

Hydrophobically associating polymers and their interactions with rod-like micelles

D. G. Peiffer

Corporate Research Laboratory, Exxon Research and Engineering Company,
Route 22 East, Clinton Township, Annandale, NJ 08801, USA
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Several families of anionic and cationic hydrophobically associating acrylamide-based copolymers have been synthesized. This study focuses on the characterization in aqueous environments of water-soluble copolymers in which low levels of alkyl, i.e. methylene, units are incorporated into the polymer chain structure. These hydrophobic monomers have built-in surfactant character; therefore, no non-polymerizable surfactants are required in the preparation of these copolymer materials. These hydrophobically associating copolymers are shown to possess both polyelectrolyte and hydrophobic character, especially as the ionic strength of the solution is varied. The results confirm that, even at low concentrations of hydrophobe (typically ≤ 1 mol%), interesting solution properties are observed, i.e. enhanced rheology as compared to its non-associating parent, marked time-dependent rheology at low shear rates, 'anti-polyelectrolyte effect' in high-ionic-strength solutions and the ability to interact preferentially with hydrophobically associating rod-like micelles. These latter materials are capable of forming highly viscoelastic solutions themselves. The rheological properties of these latter solution mixtures are very sensitive to the fraction of each component in the mixture and to the length of the alkyl chain copolymerized into the acrylamide chain backbone.

(Keywords: colloid-polymer interactions; hydrophobically associating copolymers; rod-like micelles; rheological behaviour; viscoelastic solutions)

INTRODUCTION

The need to control precisely the rheological properties of both aqueous and organic media has led to the development of polymeric materials containing low levels of associating-type functionalities¹⁻⁸. These groups can be characterized as, in qualitative terms, possessing solubility that is markedly different from the majority of the polymer chain. For example, ionic groups are effective in modifying the properties of relatively non-polar solvents, while hydrophobic moieties, i.e. oil-soluble, are especially effective in aqueous environments. In contrast to conventional polyelectrolytes in water, where the viscosity is governed by charge-charge repulsions, hydrophobically associating groups aggregate to minimize their interaction to water in a fashion that apparently is analogous to the myriad of possible structures of low-molecular-weight surfactants. The ability to form very well defined structure, however, can be constrained somewhat by the chain backbone itself. Irrespective of the detailed structure of this aggregation phenomenon, it is quite clear that such a relatively minor modification in polymer structure imparts physical properties that are dramatically different from those of its non-functionalized parent.

Presently, there are substantial synthetic efforts with regard to hydrophobically associating acrylamide copolymers in which low levels of long-chain *N*-alkyl acrylamides are incorporated^{7,8}. These copolymers are broadly characterized by enhanced viscosity combined with brine and shear stability. These copolymers are,

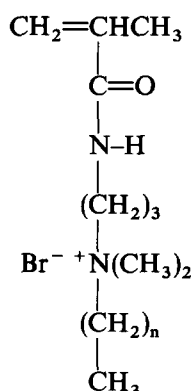
however, formed from two monomers that have markedly different solubility characteristics. Therefore, specialized synthesis procedures need to be used to ensure that both monomers are mutually copolymerized within the chain structure. To simplify these procedures and also to improve the solubility of the copolymers, the use of hydrophobic monomers with built-in surfactant character has recently been detailed⁷. It is of interest to explore the solution behaviour of water-soluble copolymers containing hydrophobically associating groups in which there are ionic functionalities also present. Therefore, in our continuing pursuit for polymeric structures capable of enhancing the rheological properties of fluids, a family of cationic long-chain alkyl-type and anionic long-chain alkyl-type monomers were synthesized and subsequently copolymerized with acrylamide via a conventional free-radical solution polymerization technique. Alcohol or surfactant homogenization, microemulsion or micellar polymerization conditions were not necessary for effective polymerization. The properties of these solutions were examined as a function of ionic strength, polymer concentration and shear rate.

Subsequently a more complex fluid system was formed with the addition of the above cationic or anionic hydrophobically associating copolymers to polymerizable viscoelastic fluids containing rod-like structures. The detailed interactions between these polymers and the rod-like colloid was examined by comparing the viscometric properties of the non-associating polymer or their associating analogues in the presence of the rod-like structures.

EXPERIMENTAL

Cationic-hydrophobic type monomer

A representative synthesis procedure is presented here. Acetone (70 ml) was added to a resin flask equipped with a water condenser, mechanical stirrer, nitrogen inlet and outlet and thermometer. Dimethylaminopropylmethacrylamide (20 g) and dodecyl bromide (29.3 g) were added and the solution temperature increased to 35°C (24 h). The monomer was isolated with the addition of anhydrous diethyl ether. The precipitate was filtered and repeatedly washed with a large excess of anhydrous diethyl ether. Elemental and n.m.r. analyses confirmed the high purity of the monomer (99%) and its chemical composition, which in the more general case is:



In the above procedure $n=11$. It is also important to note that this monomer is completely water-soluble and produces aqueous solutions having low surface tensions.

Cationic copolymer polymerization

Distilled water (500 ml) was added to a resin flask again equipped with a water condenser, thermometer, argon inlet and outlet and an air-driven mechanical stirrer. The water was deoxygenated for a period of 2 h with argon gas. The monomer, acrylamide (47.0 g, 99.0 mol%), and the previously synthesized cationic ($n=11$) monomer (2.6 g, 1.0 mol%) were subsequently added. In order to prevent hydrolysis from occurring, a room-temperature initiator (0.1 g of 2,2'-azobis(2,4-dimethyl-4-methoxyvaleronitrile)) was used. This compound was kindly supplied by DuPont (Vazo 33®). The polymerization was run for 24 h with the temperature maintained at 25°C (typical conversions were 90–100%). The copolymer was precipitated with a large excess of acetone. Subsequently, the copolymer was washed several times with a large excess of acetone and dried in a vacuum oven at 60°C for 24 h. Bromine analysis was used to determine cationic monomer incorporation. In this case, the copolymer contained 0.68 mol% (0.74 wt% bromine) of the alkyl cationic monomer. In this report the alkyl group content is synonymous with hydrophobe level. Table 1 summarizes the copolymer structures used in this study, which contains approximately equivalent bromine content, i.e. hydrophobe level, but varying alkyl chain length.

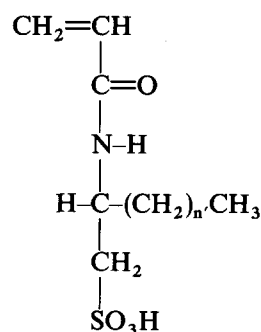
Anionic-hydrophobic type monomer

These monomers were formed via a Ritter reaction of acrylonitrile and an α -olefin. Typically, a mixture of dodecene-1 (42.0 g) and acrylonitrile (55.0 g) was added to an appropriate reaction flask and cooled to $\sim 0^\circ\text{C}$.

Table 1 Composition of the acrylamide-co-cationic hydrophobic polymers

Designation	Alkyl length, n	Bromine content (wt%)	Hydrophobe level (mol%)
11868-99A	1	0.62	0.56
11868-84C	5	0.90	0.83
11868-99B	11	0.74	0.68

Subsequently 28.0 g of 30% oleum is added over a 30 min period. The temperature of the flask was warmed slowly to room temperature and allowed to stand for 24 h. A precipitate formed and was collected by filtration, washed with an excess of acrylonitrile and dried in a vacuum oven at 25°C (24 h). Again elemental and n.m.r. analyses confirmed the high purity of the product (>99%) and its chemical composition, which in the more general case is:



In the above procedure $n'=9$. The alkyl chain length is controlled by varying the α -olefin structure. As with the cationic monomers, these compounds are water-soluble and produce aqueous solutions having low surface tensions.

Anionic copolymer polymerization

An analogous polymerization procedure was used in the preparation of these materials as described in the cationic copolymers. Essentially the only modifications were in monomer concentrations, i.e. 300.0 ml of distilled water, 47.0 g acrylamide (99.0 mol%), 2.62 g of the $n'=9$ sulphonate-containing monomer (1.0 mol%), 0.35 g sodium hydroxide and 0.05 g potassium persulphate. Polymerization temperature was 50°C and copolymer product was isolated with a large excess of acetone. Elemental analysis (sulphur) was used to determine the sulphonate content, which in this case was 0.92 mol% (0.40 wt%). This copolymer was hydrolysed under mild alkaline conditions in order to increase the charge density along the chain backbone while still retaining the identical degree of polymerization and sulphonate content.

Hydrolysis of anionic copolymers

The previously synthesized anionic copolymer (1.0 g) was dissolved in a flask containing 200.0 ml of distilled water and 0.22 g of sodium hydroxide (for example) at 50°C for 4 h. The hydrolysed copolymer was isolated with a large excess of acetone. The polymer was dried in a vacuum oven at 40°C for 48 h. The amount of base and reaction time were used to regulate the level of carboxyl groups, as shown in Table 2. The data confirm that, under these relatively mild hydrolysis conditions, it is clearly observed that the level of hydrolysis is markedly modified with increasing levels of added base, i.e. sodium hydroxide.

Table 2 Hydrolysis conditions and hydrolysis levels on an acrylamide alkylsulphonate-containing copolymer ($n' = 9$)

Designation	Sodium hydroxide (g)	Sulphonate content (mol%)	Hydrolysis level (mol%)
47BR	0.00	0.92	0.0
47BRH1	0.03	0.94	6.8
47BRH2	0.06	0.92	7.8
47BRH3	0.11	0.96	15.6
47BRH4	0.17	0.93	24.1
47BRH5	0.22	0.91	30.9
47BRH6	0.44	0.92	38.9

In addition, it is noted that the sulphonation level, and therefore the alkyl group level, remains invariant even up to high levels of hydrolysis.

Hydrophobically associating polymer-viscoelastic monomer fluid mixtures

The synthesis and properties of the viscoelastic monomer fluids were the subject of previous publications^{8,9} and, therefore, are not detailed here. The mixtures, however, were formed from the concentrated individual component solutions followed by a serial dilution to the appropriate lower concentration.

Rheological measurements

Viscosity-shear rate measurements (25°C) were performed on a Contraves Low Shear 30 instrument. All other measurements were obtained on a Brookfield viscometer (model LVT) utilizing a UL adapter for relatively low-viscosity measurements and various size spindles for higher-viscosity solutions (0.2 s⁻¹).

RESULTS AND DISCUSSION

Melting-point behaviour

Amphiphilic compounds are molecules possessing both a hydrophobic and a hydrophilic component chemically bound into a single structural entity. It is well known that the surface tension of water can be substantially reduced with the solubilization of surfactants and triblock copolymers, for example. In the most general case, these materials have different solubilities towards the solvent within the same molecule. An examination of the surface tension of the two polymerizable monomers synthesized for this study also confirms surfactant-like behaviour where the critical micelle concentration is a function of the alkyl chain length, in general. Again, this phenomenon can be detailed in terms of the dual solubility of the polar and non-polar functionalities within the monomer.

An examination of the melting point of a homologous series of the anionic alkyl-containing monomers as a function of the number of methylene groups reveals a remarkable parabolic dependence (Figure 1). These monomers were thoroughly dried prior to measurement. As was also noted by Sherrington *et al.*¹⁰ this melting-point behaviour appears to be intrinsic and the parabolic dependence on the methylene content is real. This phenomenon again is related to the dual nature of these molecules. When the methylene group length is short, then the transition is governed by the ionic, i.e. salt-like, moieties and a high melting point is exhibited. Alternatively, when the alkyl length is increased, the ionic forces

are correspondingly reduced until, of course, the alkyl chains themselves interact, causing again a rise in the melting transition. This latter effect is somewhat similar to the conventional melting transitions observed in a homologous series of normal paraffins (alkanes). As anticipated, the force of interaction of the ionic moieties can be modified through neutralization of sulphonic acid. The minimum in the curve remains invariant, but the curve is shifted upwards in temperature by approximately 50°C with the sodium counterion.

Rheology of cationic copolymers

The dual nature of these monomers is also exhibited when chemically incorporated into a water-soluble chain backbone even at relatively low levels. The effect on viscosity is particularly instructive in this regard. Figure 2 shows the viscometric behaviour as a function of polymer concentration and solvent ionic strength. The copolymer (11868-84C, Table 1) in this example has a methylene chain length of 5. A close examination of the data reveals that this copolymer behaves as a typical polyelectrolyte at salt levels below approximately 5 wt%. That is, a decrease in viscosity is observed due to screening of the charge-charge repulsions by the dissolved salt. Upon further salt addition, the modest hydrophobic nature of the monomer begins to dominate and the viscosity rises.

Doubling the methylene length has a dramatic influence on the viscosity-polymer concentration profiles (Figure 3) under identical solution conditions. Even though the hydrophobe content has been reduced by 22% (see Table 1) to 0.68 mol%, the viscosity increases above a salt level of approximately 1%. Above the critical overlap concentration, enhancement by several orders of magnitude is observed. The copolymer with the lowest hydrophobe functionality, $n = 1$, behaved as a typical polyelectrolyte in salt solutions where screening of the charge-charge repulsion dominates solution rheology, and not strong aggregation of the alkyl units.

An examination of the solubilities of these cationic alkyl-containing monomers in water also confirms that

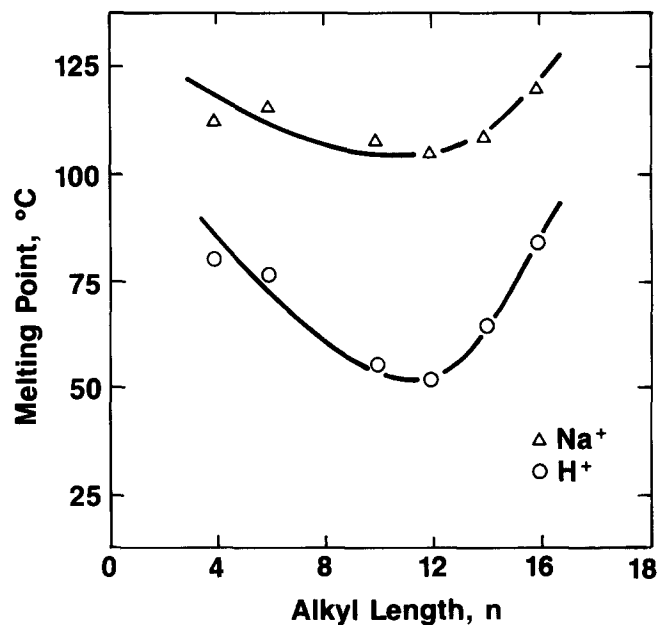


Figure 1 Plot of melting point versus alkyl chain length, n , in a series of anionic alkyl-containing monomers neutralized with sodium or in the free acid form

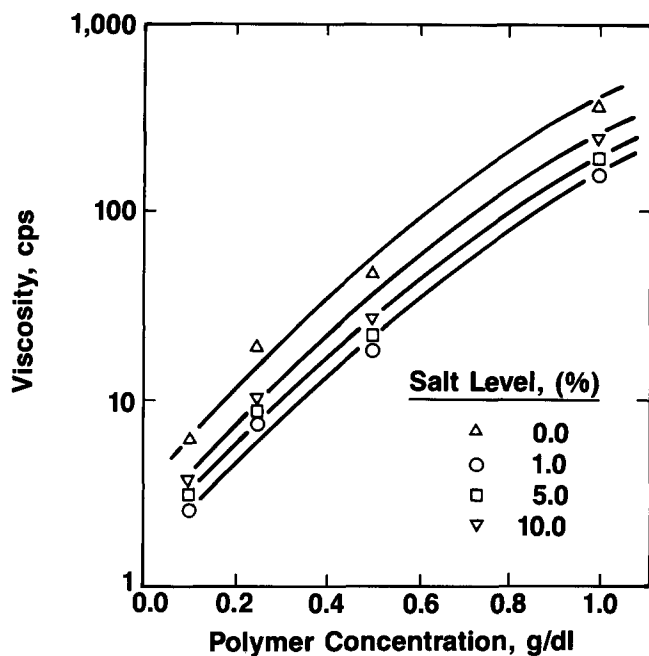


Figure 2 Viscosity-polymer concentration profiles of a cationic alkyl-containing acrylamide copolymer (11868-84C, $n=5$) as a function of salt (CaCl_2) concentration

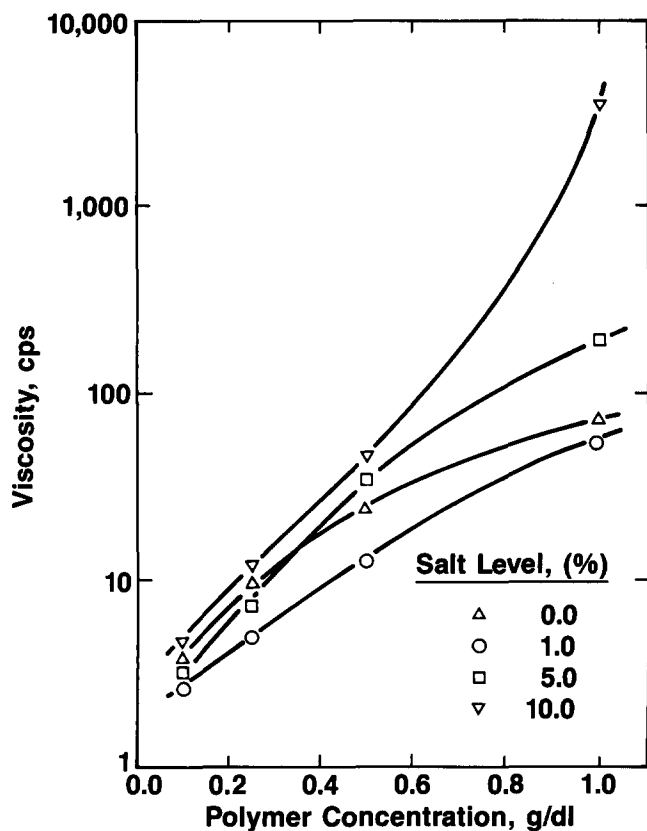


Figure 3 Viscosity-polymer concentration profiles of a hydrophobically associating cationic copolymer (11868-99B, $n=11$) as a function of salt (CaCl_2) concentration

transitions in solution behaviour of this type often occur with ionic organic compounds where the hydrophobe length is increased with respect to the methylene length. For short chain length, it was observed that these moieties were readily water-soluble. For intermediate chain lengths, the monomers were less water-soluble, as

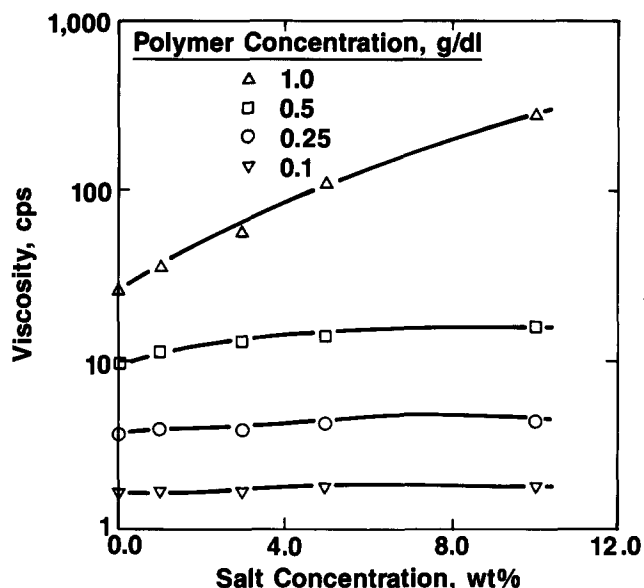


Figure 4 Viscosity-polymer concentration profiles of an anionic hydrophobically associating acrylamide copolymer (11868-47BR, $n'=9$) as a function of salt (NaCl) concentration

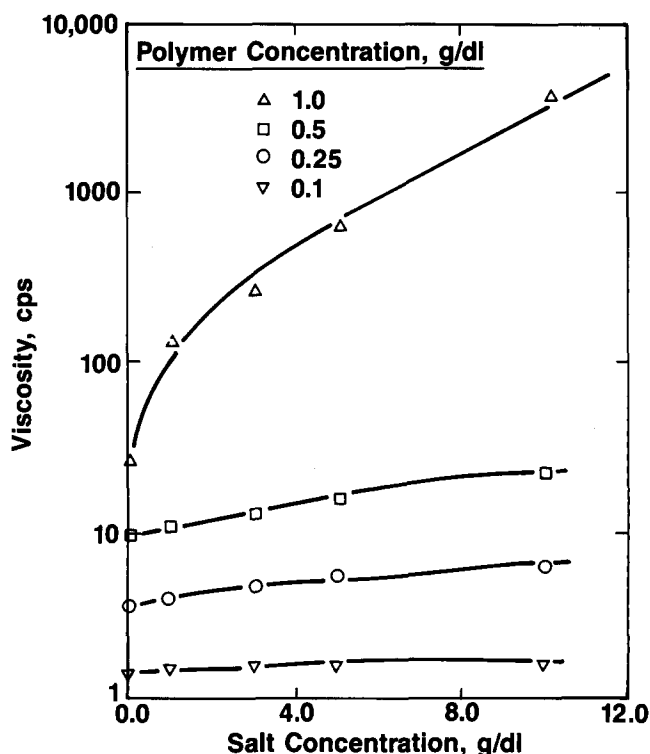


Figure 5 Viscosity-polymer concentration profiles of an anionic hydrophobically associating acrylamide copolymer (11868-47BR, $n'=9$) as a function of salt (CaCl_2) concentration

anticipated from increased hydrophobic character and apparent inability to form a micellar-type aggregate. However, for longer alkyl lengths, marked surface reduction with considerable foaming appeared. This behaviour is also manifested when these monomers are incorporated into a polymer.

Rheology of anionic hydrophobically associating polymers

In Figures 4 and 5 are shown the viscometric properties of an acrylamide copolymer containing an anionic hydrophobically associating monomer ($n'=9$). The data

confirm that, at this methylene content, hydrophobic associations dominate solution rheology. Screening of the charge-charge repulsions is unimportant but does, however, become the dominant factor at somewhat lower alkyl lengths. As expected, the strength of the hydrophobic association is a direct function of the solvent quality for the alkyl moiety. It is apparent that calcium chloride is able to enhance this association to a more significant extent than sodium chloride. At concentrations greater than the critical overlap concentration (C^*), several orders of magnitude difference is observed. It is also important to note that time-dependent rheology is observed (typically at shear rate below 100 s^{-1}) as the solvent quality for the hydrophobe is decreased.

This anionic hydrophobically associating copolymer has the unique ability of being able to be hydrolysed in order to increase the ionic charge chemically bound to the chain backbone while still retaining the hydrophobic units (Table 2). Typical fresh-water viscometric behaviour is presented in Figure 6. A salient feature of the data is a dramatic two orders of magnitude rise in the overall viscosity as the charge density is enhanced up to $\sim 30\text{ mol}\%$ followed by less abrupt viscosity reduction. This 'maximum behaviour' has been observed in a number of hydrolysed polyacrylamides¹¹. It was reported that the reduced viscosity increased sharply with an

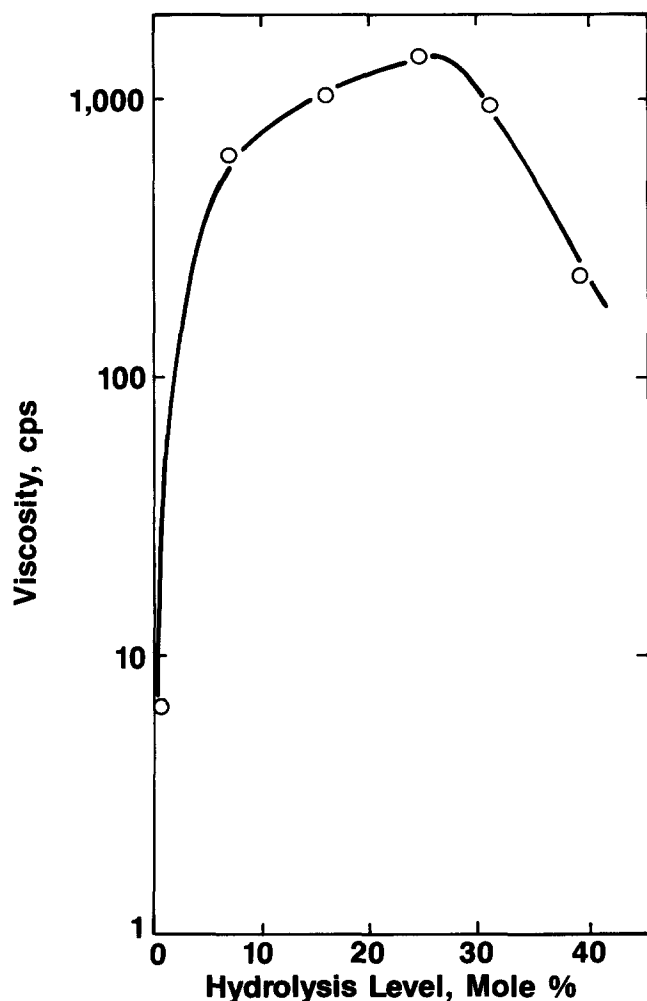


Figure 6 Comparison of the viscosities (25°C) of the 11868-47BR hydrophobically associating copolymer at several levels of hydrolysis, i.e. carboxylate content. Polymer concentration is 0.25 g dl^{-1} (shear rate of measurement is 1.0 s^{-1})

increase of sodium acrylate units up to about 40%. This phenomenon was further examined, leading to the conclusion that extensive hydrogen bonding causes the chain coils to extend. The chain dimensions rise to a maximum level at about 40 mol% acrylate content. It is important to note that the hydrophobe does not inhibit the 'maximum behaviour' of these copolymers to any great extent even though it is known that extensive multichain aggregates are formed in these associating-type polymer solutions. It can be assumed that it is quite likely that the chains retain their 'unperturbed' dimensions within an aggregate. As a result, the aggregate dimensions would increase with hydrolysis (at equivalent degrees of polymerization), resulting in a viscosity increase. A number of structural questions, however, remain unanswered as of the present time, dealing with aggregate number and size as a function of hydrolysis and polymer concentration. This work is ongoing and will be the subject of a future publication.

As noted previously, increasing the ionic strength of polyelectrolytes results in substantial dimensional decrease in coil size. This effect is also observed in these highly charged hydrophobically associating copolymers at relatively low polymer levels and salt concentrations. Again, however, the hydrophobic forces dominate solution rheology at high salt levels and also polymer concentrations. Typical results are presented in Figure 7 showing again an 'antipolyelectrolyte effect' with increasing salt concentration. The addition of hydrophobic units eliminates or at least lessens to a significant extent some of the well known limitations of polyelectrolytes and as a consequence enhances their technological utility.

Hydrophobically associating copolymer-colloidal rod mixtures

It is now well known that some specific families of amphiphilic molecules produce rather viscous aqueous solutions if the associated counterion is of the appropriate structure and binds tightly to the amphiphile itself¹²⁻²⁰. If these conditions are met, in general, rod-like micellar structures are formed. The structure and physical properties of polymerizable viscoelastic rod-like fluids have been described recently^{8,9}. An individual rod can best be described as an outer coat of ionic charge (with its associated counterion) surrounding an olephilic-hydrophobic interior comprising the majority of the alkyl tails. The olephilic region of conventional spherical micelles is well known to be capable of solubilizing a large number of organic molecules²¹. Typically, the location and distribution of solubilized species inside the micelle have been examined with an emphasis on the equilibrium distribution between a 'dissolved state' associated with the hydrocarbon core and an 'adsorbed state' arising from the outer surface, i.e. interfacial activity of the solubilize dissolved in the micelle. Therefore, it is of scientific and technological interest to examine the possible solubilization into the rod-like micelle interior of low levels of hydrophobic units copolymerized into an otherwise hydrophilic chain backbone.

The rod-like micelles used in this work are formed from the reaction of alkyl bromide with tetradecylamine with subsequent ion exchange with methylsalicylic acid. Typical viscosity-concentration profiles in fresh water of the rod-like micellar solution and the two previously described cationic hydrophobically associating copolymers are presented in Figure 8. In all instances, the

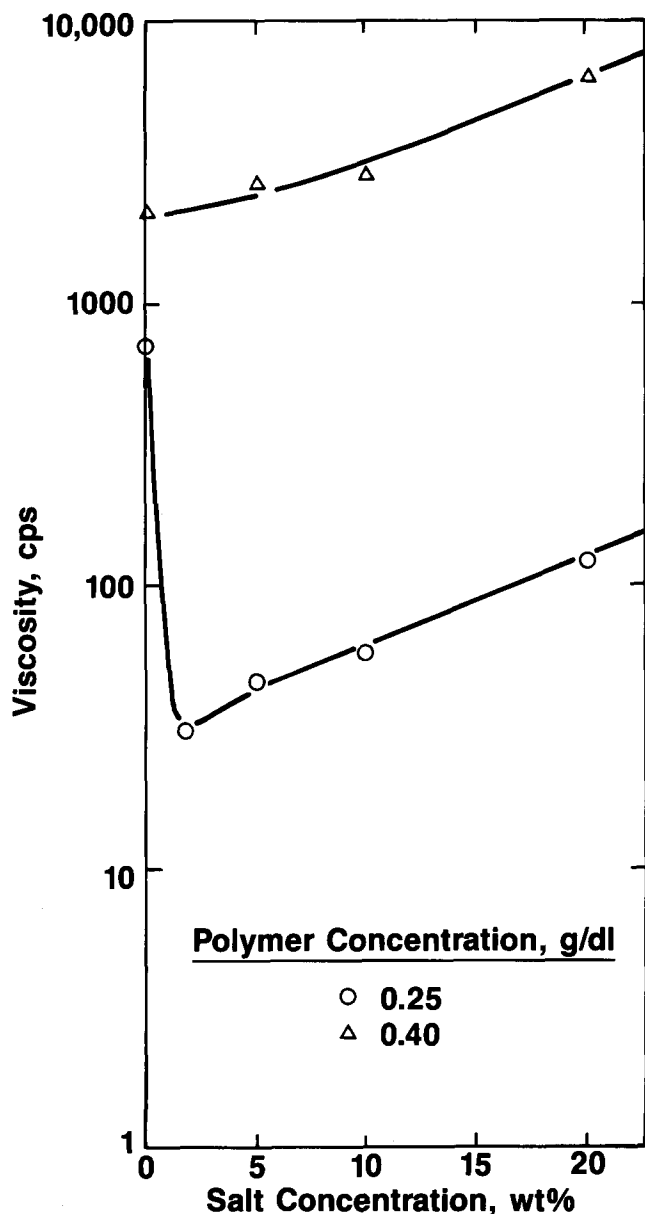


Figure 7 Comparison of the viscosities as a function of sodium chloride level at 25°C of the 11868-47BRH5 (Table 2) at two polymer concentrations

viscosity increases with monomer or copolymer concentration. From intrinsic viscosity measurements, the average degree of polymerization is approximately equivalent for the two copolymers. However, the mixing of these copolymers with rod-like structures clearly confirms that, the longer the hydrophobic methylene sequence, the higher is the overall viscosity of the mixture. Without the hydrophobe, the viscosity of the mixture is simply equivalent to the sum of the viscosity of each of the individual components. It is important to note that if the monomer units were not organized into rods but were essentially cosolvents, this would markedly reduce the viscosity of the hydrophobically associating copolymer. Effective connectivity or bridging of the monomers and the copolymer entities is certainly lacking in such solutions, but this is not the case if these monomer units are organized into a well defined structure and the hydrophobe unit on the water-soluble copolymer is of sufficient length, as shown in Figure 8.

The anchoring of the hydrophobic residues of the copolymer chains into the rod-like micelle is due primarily to the gain in free energy resulting from the transition from a partially solvent-exposed methylene chain to a system in which these units now lie in the highly hydrophobic interior of the rods. The overall structure is certainly quite dynamic in nature, but marked changes in rheological properties are clearly observed. It is also possible that only a fraction of the hydrophobic units of the copolymer are embedded in a rod-like entity (Figure 9). The exact distribution of these chain-colloid

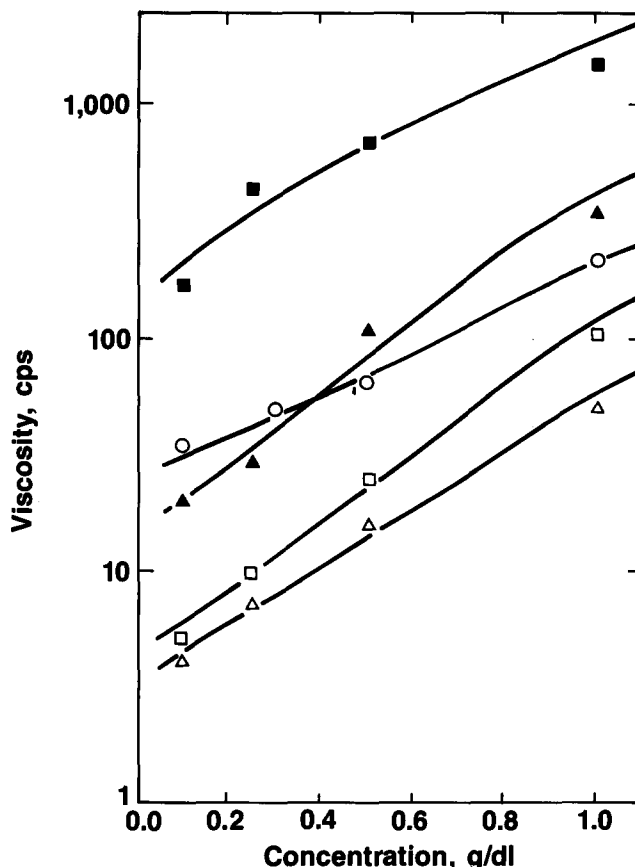


Figure 8 Comparison of the viscometric properties (1.0 s^{-1} , 25°C) as a function of concentration in fresh water of a viscoelastic monomer fluid (\circ), cationic hydrophobically associating copolymers (11868-99A, $n=1$ (\triangle) and 11868-99B, $n=11$ (\square)) and their respective 1:1 mixtures (viscoelastic monomer fluid with 11868-99A (\blacktriangle) and with 11868-99B (\blacksquare))

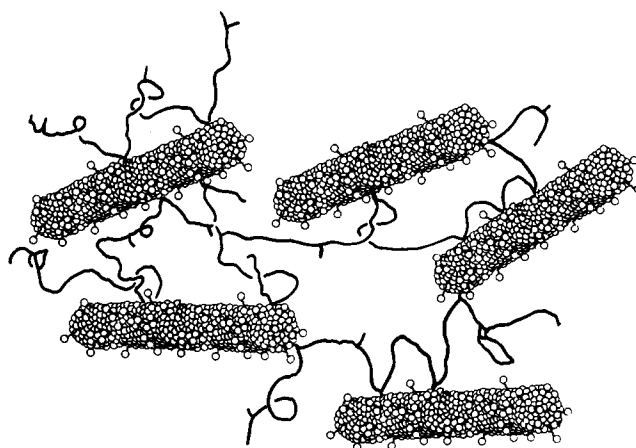


Figure 9 Schematic representation of a mixture of hydrophobically associating water-soluble copolymers and colloidal rod-like micelles

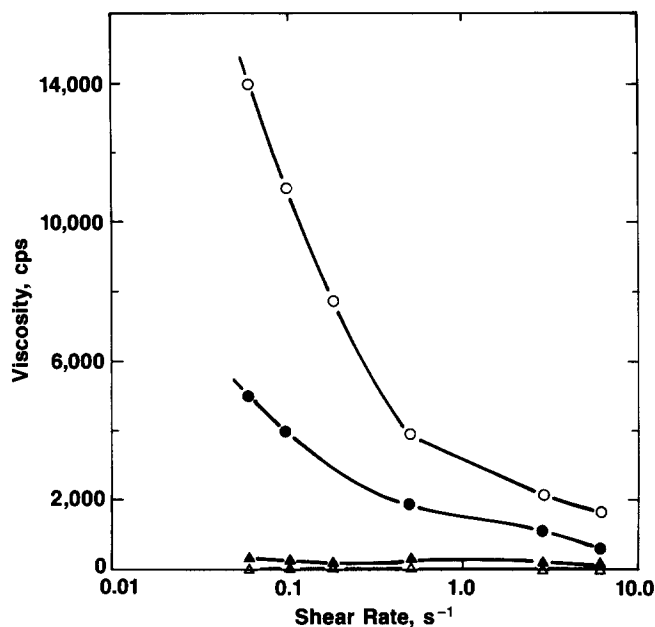


Figure 10 Viscosity-shear rate profiles in fresh water (25°C) of a viscoelastic monomer fluid (Δ , 160 ppm), an anionic hydrophobically associating acrylamide-copolymer 11868-BRH5 (\blacktriangle , 0.1 g dl⁻¹), a mixture (\bullet) of the viscoelastic monomer fluid (83 ppm) and the 11868-BRH5 copolymer (0.1 g dl⁻¹) and a mixture (\circ) of the viscoelastic monomer fluid (166 ppm) and the 11868-BRH5 copolymer (0.1 g dl⁻¹)

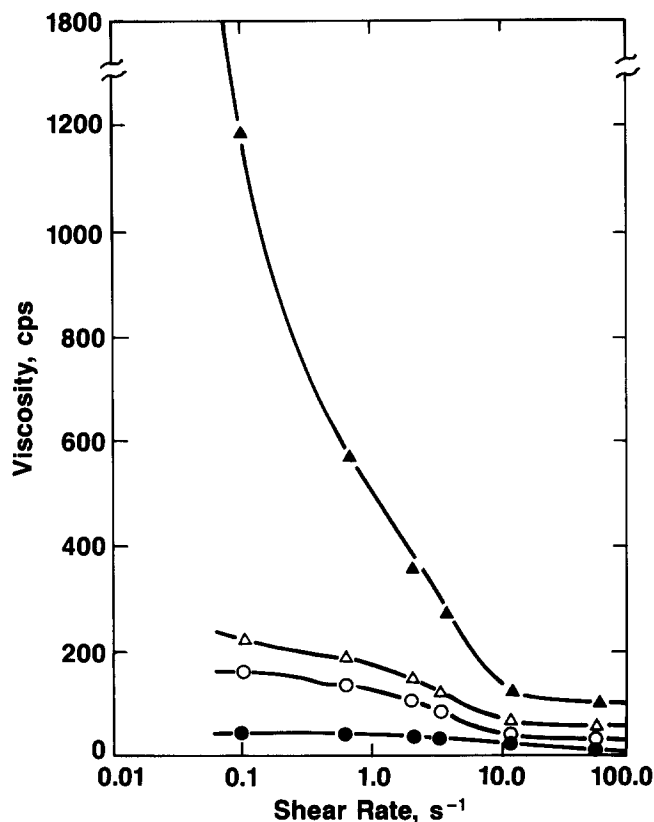


Figure 11 Comparison of the viscosity-shear rate profiles of various mixtures of the viscoelastic monomer fluid (42 ppm) with anionic hydrophobically associating copolymers (0.05 g dl⁻¹) containing increasing levels of anionic charge. The detailed composition of these copolymers is presented in Table 2. Curves: (\blacktriangle) 6.8 mol%; (Δ) 15.6 mol%; (\circ) 30.9 mol%; (\bullet) 38.9 mol%

interactions and intra- and interchain associations is unknown; but since the Laplace pressure is probably reduced in rod-like micelles²² (as compared to a spherical micelle), enhanced solubilization of the copolymer hydro-

phobes will occur. Enhanced 'bridging' and solution properties result.

These mixtures are composed of wholly cationic charge and therefore compatibility is ensured. However, it is important to examine whether anionic charge on the hydrophobic associating copolymer affects solution behaviour. Typical results are shown in Figures 10 and 11. Examination of the data clearly shows three important features of these mixtures. The first is the remarkable enhancement in viscosity as compared to the individual components of the mixture. It is readily apparent that the 'bridging phenomenon' is still very effective even at rather large anionic charge density. Secondly, these mixtures are very shear-thinning, except for marked time-dependent viscosity at low shear rates ($<0.1 \text{ s}^{-1}$). Thirdly, a modest change in the concentration of either component results in a large change in rheological behaviour. Very respectable rheology is observed even at significantly lower overall concentration. However, the improvement in properties is directly related to the hydrolysis level. These results confirm that anionic charged species reduce the structural integrity of the rod-like entities. This phenomenon parallels the fact that some ionic solubilizers interact with surfactant with opposite charge to produce insoluble products^{2,3}.

CONCLUSIONS

The main conclusion of this work is that the incorporation of hydrophobically associating groups containing also anionic or cationic moieties offers a unique pathway for the modification of the physical properties of a relatively large number of water-soluble polymeric materials and complex fluid systems. The hydrophobic groups are able to microphase-separate in such a way as to modify completely the rheology of aqueous fluids in significant ways. The improvement in viscosity with increasing ionic strength (i.e. 'anti-polyelectrolyte effect'), significant enhancement in rheology as compared to its non-hydrophobic precursors, and 'compatibilization' of the hydrophobe units (chemically attached to the chain backbone) into the hydrophobic region of rod-like micelles resulting in 'bridging' of a colloid-polymer system are a few examples of the interesting phenomena associated with these materials. Although our initial interest has been in the rheological aspects of these associating fluid systems, other avenues (bulk properties, structural modifications) are currently being investigated.

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