Quarterly Progress Report

For Innovative Copolymer Systems for In Situ Rheology Control in Advanced Oil Recovery

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by

Charles McCormick

and

Roger Hester

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The University of Southern Mississippi
Department of Polymer Science
P. O. Box 10076
Hattiesburg, MS 39406

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Abstract

Synthesis work is continuing to develop several polymer structures made from zwitterionic monomers that are potential candidates for use as mobility control agents. Solution viscosities of those polymer are shown to be responsive to solvent, pH, and ionic strength. Solution viscosity response to solvent conditions is a function of polymer monomer composition and type of monomer. Additional efforts are being made to improve the instrumentation needed to measure dilute solution viscosities of very high molecular weight, water soluble polymers. A cable rheometer has been modified to improve sensitivity and reproducibility.

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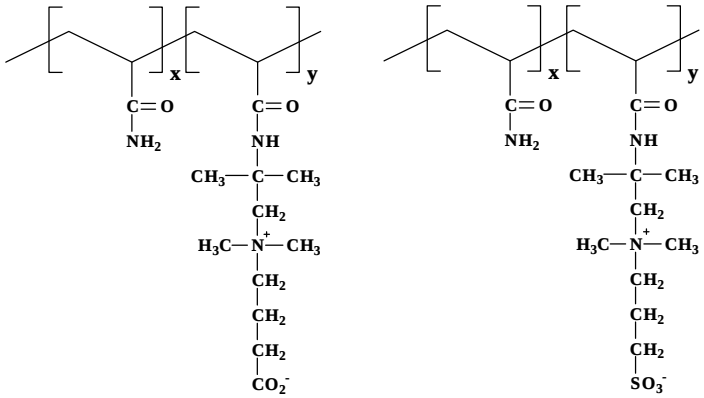
A. EXECUTIVE SUMMARY

Our research efforts have been focused on the development of stimuli-responsive water-soluble polymers designed for use in oil field applications, particularly enhanced oil recovery (EOR). This report discloses the progress of our ongoing research of polybetaines, polymers derived from zwitterionic monomers, that show the ability to sustain or increase their solution viscosity in the presence of electrolytes.[1-6] Such polymers appear to be well-suited for use under conditions similar to those encountered in EOR operations.

An old Contraves rheometer is being used to measure polymer solution shear viscosities. Replacement parts and service for this instrument are no longer provided by the vendor and, unfortunately, no commercial rheometer is presently manufactured that could replace the Contraves rheometer should it become inoperable. Because solution viscosity measurements are critical for the characterization of the polymers synthesized in this research project, a cable rheometer that could replace the Contraves is under development in our laboratory. Several cable rheometer modifications and operating procedures have been made to improve its accuracy, sensitivity, and reproducibility.

B. Task 1 Design of Co- and Terpolymers

Previously, we have reported the synthesis and characterization of copolymers of acrylamide with 4-(2-acrylamido-2-methylpropyldimethylammonio)butanoate] (DABAM series) and with 3-(2-acrylamido-2-methylpropyldimethylammonio)propanesulfonate (DAPSAM series) (*Scheme 1*). Reactivity ratios were determined and the nonlinear least squares method yielded values of $r_1 = 1.01$ and $r_2 = 0.99$, indicating random incorporation of the monomers into the final copolymers. The molecular weights of the copolymers were found to range from 3.9 to 12.0×10^6 g/mol. Preliminary studies of solution behavior examined copolymer solubility and the effects of various added electrolytes on copolymer solution viscosities. In this report, we discuss our continued investigation of the solution behavior of the DABAM and DAPSAM copolymers. The effects of pH, copolymer composition, and added electrolyte on the solution viscosity of the copolymers are described herein.



Scheme 1 Structural composition of copolymers of acrylamide with 4-(2-acrylamido-2-methylpropyldimethylammonio)butanoate (the DABAM series) and with 3-(2-acrylamido-2-methylpropyldimethylammonio)propanesulfonate (the DAPSAM series).

Solution Behavior

Effects of pH

Figure 1 shows the effects of increasing polymer concentration on the apparent viscosity of DABAM-25 and -40 at pH 3 and pH 7.5. At low pH, the carboxylate group incorporated in the AMPDAB mer unit is protonated, and the polymer acquires an overall positive charge due to the remaining ammonium group. The polycationic nature of the copolymer induces a larger hydrodynamic volume since charge-charge repulsions result in an extended conformation. As the pH is raised, the carboxylic acid is ionized and the coulombic repulsions essentially become coulombic attractions. These attractions lead to a restricted conformation and much smaller hydrodynamic volumes, as evidenced by the lower viscosity values. The effect of copolymer composition on the apparent viscosity at pH 3 is presented in *Figure 2*. The maximum viscosity occurs when approximately 20-30 mol% AMPDAB is incorporated into the copolymer. This is most likely the result of molecular weight differences, as well as charge density effects.

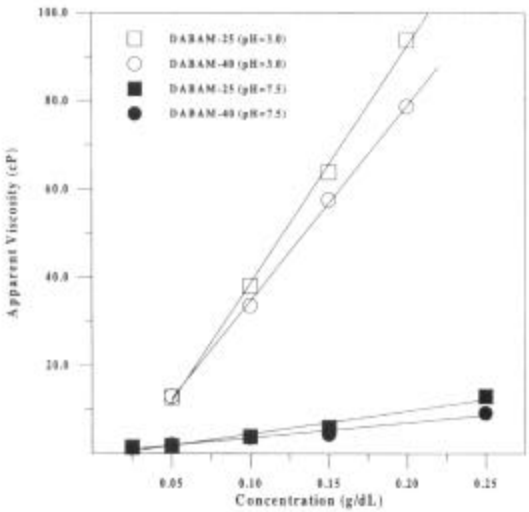


Figure 1 Apparent viscosities of DABAM copolymers at pH 3 and pH 7.5 as a function of copolymer concentration.

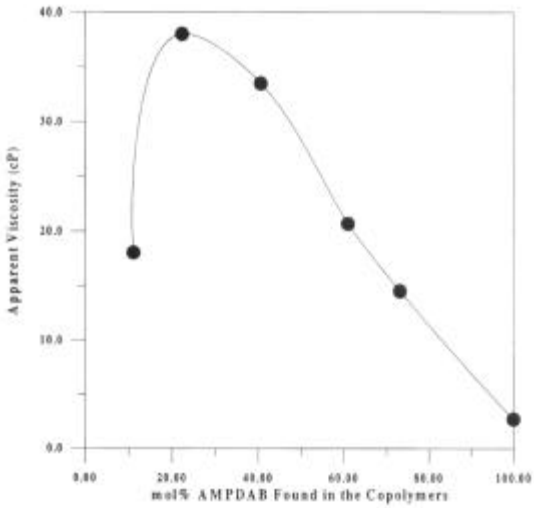


Figure 2 Apparent viscosities of DABAM copolymers as a function of the mol % AMPDAB found in the copolymers. (Determined at pH 3 and a polymer concentration of 0.1 g/dL)

The effects of added electrolytes on the solution behavior of the DABAM copolymers at pH 3 are shown in *Figure 3*. As anticipated, there is a decrease in viscosity as the concentration of NaCl increases as charge-charge repulsions are shielded and the polymer coil contracts. Linear dependency of the reduced viscosity on the inverse square root of ionic strength is typical behavior for polyelectrolytes.[7] Furthermore, the magnitude of the slope gives an indication of the degree of conformational change induced by the addition of electrolytes. From *Figure 3*, DABAM-25 exhibits the smallest slope while DABAM-75 has the highest slope. This behavior is, in part, due to enhanced hydrophobicity of the AMPDAB mer unit at low pH, due to the conversion of the carboxylate group to the carboxylic acid group. Thus, through the addition of NaCl, not only are charge-charge repulsions shielded but also hydrophobic interactions are enhanced as water structuring events lead to a "salting-out" effect. As more AMPDAB is incorporated into the copolymers, this effect is magnified.

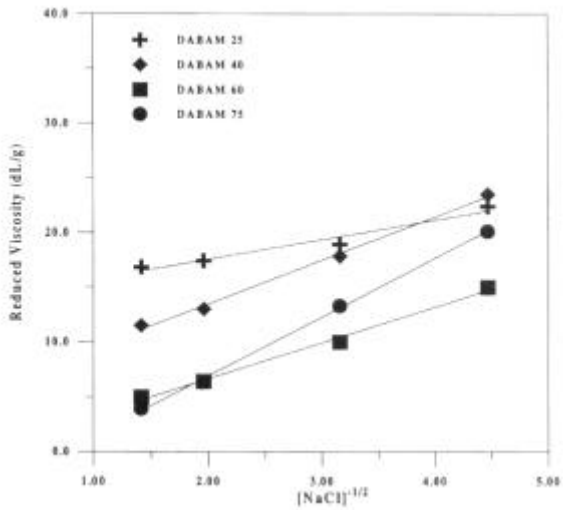


Figure 3 Reduced viscosities of DABAM copolymers as a function of the inverse square root of ionic strength. (Determined at pH 3 and a polymer concentration of 0.1 g/dL)

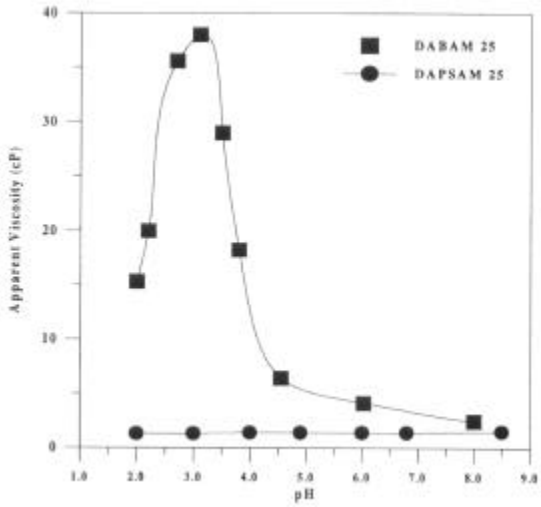


Figure 4 Apparent viscosities of DABAM and DAPSAM copolymers as a function pH (Polymer concentration of 0.1 g/dL).

The apparent viscosity as a function of decreasing pH was also examined for copolymers with different anionic substituents (*Figure 4*). DABAM-25, which incorporates the carboxylate functionality, exhibits an order of magnitude increase in the apparent viscosity as the pH is lowered from 8 to 3. DAPSAM-25, which contains the sulfonate functionality, is relatively insensitive to changes in the pH of the aqueous solution. The dramatic pH-responsiveness of the carboxybetaine mer units is in direct contrast with that of the sulfobetaine mer units. The sulfonate group is a much weaker base than the carboxylate group and cannot be protonated at pH values which will not degrade the polymer backbone. Thus, the AMPDAPS mer units of DAPSAM-25 remain in the zwitterionic state throughout the useful pH range. In contrast, DABAM-25, which contains carboxylate groups, may be converted from the zwitterionic to the cationic state by lowering of pH. At pH values less than 3, a reduction in the apparent viscosity

is observed for DABAM-25. This behavior probably results from a shielding of the cationic charges as the concentration of hydronimum and chloride ions increases as the pH is lowered. The increase in hydrophobicity as more of the carboxylate groups are protonated is also partially responsible for loss of hydrodynamic volume in aqueous media.

Conclusions

The novel series of polyampholytes based on copolymers of acrylamide (AM) and 4-(2-acrylamido-2-methylpropyldimethylammonio)butanoate (AMPDAB) exhibit complex solubility and solution behavior due to hydrogen bonding, charge-charge interactions, molecular weight, and configuration effects. The copolymers at pH 3 display polyelectrolyte behavior due to the cationic nature of the polymer. At pH 8, the copolymers exhibit both intermolecular and intramolecular interactions depending on the amount of AMPDAB incorporated into the copolymer. The poly(vinyl carboxybetaines) are more soluble in deionized water than the analogous poly(vinyl sulfobetaines) as well as being more responsive to changes in the pH of the aqueous medium.

C. Task 5a. Screen Rheometry Studies

Intrinsic Viscosity Measurements

Accurate values for intrinsic viscosity, η_{intr}, are important for characterizing high molecular weight water soluble polymer extensional flow properties since each macromolecular dilute solution prepared for the Screen Extensional Rheometer is made using a mass concentration, c*, that is a function of the intrinsic viscosity. Usually c* is equal to $1/(10\ \eta_{intr})$. Thus, an inaccurate intrinsic viscosity value results in a polymer solution deviating from expected dilute solution conditions.

Intrinsic viscosity values are determined by extrapolating a Huggins or Kraemer plot to zero polymer concentration**.** The plotted data should have linearity, otherwise, intrinsic viscosity values are subject to error. To be accurate these plots also require that solution shear viscosity measurements be made at very low fluid shear rates. The dual requirements of low fluid shear rate and dilute solution conditions combine to give low shear stress forces during viscosity measurements. Therefore, only very sensitive rheometers with transducers capable of measuring small forces can be successfully used to determine the low shear solution viscosities of high molecular weight polymers in dilute concentrations.

Contraves Rheometer

Currently, a Contraves Low Shear Model 30 rheometer, operating at a steady fluid shear rate of 5.96 sec^{-1}, is being used to collect the solution shear viscosity data necessary to calculate a polymer's intrinsic viscosity. A potential problem with this instrument is that the operating shear rates are too high for accurate shear viscosity measurements of high molecular weight polymer solutions. Lower shear rate conditions are needed with higher molecular weight polymers to ensure that solution viscosities are measured in the 1st Newtonian or "zero" shear region[1]. The Contraves can operate at lower shear rates, but unstable measurement conditions are obtained. Also, parts and service for this old instrument are no longer provided. Therefore, an accurate and reliable backup instrument for collecting polymer solution shear viscosity data is needed. Because no commercial rheometer is presently available, a cable rheometer is under development in our laboratory.

Cable Rheometer

The previously described cable rheometer[8] is currently being used to calculate the intrinsic viscosity of high molecular weight polymers. The cable rheometer provides steady shear rates that are lower than 5.96 sec^{-1}. These lower shear rates ensure that solution viscosities measurements are in the 1st Newtonian or "zero" shear region. It is critical to make viscosity measurements in this region to prevent shearing forces from altering polymer coil geometry during the measurements.

Over several months, the original cable rheometer has been modified to increase its accuracy, reproducibility, and ease of use. Modifications are illustrated in Figures 5-8. The X-Y micro-positioning stage, Figure 6, provides accurate centering of the bob inside the cup. Other improvements include incorporating an easy to read degree scale, Figure 7, that was etched into the instrument's aluminum base. Figure 8 shows the brass fitting and adjusting mechanism that directs a laser through a small opening in the bob connecting shaft. These improvements have allowed a more accurate measurement of bob deflection. Also shown in Figure 4 is a new quick disconnect that attaches the bob to the wire. This feature makes bob removal during cleaning much more convenient.

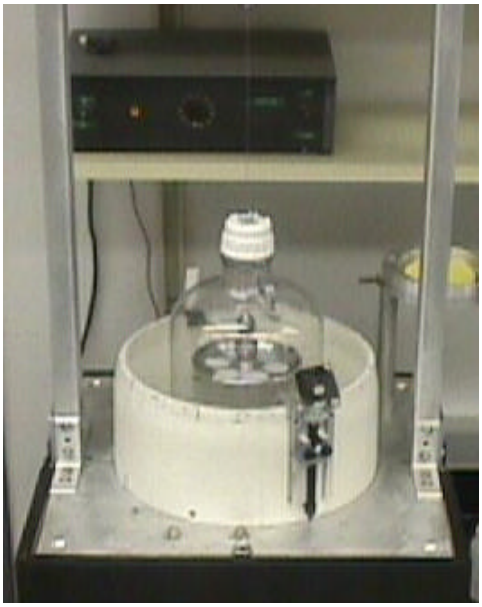


Figure 5 Fully assembled rheometer

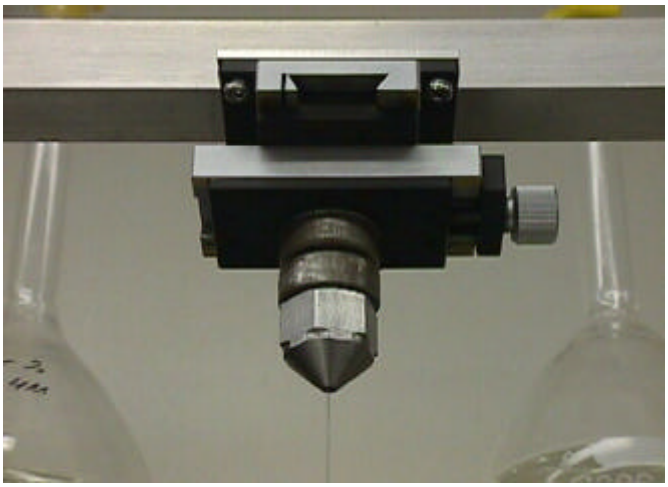


Figure 6 X-Y micropositioning stage

Figure 7 Degree Scale

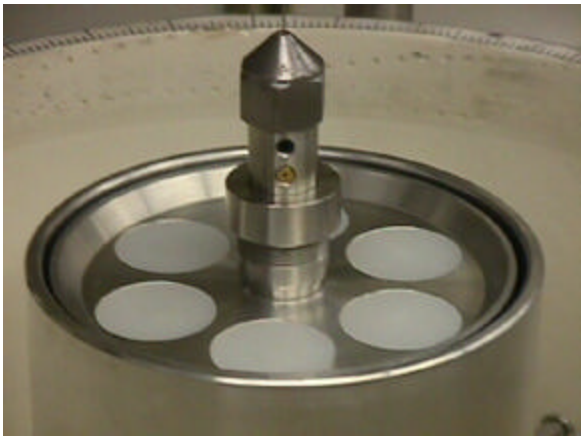


Figure 8 Cup and bob

Single Wire

After the above rheometer modifications were completed, further force sensitivity improvements were desired. The old cable, which contain forty nine stranded wires, was exchanged with a cable having a single wire with a diameter of 0.007 inches. It was expected that the single wire cable will be more sensitive because the torque applied to the cable would produce more twist than the larger diameter stranded cable.

Instrument Constant "K"

The instrument constant or cable modulus, K, was determined using 2-Ethyl-1-Hexanol (shear viscosity = 0.0965 poise at room conditions) and the results from the stranded wire cable and single wire cable are reported in Table I. The lowest motor speed (2.16 rpm) was used to collect the

data for the instrument constant. As expected, the data from Table I shows that at a given torque more twist is developed with the single wire cable as compared to the stranded wire cable.

Table 1. Instrument Information

Parameter	Single wire cable	Stranded wire cable (7x7)
Deflection Angle (degrees)	147.5	85.5
Cup Speed (rpm)	2.16	2.75
"K" constant value (psi)	2.486×10^{-8}	4.517×10^{-8}
Cable Diameter (in)	0.007	0.024

The "K" constant values are basically the same. The difference between the two constants can be attributed to the difference in the cup speed and wire geometry (single strand cable versus multi-stranded cable). Using the instrument constant for the single wire cable, solution viscosities of a 4.1 million molecular weight Polyethylene Oxide (PEO) were measured on the rheometer using both the single wire cable and the stranded wire cable.

Solution Intrinsic Viscosity

Five solution concentrations of the 4.1×10^6 g/mol PEO were tested on the rheometer. Huggins plots of reduced viscosity versus concentration were generated using both the single wire cable and the stranded wire cable and are shown in Figures 9 and 10, respectively. Linear data must be obtained so a correct intrinsic viscosity value can be acquired through extrapolation to the ordinate. As shown in Figure 9, the data from the single wire cable did not result in a linear plot. Since the plot was not linear, an accurate intrinsic viscosity could not be obtained. In contrast to the single wire cable data, data from the stranded wire cable was linear as shown in Figure 10.

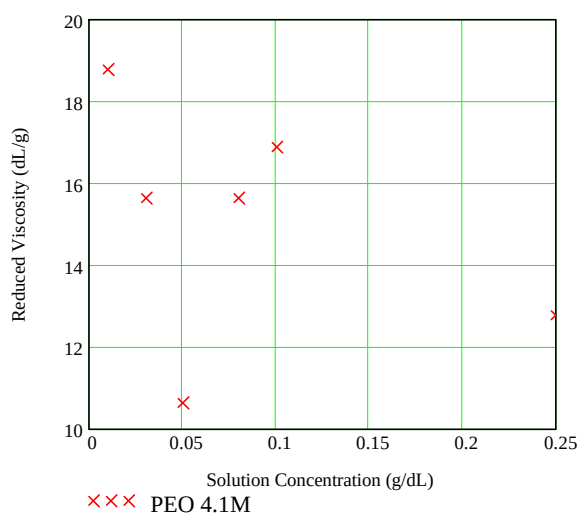


Figure 9 Single stranded wire data

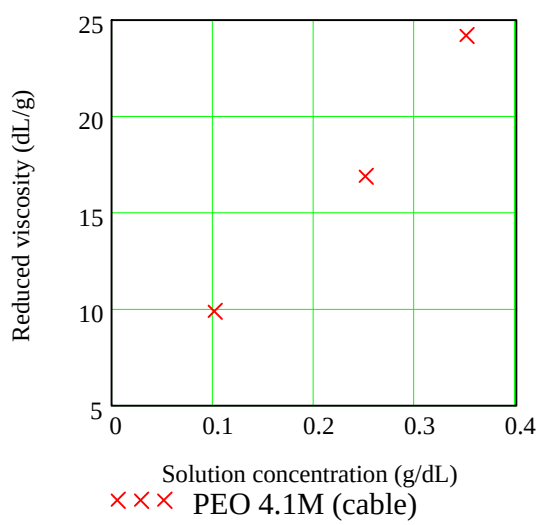


Figure 10 Cable data

Since the data from the stranded wire cable resulted in a linear fit, an accurate intrinsic value for the PEO could be determined.

Experimentation also revealed that at very low cup rotational speeds the stranded wire cable's response was not as good as the single wire cable. However as the motor speed was increased, the stranded wire cable response improved. After testing both the single wire and cable it was determined that the stranded wire cable will give more accurate intrinsic viscosity values since the viscosity data results in linear plots. However, the instrument configured with the stranded wire cable is less sensitive than the single wire cable at low cup rotational speeds.

Future Cable Rheometer Modifications

Other instrument improvements are still needed before reliable viscosity measurements can obtained with the cable rheometer. As it is currently designed, the bottom surface of the bob has a conical cavity which houses an air pocket. This pocket was designed to eliminate the fluid friction on the cup's bottom surface. This assures that only fluid shear forces around the cup's curved side are active in producing fluid torque on the cable. It is now suspected that the air pocket volume may not be constant. The pocket volume appears to be dependent upon how the bob is lowered into the fluid contained within the cup. Sometimes, as the bob is lowered, one or more large air bubble rises from the cavity. This indicates that the amount of air in the cavity is probably not consistent over the course of several experiments.

The effect that a variable air pocket volume could have on the viscosity measurement is two-fold. First, as more air escapes and fluid fills the bob cavity, there is an increased area of fluid-to-bob bottom surface contact. This extra area is not accounted for in the viscosity calculations. Thus, viscosity measurements would vary with air pocket volume. Another effect of variable air pocket volume is a variation in bob weight introduced by changing buoyant forces. As the effective weight of the bob changes there is variation in the twist angle produced at a given cable torque. When a weight is suspended from the stranded wire cable, the cable tends to untwist to some equilibrium point. If the bob weight varies, this equilibrium deflection changes and the torque due to a given shear force produces a different cable twist angle.

These inconsistencies will be eliminated by removing the cup's air pocket. A new bob and cup will be fabricated such that the bottom surface will be slightly tapered, similar to that used in the Contraves rheometer. Using this geometry, no air can be trapped under the bob. Also, the surface area of fluid to bob contact will be increased by about thirty percent. This should result in an increase in instrument sensitivity.

D. References

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