

Evaluation of Hydrophobically Associated Polyacrylamide-Containing Aqueous Fluids and Their Potential Use in Petroleum Recovery

Beatriz S. Chagas,¹ Dilon L. P. Machado Jr.,¹ Roberto B. Haag,² Celso R. de Souza,² Elizabete F. Lucas¹

¹*Instituto de Macromoléculas/Universidade Federal do Rio de Janeiro, CT, Bl. J, Ilha do Fundão, P.O. Box 68525, 21945-970, Rio de Janeiro, Brazil*

²*CENPES/PETROBRAS, Cidade Universitária, Q.7, 21949-900, Rio de Janeiro, Brazil*

Received 30 May 2003; accepted 17 September 2003

ABSTRACT: Acrylamide and tridecyl acrylate copolymers were synthesized by micellar copolymerization to obtain water-soluble, hydrophobically modified polymers. Rheological properties of the obtained polymer solutions were evaluated and compared to those of solutions of a commercial polyacrylamide currently used in the petroleum industry. The behavior of the copolymer solutions was studied as a function of the variation of hydrophobic monomer content incorporated in the copolymer as well as the salt content of the aqueous medium, for diluted and semi-diluted regimens. Comparative studies of such effects on the intrinsic viscosity and the critical concentration of those polymers were conducted. The increase in hydrophobic monomer content produced a sudden increase in the bulk and absolute viscosity of the polymeric solutions, a trend that was more intense from a certain concentration typical

for each polymer. Salt addition led to lower bulk viscosity caused by a stronger interaction among hydrophobic groups, resulting from minimized exposure of such groups and water. The same effect was observed for the critical concentration. A comparison of the synthesized polymers with industrial polyacrylamide showed that the synthesized polymers were characterized by advantageously high shear strength and high salt resistance. However, in the absence of salts, higher copolymer amounts were needed to prepare solutions whose viscosity was the same as that of commercial polyacrylamide. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3686–3692, 2004

Key words: water-soluble polymer; micellar polymerization; acrylamide copolymer; hydrophobic interactions; thickeners

INTRODUCTION

The use of polymers in the petroleum industry encompasses various areas of the activities of petroleum exploration, drilling, production, treatment, transportation, and storage, performing functions such as flocculating, stabilizer and thickening agent, organic deposition inhibitor, friction-reducing agent, and filtration aid, for example. Commonly used polymers for preparing service fluids are frequently water soluble and may be of natural origin, synthetic origin, or naturally modified.^{1,2}

The main role of a polymer used in petroleum recovery is to increase the viscosity of the aqueous

phase. Such increased viscosity may improve the efficiency of the lines during the process of oil recovery. One of the techniques used to recover petroleum from the rock formation is water injection into the producing field. The role of water is to propel the oil toward the producing well. Because water mobility is higher than that of petroleum, the injection of pure water causes the exit of this same water through the producing well instead of the exit of oil. To render the mobility of water similar to that of oil, thickening agents are used, more specifically, water-soluble polymers.²

Commercially, partially hydrolyzed polyacrylamide (HPAM) and biopolymers such as xanthan gum are used in the petroleum industry as thickening agents. Conventional polymers rely on chain extenders and physical entanglements of solvated chains to increase solution viscosity. In HPAM, carboxylated groups promote chain expansion as a result of ionic group repulsion, leading to higher solution viscosity. When all other factors are kept constant, the viscosity of a HPAM solution increases with the increase in molecular weight. As a result, oil field operations make use of high molecular weight HPAM, thus increasing the solution viscosity at a definite polymer concentration.

Correspondence to: E. Lucas (elucas@ima.ufrj.br).

Contract grant sponsor: National Research Council, Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Brazil.

Contract grant sponsor: José Bonifácio University Foundation.

Contract grant sponsor: Petrobras' R&D Center (CENPES/PETROBRAS).

However, when submitted to high shear rates, such as those encountered in pumping environments, high molecular weight HPAMs undergo irreversible degradation. High shear rates lead to a break of the polymer chain, with an irreversible decrease in viscosity. The higher the HPAM molecular weight, the easier shear degradation will be. However, high molecular weights are required to yield high viscosity at reduced concentrations. Besides, HPAM viscosity quickly decreases with increased salinity and hardness of the water used to make the solution, that is, as a result of the neutralization of ionic groups responsible for the repulsion, thus leading to chain contraction. The complexing capacity of the HPAM carboxylated groups may lead to polymer precipitation at high divalent ion concentration. In many oil reservoirs, water bears a high sodium chloride and divalent ion concentration, requiring the use of extremely costly and easily biodegradable xanthan biopolymers.²⁻⁴

Hydrophobically modified water-soluble polymers are water-soluble polymers that contain a small amount of hydrophobic groups directly linked to the main chain. In aqueous solutions, hydrophobic groups of these polymers tend to associate to minimize their exposure to the aqueous medium, analogous in a way to the micelle formation of a surface agent above its critical micellar concentration. Such associations result in an increase of the hydrodynamic size, which increases solution viscosity. Because the high viscosity conveyed by these polymers is attributed to molecular association, on shearing the fluids just disrupt these associations, which are reset when shear is interrupted and initial viscosity is recovered.⁵⁻¹⁰

Hydrophobically modified water-soluble polymers (HMWPs) belong to two categories: (1) those that make intramolecular associations and (2) those that make intermolecular associations. Each kind has unique features in solution based on hydrophobic interactions and associations as well as on ordination associations in water. Determination of parameters of the inter- and intramolecular aggregations includes the mole percentage of hydrophobic groups, the molar volume of the substituting group, chemical composition, and, particularly, the relative localization of hydrophobic groups, hydrophilic moiety length and hydration, and overall molecular weight.² HMWPs are usually prepared from acrylamide and a hydrophobic monomer by means of free-radical polymerization. Acrylamide is the most useful monomer for obtaining water-soluble high molecular weight polymers so that its copolymers are among the most extensively investigated.⁸⁻¹³ In spite of the fact that different polymers are used to prepare associated polymers, acrylamide is the most suitable one because its copolymers show the desired effect at polymer concentrations below 1% by weight.

HMWPs are usually prepared by two main methods: (1) copolymerization of hydrophilic and hydrophobic monomers and (2) polymer chemical modification to introduce hydrophobic and hydrophilic groups. Copolymerization by the technique known as micellar polymerization is the most common method applied for the synthesis of associated polymers.⁵ The micellar process¹⁴ for obtaining amphiphilic copolymers overcomes the experimental drawbacks of conventional copolymerization. Particularly, it renders possible the polymerization of water-soluble polymers, such as acrylamide, and of water-insoluble monomers, such as the alkyl acrylamides, yielding copolymers useful as thickening agents for aqueous media. The process adds the water-insoluble monomer in the predominantly aqueous medium with the aid of a suitable water-soluble surface agent, such as sodium dodecyl sulfate (SDS). Although other surface agents may be used, SDS is the most commonly employed because, among other reasons, it is available in a high degree of purity. Impurities, such as alcohol or heavy metal cations, may intervene in the polymerization, yielding reduced molecular weight polymers.

The aim of this work was the synthesis of hydrophobically modified acrylamide with tridecyl acrylate by of the technique of micellar polymerization. Further, to determine the shear strength and salinity resistance of the fluid the rheological behavior of the obtained polymer solutions was evaluated as a function of their concentration and copolymer composition.

EXPERIMENTAL

Synthesis of copolymers

The synthesis of the acrylamide-tridecyl acrylate copolymers was performed in a polymerization unit with 12-flask capacity consisting of a thermostatic bath and a turning base provided with controlled speed.

At first a 3 w/v % aqueous solution of SDS was prepared. To this solution 3 w/v % acrylamide solution and tridecyl acrylate were added in the amounts set forth in Table I. Potassium persulfate was used as initiator, at a concentration of 0.005 w/v %. After purging with nitrogen, the polymerization system was maintained at 60°C for 9 h.

Only Sample 03 was purified. The polymer was recovered by methanol precipitation, followed by filtration and oven drying at 50°C. Later, copolymer dissolution was carried out in an aqueous SDS solution at 3 w/v %.

Rheological evaluation

Viscosity measurements were obtained from three different apparatuses:

TABLE I
Reaction Conditions of Copolymerization Batches for
Acrylamide and Tridecyl Acrylate Using the
Technique of Micellar Copolymerization

Identification code	Amount of tridecyl acrylate relative to acrylamide weight	
	wt %	mol %
Sample 01	0.69	0.24
Sample 03	1.03	0.35
Sample 04	1.22	0.42
Sample 05	1.40	0.48
Sample 06	1.54	0.53
Sample 08	1.99	0.69
Sample 09	2.33	0.81
Sample 10	2.73	0.95

1. Haake rheometer, RheoStress RS 100 model (Bersdorff, Germany): cone and plate geometry (60 mm, 2°), with shear stress in the range 0.15–0.0025 Pa and shear rate in the range 1000–0.01 s⁻¹, at a temperature of 25°C.
2. Contraves rheometer, Low Shear LS 40 model (Greisensee, Switzerland): cylinder rotational system of the Couette type, with shear stress in the range 0.00265–0.165 Pa and shear rate in the range 10–0.01 s⁻¹, at a temperature of 30°C.
3. Brookfield viscometer, Model LVT (Middleboro, MA): coupled with a small sample adapter and SC4 31/13R spinkler, in the shear rate range 1–0.05 s⁻¹, at a temperature of 25°C.

Intrinsic viscosity values were determined by extrapolating from viscosity reduced to zero concentration.

Critical concentrations were obtained by the intersection of straight lines from specific viscosity η_{sp} graphs (at zero shear rate), as a function of the product of the solution intrinsic viscosity by its concentration, $c[\eta]$.

Variable concentration solutions were obtained through successive dilutions. Concentrations were corrected by adding a 1-mL aliquot to a previously tared flask, which was then placed in an oven at 50°C until constant weight (the maximum oven temperature was 50°C because of SDS degradation above that temperature). To calculate solution concentration, the theoretical amount of SDS present was subtracted.

RESULTS AND DISCUSSION

Synthesis of copolymers

Solutions resulting from copolymerization appeared as transparent, homogeneous, colorless, and clear. In view of the problems for purifying and quantifying these polymers,^{12,15,16} solutions resulting from polymerization reactions were used in the rheological

studies. Because all the reactions were run under constant conditions (initiator amount, temperature, and reaction time) and the hydrophobic monomer content varied within narrow limits, for purposes of the present study, it was considered that molecular weights of the obtained copolymers were similar.

Rheological studies

Absolute viscosity of polymeric solutions resulting from micellar polymerization

Figure 1 illustrates how absolute viscosity varies as a function of the shear rate of solutions of copolymers obtained by making use of the micellar copolymerization technique. As expected, it may be observed that viscosity increased as a result of the increase in hydrophobic monomer content in the feed. That is, Sample 10, which had the highest amount of hydrophobic monomer, showed the highest absolute viscosity value, whereas Sample 01, which had the lowest amount of hydrophobic monomer, showed the lowest viscosity value. The observed viscosity value occurs because copolymers having higher amounts of hydrophobic monomer tend to a higher association among molecules, thus increasing the aggregate volume, and as a consequence increasing the medium viscosity.

These results led us to consider that systems having a larger amount of hydrophobic monomer in the feed resulted in copolymers having a higher amount of hydrophobic monomer incorporated in their chain, even if the composition figures in the feed and in the copolymer are not essentially the same. Figure 1 results were obtained from the higher to the lower shear rate, which demonstrates that the fluid could recover viscosity even after having been sheared. This means that, when submitted to high shear rates, the molecular weight of such molecules is not reduced, only the

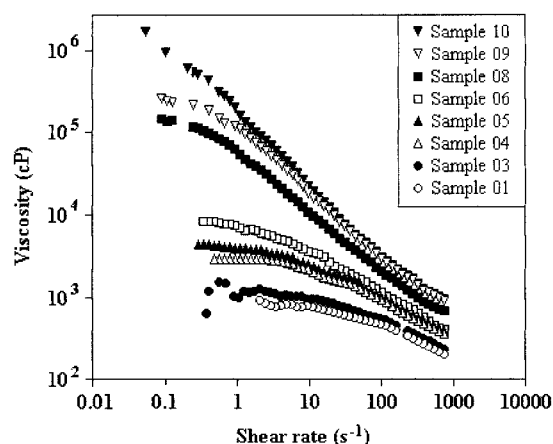


Figure 1 Curves of apparent viscosity versus shear rate for samples 01 to 10, from a Haake rheometer, at 30°C.

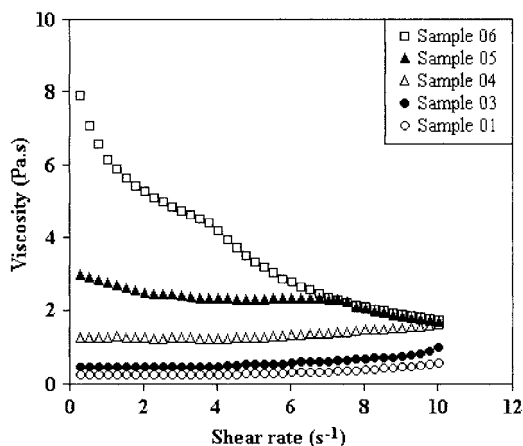


Figure 2 Curves of apparent viscosity versus shear rate for samples 01 to 06, from a Low Shear rheometer, at 30°C.

interchain association of copolymer hydrophobic groups is broken and subsequently restored.

A similar rheological study was run in the Low Shear 40 rheometer for Sample 01 and Sample 06. In this case viscosity measurements were made following a low-shear regimen. Figure 2 shows the results for absolute viscosity versus shear rate. It may be observed again that absolute viscosity is increased when the amount of hydrophobic monomer is increased. From Sample 05 on, behavior progressively moves away from Newtonian, which could be observed for samples having a lower amount of hydrophobic monomer.

In view of the fact that the surface agent amount was kept constant for all the reactions, it may be suggested that from Sample 05 on the size of hydrophobic blocks in the polymer chain causes it to be more sensitive to the shearing effects at the actual solution concentration (~ 3 w/v %).

Intrinsic viscosity

Intrinsic viscosity of the samples was also determined to evaluate the influence of SDS and NaCl contents on

the behavior of nonaggregated systems. At first a standard salt (NaCl) concentration had to be determined that would not cause precipitation in those systems. Solubility tests established that concentration as 0.1M (0.58 w/v % NaCl).

Thus, to determine intrinsic viscosity values of the polymer solutions, bulk viscosity analyses of each dilution were run in a Low Shear rheometer. A Newtonian behavior was observed for viscosity as a function of shear rate for the polymer concentration ranges used for all solutions as well as increased viscosity with increase in polymer concentration. Reduced viscosity values were taken in the Newtonian portion of the viscosity versus shear rate curves. Intrinsic viscosities were obtained from the Huggins equation¹⁷ with a reasonable match. Table II shows intrinsic viscosity values of copolymer solutions of varying SDS and NaCl concentrations, and copolymers of different amounts in hydrophobic monomer.

A comparison was made among the values of intrinsic viscosity for solutions of Sample 03, Sample 06, and Sample 09 copolymers, prepared from nonpurified solutions and containing the same content of added SDS (3 w/v%). Evaluation of the data led to the conclusion that intrinsic viscosity values are increasingly dependent on the increase of hydrophobic monomer content in the copolymers. The same behavior was observed when 0.1M NaCl-containing systems were compared with each other. Such results match literature data,^{5,6,13,14} given that at infinite dilution there is no intermolecular interaction, that is, the molecule behaves as if it were by itself in the solution, whereas the interaction of the molecular hydrophobic moieties, which minimize its exposure to water, promotes chain contraction. The higher the hydrophobic monomer content in the copolymer, the higher the chain contraction and the lower, intrinsic viscosity of solution.

A comparison between results obtained for nonpurified Sample 03 and purified Sample 03, both solutions containing 3 w/v % SDS, shows that after purification the polymer hydrodynamic volume was re-

TABLE II
Intrinsic Viscosity Values Obtained for Polymer Solutions

Sample code	Purification ^a	SDS (% w/v)	NaCl (mol %)	Intrinsic viscosity ^b (dL/g)	[η] Reduction (%)
Sample 03	Yes	3	—	2.31	—
Sample 03	No	3	—	7.93	60
Sample 06	No	3	0.1	3.23	
		3	—	5.90	49
Sample 09	No	3	—	3.04	
		3	0.1	4.22	45
		3	—	2.33	
		0.5	—	17.87	—

^a Yes = purified sample; No = nonpurified sample.

^b Huggins's extrapolation.

TABLE III
Critical Concentrations of Tridecyl Acrylate-Modified Acrylamide Copolymer Solutions

Sample code ^a	Estimated hydrophobe content in copolymer (mol %)	c^* for samples diluted in 3% w/v SDS, no NaCl (g/dL)	c^* for samples diluted in 3% p/v SDS and 0.1M NaCl (g/dL)	c^* for samples diluted in 0.5% w/v SDS, no NaCl (g/dL)
COP-C13-09	1.12	0.30	0.22	0.15
COP-C13-06	0.73	0.37	0.28	—
COP-C13-03	0.49	— ^b	0.41	—

^a Nonpurified solutions.

^b c^* did not occur in the tested concentration range (0.019–0.30 g/dL).

duced. This may be explained by the fact that the solid obtained after methanol precipitation was insoluble in aqueous media, that is, the copolymer chains had undergone a high degree of contraction. The chain hydrophobic groups are so strongly linked that the entry of water molecules to promote dissolution is highly impaired. Even upon addition of a surface agent to the aqueous medium there is a strong resistance to the dissolution process, with agitation and exposure to the dissolution medium being required for more than 24 h, until all the copolymer is again dissolved. Whenever the copolymer is dissolved, it is not necessary that its chains have the same hydrodynamic volume than that shown in solutions of nonpurified samples. Sadicoff and coworkers,^{15,16} based on a study on poly(propylene oxide) (PPO)-modified acrylamide, observed a behavior opposite to that of the present work, that is, solutions from purified copolymer had intrinsic viscosities equal or slightly superior to those of copolymers solutions prepared from a nonpurified solution. The observed discrepancy relative to the tridecyl acrylate-modified acrylamide copolymers may be explained by the fact that the hydrophobic character of the tridecyl acrylate monomer is stronger than that of PPO.

Still in Table II, comparing with Sample 09, in the absence of salt, containing different amounts of SDS (3 and 0.5 w/v%), it may be observed that the lower surfactant amount in the medium leads to an increase in intrinsic viscosity values. In principle, it could be expected that a reduction in SDS concentration would cause lower copolymer solubility in the medium and therefore lower intrinsic viscosity. The triplicate-run experiment confirmed that $[\eta]$ increases with SDS reduction. Such an unexpected result may be explained if one considers that because of the high degree of incompatibility of the copolymer hydrophobic branches with the medium, containing a lower content of surfactant agent, molecules tend to form molecular agglomerates that are difficult to break apart. Such agglomerates mask the actual intrinsic viscosity value; that is, the resulting viscosity would be relative to a molecular aggregate and not only to a single molecule. In this case, it is suggested that the solutions under investigation were not in the concentration range of a

diluted regimen, which was checked later in the determination of the critical system concentration.

Now, upon comparing systems containing 3% SDS, in the presence and in the absence of NaCl, it is observed that the presence of salt in the diluting solution, at the concentration of 0.1 mol, decreased the intrinsic viscosity for all studied samples. Salt present in the aqueous medium is a strong competitor with the polymer chain toward water, leading to lower polymer solubility, which in turn causes molecular contraction. However, it is seen that the reduction in viscosity is less marked as the hydrophobic monomer content in the copolymer is augmented (Table II). This indicates that the decrease in intrinsic viscosity could be minimized or even impaired by the increase in content of hydrophobic monomer that is modifying polyacrylamide. Therefore, there is a content in hydrophobic monomer in the copolymer chain that may be sought for which the polymer solutions do not show any viscosity loss in the presence of salt.

Critical concentration

Analyses of $[\eta]$ obtained with a Low Shear rheometer allowed collection of data for assessing the critical concentration for Sample 03, Sample 06, and Sample 09 copolymers, in the presence of SDS and in the absence and presence of salt (0.1M NaCl) (Table III). It may be observed that a higher content in hydrophobic monomer leads to a lower copolymer critical concentration. For the same surfactant agent concentration in the dilution medium, it is expected that the solubility of the tridecyl acrylate-modified acrylamide copolymers be reduced with the increase in the hydrophobic content with a consequent decrease in the values of c^* . An increase in the hydrophobic chain domains should be responsible for the increase in solubility of such chains in the aqueous medium, so that the polymer concentration range in a diluted regimen becomes narrower. According to literature data,⁵ the presence of salt introduces even deeper modifications in the solubility of hydrophobic groups, so as to intensify intermolecular interactions, thus increasing viscosity and consequently reducing the value of c^* , compared to the values obtained for a nonsaline medium.

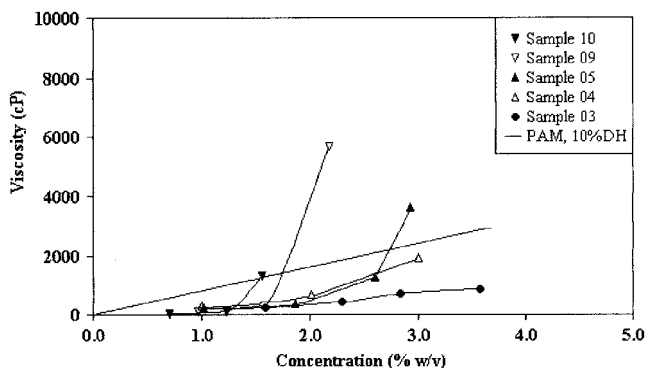


Figure 3 Curves of absolute viscosity versus concentration of the acrylamide and tridecyl acrylate copolymer compared to the curve of commercial polyacrylamide solution (FLOPAAM), from a Brookfield viscometer, at 25°C.

Absolute viscosity as a function of copolymer concentration and comparison with a commercial polyacrylamide

Aiming at comparing the rheological behavior of tridecyl acrylate–modified acrylamide copolymers in the semi-diluted regimen range, and using a commercial product marketed as FLOPAAM, polymeric solutions resulting from the micellar polymerization were diluted and their absolute viscosities were measured in a Brookfield viscometer. Tests were run in both the absence (Fig. 3) and the presence of salts (Table IV).

Figure 3 illustrates curves of absolute viscosity versus solution concentration for Sample 03, Sample 04, Sample 05, Sample 09, and Sample 10 copolymers, as well as for the commercial FLOPAAM sample, obtained for the shear rate of 0.5 s^{-1} . Some samples (the more viscous, having a higher amount of hydrophobic moieties) could not have their viscosity determined in the Brookfield viscometer because the values would be much beyond the sensitivity of the apparatus. Those samples required a deeper dilution to allow reading their solution viscosity. For the less-viscous batches, less-diluted solutions were prepared, with their concentrations being nearer to that of the polymerization-prepared batches.

It could be observed that, although for commercial polyacrylamide the increase in viscosity solution is practically linear based on polymer concentration, for tridecyl acrylate–modified polyacrylamide the increase in viscosity occurs according to a nonlinear pattern, being more intense with the increase of hydrophobic monomer content in the copolymer. A sharp change in the viscosity versus copolymer concentration curve occurs from a certain concentration, a behavior that is typical of each copolymer.

The effects of the hydrophobic groups on the rheological properties of their solutions depend on the polymer concentration. The occurrence of intermolecular interactions, intramolecular interactions, or both,

will determine the possible modifications observed in this typical rheological behavior.² The increase of hydrophobic monomer content during the copolymer synthesis, keeping constant the concentration of reaction surface agent, leads to larger hydrophobic blocks, thus causing an increase in the hydrophobicity of the copolymer.¹⁸ For more highly concentrated polymeric solutions in the semi-diluted regimen, it is expected that intermolecular interactions are intensified, thus increasing the occurrence of molecular aggregates and leading to a sudden increase in the absolute viscosity of such solutions. For copolymers having larger hydrophobic blocks, these more-intense interactions will probably occur at lower polymer concentrations caused by the increase in hydrophobic domains.

Commercial polyacrylamide marketed as FLOPAAM (degree of hydrolysis = 10%), used as a thickener in petroleum tertiary recovery fluids, served as a comparative parameter for the copolymers investigated in this work. Solutions of this commercial copolymer showed a behavior typical for commercial polyacrylamides cited in various literature studies.^{2–13} For low shear rates a Newtonian behavior may be observed in the test concentration range (0.01–1.5 g/dL). In this Newtonian region, solution viscosity varies linearly with the variation of the polyacrylamide concentration. From a viscosity versus concentration plot it is seen that a value of 0.04 g/dL for the concentration is required to attain a viscosity of 19 cP, which is the viscosity of injection fluids used in petroleum tertiary recovery. By drawing a straight line parallel to the axis of the polymer concentration and crossing the 19 cP viscosity of Figure 3 it may be seen that several copolymers show viscosities of this order, for concentrations that are higher than that used with the FLOPAAM acrylamide.

Table IV lists values for absolute viscosity measured in a Brookfield viscometer in the presence and in the absence of salt, at a shear rate of 0.5 s^{-1} , of a commercial polyacrylamide solution of FLOPAAM and of Sample 05 and Sample 09 copolymers. It may be observed that 1 g/dL of Sample 05 copolymer is required to obtain the same absolute viscosity ($\sim 30 \text{ cP}$) achieved by commercial polyacrylamide at a concen-

TABLE IV
Absolute Viscosity of Polymeric Solutions as Measured in a Brookfield Viscometer, at 0.5 s^{-1} , in the Presence and in the Absence of Salt

Sample code	Polymer concentration (g/dL)	Absolute viscosity (cP)	
		No salt	Salt added (0.1M NaCl)
FLOPAAM	0.04	30	4
COP-C13-07	0.96	30	38
COP-C13-09	1.0	34	36

tration of only 0.04 g/dL. Such higher polymer concentration required for obtaining the same viscosity as that obtained with commercial polyacrylamide may possibly be attributed to different molecular weights. Salt addition to the medium caused a sudden decrease in viscosity of the polyacrylamide solution. On the contrary, copolymer solutions have shown a viscosity increase in a saline medium. This behavior, observed for all samples, is in agreement with literature data² found for similar polymers. Polyacrylamide viscosity is reduced because this polymer is partially hydrolyzed and ions present in solution reduce the electrostatic repulsion of the hydrolyzed groups present in the chain, resulting in chain contraction. As for the acrylamide and tridecyl acrylate copolymers, the presence of salt decreases molecular solubility as a whole but intensifies intermolecular interactions, thus ultimately leading to an increase in the hydrodynamic volume and consequently an increase in viscosity.

A few modifications should still be introduced in reaction conditions to obtain copolymers having viscosities of the order of 19 cP, by using a concentration similar to that of commercial polyacrylamide. On the other hand, advantages inherent to copolymers compared to those of polyacrylamide, mainly with respect to salt sensitivity, may certainly compensate for the use of more highly concentrated polymer solutions in highly saline fields.

CONCLUSIONS

Use of copolymers from the described polymerizations yielded highly viscous solutions of high shear strength and high salt resistance, which indicates excellent potential use in tertiary petroleum recovery. To be used in the petroleum industry, in wells without the presence of salts, such copolymers should have molecular weights slightly higher than those obtained in the present work, to reduce solution concentration, while keeping a viscosity level suitable for petroleum recovery operations.

The addition of salt to tridecyl acrylate-modified acrylamide copolymer solutions, in the diluted-regi-

men range, led to a decrease in intrinsic viscosity values, which may be attributed to changes in hydrophobic group solubility. However, this lower intrinsic viscosity was minimized through an increase in hydrophobic monomer content in the copolymer. The critical concentration of copolymer solutions was reduced upon increasing the hydrophobic monomer content, probably because of solubility modifications caused by hydrophobic blocks.

The authors are indebted to the National Research Council, Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Brazil; José Bonifácio University Foundation; and Petrobras' R&D Center (CENPES/PETROBRAS) for support of this work.

References

1. Borchardt, J. K. In: *Encyclopedia of Polymer Science and Engineering*; Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, G., Eds.; Wiley: New York, 1987; Vol. 10, p. 328.
2. McCormick, C. L.; Bock, J. E.; Schulz, D. N. In: *Encyclopedia of Polymer Science and Engineering*; Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, G., Eds.; Wiley: New York, 1989; Vol. 17, p. 730.
3. Biggs, S.; Selb, J.; Candau, F. *Polymer* 1993, 34, 580.
4. McCormick, C. L.; Nonaka, T.; Johnson, C. B. *Polymer* 1988, 29, 731.
5. Taylor, K. C.; Nasr-El-Din, H. A. *SPE* 29008 1995, 675.
6. Schulz, D. N.; Kaladas, J. J.; Maurer, J. J.; Bock, J.; Pace, S. J.; Schulz, W. W. *Polymer* 1987, 28, 2110.
7. Lacík, I.; Selb, J.; Candau, F. *Polymer* 1995, 36, 3197.
8. Candau, F.; Volpert, E.; Lacik, I.; Selb, J. *Macromol Symp* 1996, 111, 85.
9. Volpert, E.; Selb, J.; Candau, F. *Macromolecules* 1996, 29, 1452.
10. Uemura, Y.; McNulty, J.; MacDonald, P. M. *Macromolecules* 1995, 28, 4150.
11. Branham, K. D.; Davis, D. L.; Middleton, J. C.; McCormick, C. L. *Polymer* 1994, 35, 4429.
12. Hill, A.; Candau, F.; Selb, J. *Macromolecules* 1993, 26, 4521.
13. Volpert, E.; Selb, J.; Candau, F. *Polymer* 1998, 39, 1025.
14. Turner, S. R.; Siano, D. B.; Bock, J. U.S. Pat. 4,528,348, 1985.
15. Sadicoff, B. L.; Brandão, E. M.; Lucas, E. F. *Int J Polym Mater* 2000, 47, 399.
16. Sadicoff, B. L.; Brandão, E. M.; Amorim, M. C. V.; Lucas, E. F. *Polím Ciência Tecnol* 2001, 11, 41.
17. Cowie, J. M. G. *Polymers: Chemistry and Physics of Modern Materials*, 2nd ed.; Chapman & Hall: New York, 1991; p. 208.
18. Chatterji, J.; Borchardt, J. K. *J Petrol Technol* 1981, 33 2042.