Modified Acrylamide Polymers for Enhanced Oil Recovery

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Synopsis

Copolymers of sodium acrylate and N-methyl-, N-isopropyl-, N-n-butyl-, and N-t-butylacrylamide were prepared. The viscosities of these copolymers in 0.01% and 2.00% NaCl and their resistances to shear were compared with those of several partially hydrolyzed polyacrylamides. The poly(N-alkylacrylamide-co-sodium acrylate) demonstrated somewhat better retention of viscosity in brine than did analagous partially hydrolyzed polyacrylamides. N-alkyl substitution increased sensitivity to shear in low salt solutions.

INTRODUCTION

Rising oil prices make tertiary oil recovery economically feasible. Efforts are underway in the United States and elsewhere to improve enhanced oil recovery (EOR) methods. Polymers play an important role in this process by thickening water in both surfactant/polymer and polymer flooding. Xanthan gum and partially hydrolyzed poly(acrylamide) (HPAM) have been used in these capacities. HPAM is the most widely used of these two polymer types despite characteristics such as viscosity loss in brines and shear stability. Two possible approaches for improving HPAM type polymers are (a) stiffening the polymer backbone and (b) substituting alkyl groups for one or both of the hydrogens on the amide nitrogen. The first approach is discussed in another paper by this group.[1] The latter method (b) will be discussed in this paper.

Hester et al.[2] have synthesized N,N-dimethyl and N,N-diethylacrylamide polymers for EOR evaluation, but surprisingly there is little work reported in the literature on the synthesis and testing of N-mono-substituted acrylamide polymers for this application. The present investigation consisted of the synthesis and evaluation of two homopolymers and four copolymers for possible use in EOR. The polymers studied were the following: (1) poly(N-methylacrylamide), (2) poly(N-isopropylacrylamide), (3) poly(N-methylacrylamide-co-sodium acrylate), (4) poly(N-isopropylacrylamide-co-sodium acrylate), (5) poly(N-butylacrylamide-co-sodium acrylate), (6) poly(N-t-butylacrylamide-co-sodium acrylate).

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EXPERIMENTAL

The homopolymers and copolymers were prepared by aqueous solution polymerization, using potassium persulfate $(K_2S_2O_8)$/sodium metabisulfite $(Na_2S_2O_5)$ as initiator/activator. Commercial monomers were purified either by distillation under reduced pressure or by recrystallization. The reactions were carried out in a nitrogen atmosphere, and the water used as the polymerization solvent was deaerated. Polymeric products were isolated and purified by reprecipitation and washing.

Synthesis of Homopolymers. The experimental procedure followed to prepare these polymers was a very simple one. A weighed amount of monomer was dissolved in an appropriate amount of distilled, deaerated water in a 50-mL serum bottle. The bottle was flushed and sealed under a nitrogen stream. The initiator solution was then introduced into the bottle by syringe. At the appropriate stage, the reaction was terminated by pouring the viscous solution into a constantly stirred nonsolvent. When copolymers were made, the polymerization reactions were terminated at conversions of 30% or less, so that the copolymers isolated would be relatively uniform in composition.

In the homopolymer synthesis work, it was found that lower reaction temperatures, lower percentages of initiator, and higher concentrations of monomer in the aqueous solutions helped produce polymers of higher viscosity. In general, high purity monomers were necessary to obtain high molecular weight polymers. Use of an activator did catalyze the polymerization reaction effectively but yielded lower viscosity polymers. The polymers usually were precipitated in methanol, ethanol, or acetone. However, the precipitation of poly(N-isopropylacrylamide) involved problems. Methanol, ethanol, dioxane, tetrahydrofuran, dimethylsulfoxide, and acetone all were either ineffective or very poor precipitants. The poly(N-isopropylacrylamide) was precipitated successfully by warming the aqueous solution to 80°C, or by removing the water azeotropically with toleune.

Synthesis of Copolymers. Copolymers were prepared from N-substituted acrylamides and sodium acrylate or acrylic acid. Efforts were made to establish optimum reaction conditions by varying the proportions of monomer:initiator:activator (MIA) and by varying the aqueous solution concentration, temperature, and other factors.

The reactions of poly(N-methylacrylamide-co-sodium acrylate) were first conducted at "high" MIA proportions of 100:40:4. The MIA was then progressively changed to a ratio of 100:0.1:0.05. It was observed that very high and very low MIA proportions yielded only low viscosity copolymers. MIA proportions of 100:0.5:0 (no activator) yielded the highest viscosity copolymers. For copolymers of nearly the same acid content, increases in the MIA proportions caused marginal decreases in the reduced viscosity of the copolymers in 0.01% sodium chloride brine. The optimum temperature range for copolymerization reactions was 15–25°C. For the N-methylacrylamide copolymer system, MIA proportions representing initiator fractions lower than 100:0.5:0 generated low viscosity polymers. However, for the N-isopropylacrylamide copolymer system, MIA proportions representing lower initiator fractions led to copolymers displaying higher viscosities.

In the preparation of poly(N-n-butylacrylamide-co-sodium acrylate), sodium dodecyl sulfate (lauryl sulfate) was added to the reaction mixture as

an emulsifier. The optimum MIA proportions were 100:0.1:0.05. In two emulsion copolymerizations with N-n-butylacrylamide, the amounts of sodium acrylate added to the monomer feed solution were the equivalent of 50% and 60% acrylic acid. However, the copolymers isolated at low conversions contained over 75% acrylic acid.

N-t-butylacrylamide was found to be soluble in dimethylformamide–water. Therefore, N-t-butylacrylamide was copolymerized in that mixed solvent system by following the usual redox recipe.

Seven samples of poly(N-methylacrylamide-co-sodium acrylate) were prepared by hydrolysis of homopolymers in basic aqueous solutions, and were precipitated using the methods discussed above. The sodium salt form of the resulting copolymers contained sodium acrylate residues ranging from 8.4 to 41.5 wt %. For hydrolysis of poly(N-methylacrylamide), drastic conditions such as high temperature, excess sodium hydroxide, and extended heating periods were necessary to achieve the desired degree of hydrolysis (Table I). In contrast, hydrolyzed polyacrylamide can be prepared by using only the stoichiometric amount of sodium hydroxide needed to hydrolyze the desired fraction of amide unit at 60°C.[3]

Screening Procedure. The polymers were dissolved in 0.01 and 2% aqueous NaCl and capillary flow times were measured at 25°C using a Cannon-Ubbelohde type capillary viscometer. This simple screening procedure[4] provided data on the viscosity loss in brine by comparing the ratios of the reduced viscosity in 2% NaCl to that in 0.01% NaCl. Shear degradation was estimated by comparing reduced viscosity in each brine before and after passage through a screen-shear apparatus.[4] Results of extensive testing obtained with this screening procedure are discussed elsewhere.[4-6]

DISCUSSION

Effect of N-Substitution. Poly(N-methylacrylamide-co-sodium acrylate) tends to retain a slightly larger fraction of its specific viscosity in 2% NaCl than do the unsubstituted analogs. However, the N-methyl substitution seems to make the copolymers more sensitive to shear degradation (Tables II and III). Although these differences involving N-methyl-substi-

TABLE I
Hydrolysis of Homopoly(N-Methylacrylamide)

Sample no.	Poly(N-methyl-acrylamide) (g)	Sodium hydroxide 1N solution (mL)	Temp. (°C)	Time (h)	Degree of hydrolysis[a]
147	2.00	7.40	60	2	11.1
160	0.50	2.10	60	24	8.4
164	1.80	8.10	96	48	22.3
167	1.17	7.20	98	95	24.3
169	1.30	12.00	98	88	30.6
179	0.60	10.00	98	140	41.5
166	0.75	5.00	96	24	20.5

[a] As measured by the weight percent of sodium acrylate residues found by acid-base titration of the isolated polymer.

Sample no.	Polymer concn. (g/dL)	Sodium acrylate content (wt %)	Reduced Viscosity in		Viscosity shear[a] (%)	Retention brine[a] (%)
			0.01% NaCl (dL/g)	2.0% NaCl (dL/g)		
Polymers made by copolymerization						
79	0.0151	9.5	35.69	12.97	80.7	36.3
78	0.0151	16.1	74.94	13.17	75.1	17.6
122	0.0160	24.3	63.46	10.00	89.8	15.8
76	0.0147	28.4	76.66	10.11	89.1	13.2
124	0.0169	31.8	24.96	4.30	92.6	17.2
74	0.0141	36.2	81.20	9.89	91.0	12.2
75	0.0149	36.4	102.73	13.00	80.4	12.7
121	0.0157	36.8	36.49	5.38	83.4	14.8
46	0.0151	42.7	103.85	13.04	80.0	12.6
45	0.0152	46.6	113.12	14.79	73.3	13.1
Polymers made by hydrolysis						
166	0.0117	20.5	85.90	10.36	96.8	12.1
164	0.0129	22.3	40.58	3.66	99.5	9.0
167	0.0132	24.7	85.65	10.02	97.2	11.7
169	0.0127	30.6	94.81	10.72	98.4	11.3
179	0.0125	41.5	87.05	9.10	97.2	10.4

[a] Shear effect $= [(\eta_{sp})_{0.01}]_s/[(\eta_{sp})_{0.01}]_u \times 100$ and brine effect $= (\eta_{sp})_2/(\eta_{sp})_{0.01} \times 100$, where $(\eta_{sp})_2 =$ specific viscosity in 2% NaCl, $(\eta_{sp})_{0.01} =$ specific viscosity in 0.01% NaCl, $[\eta_{sp}]_s =$ specific viscosity of sheared polymer solution, $[\eta_{sp}]_u =$ specific viscosity of unsheared polymer solution.

tuted vs. unsubstituted copolymers are small, the best matched comparisons show these differences, especially the difference in NaCl sensitivity, to be statistically significant. When compared with analogous unsubstituted copolymers, poly(N-isopropylacrylamide-co-sodium acrylate) samples exhibited slight improvements in resistance to both NaCl and shear (Tables III and IV).

Effect of Charge-to-Mass Ratio of Polyanion. For each polymer type studied, the copolymer composition has been varied in order to obtain copolymers whose anions have varying charge-to-mass ratios or degrees of hydrolysis. This structural variation is very important when considering viscosity loss in brine (2% NaCl). Solutions of nonionic polymers exhibit little or no sensitivity to NaCl concentration, but many solutions of ionic polymers lose more than 90% of their specific viscosity when the NaCl concentration is increased from 0.01 to 2%. The relationship between degree of hydrolysis and viscosity loss in brine for the N-substituted analogs follows the general trend commonly observed with HPAM-type polymers (Tables II–IV).

Effects of Possible Sequence Variation. Variations in the structural details of copolymer chains may result when different synthetic methods are used in the preparation of the copolymers. Most of the N-alkyl-substituted copolymers were synthesized by copolymerization, but some poly(N-methylacrylamide-co-sodium acrylate) samples were synthesized by partial

TABLE III
Screening Data for Poly(acrylamide-co-Sodium Acrylate)

Sample no.	Polymer concn. (g/dL)	Sodium acrylate content (wt %)	Reduced Viscosity in		Viscosity shear[a] (%)	Retention brine[a] (%)
			0.01% NaCl (dL/g)	2.0% NaCl (dL/g)		
309	0.0170	16.1	106.19	14.76	91.4	13.9
184	0.0187	18.8	11.72	0.86	94.4	7.4
184	0.0187	18.8	11.72	0.86	94.4	7.4
185	0.0152	14.2	14.43	1.34	98.6	9.3
6	0.0608	19.6	103.92	9.07	94.5	8.7
310	0.0179	28.8	122.71	12.72	94.1	10.4
181	0.0207	31.5	15.16	1.25	98.7	8.2
132	0.0173	41.7	115.57	10.46	92.4	9.0
178	0.0146	41.7	103.71	11.11	95.9	10.7
16	0.0069	43.0	151.33	16.41	96.0	10.8
7	0.0086	50.8	143.86	13.66	90.3	9.5
40	0.0126	52.9	64.02	4.93	94.3	7.7

[a] See footnote to Table II.

TABLE IV
Screening Data for Poly(N-isopropylacrylamide-co-Sodium Acrylate)

Sample no.	Polymer concn. (g/dL)	Sodium acrylate content. (wt %)	Reduced Viscosity in			Viscosity shear[a] (%)	Retention brine[a] (%)
			0.01% NaCl (dL/g)	2.0% NaCl (dL/g)			
69	0.0151	17.6	16.13	2.27		97.6	14.1
58	0.0169	28.9	71.64	12.25		89.0	17.1
43	0.0125	31.5	40.58	4.81		89.5	11.9
57	0.0153	33.0	48.83	6.19		95.5	12.7
56	0.0152	45.3	85.96	11.64		92.0	13.5
61	0.0154	46.8	88.83	11.27		88.1	12.7
13	0.0081	51.3	85.54	12.38		85.5	14.5

[a] See footnote to Table II.

hydrolysis of poly(N-methylacrylamide) (Table I). Although both synthetic methods should produce essentially random copolymers, those synthesized by one method may have an increased number of like-monomer sequences (more nearly like block copolymers), and those prepared by the other method may be more nearly like alternating copolymers. The samples synthesized by partial hydrolysis tend to lose a somewhat larger fraction of their viscosity when subjected to increased NaCl than do samples of the same polymer type synthesized by copolymerization (Tables II and V).

Poly(N-alkylacrylamide-co-sodium acrylate) samples with the alkyl substituent being either a methyl or isopropyl group have shown a small improvement in viscosity retention in 2% NaCl when compared with poly(acrylamide-co-sodium acrylate) samples. This improvement may be the result of the alkyl substitution or a variation in the sequencing of the ionic changes on the polymer chain.

Poly(N-n-butylacrylamide-co-sodium acrylate) samples of sufficiently high viscosity may exhibit a small improvement in viscosity retention in NaCl brine, compared with what would be expected from other copolymers having similar weight percent sodium acrylate residues, but a direct comparison is not possible for two reasons. Because of the water insolubility of N-n-butylacrylamide, these samples were synthesized by an emulsion polymerization method, rather than the solution polymerization method used for other polymer types. Also, all of these poly(N-n-butylacrylamide-co-soium acrylate) samples have higher percentages of sodium acrylate residues than most of the other samples being compared.

Berea Core Tests. Several flow tests in Berea core were conducted to compare the effect of N-alkyl substitution on adsorption (or retention) of acrylamide polymers. These tests showed some interesting results. In the initial tests, homopolymers of acrylamide and N-methylacrylamide of nearly equal viscosity were utilized (Table VI and Fig. 1). The data from these tests indicate that the N-methyl substitution of acrylamide polymers reduces the amount of polymer retention in the Berea core sample. This suggests either that the N-substituted acrylamide is adsorbed less on the rock surfaces than is polyacrylamide or that there is less mechanical entrapment of the N-substituted polymer.

Similar tests (Table VI and Fig. 2) also were carried out utilizing the following copolymers: (1) poly(N-methylacrylamide-co-sodium acrylate); (2) poly(N-isopropylacrylamide-co-sodium acrylate); (3) poly(acrylamide-co-sodium acrylate). Several tentative hypotheses may explain the behavior observed. Consider the data of Figure 1, which compares acrylamide and N-methylacrylamide homopolymers. Because of the presence of a methyl group on the amide nitrogen, the poly(N-methylacrylamide) polymer molecules may be slightly more basic than the analogous unsubstituted polymer molecules. As a result, rock surfaces, which are generally basic in nature, may attract the N-substituted polymer molecules less than the unsubstituted polymer molecules. This attraction might involve the hydrogens of the amide groups acting as hydrogen-bond donors to chemically combined oxygen at the rock surface. If so, the decreased number of amide hydrogens and the steric bulk of the methyl groups of the N-substituted polymer also might play a role in the reduced attraction. It is likely that the polyacry-

TABLE V
Comparative Screening Data for Poly(acrylamide-co-Sodium Acrylate)

Sample no.	Polymer concn (g/dL)	Sodium acrylate content (wt %)	Reduced Viscosity in		Viscosity shear[a] (%)	Retention brine[a] (%)
			0.01% NaCl (dL/g)	2.0% NaCl (dL/g)		
Commercial polymers made by hydrolysis						
203	0.0155	17.5	90.7	12.5	87.2	13.8
204	0.0160	18.5	74.1	9.0	88.8	12.1
34	0.0101	29.1	115.6	12.6	84.4	10.9
25	0.0116	31.1	164.8	18.3	66.2	11.1
132	0.0173	41.7	115.6	10.5	92.4	9.0
32	0.0143	41.9	209.4	18.5	67.1	8.8
Commercial polymers made by copolymerization						
205	0.0148	33.2	102.2	12.0	89.6	11.8
207	0.0157	36.3	111.1	14.2	92.5	12.8
206	0.0151	38.6	118.5	15.8	88.4	13.3
208	0.0152	41.5	205.0	24.1	71.2	11.8

[a] See footnote to Table II.

TABLE VI
Berea Core Tests

Sample no.	Polymer type	Sodium acrylate content (wt %)	Reduced viscosity in 0.01% NaCl (dL/g)
38	Poly(N-methylacrylamide)	0	4.77
9	Polyacrylamide	0	6.12
46	Poly(N-methylacrylamide-co-sodium acrylate)	42.7	103.12
61	Poly(N-isopropylacrylamide-co-sodium acrylate)	46.8	88.83
17	Poly(acrylamide-co-sodium acrylate)	40.7	117.70

lamide polymer chains in solution extend more than poly(N-methylacrylamide) chains, due to better solvation by water of the more polar polyacrylamide. This chain extension changes the hydrodynamic size of the unsubstituted polymer molecules, which may cause more mechanical entrapment of the polyacrylamide during flow.

The decreased retention of poly(N-methylacrylamide-co-sodium acrylate) compared to poly(acrylamide-co-sodium acrylate) shown in Figure 2 can be explained by the phenomena discussed above. However, the increased retention of poly(N-isopropylacrylamide-co-sodium acrylate) indicates that another factor besides those mentioned previously becomes important when the size of the N-alkyl substituent is larger than methyl.

Acrylamide, N-methylacrylamide, N-ethylacrylamide, N-isopropylacrylamide, and their homopolymers and copolymers with acrylic acid are soluble in cold water whereas the homopolymers of N-n-butylacrylamide and N-t-butylacrylamide are not. Since poly(N-isopropylacrylamide) is insoluble in *hot* water, it appears that the isopropyl substituent is the limiting size of
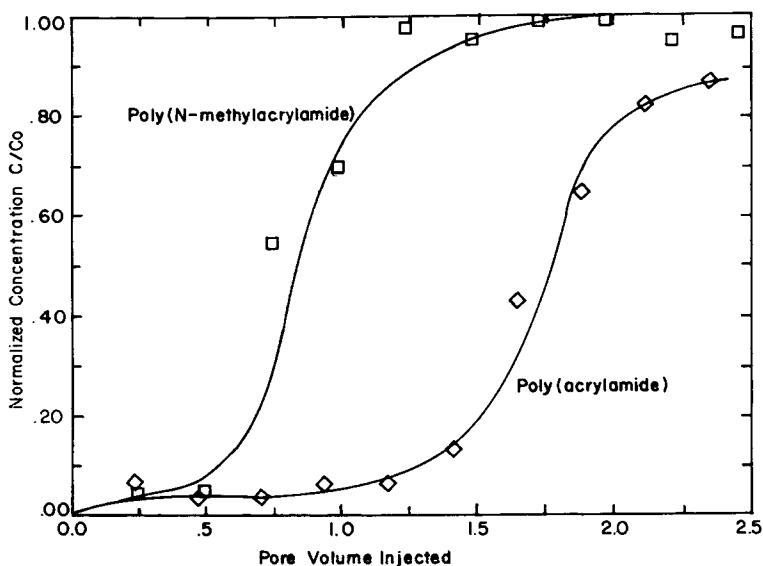

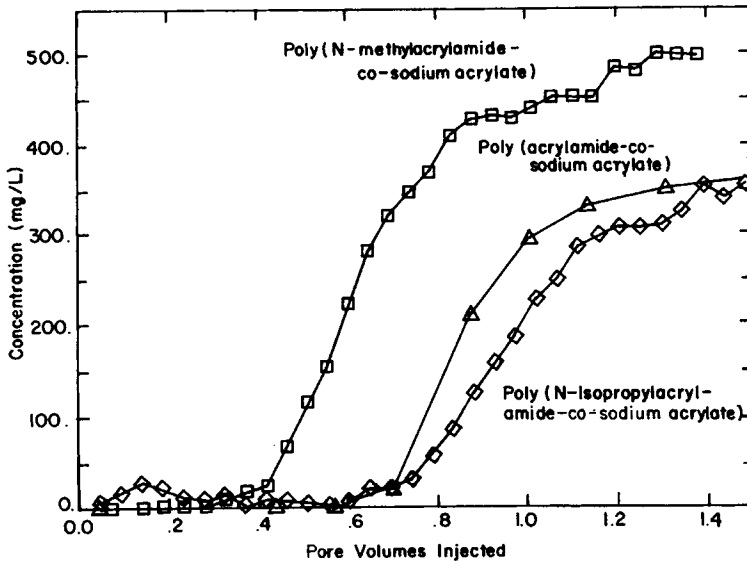Fig. 1. Polymer breakthrough curves for homopolymer.

Fig. 2.   Polymer breakthrough curves for copolymers.

an alkyl group for solubility of N-substituted acrylamide homopolymers in cold water. Thus, the decreased hydrophilicity of poly(N-isopropylacrylamide-co-sodium acrylate) may be an important factor in its behavior in the core tests. The poly(N-isopropylacrylamide-co-sodium acrylate) molecules may have a strong tendency to adsorb on the rock surfaces owing simply to their poor solvation by water. This factor may dominate and cause the poly(N-isopropylacrylamide-co-sodium acrylate) to adsorb more on the Berea core than poly(N-methylacrylamide-co-sodium acrylate) or poly(acrylamide-co- sodium acrylate).

CONCLUSIONS

1. Aqueous solutions of poly(N-alkylacrylamide-co-sodium acrylate) polymers show somewhat better retention of viscosity in salt solution than do analogous unsubstituted polymers.

2. However, N-methyl substitution makes the polymers more shear sensitive in low salt solutions.

3. The N-methyl substitution of acrylamide polymers reduces the amount of polymer retention in Berea core, but N-isopropyl substitution increases retention.

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