity. This increases H and thus fluid resistance to flow. 2) Have a coil viscosity which is low. This always increases H ,which is desirable, but also lowers the coil response time, λ , which is undesirable because a greater fluid extensional flow field stress is required to elongate the polymer. These stresses are not usually present when flooding a reservoir. 3) Have a coil modules which is low. This enables polymer extension at lower fluid flow field extensional stresses which occur at lower fluid flow rate through the porous media.

Polymer analysis using the solution extensional flow model is presently being performed. Table I list the polymer systems that have been studied to date and the model parameters associated with each polymer. After additional polymers have been analyzed a universal relationship between intrinsic viscosity and coil viscosity may be found. If so, then polymer performance in enhancing fluid resistance during flooding will be made more predictable and efforts to synthesize polymers with desired solution rheological properties can be better directed.

NOMENCLATURE

Table I

Symbol Descriptions

Symbol	Description
c	mass concentration of polymer in solution
De	Deborah Number, equal to $\omega\ \eta\ /\ G$
d	packing spherical diameter
G	polymer coil modules
H	dimensionless coil viscosity, equal to $[\rho\,\mu_o\eta_{intr}]\,/\,\eta$
NSFR	$\Delta P_s - \Delta P_o(1+\eta_{intr}c)/[\Delta P_o(1+\eta_{intr}c)\eta_{intr}c]$

Q	fluid volummetric Flow Rate
t	time
ΔP_o	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 d, equal to 3/4
λ	coil response time
μ_o	solvent shear viscosity
ρ	polymer monomer density
ω	coil cycle frequency
ψ	packed bed tortuosity

REFERENCES

1. Hester, R. D., C. L. McCormick, DOE Quarterly Report for DE-AC22-92BC-14882, June 23, 1995

2. Durst, F., R. Hass, *Rheol. Acta 20,* 179, 1981.

3. McCormick, C. L., K. P. Blackman, *J. Poly. Sci., Poly. Chem, A24,* 2635, 1986.

4. McCormick, C. L., K. P. Blackman, *D. L. Elliott, J. Poly. Sci., Poly. Chem, A24,* 2619, 1986.

TABLE I ;Packed Bed Extensional Results for Polymer Solutions Using 0.5 M NaCl Solvent

Polymer Type	Mol. Wt. g / mole x 10^{-6}	Intrinsic Viscosity cm^3 / g	Solution Conc. g / cm^3 x 10^{-6}	Packing Sphere Size cm x 10^3	Coil Viscosity poise	Coil Modulus dyne / cm^2 x 10^{-3}	Coil Response Time msec	Coil Hydro. Diameter Å	Dimen sionless Conc.
AM/AMBA[a]	14	4600	54	29	10	11	1.0	4300	0.25
AM/AMBA[a]	14	4600	54	15	9.4	7.7	1.2	4300	0.25
AM/AMBA[a]	14	4600	166	29	13	9.0	1.4	4300	0.76
AM/AMBA[a]	14	4600	166	15	11	8.8	1.3	4300	0.76
AM/AMBA[a]	14	4600	466	29	20	11	1.9	4300	2.14
AM/AMBA[a]	14	4600	466	15	18	6.8	2.7	4300	2.14
AM/AMBA[b]	14	4600	0	15/29	8.4	9.2	0.90	4300	0
PAM[c]	19	2900	50	39	3.4	2.7	1.2	4100	0.145
PAM[c]	19	2900	25	39	3.1	2.6	1.2	4100	0.073
HPAM[d]	11	2200	50	39	3.5	6.1	0.57	3100	0.11
HPAM[d]	11	2200	25	39	2.9	6.4	0.56	3100	0.055
HPAM[e]	3.5	1200	50	39	3.5	16	0.22	1700	0.060
PEO[f]	2.8	960	50	29	7.6	150	0.051	300	0.048
PEO[f]	2.8	960	100	29	9.8	110	0.088	300	0.096
PEO[f]	7.6	2100	50	29	33	840	0.039	2700	0.105
PEO[f]	7.6	2100	100	29	44	310	0.14	2700	0.21

a) Copolymer from C. L. McCormick, synthesized from acrylamide and 3-acrylamido-3-methylbutanoic acid monomers[3,4]
b) Results obtained by extrapulating AM/AMBA data to zero polymer concentration (see Figure 1) c) Polyacrylamide data from Durst paper[2] d) Hydrolyzed polyacrylamide with 3 % hydrolysis, data from Durst paper[2] e) Hydrolyzed polyacrylamide with 13 % hydrolysis, data from Durst paper[2] f) Poly(ethylene oxide) from Polysciences, Inc.

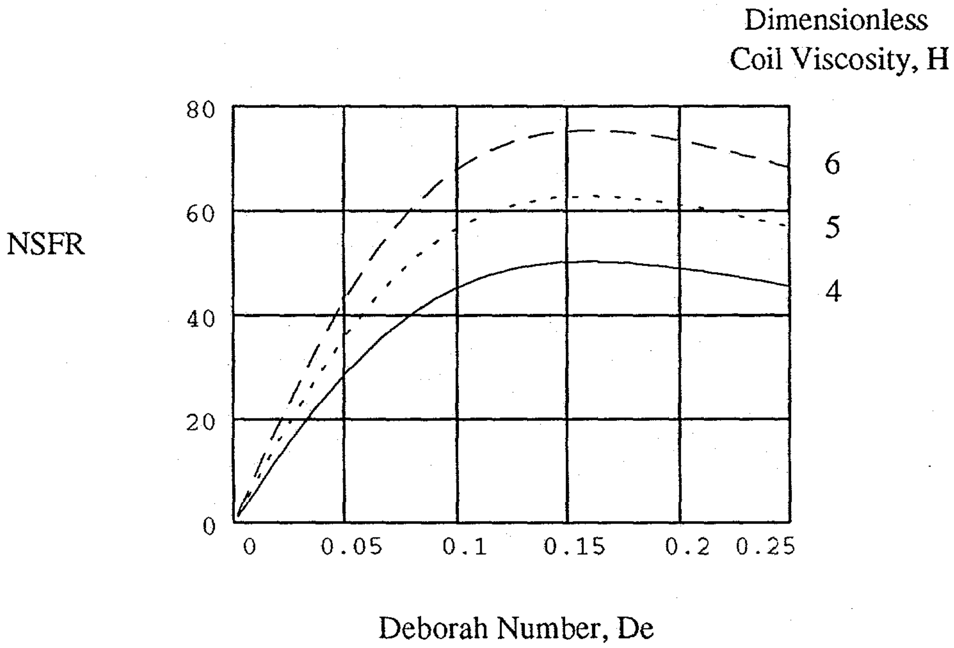

Figure 1 : Normalized Solution Flow Resistance (NSFR) Dependence Upon Deborah Number and Dimensionless Coil Viscosity