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Water-Soluble Random and Graft Copolymers for Utilization in Enhanced Oil Recovery

C. L. McCormick[a]
[a] Department of Polymer Science, University of Southern Mississippi, Hattiesburg, Mississippi

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Water-Soluble Random and Graft Copolymers for Utilization in Enhanced Oil Recovery

C. L. McCORMICK

Department of Polymer Science
University of Southern Mississippi
Hattiesburg, Mississippi 39406-0076

ABSTRACT

Copolymer structure has a marked effect on solution properties and thus behavioral characteristics of water-soluble copolymers utilized in enhanced oil recovery. The ability of random and graft copolymers to maintain large hydrodynamic volumes in dilute solutions in the presence of mono- and divalent electrolytes is critical for mobility control. The differences in viscosity behavior are described for a series of random and graft copolymers of acrylamide with sodium-2-acrylamido-2-methylpropane sulfonate (NaAMPS), diacetone acrylamide (DAAM), and sodium acrylate (NaA) as a function of polymer microstructure, temperature, concentration, and added electrolytes. Copolymers of AM-NaAMPS show enhanced salt tolerance and phase stability over their AM-NaA counterparts with similar compositions and molecular weights. The AM-DAAM copolymers show unusual solution behavior with increases in viscosity in the presence of added salt.

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I. INTRODUCTION

Dwindling domestic reserves, high prices, and uncertainties of future feedstocks have encouraged scientists and engineers to explore new avenues for recovering additional petroleum from reservoirs depleted by conventional recovery techniques. These methods, collectively referred to as enhanced oil recovery (EOR), may account for over 25% of the total United States crude oil production by the year 2000 according to some estimates [1, 2].

A. Enhanced Oil Recovery Technology

A newly drilled oil formation generally has enough natural pressure to force the reservoir oil to the well bore where it rises or is pumped to the surface. Upon depletion of the natural pressures, only 20-30% of the original oil in place is normally recovered during this primary production phase. Increased oil recovery is possible by pressure maintenance during the latter stages of primary production or repressurization after depletion of the natural drive energy.

Injection of fluids (generally water solutions) into the formation significantly improves the sweep of oil from the porous rock toward producing wells. Water flooding has proven to be the most practical approach and currently represents approximately half of the current United States daily oil production [1].

Substantial quantities of oil remain trapped in the pore space of reservoir rock even after water flooding. Therefore, a number of additional enhanced oil recovery methods are currently used such as: Thermal, carbon dioxide, and chemical flooding. Chemical flooding techniques include the use of surfactants, miscible hydrocarbons, alcohols, alkali, and polymers. This report will deal only with polymers potentially useful in simple polymer flooding or micellar polymer flooding.

The major problems encountered in simple water flooding are related to "fingering" of the injected water through the mobile fluid front, resulting in premature breakthrough to the production wells. The produced water-to-oil ratio then climbs until oil recovery is no longer economically feasible. To reduce fingering, high molecular weight, water-soluble polymers may be added to the injection water to increase viscosity. The solution becomes less mobile than the oil, resulting in increased sweep efficiency. Additionally, surfactants may be injected to precede a polymer flood (micellar polymer flooding) for even more efficient recovery. The relative merits of chemical methods, ongoing field projects, and some economic calculations have recently been reviewed [3].

In order to obtain mobility control in a flood, the displacing fluid should have a mobility equal to or lower than the mobility of the oil. The mobility ratio, M, is normally expressed:

$$M = \frac{\lambda_w}{\lambda_0} = \frac{k_w/\mu_w}{k_0/\mu_0} \qquad (1)$$

λ_w and λ_0 represent the mobility of the water and oil, respectively; k represents permeability of reservoir rock to each phase; and μ represents viscosity. The addition of certain water-soluble polymers increases viscosity of the water phase and may in some instances reduce the permeability of the porous rock to water. In heterogeneous reservoirs of various porosities and fracture zones, the resistance to water can be significantly increased and the degree of fingering reduced so that a more uniform fluid front is developed.

The physical and chemical interactions that polymer solutions encounter in the field are extremely complex. The polymer must perform at relatively high temperatures for long periods of time under various conditions of pH, ionic strength (with various ion types), pressure, flow rate, and substrate heterogeneity. The polymer must resist shear degradation and must not adsorb permanently to the rock surface. Multivalent cations present in the aqueous solution can lead to intermolecular interactions on charged polymers causing cross-linking, gel formation, precipitation, and pore clogging. The variety of pore sizes in reservoir rock can cause chromatographic effects on the macromolecules. Since the larger molecules are excluded from smaller pores, they bypass them in route to larger pores. Polymer slug dispersion eventually occurs, resulting in loss of mobility control. Additionally, oil entrapped in small pores may be completely bypassed. This portion of the rock is referred to as "excluded" pore volume or "inaccessible" pore volume.

In order for a polymer to be economical in EOR, it must produce large viscosity increases at low concentrations (i.e., < 1000 ppm); therefore, large solution dimensions of the macromolecules must be maintained. Several commercially available polymers are being field tested. Most data, to date, have been obtained for polyacrylamides and biologically produced polysaccharides. High molecular weight polyacrylamides and their partially hydrolyzed derivatives are available at 2.0 ± 0.30 \$/lb, while the polysaccharides may require 2.5 ± 0.35 \$/lb. At 2.0 \$/lb the cost of a 1000 ppm solution of polymer would be 0.69 \$/barrel [4, 5].

B. Structural Requirements of EOR Polymers

The possibility of increased efficiency and thus better economics in future years will depend upon new laboratory discoveries. Present commercial polymers, with one or two exceptions, have not been tailored for EOR use. The most important requirements for candidate water-soluble polymers for EOR can be related to the fundamental parameter hydrodynamic volume (HDV). HDV has a firm theoretical basis and is measurable by a number of techniques including classical light scattering, quasi-elastic light scattering, viscometry, and ultracentrifugation. Measurements of polymer microstructure, polymer-solvent interaction, chain extension, etc. can be used to correlate polymer performance under specific conditions to HDV.

The importance of HDV can be readily seen by examining Eq. (1). Mobility control ratio values are smaller as the viscosity of the water phase is higher. Large viscosity increases at low concentrations can be realized only with molecules maintaining large solution dimensions. Therefore, the polymer should not drastically lose viscosity at operating temperature or in the presence of NaCl, $CaCl_2$, or other electrolytes.

Dimensions of macromolecules may be too large for adequate permeability. The size of the polymer in solution affects its degree of entrapment and adsorption during flow through the porous reservoir rock. Additionally, the pore size distribution of the medium determines the extent of permeation, resulting in chromatographic separation of chains of different size (size exclusion chromatography).

Obviously, choice of polymer can have a large effect on performance based on the above considerations alone. Other practical considerations aside from cost include: method of dissolution; shearing effects during mixing or injection; gellation; and biological, thermal, or oxidative degradation.

The structures of a variety of commercial and some selected laboratory polymers with potential in EOR are illustrated in Fig. 1. Synthetic polymers (I-III) can be polymerized to high molecular weights and exhibit exceptionally high solution viscosities, but shear degradation and viscosity loss in the presence of electrolytes (especially a problem with Type II) can lead to loss of mobility control. Biopolymers IV and V and other related polysaccharides have moderately high viscosities due to their extended chain structures in solution and are not as sensitive to viscosity loss in the presence of electrolytes. However, they are prone to biological degradation and present some handling and filtration problems. Modified natural polymers, including starch derivatives and cellulose derivatives VI and VII, have been used for a number of oil field applications but lack properties necessary for mobility control in EOR. A recent review of the uses of polymers II and IV-VII, in the oil field, is given in Ref. 6.

The extended chain dimensions of natural polysaccharides and the immense viscosity increases observed in our laboratories for certain acrylamide copolymer compositions have led to investigations of both synthetic copolymers and graft copolymers derived from natural polymers [7-17]. The promising solution properties of copolymers VIII-X of Fig. 1 will be discussed in relationship to molecular structure, grafted chain length, and composition in this report.

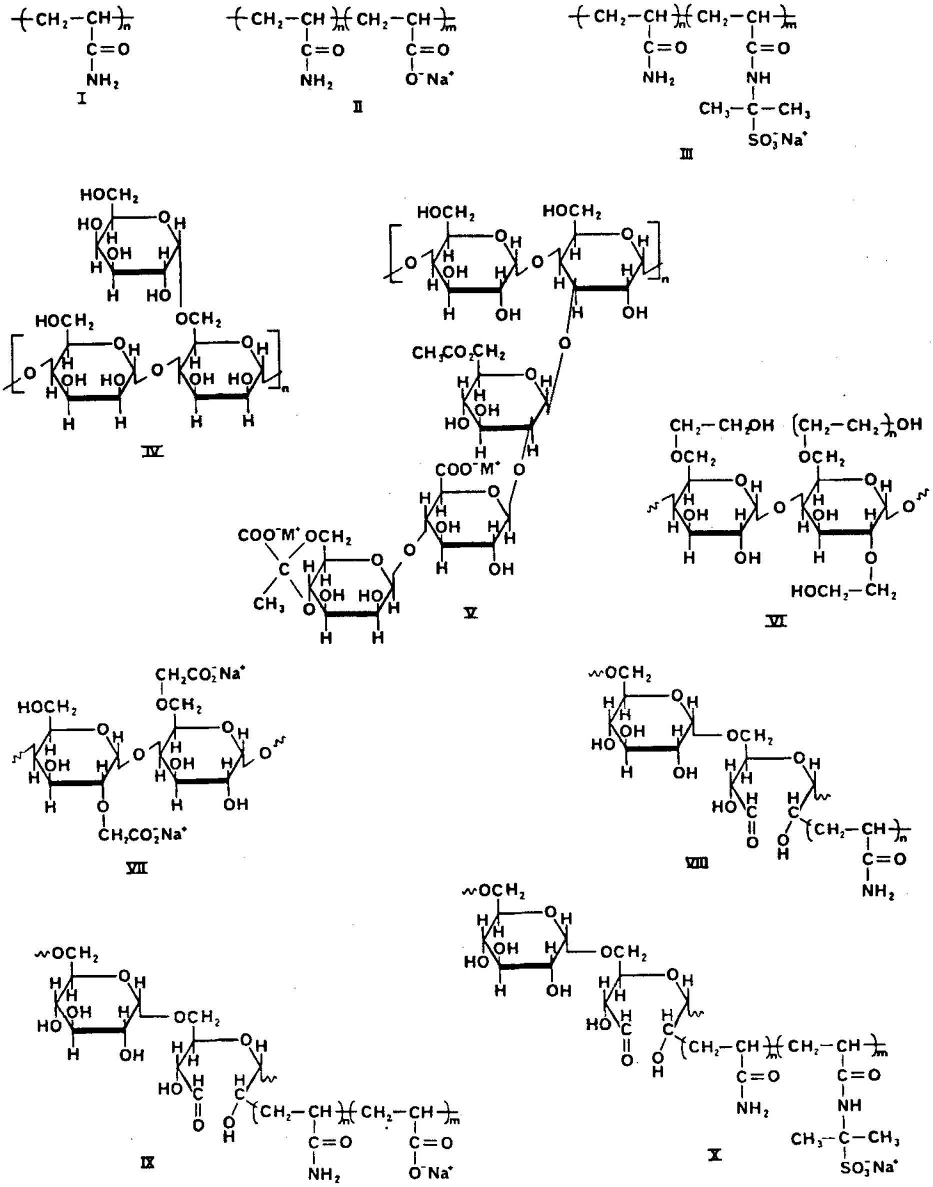

FIG. 1. Synthetic and natural polymers for potential utilization in oil field applications.

II. EXPERIMENTAL

A. Syntheses of Random and Graft Copolymers

Random copolymers of acrylamide with sodium acrylate (NaA) [7, 16], sodium-2-acrylamido-2-methylpropane sulfonate (NaAMPS) [7, 11-13, 16], and diacetone acrylamide (DAAM) [16] were synthesized in aqueous solutions with persulfate initiators as previously reported. Graft copolymers of dextran with polyacrylamide [8-10, 17], poly(acrylamide-co-NaA) [15, 17], and poly(acrylamide-co-NaAMPS) [14, 17] were prepared utilizing controlled Ce(IV) initiation.

B. Structural Determinations and Viscosity Measurements

Elemental analyses were performed by Galbraith Laboratories of Knoxville, Tennessee. Infrared spectra were obtained using a Perkin-Elmer 567 Grating Infrared Spectrophotometer. Carbon-13 nuclear magnetic resonance spectrometry experiments were conducted with a JEOL FX-90Q Spectrometer. A Knauer Membrane Osmometer was utilized to determine number-average molecular weights. Gel permeation chromatography measurements were conducted with a Waters Associates ALC 300 with Model R401 refractive index detector. A series of controlled porous glass columns were used with 0.4 M Na_2SO_4 as the mobile phase. Viscosity measurements were performed with Cannon-Ubbelohde four-bulb shear dilution capillary viscometers.

III. STRUCTURE-PROPERTY RELATIONS OF TAILORED MODEL COPOLYMERS

In order to assess the effects of molecular structure on solution behavior, several series of synthetic copolymers were prepared with controlled microstructures and molecular weights. Three comonomers, sodium acrylate (NaA), sodium-2-acrylamido-2-methylpropane sulfonate (NaAMPS), and diacetone acrylamide (DAAM), were utilized to prepare random copolymers with acrylamide (AM). Further, dextran was grafted with those comonomers at feed compositions resulting in optimal viscosity enhancement. Selected structural and behavioral properties of these copolymer systems are presented in the following discussion. Emphasis has been placed on viscosity, phase behavior, and salt tolerance.

A. Random Copolymers of Acrylamide

1. Reactivity Ratios, Microstructure, and Molecular Weight

Reactivity ratio studies were conducted utilizing classical Fineman-Ross [18], Kelen-Tüdös [19], and Mayo-Lewis [20] approaches for the AM-NaA, AM-NaAMPS, and AM-DAAM monomer pairs. As expected, these comonomers (Table 1) copolymerize randomly in aqueous conditions with added electrolytes. Under these conditions, copolymer compositions were varied by changing feed compositions (Table 2). Copolymer compositions were confirmed by elemental analyses, infrared spectroscopy, and carbon-13 NMR spectrometry. Mean sequence lengths, μ, were then determined statistically utilizing the method of Igarashi [21]. Molecular weights were measured by membrane osmometry.

2. Solution Properties and Phase Behavior

Typical polyelectrolyte behavior is observed for the AM-NaA (Fig. 2) and AM-NaAMPS (Fig. 3) copolymers with added electrolyte. Linear relationships between zero-shear intrinsic viscosity, $[\eta]_0$, and the inverse square root of ionic strength are observed in aqueous sodium chloride solutions for both copolymer types. The slopes of the line and the magnitude of $[\eta]_0$ are measures of salt sensitivity and are quite dependent on polymer structure. At high ionic strengths, charge-charge repulsions along the macromolecular backbone are minimized and chain dimensions become smaller.

The effects of comonomer structure were, therefore, evaluated in NaCl solutions of 0.257 M. Interestingly, the highest viscosities were found for NaA-10-4 in the AM-NaA series and AMPS-1-4 in the AM-NaAMPS series (Table 3). In fact, maxima in the respective plots of $[\eta]_0$ vs mol% charged comonomer occurred at approximately 10 mol% (Figs. 4 and 5).

The absolute values of $[\eta]_0$ were higher in 0.257 M NaCl solutions for the AM-NaAMPS copolymers as compared to AM-NaA copolymers of similar microstructures (Table 3), despite the fact that these copolymers have similar molecular weights. Copolymer AMPS-1-5 with a mean sequence length ratio of 8.2 exhibited a viscosity twice as large as that of NaA-10-4 with a mean sequence length ratio of 8.8.

Although it is tempting to explain the above results or differences in ion binding due to pK_a differences in the sulfonated and carboxylated comonomers, other factors including hydrophobicity and conformation are certainly important.

The AM-DAAM series was synthesized (Table 2) in order to probe hydrophobic effects. The DAAM comonomer mimics the NaAMPS

TABLE 1. Reactivity Ratios

	Fineman-Ross		Kelen-Tüdős		Mayo-Lewis	
M_1-M_2	r_1	r_2	r_1	r_2	r_1	r_2
AM-NaAMPS	0.98 ± 0.09	0.49 ± 0.02	1.00 ± 0.08	0.52 ± 0.07	1.02 ± 0.01	0.50 ± 0.01
AM-DAAM	0.83 ± 0.04	0.95 ± 0.06	0.82 ± 0.04	0.92 ± 0.05	0.76 ± 0.02	0.99 ± 0.04
AM-NaA	1.05 ± 0.08	0.19 ± 0.04	1.11 ± 0.10	0.32 ± 0.09	- -	- -

TABLE 2. Structural Information

Sample number	Composition[a]		$\overline{M}_n \times 10^{-6}$ [b] g/mol	Mean sequence length[c]	
	Mol% AM	Mol% comonomer		μ_{AM}	$\mu_{comonomer}$
AMPS-1-5	90.5	9.5	1.11 ± 0.05	9.0	1.1
AMPS-2-5	81.0	19.0	1.08 ± 0.06	4.6	1.1
AMPS-3-5	72.1	27.9	0.92 ± 0.06	3.1	1.2
AMPS-7-5	34.3	65.7	0.80 ± 0.04	1.4	2.1
DAAM-11	88.9	11.1	0.76 ± 0.04	8.4	1.1
DAAM-21	77.2	22.8	0.73 ± 0.04	4.3	1.2
DAAM-31	68.6	31.4	0.70 ± 0.03	2.9	1.4
DAAM-41	58.8	41.2	0.65 ± 0.03	2.2	1.6
NaA-10-4	90.1	9.9	0.96 ± 0.05	10.8	1.0
NaA-20-4	84.2	15.8	0.77 ± 0.05	5.4	1.1
NaA-35-5	58.3	31.7	0.69 ± 0.04	2.9	1.2
NaA-50-4	58.3	41.7	0.43 ± 0.03	2.0	1.4
NaA-65-4	46.8	53.2	0.25 ± 0.02	1.5	1.7

[a] From elemental analysis.
[b] From membrane osmometry.
[c] Statistically calculated from reactivity ratios.

monomer with the exception that it has no formal ionic charge. Surprisingly, these copolymers at certain compositions actually exhibit viscosity increases with addition of NaCl to their aqueous solutions (Fig. 6). In 0.257 M NaCl a maximum in the $[\eta]_0$ vs mol% DAAM plot (Fig. 6) is observed. This maximum, however, appears near 20% rather than near 10% as observed for the charged copolymers. Since light-scattering measurements indicate lower values of the second virial coefficient in aqueous NaCl as compared to distilled water, chain extensions due to conformational restrictions and/or cooperative associations are obviously important in viscosity behavior.

The effects of ion binding on divalent calcium ions are readily observed with AM-NaA copolymers. Solution turbidimetry studies were

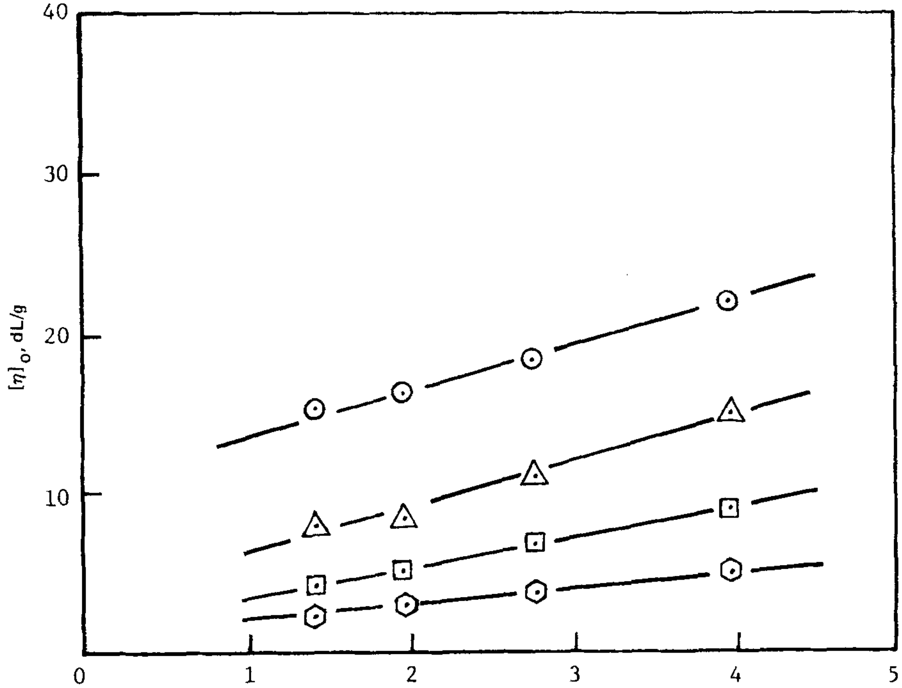

FIG. 2. Zero-shear intrinsic viscosity of AM-NaA copolymers as a function of ionic strength $^{-1/2}$ in NaCl aqueous solution (⊙ = NaA-10-4, ◬ = NaA-35-5, ⊡ = NaA-50-4, ⬡ = NaA-65-4).

conducted to assess phase behavior as a function of polymer concentration, $CaCl_2$ concentration, and temperature. Figure 7 illustrates typical phase separation of copolymer NaA-30-4 at 1500 ppm. The critical temperature for phase separation is plotted as a function of wt% $CaCl_2$. Above T_c, turbidity is observed and little viscosity is retained. This phenomenon is extremely important since the most widely used mobility control polymers in EOR are of the AM-NaA type.

Previous studies in our labs have shown that phase behavior is also a function of copolymer composition for the AM-NaA copolymers [17]. Quite significant is the fact that no separation of phases was observed for either the AM-NaAMPS series or the AM-DAAM series.

Temperature effects on viscosity are also important for practical applications of polymers in EOR since many petroleum reservoirs

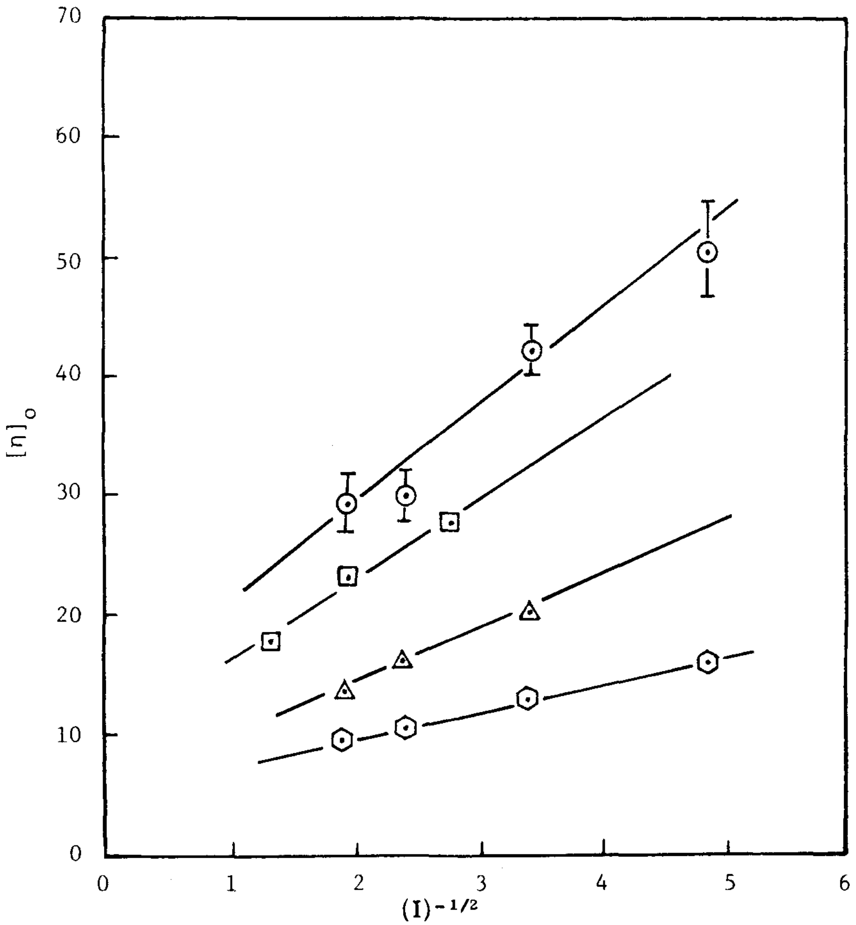

FIG. 3. Zero-shear intrinsic viscosity of AM-NaAMPS copolymers as a function of ionic strength$^{-1/2}$ in aqueous solutions (⊙ = AMPS-1-5, ⊡ = AMPS-2-5, △ = AMPS-3-5, ⬡ = AMPS).

reach elevated temperatures. Figure 8 shows the relative insensitivity of two AM-NaAMPS copolymers over the 30 to 70°C range. The AM-NaA polymers are more sensitive; however, the AM-DAAM copolymers show the greatest loss in viscosity over that range (Fig. 9).

TABLE 3. Structural Information

Sample number	Composition^a		$[\eta]_0$ in 0.257 M NaCl, dL/g	$\mu_{AM}/\mu_{comonomer}$
	Mol% AM	Mol% comonomer		
AMPS-1-5	90.5	9.5	29.5	8.2
AMPS-2-5	81.0	19.0	23.0	4.2
AMPS-3-5	72.1	27.9	13.2	2.6
AMPS-7-5	34.3	65.7	12.8	0.7
DAAM-11	88.9	11.1	14.3	7.6
DAAM-21	77.2	22.8	15.8	3.5
DAAM-31	28.6	31.4	14.6	2.1
DAAM-41	58.8	41.2	8.8	1.4
NaA-10-4	90.1	9.9	14.1	10.4
NaA-20-4	84.2	15.8	9.0	5.0
NaA-35-5	68.3	31.7	8.6	2.4
NaA-50-4	58.3	41.7	5.2	1.5
NaA-65-4	46.8	53.2	3.2	0.9

^{a}From elemental analysis.

B. Graft Copolymers of Dextran

1. Dextran-g-Poly(Acrylamides)

The effects of combining polysaccharides with known chain extending capability and high viscosity random copolymers were examined by utilizing a modified Ce(IV) grafting technique [7, 10, 17]. Dextran, a well-characterized, water-soluble polysaccharide of $\overline{M}_w = 500{,}000$, was chosen as a substrate on which acrylamide was to be grafted. The copolymers (Type VIII, Fig. 1) were prepared under specified conditions to eliminate homopolymer formation and to control the number and length of the grafted chains as well as total molecular weight. Copolymers were characterized by viscometry, size exclusion chromatography, and elemental analysis. Enzymatic and chemical hydrolysis techniques were used to separate the poly(acrylamide) grafts from

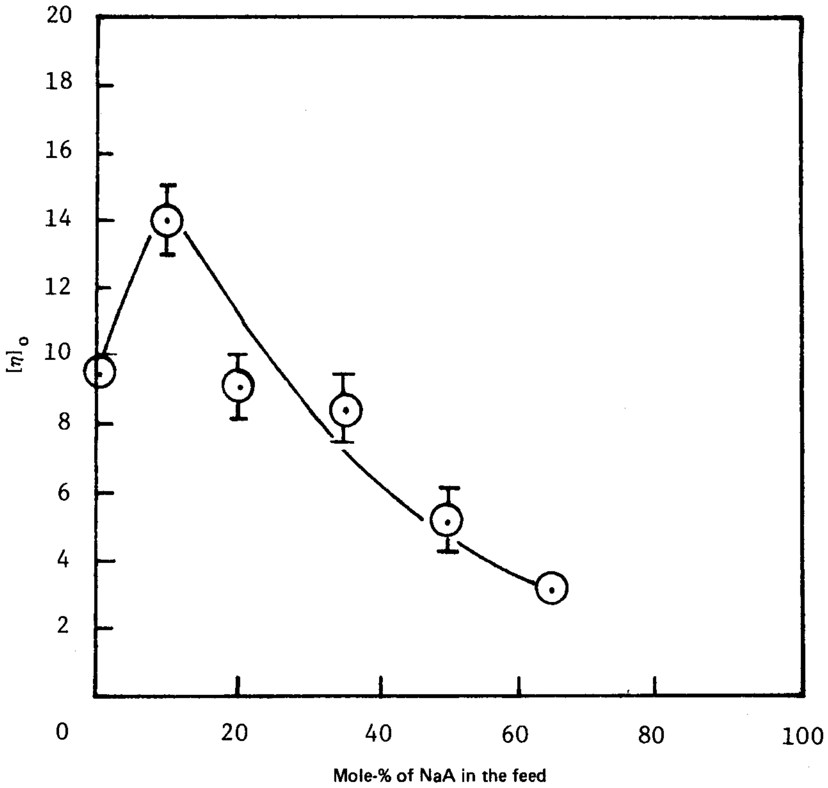

FIG. 4. Effect of feed composition on zero-shear intrinsic viscosity in 0.257 M NaCl of AM-NaA (⊙) copolymers at high conversion.

the backbone. Subsequent molecular weight analysis allowed calculation of grafting efficiency [7, 10, 17]. Structural data for the model graft copolymers are given in Table 4.

Total molecular weights of the graft copolymers varied from 1.5 to 7.0 million. As the number of grafting sites increases for these polymers of similar molecular weight, the hydrodynamic volume decreases as measured by the size exclusion chromatograms in Fig. 10. Those polymers with largest dimensions elute near the void volume of the column set. Interestingly, graft copolymer PC-5, with an average number of grafting sites of 2.5 per dextran chain and a

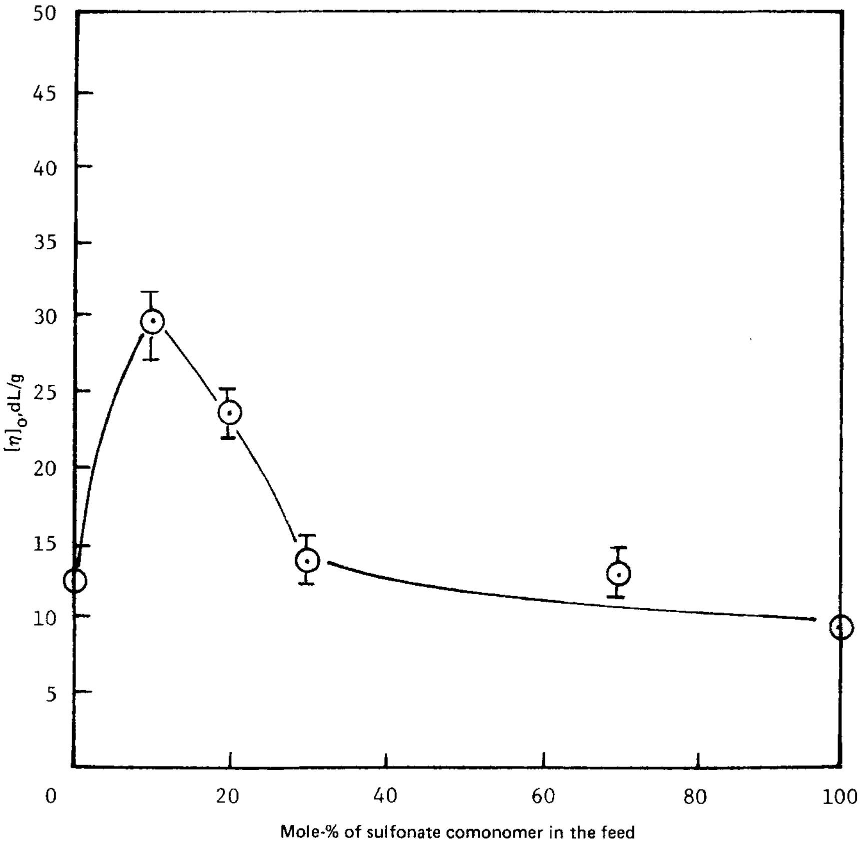

FIG. 5. Effect of feed composition on the zero-shear intrinsic viscosity in 0.257 M NaCl of AM-NaAMPS (⊙) copolymers at high conversion.

molecular weight of 3.2 million, shows a larger kinematic viscosity (Fig. 11) over all shear rates than homopolyacrylamide of molecular weight 5-6 million. Similar comparisons can be made with PC-3 or PC-4 and homopolyacrylamide of 4.0 million molecular weight. Apparently, for low numbers of long-chain grafts, chain extension by the polysaccharide backbone can be significant. Similar behavior has been reported by Butler et al. [22] for acrylamide-grafted starch copolymers.

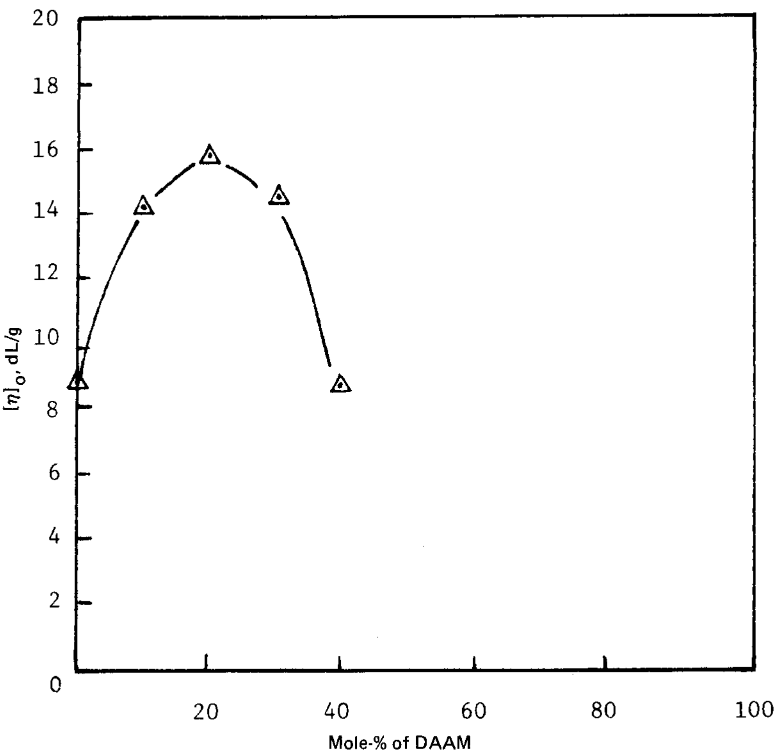

FIG. 6. Effect of feed composition on zero-shear intrinsic viscosity for AM-DAAM (△).

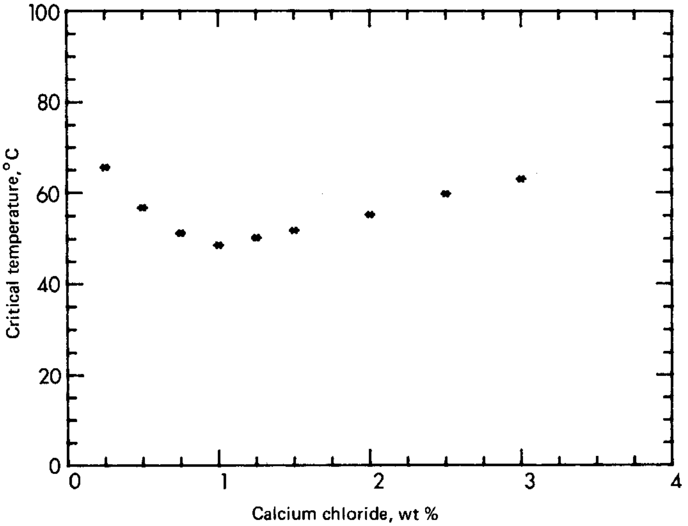

FIG. 7. Phase behavior of the random copolymer of acrylamide and sodium acrylate (1:1).

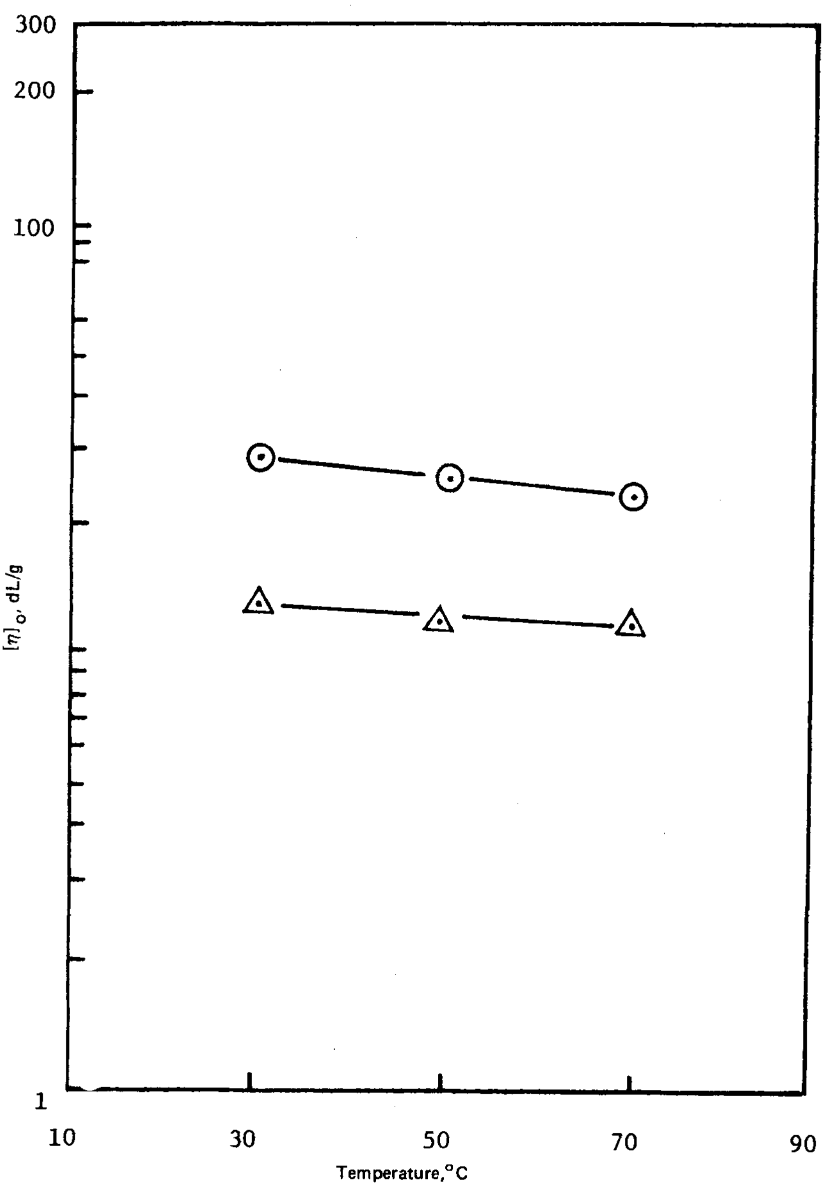

FIG. 8. Zero-shear intrinsic viscosity in aqueous 0.257 M NaCl solution as a function of temperature. Copolymer samples: ⊙ = AMPS-1-5, △ = AMPS-3-5.

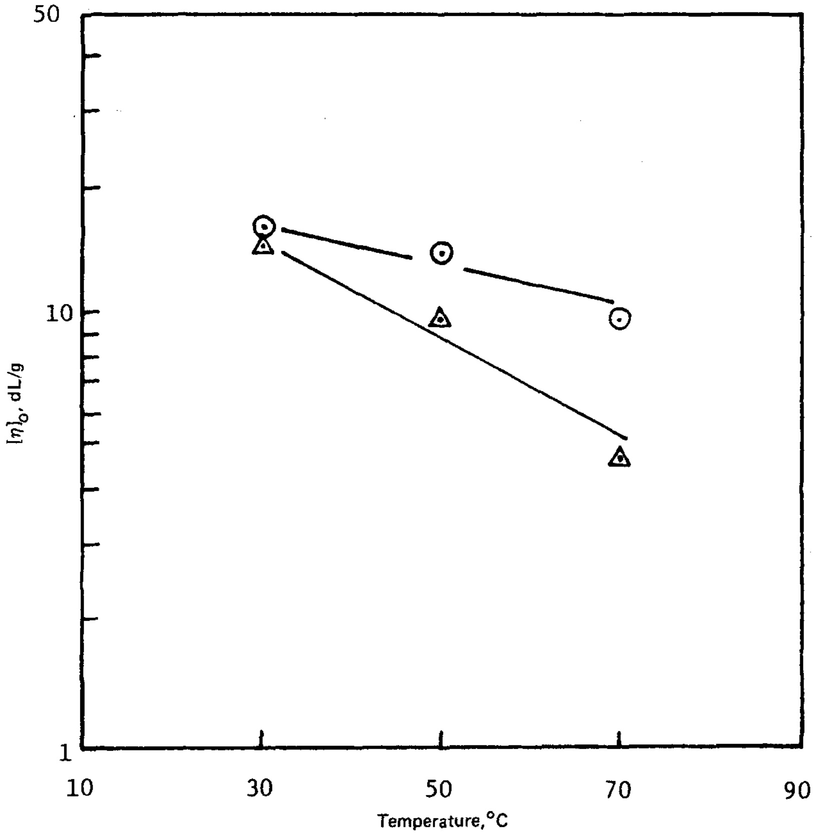

FIG. 9. Zero-shear intrinsic viscosity in 0.257 M $NaCl_{(aq.)}$ as a function of temperature. Copolymer samples: ⊙ = DAAM-21, ⚠ = DAAM-31.

2. Dextran-g-Poly(Acrylamide-co-Sodium Acrylates)

Graft copolymers of Type IX (Fig. 1) seem potentially useful for EOR since they should offer large dimensions due to backbone rigidity, side-chain copolymer composition, and anionic charge. Additionally, the possibility of intrachain chelation of divalent species could possibly prevent crosslinking, precipitation, and eventual pore clogging.

Attempts to synthesize Type IX systems from Ce(IV) grafting of comonomers AM and NaA onto dextran were unsuccessful due to binding of Ce(IV) to NaA. However, selective hydrolysis of the side chains of model graft copolymers (Type VIII) yielded Type IX copolymers. The

TABLE 4. Structural Data for Dextran-g-Poly(Acrylamides)[a]

Sample number	Elemental analysis, %			W_{PAM}	Molecular weight of PAM graft ($\times 10^{-6}$ daltons)			$\overline{M}_w$[d] of graft copolymers ($\times 10^{-6}$ daltons)	Average number of grafting sites	Initiation efficiency
	C	H	N		$\overline{M}_n$[a]	$\overline{M}_n$[b]	$\overline{M}_w$[c]			
PC-0	44.15	6.44	14.92	0.853	8.62	4.28	6.50	7.00	1.00	-
PC-1	43.54	6.37	11.22	0.633	6.47	3.00	4.52	5.02	1.00	-
PC-2	45.08	6.41	14.64	0.816	3.34	2.14	3.20	3.70	1.00	-
PC-3	44.69	6.49	14.86	0.838	2.53	1.55	2.30	3.09	1.13	0.37
PC-4	44.80	6.63	14.89	0.838	1.76	1.02	1.50	3.09	1.13	0.43
PC-5	44.56	6.37	14.91	0.844	1.30	0.76	1.10	3.21	2.46	0.49
PC-6	44.31	7.52	15.29	0.873	0.57	0.38	0.55	3.94	6.25	0.63
PC-7	44.17	7.58	15.22	0.872	0.40	0.27	0.38	3.91	8.97	0.45
PC-8	44.68	7.55	15.10	0.853	0.29	0.18	0.25	3.40	11.60	0.39
PC-9	44.78	7.45	15.03	0.847	0.21	0.14	0.19	3.27	14.60	0.37
PC-10	44.67	7.65	14.95	0.844	0.19	0.12	0.17	3.21	15.90	0.32
PC-11	45.69	7.26	14.50	0.795	0.08	0.07	0.10	2.44	19.40	0.19
PC-12	44.95	7.23	12.43	0.683	0.05	0.04	0.05	1.58	21.50	0.11

[a] Theoretically predicted values from elemental analysis.

[b] Experimentally determined from $[\eta]_0 = 6.5 \times 10^{-5} \overline{M}_n^{0.82}$.

[c] Experimentally determined from $[\eta]_0 = 6.31 \times 10^{-5} \overline{M}_w^{0.80}$.

[d] Weight-average molecular weight calculated from elemental analysis.

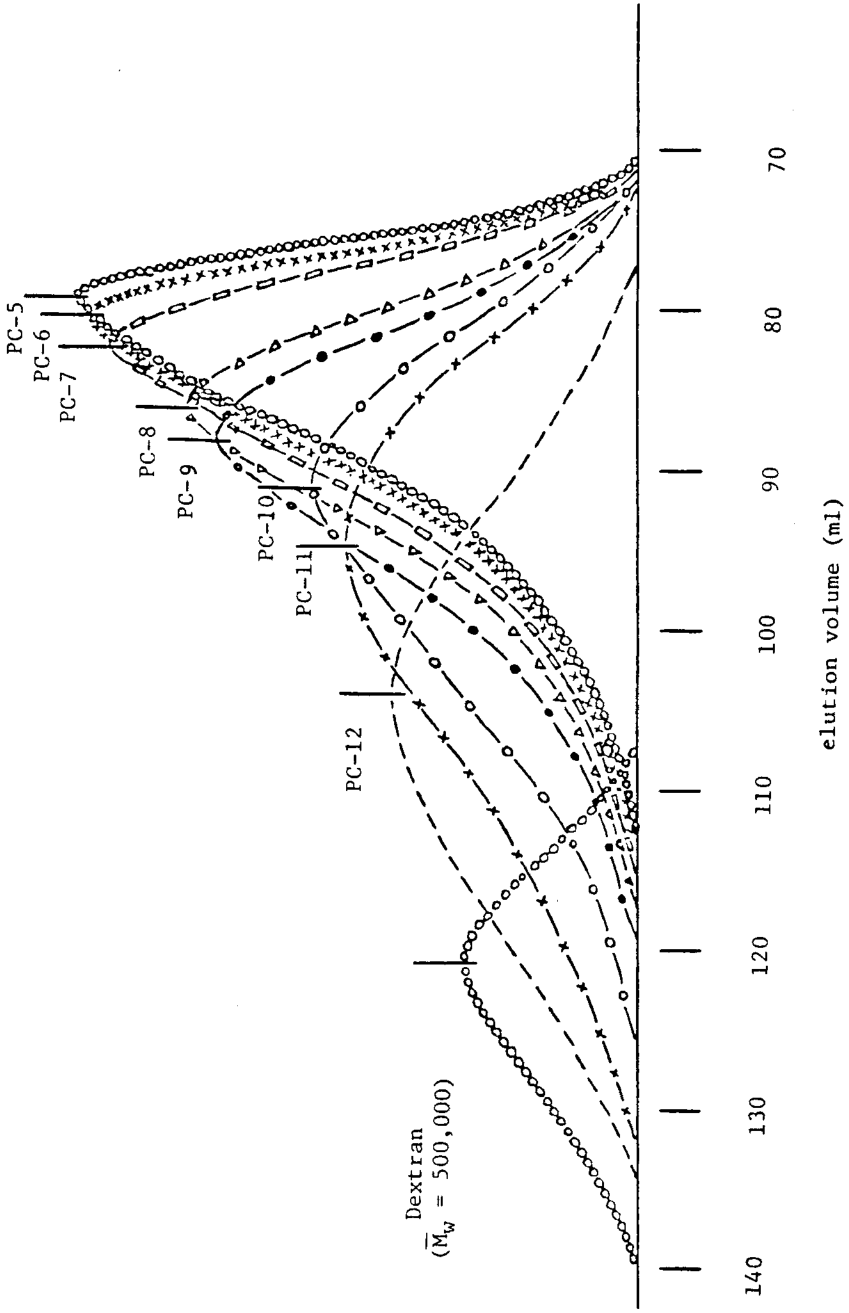

FIG. 10. Aqueous size exclusion chromatograms of model graft copolymers (PC-5 to PC-12).

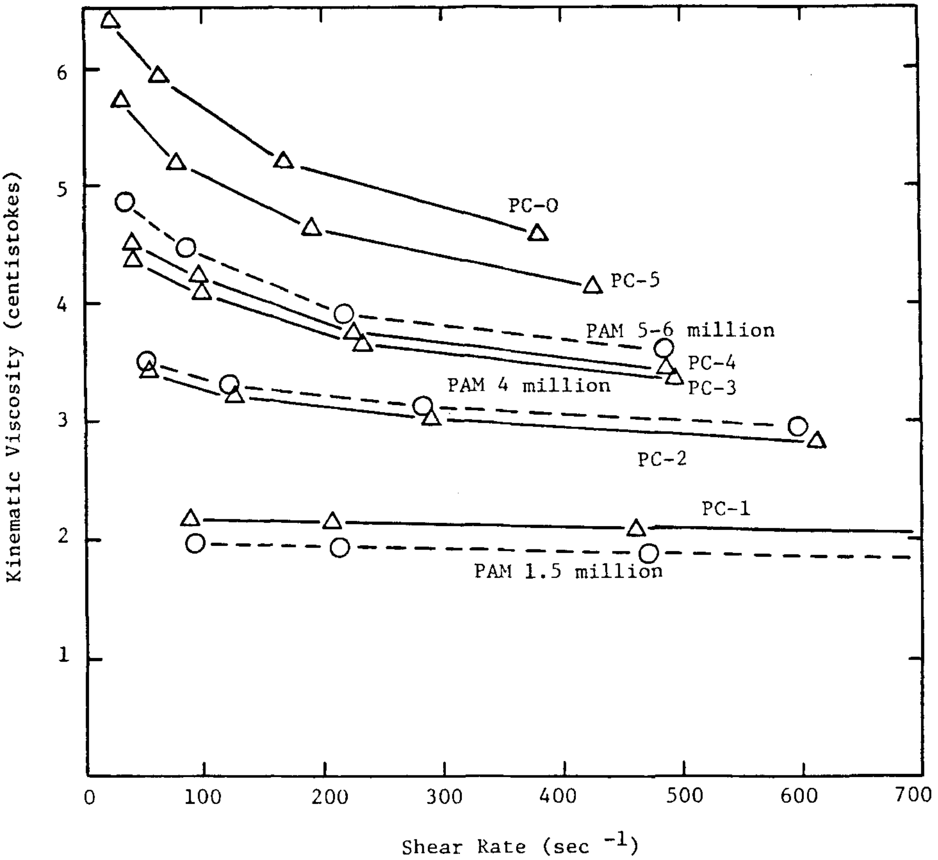

FIG. 11. Kinematic viscosity as a function of shear rate for model graft copolymers PC-0 to PC-5 in H_2O at 25°C, c = 0.20 g/dL.

degrees of hydrolysis varied from 25 to 60%. Mole fractions of the acrylamide, sodium acrylate, and anhydroglucose units are given in Table 5 along with structural data for partially hydrolyzed polyacrylamide (HP series). Data for the parent graft copolymers are given in Table 4.

The effect of graft copolymer structure on aqueous solution viscosity is shown in Fig. 12. The zero-shear intrinsic viscosity at 30°C in 0.5 M NaCl increases as the sodium acrylate content of the graft copolymer increases. Since samples in the PC-0 series and the PC-5 series exhibit higher viscosity than those in the PC-7

TABLE 5. Structural Data for Dextran-g-Poly(Acrylamide-co-Sodium Acrylates) and Poly(Acrylamide-co-Sodium Acrylates) Prepared by Partial Hydrolysis Utilizing Aqueous NaOH

Sample number	Elemental analysis, %			Copolymer composition			Hydrolysis, %
	C	H	N	F_{AG}[a]	F_{AM}[b]	F_{SA}[c]	
PC-01	41.85	5.78	10.05	0.070	0.661	0.269	28.9
PC-02	40.77	5.37	9.24	0.070	0.624	0.306	32.9
PC-03	39.48	5.53	5.72	0.070	0.399	0.531	57.1
PC-51	41.23	5.80	10.31	0.075	0.691	0.234	25.3
PC-52	40.62	5.56	9.24	0.075	0.629	0.296	32.0
PC-53	40.45	5.33	5.43	0.075	0.371	0.554	59.9
PC-71	42.27	6.09	10.31	0.060	0.665	0.275	29.3
PC-72	41.39	5.54	9.06	0.060	0.597	0.343	36.5
PC-73	37.97	5.01	5.37	0.060	0.386	0.554	59.0
HP-1	41.20	5.42	10.31	-	0.644	0.356	35.6
HP-2	41.85	5.89	10.36	-	0.637	0.363	36.3
HP-3	40.84	5.16	9.03	-	0.569	0.431	43.1
HP-4	39.45	5.07	8.40	-	0.548	0.452	45.2

[a] Mole fraction of anhydroglucose units.
[b] Mole fraction of acrylamide units.
[c] Mole fraction of sodium acrylate units.

series over a wide range of charge density, the length of the grafted chain seems more important than total molecular weight of the graft copolymer. The graft copolymers of the PC-5 series, having few long chains, exhibit higher viscosity than comparative linear models (HP series), although the latter have higher molecular weights (5-6 million) than the former (3.2 million). These effects are similar to those observed for the unhydrolyzed graft copolymers (Type VIII) and seem to indicate some structural advantages of grafting.

The effects of added electrolytes on solution viscosity were investigated (Fig. 13) while maintaining a constant shear rate of 100

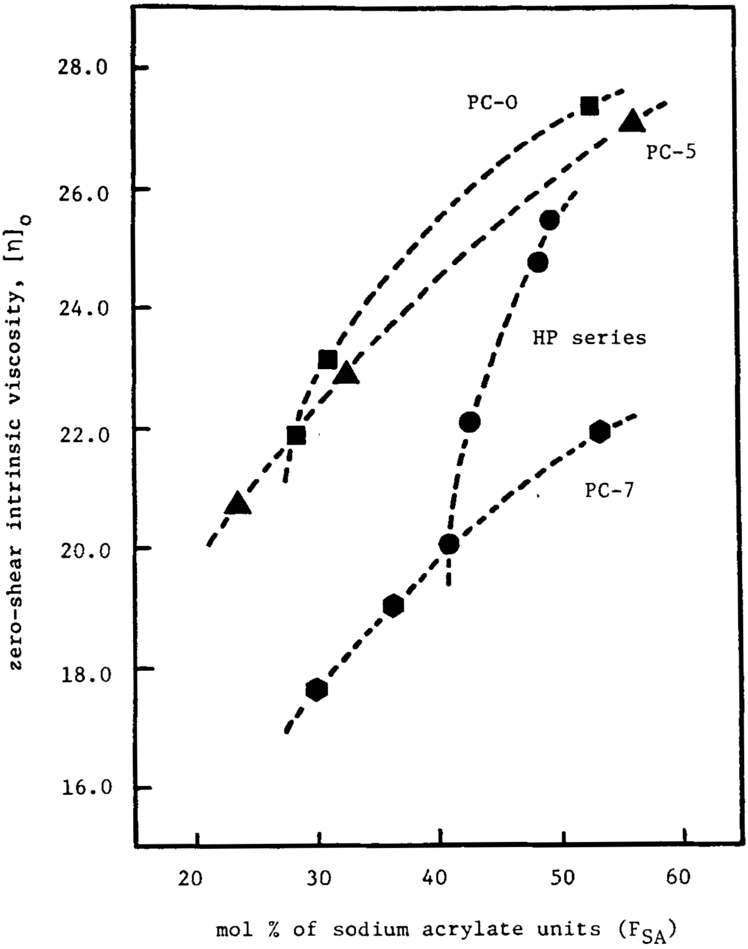

FIG. 12. Zero-shear intrinsic viscosities of hydrolyzed polymer samples as a function of charge density (F_{SA}) at 30°C, 0.5 M NaCl aqueous solution.

s^{-1}. The divalent calcium ion had a much stronger effect in reducing viscosity than the sodium ion. The viscosities of the polymer samples decreased rapidly with addition of small amounts of $CaCl_2$, showing the effects of ion-binding to the carboxylate side chains.

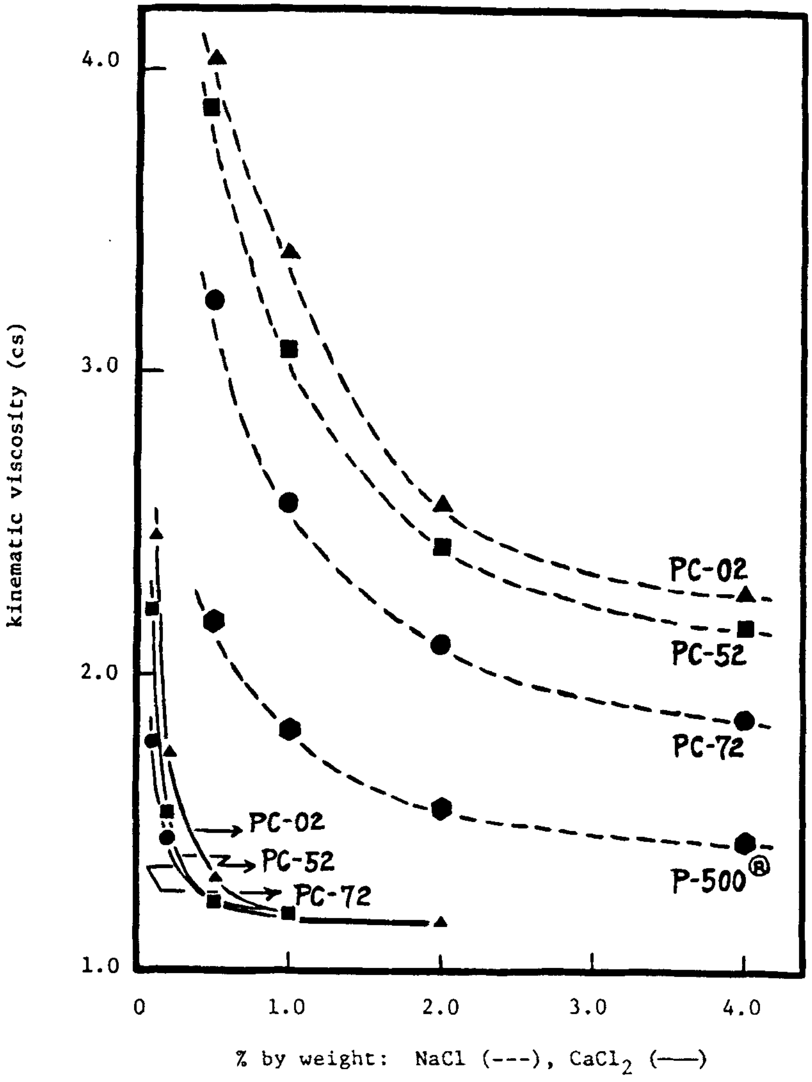

FIG. 13. Effect of salts on solution viscosity of hydrolyzed samples at 30°C (C_p = 500 ppm, and shear rate of 100 s^{-1}).

TABLE 6. Structural Data for Model Dextran-g-Poly(AM-co-NaAMPS) Samples

Sample number	Elemental analysis, %		Graft copolymer composition (mole draction)			W_g [a]	$\overline{M}_{w,g}$ [b] ($\times 10^{-6}$)
	N	S	F_{AG}	F_{AM}	F_{NaAMPS}		
LS-V-411	12.67	1.44	0.163	0.795	0.042	0.715	1.75
LS-V-412	11.59	2.95	0.166	0.741	0.093	0.733	1.87
LS-V-421	10.95	3.55	0.175	0.708	0.117	0.731	1.86
LS-V-422	9.99	4.40	0.193	0.652	0.155	0.724	1.81
LS-V-431	9.53	4.87	0.200	0.621	0.179	0.724	1.81
LS-V-432	8.27	6.56	0.212	0.515	0.273	0.743	1.94
LS-V-441	7.27	7.44	0.240	0.420	0.340	0.735	1.89
LS-V-442	5.73	8.63	0.301	0.239	0.460	0.715	1.75

[a] Weight fraction of grafted chains in the copolymer.

[b] Weight-average molecular weight of the graft copolymer.

3. Dextran-g-Poly(Acrylamide-co-Sodium-2-Acrylamido-2-Methylpropane Sulfonates)

Dextran-g-poly(AM-co-NaAMPS) (Type X) copolymers were synthesized utilizing a modified Ce(IV) grafting technique in which AM and NaAMPS were grafted onto a precomplexed dextran. The study was complicated by binding of the Ce(IV) ion with NaAMPS and by homopolymerization of NaAMPS. However, controlled oxidation of the dextran prior to grafting gave higher monomer conversion and better control of the number of grafting sites.

Structural compositions of the graft copolymers are given in Table 6 including the total weight-average molecular weight, the weight fraction of the grafted chains [7, 14, 17], and the mole fractions of the respective anhydroglucose, AM, and NaAMPS units. Kinematic viscosities in 0.1 M NaCl and 0.5 M NaCl solutions at 100 s^{-1} are shown in Table 7.

Those graft copolymers with low mole fractions of NaAMPS exhibit the highest viscosities in sodium chloride solutions. The higher values in 0.1 M NaCl, as compared to 0.5 M NaCl, are due to incomplete charge masking along the backbone. The increased viscosity of

TABLE 7. Physical Data for Dextran-g-Poly(AM-co-NaAMPS)

Sample number	F_{NaAMPS}[a]	F_{NaAMPS}[b]	$M_w \times 10^{-6}$	η,[c] cS	η,[d] cS
LS-V-411	0.042	0.050	1.75	2.84	2.84
LS-V-412	0.093	0.112	1.87	3.24	2.80
LS-V-421	0.117	0.142	1.86	3.83	2.74
LS-V-422	0.155	0.192	1.81	4.06	2.67
LS-V-431	0.179	0.224	1.81	3.21	2.13
LS-V-432	0.273	0.346	1.94	3.03	2.04
LS-V-441	0.340	0.447	1.89	2.92	1.95
LS-V-442	0.460	0.658	1.75	2.03	1.47

[a] Mole fraction NaAMPS in the polymer.

[b] Mole fraction NaAMPS in the grafted chains.

[c] Kinematic viscosity of polymer in 0.1 M NaCl/H_2O, C = 1000 ppm, $\dot{\gamma} = 100\ s^{-1}$, T = 30°C.

[d] Kinematic viscosity of 0.5 M NaCl/H_2O, C = 1000 ppm, $\dot{\gamma} = 100\ s^{-1}$, T = 30°C.

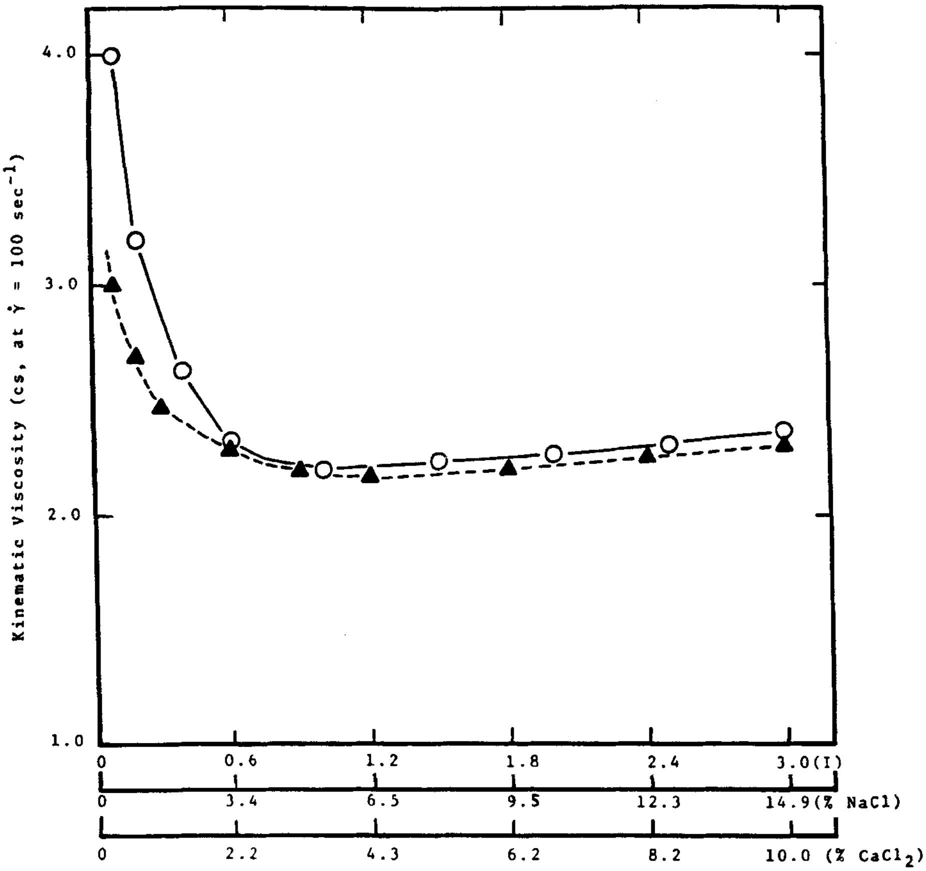

FIG. 14. Effect of added electrolytes on the kinematic viscosity of graft copolymer LS-V-421 scales: ionic strength (I), weight % NaCl (○), and $CaCl_2$ (△).

these compositions in salt, as compared to the homopolymers of AM and NaAMPS (especially those graft copolymers having less than 10 mol% NaAMPS in the side chain), has also been observed for random copolymers of AM with NaAMPS (Type III) [7, 13, 16].

Salt sensitivity studies have been conducted for the dextran-g-poly(AM-co-NaAMPS) containing 11.1% NaAMPS at a concentration of 1000 ppm (Fig. 14). This copolymer exhibited viscosity loss up to an ionic strength of 0.6 (approximately 3.4% NaCl or 2.2% $CaCl_2$ by weight). Of considerable importance, however, is the fact that no phase separation occurs for any of the AM-NaAMPS-grafted dextran compositions up to 10 wt% $CaCl_2$. The copolymers of Types II and IX with sodium acrylate units are, by contrast, highly susceptible to phase separation.

IV. CONCLUSIONS

Copolymer structure has a marked effect on solution behavior of water-soluble, random, and graft copolymers synthesized in this work. Large hydrodynamic volumes are measured in aqeuous solutions of random copolymers of acrylamide with NaA, NaAMPS, and DAAM comonomers. The ability of these copolymers to maintain large dimensions in the presence of sodium chloride and calcium chloride can be directly related to copolymer composition and, more appropriately, microstructure. The differences in salt sensitivity of the AM-NaA copolymers, as compared to the AM-NaAMPS copolymers of similar composition, can be attributed to differences in ion binding of sodium and calcium ions to the carboxylate and sulfonate anions, respectively. However, the distance of the charged group from the backbone certainly influences conformation and chain extension, especially in electrolyte solutions. This effect is clearly demonstrated by the nonionic DAAM copolymers. Properties of the grafted-dextran copolymers such as salt sensitivity and viscosity are largely due to the composition and length of the grafted chains. In some cases, however (those with reasonably large dextran backbones and a few long chain grafts), molecular dimensions appear to be greater than those of the random copolymers of the same composition and comparable molecular weights. Although all the copolymers of polyelectrolyte nature show viscosity loss with added electrolytes, those containing NaAMPS units do not phase separate in the presence of $CaCl_2$ over a wide range of solution temperatures. Polymers, therefore, of AM-NaAMPS and dextran-g-AM-co-NaAMPS can be prepared which show increased salt tolerance and phase stability as compared to their AM-NaA counterparts. In addition to seeking a theoretical basis for these observations, further studies will be conducted on adsorption, entrapment, and polymer-surfactant compatibility for these systems. An optimization of cooperative effects along the macromolecular backbone such as those present in proteins and nucleic acids may lead to tailoring of more efficient systems for use in enhanced oil recovery.

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REFERENCES

[1] H. K. Van Poolen and Associates, *Enhanced Oil Recovery*, Penwell, Tulsa, Oklahoma, 1980.

[2] *Enhanced Oil Recovery*, National Petroleum Council Report, December 1976.

[3] W. B. Gogarty, Part I, *J. Pet. Technol.*, p. 1563 (September 1983); Part II, *Ibid.*, p. 1767 (October 1983).

[4] "Enhanced Oil Recovery–Secondary and Tertiary Methods," in *Chemical Technology Review #103*, 49, Noyes, Park Ridge, New Jersey, 1978.

[5] Lewin and Associates, *The Potential and Economics of Enhanced Oil Recovery*, Washington, D.C., 1976.

[6] J. Chatterji, *J. Pet. Techol.*, p. 2042 (November 1981).

[7] C. L. McCormick et al., *Improved Polymers for Enhanced Oil Recovery*, Annual Reports, BETC-5603-5 (1978), BETC-5603-10 (1979), BETC-5603-15 (1980), BC-10321-5 (1981), BC-10321-12 (1982), U.S. Department of Energy, Bartlesville, Oklahoma.

[8] C. L. McCormick and L. S. Park, *J. Appl. Polym. Sci.*, 26, 1705 (1981).

[9] C. L. McCormick and K. C. Lin, *J. Macromol. Sci.–Chem.*, A16(8), 1441 (1981).

[10] C. L. McCormick and L. S. Park, *J. Polym. Sci., Polym. Chem. Ed.*, 19, 2229 (1981).

[11] C. L. McCormick and G. S. Chen, *Ibid.*, 20, 817 (1982).

[12] C. L. McCormick and B. H. Hutchinson Jr., *J. Appl. Polym. Sci.*, 27, 3103 (1982).

[13] C. L. McCormick, G. S. Chen, and H. H. Neidlinger, *Ibid.*, 29, 1159 (1984).

[14] C. L. McCormick and L. S. Park, *J. Polym. Sci., Polym. Chem. Ed.*, 22, 49 (1984).

[15] C. L. McCormick, L. S. Park, and R. D. Hester, *Polym. Eng. Sci.*, 24(2), 163 (1984).

[16] G. S. Chen, PhD Dissertation, University of Southern Mississippi, Hattiesburg, 1982.

[17] L. S. Park, PhD Dissertation, University of Southern Mississippi, Hattiesburg, 1982.

[18] M. Fineman and S. D. Ross, *J. Polym. Sci.*, 5, 259 (1950).

[19] T. Kelen and F. Tüdös, *J. Macromol. Sci.–Chem.*, A9, 1 (1975).

[20] F. R. Mayo and F. M. Lewis, *J. Am. Chem. Soc.*, 66, 1594 (1944).

[21] S. Igarashi, *J. Polym. Sci., Polym. Lett. Ed.*, 1, 359 (1963).

[22] H. Pledger, J. J. Meister, T. E. Hogen-Esch, and G. B. Butler, *Soc. Pet. Eng. Paper 8422*, Las Vegas, September 1979.