Copolymers of acrylamide/*N*-alkylacrylamide in aqueous solution: the effects of hydrolysis on hydrophobic interactions

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Two copolymers of acrylamide/*N*-4-ethylphenylacrylamide have been prepared by an aqueous micellar copolymerization technique with two different amounts of an anionic surfactant (sodium dodecyl sulphate). Such changes in the polymerization medium give copolymers with different microstructures. Samples of each copolymer were subsequently hydrolysed to 10, 20 and 40% completion. Hydrophobic interactions of all the samples in aqueous solution were then studied in the semi-dilute concentration range near to and above the chain overlap concentration, c^*, via rheological and fluorescence techniques. The samples were each studied as a function of concentration, salt concentration, surfactant concentration and temperature. In all cases, the rheological and the fluorescence data were consistent and directly related to the number of interchain liaisons in solution. The number of interchain liaisons increased with increase in the copolymer hydrophobicity and were hence related to the hydrolysis level and the blockiness of the copolymer.

(Keywords: hydrolysed polyacrylamides; hydrophobic interactions; associative polymers; thickeners; fluorescence)

INTRODUCTION

The modification and control of aqueous viscosity with polymeric molecules has, in recent years, become an area of great industrial importance[1,2]. One such area of interest concerns the possibilities for tertiary oil recovery of water-based systems with controllable rheological properties under a variety of physical conditions. Such viscosity control can be achieved using high-molecular-weight polymers or polyelectrolytes ($M_w \approx 10^7$). However, these materials are susceptible to shear degradation at elevated shear rates, leading to a loss of viscosity if the sample is returned to zero-shear conditions. Alternatively, to avoid shear degradation, similar viscosification can be obtained with lower-molecular-weight polymers ($M_w \approx 10^6$) containing small amounts of a hydrophobic monomer[3–13]. In aqueous solutions the hydrophobic groups associate, owing to the unfavourable solvent conditions, which causes the formation of physical linkages between the copolymer chains. These physical links will be broken at high shear rates but they may re-form on returning to low-shear conditions. As a result, the syntheses of copolymers containing a water-soluble polymer backbone and which have low amounts of a hydrophobic monomer dispersed along their length have been developed. The synthetic routes most often employed to obtain such copolymers are either micellar copolymerization[6–11,14,15] or the chemical modification of a water-soluble precursor polymer[3,12,13].

Copolymers based on acrylamide have been those most extensively investigated[4–11,14–17]. These copolymers are usually prepared in an aqueous micellar medium by free-radical copolymerization. In such copolymers the presence of only very small amounts of the hydrophobic comonomer (< 1 mol%) is sufficient to alter dramatically the solution rheological properties. In order to understand the solution properties, a knowledge of the copolymer composition and the distribution of the hydrophobe within the copolymer is very important. Obviously, the use of such low amounts of comonomer causes large problems in such determinations. However, accurate composition analysis has been shown to be possible when using a hydrophobic monomer that is u.v.-active[9,14,17]. Furthermore, it has been reported that the solution properties of these copolymers can be directly related to their microstructure[9,10]. Consequently, using a u.v.-active monomer, we have recently reported the effects of micellar copolymerization conditions on the subsequent copolymer microstructure as well as proposing a reaction mechanism[17]. It was found that the use of a micellar reaction medium leads to copolymers that have an essentially block-like structure, the hydrophobe being in what can be considered as hydrophobe-rich regions of the acrylamide backbone. The incorporation rate of the hydrophobic monomer into the copolymer chains, and hence the size of these hydrophobe-rich regions, was found to increase upon increasing the initial ratio of hydrophobic monomer to surfactant in the reaction medium. Increased initial incorporation rates were also shown to lead to greater polydispersity of the resultant copolymer samples in terms of their composition.

Recently, as a result of this expanding interest in hydrophobically associating copolymers, there have been an increasing number of reports into the effects of introducing charge onto the copolymer back-

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bone[5,13,15,18–20]. However, as yet, no systematic study of the effect of introducing charge on copolymers of differing hydrophobicities has been published. McCormick and coworkers have, in a series of publications[21], investigated a range of different charged associating polymers. Their polymers were in general, however, much more complex, often being polyampholytic in nature. The water-soluble polymer backbones were modified with a relatively high number of weakly hydrophobic groups, which leads to a higher number of intrachain liaisons and less of an interchain nature than seen for the copolymers referenced above.

In this paper we present the results of a study into the effects of the microstructure on the solution properties of copolymers of acrylamide/*N*-4-ethylphenylacrylamide (AM/eϕAM) in which the acrylamide backbone is partially hydrolysed. The properties of these solutions were studied as a function of copolymer concentration in the semi-dilute range. The chain overlap concentration c^* can be estimated to 0.15 wt% by assuming that $c^*[\eta]$ is of the order of unity ($[\eta]$ being the intrinsic viscosity of the polymer). The polymer concentrations investigated (from 0.25 to 2 wt%) are therefore near to and above c^*. Solution properties as a function of added salt concentration (sodium chloride), added surfactant concentration (sodium dodecyl sulphate (SDS)) and temperature were also investigated. In each case, measurements of the apparent solution viscosities were performed both as a function of shear rate $\dot{\gamma}$ and also as a function of shear time at a given constant shear rate. The rheological data obtained were correlated to fluorescence data for the systems to obtain further information on the nature of the interactions.

EXPERIMENTAL

Materials

Synthesis and characterization of the copolymers. The acrylamide/*N*-4-ethylphenylacrylamide (AM/eϕAM) copolymers were prepared by an aqueous micellar copolymerization technique, which has been well detailed elsewhere[14,17]. Therefore, only a brief summary will be given here. The hydrophobic monomer, at 1 mol% relative to the total feed of monomers, was solubilized in 300 cm^3 of an aqueous sodium dodecyl sulphate solution containing enough acrylamide monomer to give 9 g in total weight of monomers. The surfactant concentration was either 1.5 or 3% w/v. When the solution was completely homogeneous, the reaction was initiated, at 50°C, with potassium persulphate (0.3 w/w relative to the monomers). After 7 h the reaction was terminated by cooling to room temperature followed by the immediate precipitation of the copolymer product in an excess of methanol. The product was filtered and washed repeatedly in methanol before being dried at 50°C for >4 days. The copolymers were characterized by static light scattering and u.v. spectroscopy. The physical details of the products are given in *Table 1*; the details of a polyacrylamide prepared by the same technique but in the absence of ethylphenylacrylamide are also given.

Hydrolysis of the copolymers. Hydrolysis of polyacrylamide, with sodium hydroxide, to give carboxylate functionalities in the copolymer chain is a well known reaction[22–25]. The degree of hydrolysis can be controlled by varying the polymer concentration, the concentration of basic ions, the temperature or the duration of the reaction.

Using the known kinetic data for the hydrolysis of polyacrylamide, each of the two copolymers was reacted to obtain three levels of hydrolysis (i.e. 10, 20 and 40%). In this work the concentration of the copolymers must be kept low during reaction to prevent too much interaction and, hence, very high viscosities. Therefore, in order to obtain realistic reaction times, the degree of hydrolysis was primarily controlled by varying the temperature. All hydrolysis reactions were performed at a (co)polymer concentration of 0.7% by weight (i.e. 0.1 M acrylamide) and an alkali concentration of 0.25 mol l^{-1}. A level of 10% hydrolysis was achieved by performing the reaction for 1 h at 30°C; for 20% hydrolysis the reaction duration was 2 h at 30°C; and for 40% hydrolysis, 2.5 h at 50°C.

Immediately after the required reaction time, the medium was cooled and the product precipitated in methanol. After filtration, the copolymer was washed and filtered three or four times in an excess of methanol to remove all traces of the reactants. The resultant product was then dried for 4 days at 50°C before being analysed by elemental analysis. The degree of hydrolysis was estimated from the amounts of carboxylic acid and sodium carboxylate groups present, determined by potentiometry and sodium elemental analysis, respectively. The presence of carboxylic acid groups must also be taken into account since such groups have been shown to be present in the polymers after alkaline hydrolysis and recovery in methanol[26]. Data on the degrees of hydrolysis

Table 1 Synthetic details and physical properties of the (co)polymers

	Synthetic details			Analysis data	
(Co)polymer code	SDS[a] (%)	[eϕAM] in feed[b] (%)	Hydrophobe molecules per micelle[c]	[eϕAM] in copolymer[d] (%)	M_w[e] ($\times 10^{-6}$)
S1.5	1.5	1.0	5.8	0.98	2.9
S3	3	1.0	2.6	1.03	2.7
PAM	1	0	0	0	2.3

[a] Percentage in feed, weight/volume
[b] Mole percentage of hydrophobic monomer based on total moles of monomer
[c] Calculated using a c.m.c. = 9.2×10^{-3} mol l^{-1} and an aggregation number of 60 at 50°C (ref. 27)
[d] Determined by u.v. analysis (see refs 14 and 17)
[e] Determined from static light scattering measurements in formamide (see refs 10 and 17)

Table 2 (Co)polymer hydrolysis data

(Co)polymer code	Hydrolysed code	Analysis data (mol%)				Hydrolysis (%)
		[eϕAM]	AM	COOH	COONa	
S1.5	S1.5(1)	1.0	88.6	1.9	8.5	10.5
	S1.5(2)	1.0	80.7	2.9	15.4	18.5
	S1.5(4)	1.0	57	5.4	36.6	42.5
S3	S3(1)	1.0	88.4	1.4	9.2	10.8
	S3(2)	1.0	80.2	2.4	16.4	18.9
	S3(4)	1.0	55.2	4.4	39.4	44.2
PAM	HPAM	0	84.0	8.4	7.6	16.0

obtained are given in *Table 2*. In all cases, the calculations were performed after taking into account the amount of water present in the sample, since such samples are very hygroscopic (4–7 wt% H_2O). Data for the hydrolysis of the polyacrylamide sample are also given in *Table 2*.

Other materials. Sodium dodecyl sulphate (SDS) (Touzart and Matignon, >99.5% pure) was used as received without further purification. The critical micelle concentration (c.m.c.) determined at a temperature of 25°C by conductivity was 8×10^{-3} mol l^{-1} and by fluorescence 8.2×10^{-3} mol l^{-1}. Both values agree well with literature data[27], confirming the purity.

Sodium chloride (Prolabo, >99.5% pure) was also used as received with no further purification.

Pyrene was zone refined and was kindly given by Dr A. Malliaris, NRC Democritos, Athens, Greece.

All water used here was deionized and distilled from an all-glass apparatus.

Methods

Rheological measurements. Viscosity–time and viscosity–shear rate measurements were performed using a Contraves Low Shear 30 instrument interfaced to a personal computer and driven by a software package supplied by the manufacturers. Dependent on the apparent viscosity η, two measuring systems were employed, either the 2T–2T ($\eta < 10$ mPa s) or the 1–1 ($\eta > 10$ mPa s).

Copolymer solutions were prepared by the dissolution of the copolymers, at appropriate concentrations, in stock aqueous solutions either in the presence or in the absence of SDS and/or sodium chloride. All the samples examined by rheology were prepared using water saturated with pyrene for subsequent analysis by fluorescence techniques. Agitation by magnetic stirring was applied during the first 24 h of dissolution. Before measurement, the samples were left for a further 24 h with no agitation.

Fluorescence. Steady-state fluorescence measurements of the emission spectra of these samples were performed using a Hitachi F-4010 spectrophotometer. The ratio I_3/I_1 of the intensities of the third and first vibronic peaks for the emission spectrum of pyrene provides an estimate of the local environment, i.e. hydrophobic or hydrophilic, sensed by the fluorescent probe[28].

Samples were thermostatted at the appropriate temperature and were excited at a wavelength of 335 nm with a bandwidth of 1.5 nm.

Table 3 Solubility of *N*-4-ethylphenylpropionamide as a function of salt content in brine solutions

Sodium chloride molarity	Dissolved concentration (mol l^{-1}) × 10^4 (±0.1)
0 M	17.2
1.0 M	9.7
2.0 M	4.9

Solubility of N*-4-ethylphenylpropionamide in aqueous salt solutions.* The solubility of the saturated homologue of the hydrophobic monomer employed here was measured as a function of salt content using a u.v. technique detailed elsewhere[10,14,17]. The u.v. spectra were examined in the range 200–300 nm, the hydrophobe giving an absorbance maximum between 245 and 247 nm. A calibration curve of the absorbance as a function of concentration in water/2% ethanol solution was performed initially following the technique of Valint *et al.*[14]. Subsequently, saturated solutions of the hydrophobic homologue were prepared as a function of salt content by agitation of an excess of the homologue in appropriate aqueous salt solutions for 48 h. After filtration, the absorbance maxima were recorded and the dissolved amounts calculated from the calibration curve. Each measure was performed twice to check reproducibility, and the absence of any effects of the salt on the absorption coefficient was verified. Data for the dissolved amounts of hydrophobe as a function of salt concentration are given in *Table 3*.

RESULTS AND DISCUSSION

Effects of copolymer structure and hydrolysis degree

Figures 1 and *2* show the effect of copolymer concentration on the apparent solution viscosities, measured at a shear rate $\dot{\gamma} = 0.5$ s^{-1} and at 25°C, for the two copolymer samples investigated at all the hydrolysis levels. It should be noted that the data given in *Figure 1* cover a concentration range of up to 1% (w/w), while those of *Figure 2* are up to 2% (w/w). Examination of samples of copolymer S1.5 was impossible at higher concentrations owing to the very high apparent viscosities. Corresponding data of I_3/I_1 measured by fluorescence are given in *Table 4*. As shown in *Table 1*, the copolymer samples discussed here will be designated either as S1.5 or S3 depending upon the percentage of SDS used in the synthesis. The degree of hydrolysis will

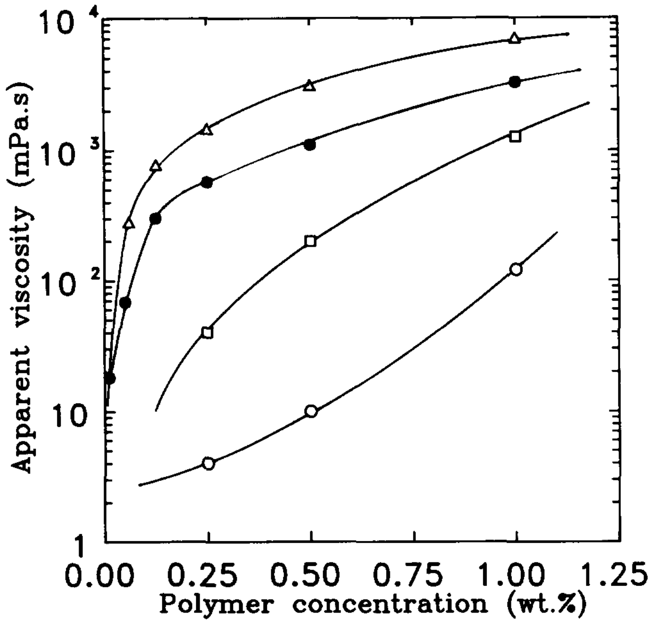

Figure 1 Variation of the apparent viscosity as a function of copolymer concentration for copolymer sample S1.5 at four levels of hydrolysis: 0% (○); 10.5% (□); 18.5% (△); 42.5% (●). ($\dot{\gamma} = 0.5\ \mathrm{s}^{-1}$; $T = 25$°C)

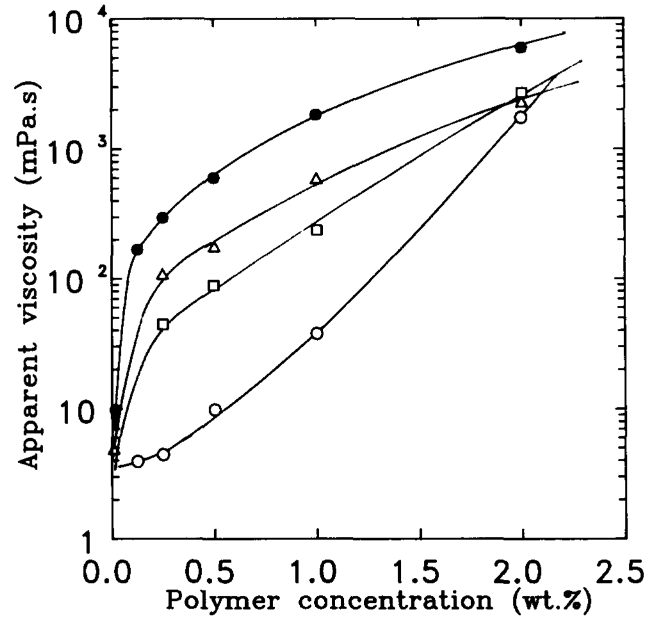

Figure 2 Variation of the apparent viscosity as a function of copolymer concentration for copolymer sample S3 at four levels of hydrolysis: 0% (○); 10.8% (□); 18.9% (△); 44.2% (●). ($\dot{\gamma} = 0.5\ \mathrm{s}^{-1}$; $T = 25$°C)

be indicated in parentheses, after the copolymer name, by using the numerals 0, 1, 2 and 4 (*Table 2*).

Before discussion of the effects of hydrolysis, it is necessary to compare the two unhydrolysed copolymers. Clearly, at concentrations greater than 0.25% (w/w), copolymer S1.5(0) shows a greater increase in the apparent solution viscosity as a function of concentration. While it is true that its molecular weight is slightly greater (*Table 1*), the differences in apparent viscosities, especially at 1% (w/w) concentration, are too large to be explained simply by this. The data suggest, in fact, a greater degree of interaction between its hydrophobic groups than seen for S3(0), leading to more interchain crosslinking. Further evidence for the increased level of hydrophobic interactions in solutions of copolymer S1.5(0) is seen in the fluorescence data (*Table 4*), where the higher the value of I_3/I_1 the greater the hydrophobic character of the system. Once again, the values of copolymer S1.5(0) are superior to those of copolymer S3(0) at all concentrations. The reason for this increased hydrophobic character of one copolymer when compared to the other, despite an equivalence in the amount of incorporated hydrophobe, is a result of the differing quantities of SDS in the reaction medium (*Table 1*). As has been shown previously[14,17,29], copolymerization in an aqueous micellar medium where the hydrophobe is solubilized within micelles causes an increased initial rate of incorporation of the hydrophobic monomer into the copolymer samples, the rate augmentation increasing as the ratio of hydrophobe to SDS in the initial reaction mixture increases. A result of this rate increase is to give hydrophobic-rich regions of the copolymer chains, which contain greater mumbers of hydrophobes than the average found in any one micelle at the beginning of the reaction (*Table 1*). It was also noticed that the number of hydrophobes incorporated initially into each hydrophobic-rich region of the copolymers increases disproportionately with increasing numbers of hydrophobes per micelle. Obviously rearrangement of the reaction components during polymerization means a falling number of hydrophobes per micelle, which leads to a decreasing rate of incorporation with increasing overall monomer conversion. Thus the copolymer prepared in a reaction medium containing lower levels of SDS (copolymer S1.5(0)) will have, on average, a lower number of larger hydrophobically rich blocks per acrylamide chain. However, it should also be noted that its compositional polydispersity can be expected to be greater as well[17].

It is expected that hydrophobic monomer units in a water-soluble copolymer will have a higher hydro-

Table 4 I_3/I_1 values as a function of (co)polymer concentration for hydrolysis degrees[a] of 0, 10%, 20% and 40% for copolymers and 0 and 16% for homopolymer

(Co)polymer concentration (wt%)	Copolymer S1.5				Copolymer S3				Homopolymer	
	0	10%	20%	40%	0	10%	20%	40%	0	16%
0.125	0.61	0.56	0.54			0.55	0.58			
0.25	0.64	0.58	0.58	0.56	0.58	0.57	0.58	0.56	0.54	
0.50	0.71	0.63	0.62	0.58	0.62	0.60	0.57	0.59	0.55	0.56
1.00	0.78	0.67	0.63	0.60	0.65	0.66	0.60	0.58	0.58	0.60
2.00					0.71	0.69	0.63	0.60	0.62	0.63

[a] Approximate values, for real data see *Table 2*

phobicity when grouped together than when dispersed as discrete units. This has been demonstrated previously for copolymer samples such as those used here[9,10]. A copolymer in which the hydrophobe was distributed as discrete units had a similar viscosifying capability as polyacrylamide of equivalent molecular mass whereas a 'block-like' copolymer gave solutions with greatly enhanced viscosities. Thus, in the copolymer with generally fewer but larger regions of hydrophobe, the hydrophobicity can be considered to be greater, and hence there will be higher number of the hydrophobic units involved in hydrophobic interactions leading to higher apparent viscosities at equivalent concentrations and hydrophobe levels.

Partial hydrolysis of the acrylamide units in the copolymer samples can be considered to have a number of effects on the solution properties, including an increased solubility of the copolymer, as evidenced by increased values of the intrinsic viscosity and the exponent of the Mark–Houwink relation for hydrolysed polyacrylamides in aqueous salt solutions[30]. The polymer chains will also undergo an expansion in solution, the magnitude of which depends on the concentration (as a cause of inter- and intrachain charge interactions). There may also be a hindrance of any hydrophobic interaction by repulsions between neighbouring charged groups on the copolymer backbones.

In *Figures 1* and *2*, it is clear that, for copolymer S1.5 or copolymer S3, at all concentrations examined and at the three levels of hydrolysis, the presence of charge leads to a higher viscosity than seen for the non-charged copolymer. It should also be noted that the curve shape is different for the charged copolymers compared to the uncharged samples. The former increase rapidly at low concentrations but tend towards a plateau at higher concentrations, whereas the latter have a more 'exponential-like' response to increasing concentration. The tendency towards a plateau in the charged-polymer solutions is typical of polyelectrolyte solutions, where initial viscosity increases are attributed to chain expansion due to charge–charge repulsions within the chains and the levelling off of the viscosity at higher concentrations is due to autoscreening of the charges. Thus, polymers with a higher charge density can be expected to reach this plateau at a lower concentration than those with less charge. This is confirmed in both *Figures 1* and *2*, where increasing charge clearly leads to an earlier attainment of a plateau value.

Examination of the fluorescence data in *Table 4* reveals that increasing levels of hydrolysis, at any given copolymer concentration for either of the two copolymers, leads in general to a decrease in the number of hydrophobic domains within the solution. However, increasing charge was also seen to cause an increase in copolymer coil dimensions and hence viscosity. Therefore, an increase in the degree of hydrolysis is seen to have two opposing effects on the properties of the copolymers as aqueous viscosifiers.

The presence of these two opposing effects is evidenced upon closer examination of the viscosity and fluorescence data for both copolymers. From *Table 4*, it is clear that for copolymer S1.5(4) at $\approx$40% hydrolysis there are no significant differences in its I_3/I_1 values with those of either hydrolysed or non-hydrolysed homopolyacrylamide. A similar result was observed for copolymer S3, although this time at both $\approx$20% and $\approx$40% hydrolysis. This suggests that, for these samples, the presence of charge on the copolymer backbone leads to a complete loss of hydrophobic interactions. Furthermore, in *Figure 1* it can be seen that the solution viscosity is higher, at all concentrations, for copolymer S1.5 at $\approx$20% hydrolysis than for that at 40%. This is contrary to what we might expect based solely on the polyelectrolyte character, where a higher charge should lead to a higher apparent viscosity in solution. However, the presence of hydrophobic interactions at $\approx$20% hydrolysis combined with the expanded chain dimensions gives two complementary viscosifying effects and, hence, a much increased viscosity.

Examination of the apparent solution viscosities for both copolymers at $\approx$40% hydrolysis (S1.5(4) and S3(4)) and at equivalent concentrations reveals a close similarity in the values, the values of copolymer S3(4) being slightly lower as a result of its slightly smaller molecular-weight average (*Table 1*). This is further evidence for the absence of any hydrophobic interaction in either sample, whereas at $\approx$20% hydrolysis the lack of hydrophobic interactions leads to the apparent viscosities of copolymer S3(2) being much lower than those of S1.5(2), in which hydrophobic interactions are present. At $\approx$10% hydrolysis, where both copolymers exhibit hydrophobic interactions, despite being charged, the apparent viscosities for copolymer S1.5(1) are always greater, at equivalent concentrations, than those of S3(1) owing to the higher hydrophobicity discussed above.

It is clear, therefore, that larger hydrophobic regions in the copolymer samples, at a constant level of hydrophobe, lead to a higher hydrophobicity and hence a higher viscosifying capability in aqueous solution. This higher hydrophobicity also allows the incorporation of a higher degree of charge onto the copolymer chains before all hydrophobic interactions are suppressed. The loss of hydrophobic interactions and the greater chain expansion with increasing charge mean that, for any given copolymer sample, there will be a certain level of charge that gives the maximum combined viscosification due to both effects[20]. The suppression of hydrophobic interactions due to the presence of charge may be attributed either to an increased solubility of the copolymer chains or to charge–charge repulsions between the chains or to a combination of the two. While it would seem probable that a combination of the two effects may be responsible for this interaction loss, no data have been determined here, and so this remains a hypothesis.

Effects of additives on the solution rheological properties

Sodium chloride salt. The effects on the solution reduced viscosities of the addition of various amounts of sodium chloride as a function of concentration for copolymer S1.5(1) at $\approx$10% hydrolysis are shown in *Figure 3*. Similar data were obtained for both copolymer samples at all degrees of hydrolysis, although for samples at higher hydrolysis levels the high apparent viscosities made solution preparation and viscosity determination difficult. In *Figures 4* and *5* the reduced viscosity and I_3/I_1 fluorescence data, respectively, are given as a function of salt molarity at 1% (w/w) copolymer concentration for both copolymers at 0% and $\approx$10% hydrolysis. For reference, viscosity and fluorescence data of a polyacrylamide both hydrolysed and non-hydrolysed are also given.

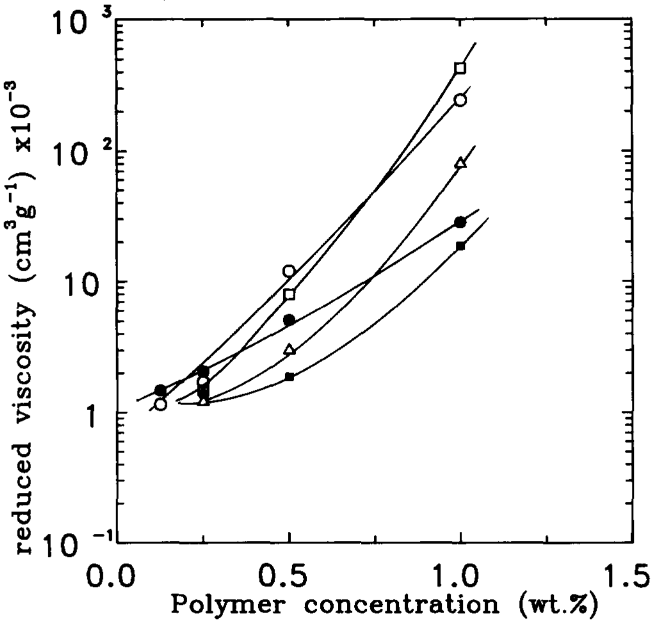

Figure 3 Variation of the reduced viscosity as a function of copolymer concentration for sample S1.5(1) in aqueous sodium chloride solutions: 0.1 M (■); 0.6 M (●); 1.0 M (△); 1.6 M (□); 2.0 M (○). ($\dot{\gamma} = 0.5\,s^{-1}$; $T = 25°C$)

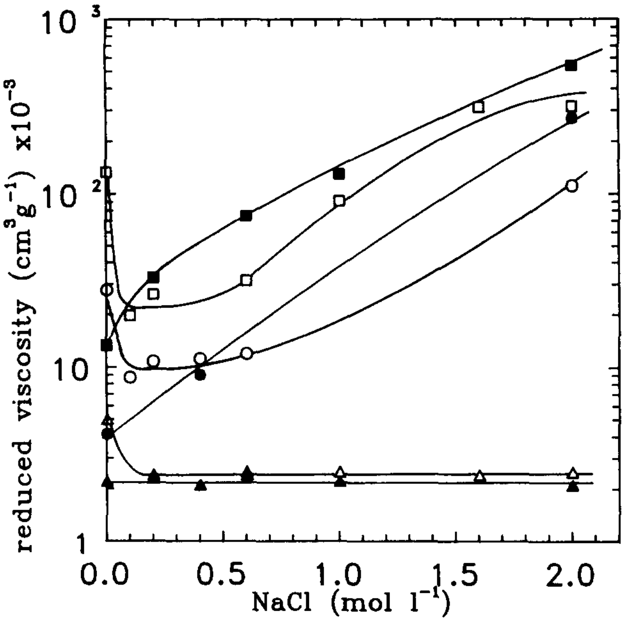

Figure 4 Effects of the presence of sodium chloride ($mol\,l^{-1}$) on the reduced viscosities of (co)polymer solutions, at a fixed (co)polymer concentration of 1% (w/w). Filled symbols represent non-hydrolysed samples, open symbols represent their hydrolysed analogues: S3(0) (●); S3(1) (○); S1.5(0) (■); S1.5(1) (□); PAM (▲); HPAM (△); ($\dot{\gamma} = 0.5\,s^{-1}$, $T = 25°C$)

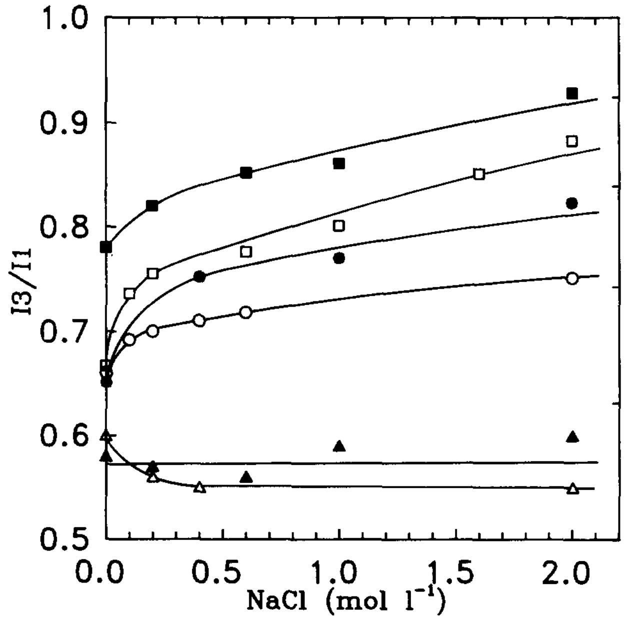

Figure 5 Variation of I_3/I_1 for a pyrene fluorescent probe in aqueous (co)polymer solutions as a function of the added salt molarity. Filled symbols represent non-hydrolysed samples, open symbols represent their hydrolysed analogues: S3(0) (●); S3(1) (○); S1.5(0) (■); S1.5(1) (□); PAM (▲); HPAM (△). (Polymer concentration = 1% (w/w); $T = 25°C$)

At all molarities of salt examined (0.1 M < [NaCl] < 2 M) the curve shapes as a function of copolymer concentration (*Figure 3*) resembled that of the non-hydrolysed copolymer, i.e. 'exponential-like' increase in viscosity in the semi-dilute concentration regime. This suggests that, even at 0.1 M NaCl, the charge on the chain is completely screened and the copolymers act as simple uncharged associating copolymers. Clearly, increasing the amount of salt leads to an increase of the viscosity at each concentration, the increase between each salt concentration becoming larger at higher copolymer concentrations. The increasing viscosity as a function of salt content, at a fixed copolymer concentration (*Figure 4*), is apparent for both the charged and uncharged copolymers. For the charged copolymers there is an initial sharp loss in viscosity due to the effects of charge screening by the salt, and hence contraction of the expanded polymer chains. After this, the copolymers, whether charged or uncharged, have similar behaviour, although the viscosities of the non-charged samples increase more rapidly. This increase of solution viscosity has been observed previously by a number of authors[7,18–20,31] for both charged and non-charged samples. For the former samples, this effect was generally assumed to arise from a screening of the repulsive electrostatic forces, thus promoting a greater number of hydrophobic interactions. For the latter, this can be attributed to a decreasing solubility for the hydrophobic regions. As a consequence, we have measured the solubility of the saturated homologue of our hydrophobic monomer, *N*-4-ethylphenylpropionamide, as a function of the salt concentration. The results, presented in *Table 3*, clearly show that the solubility decreases with increasing salt concentration, confirming this earlier hypothesis. The 'salting-out' effect, i.e. the lowering of the solubility of non-ionic hydrocarbon compounds in water by addition of inorganic salts, is a well known phenomenon extensively studied for many years[32]. Further proof that the salt effect acts primarily on the hydrophobe and not on the acrylamide backbone, after complete charge screening, is seen in the viscosity data for a polyacrylamide and a hydrolysed polyacrylamide as a function of [NaCl] (*Figure 4*). After complete charge screening ([NaCl] > 0.1 M), the viscosities of the two homopolymer samples are practically flat as a function of salt content, the values of the hydrolysed polymer being slightly higher than those of the non-hydrolysed.

Once again, the fluorescence data (*Figure 5*) support the conclusions drawn from the viscosity results. As the salt level is increased, the values of I_3/I_1 increase as well, indicating an increased number of hydrophobic domains in the solution. For both copolymers the non-charged samples show higher values of I_3/I_1 than their charged homologues at all salt concentrations, which is again in agreement with the higher viscosities seen for the non-charged copolymers (*Figure 4*).

Surfactant (SDS). The effects of adding surfactant to semi-dilute solutions of uncharged hydrophobically associating copolymers at surfactant concentrations equal to or less than its c.m.c. have previously been reported by a number of authors[12,33–39]. In *Figure 6*, the apparent viscosities obtained as a function of surfactant (SDS) concentration, at a fixed shear rate ($\dot{\gamma} = 0.5\,s^{-1}$) and at 0.5% (w/w) copolymer concentration, for the two uncharged parent copolymers are given. In both cases a maximum in the apparent viscosity was observed. Reasons for this maximum have been adequately presented previously[12,39] and will not, therefore, be covered in detail here. In brief, the addition of surfactant is thought to lead to the formation of mixed micelles with the copolymer hydrophobe regions, which initially facilitate interchain linkages between the chains and hence increase the viscosity. As the surfactant c.m.c. is approached, enough surfactant is present to solubilize each region of hydrophobe within a single micelle and so interchain liaisons are impeded and the viscosity falls.

For the uncharged samples the viscosity maxima were found at approximately the same concentration of SDS (i.e. between 0.1% and 0.15%) just below the surfactant c.m.c. (0.23% w/w). Once again, however, the magnitude of the observed apparent viscosities for the copolymer with the higher hydrophobicity were much greater. This suggests that even in the presence of SDS, which is believed to encourage interchain liaisons by forming mixed micelles with the hydrophobic regions[39], not all of the available hydrophobe is involved in interchain links. Thus, here again the larger hydrophobic regions are favoured in interchain linking, leading to a much higher proportion of the total hydrophobe being involved in such liaisons and hence a greater viscosity maximum. In the less hydrophobic copolymer sample, a high proportion of the hydrophobe is probably found either as single units or as very small 'blocks'[9,10,17] and can therefore be solubilized without forming either intra- or interchain liaisons. The addition of SDS will have very little or no effect on such hydrophobe regions but rather will associate with the less 'soluble' larger regions, of which there are considerably fewer in copolymer sample S3(0).

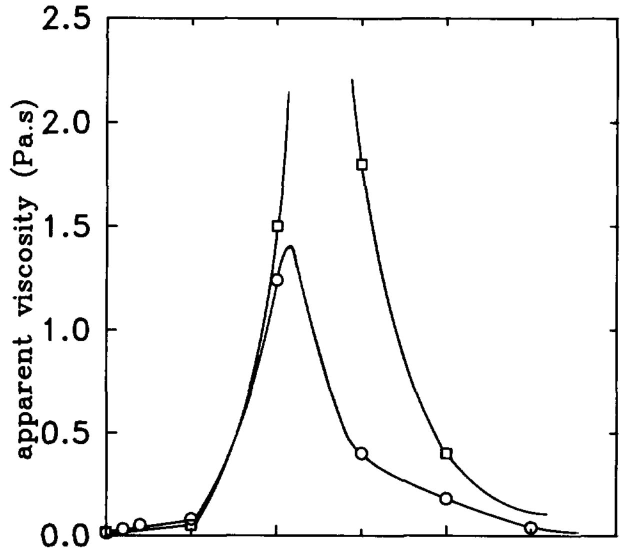

Figure 6 Apparent viscosities as a function of SDS concentration for the two non-hydrolysed copolymer samples: S1.5(0) (□); S3(0) (○). (Copolymer concentration = 0.5% (w/w); $\dot{\gamma} = 0.5\,s^{-1}$; $T = 25°C$)

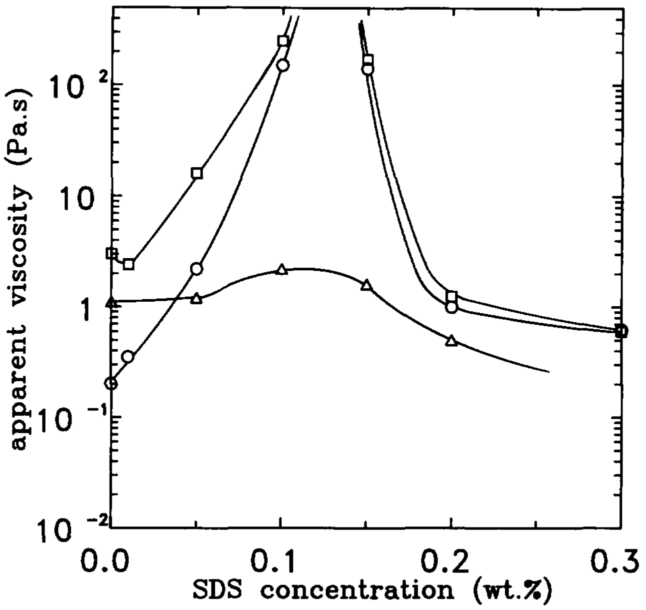

Figure 7 Apparent viscosities (log scale) as a function of SDS concentration for copolymer S1.5 at three levels of hydrolysis: 10.5% (○); 18.5% (□); 42.5% (△). (Copolymer concentration = 0.5% (w/w); $\dot{\gamma} = 0.1\,s^{-1}$; $T = 25°C$)

A number of interesting effects may be considered as possible when adding the anionic surfactant to the negatively charged hydrolysed copolymer samples due to charge repulsions between the copolymers and the surfactant. In *Figure 7* results for the apparent viscosities, at a fixed shear rate ($\dot{\gamma} = 0.1\,s^{-1}$), as a function of surfactant concentration for copolymer S1.5 at the three hydrolysis levels are given. Similar data were also obtained for copolymer S3, although, as usual, at less significant viscosities. The peak maxima at all levels of hydrolysis were once again centred between 0.1% and 0.15% (w/w) of surfactant added. Interestingly, at all three hydrolysis levels, a maximum as a function of surfactant concentration was observed, even for the sample at 40% hydrolysis, which had ostensibly no hydrophobic interactions in pure aqueous solution. While it is true that the augmentation of apparent viscosity is considerably less important in this case than at the other two hydrolysis levels, the fact that we do have an increase suggests that, as previously hypothesized, surfactant positively encourages interchain linkages by mixed micelle formation. Clearly, as was observed in a previous study by us[39], the surfactant associates directly with the hydrophobe regions in a non-cooperative binding process that leads to the formation of mixed micelles capable of causing interchain links. This appears to remain possible even when an unfavourable charge is introduced onto the chain backbone, proving the specificity of the surfactant for the hydrophobe regions in such copolymer samples. This apparent lack of hindrance has also been reported for the interaction between a negatively charged hydrophobically modified poly(acrylic acid) and SDS[38].

Addition of salt to solutions of hydrolysed copolymer and surfactant was observed to have the following two effects: (i) the peak maximum was moved to the left (i.e. lower surfactant concentrations), and (ii) the magnitude of the maximum sharply diminished. Typically representative curves are given in *Figure 8*. The first effect is related to the c.m.c. of SDS, higher salt levels decreasing the c.m.c.[27] and hence the position of the maximum, which is always at concentrations of surfactant just below the c.m.c. The second effect is caused simply by charge screening, which gives copolymers with much reduced coil dimensions and hence lower apparent viscosities.

For all samples in the region of the peak maxima, whether charged or uncharged and whether in the presence or absence of salt, complex rheological behaviour as a function of shear time, at a constant shear rate, was seen. In *Figure 9*, a representative curve showing rheopectic/thixotropic effects is shown. These effects, caused by a changing balance of intra- and interchain liaisons, have been extensively discussed previously and, therefore, will not be considered here in more detail[39]. It should be noted, however, that the presence of such time-dependent shear effects means that all the viscosity values presented previously (*Figures 6–8*) are those values obtained at the plateau (*Figure 9*) when the viscosity reaches an equilibrium value.

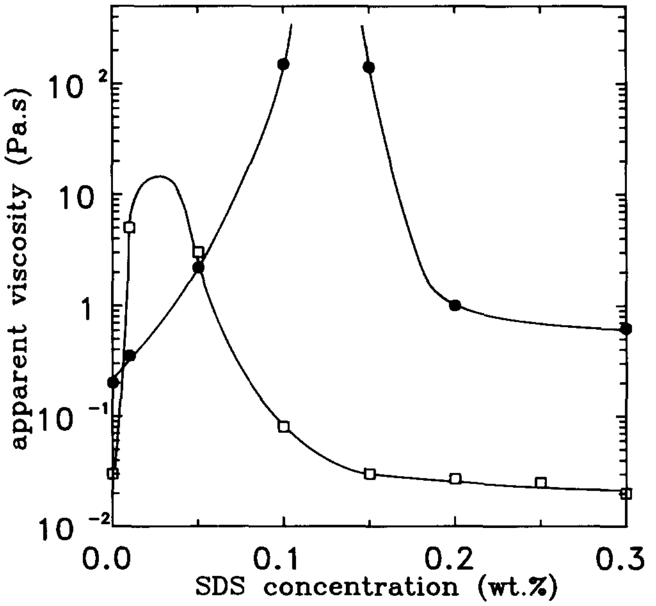

Figure 8 Apparent viscosities (log scale) as a function of SDS concentration for copolymer S1.5(1) at two molarities of sodium chloride: 0 M (●); 0.6 M (□). (Copolymer concentration = 0.5% (w/w); $\dot{\gamma} = 0.5\,s^{-1}$)

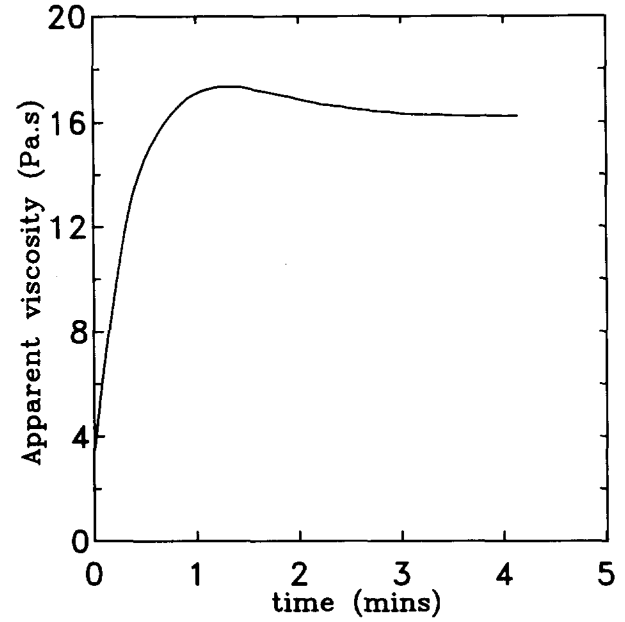

Figure 9 Apparent viscosity as a function of shear time at a constant shear rate ($\dot{\gamma} = 0.5\,s^{-1}$): copolymer sample S1.5(2); concentration = 0.5% (w/w); SDS concentration = 0.05% (w/w)

Effects of temperature

Temperature effects on the rheology of the copolymer solutions were investigated by measuring the apparent viscosity as a function of shear rate at four different temperatures. In all cases, the apparent viscosity, at any given shear rate, was seen to decrease with increasing temperature. This result is not surprising, however, since the viscosities of either water or brine solutions are known to be very temperature-sensitive. Therefore, in order to examine only the changing behaviour of the copolymers with temperature, it is necessary to consider the reduced solution viscosities, η_{red}. In this part of the discussion, only data for the samples of copolymer S1.5 will be considered, since the data for copolymer S3 were, in general, directly comparable but the viscosities were lower and the changes less marked.

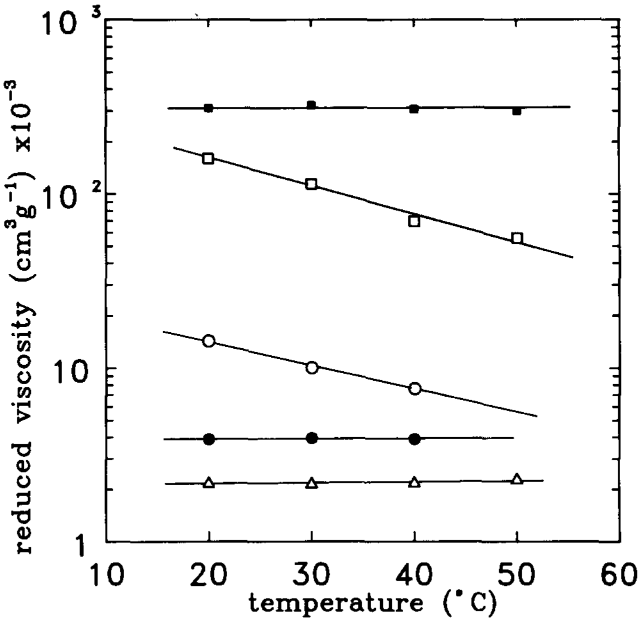

Figure 10 Effect of temperature on the reduced viscosities (log scale) of a polyacrylamide and a copolymer (sample S1.5) at various levels of hydrolysis: PAM (△); HPAM (●); S1.5(0) (○); S1.5(1) (□); S1.5(4) (■). (Copolymer concentration = 1% (w/w); $\dot{\gamma} = 0.5\,s^{-1}$)

In *Figure 10*, the reduced viscosities, at a copolymer concentration of 1% (w/w), as a function of temperature are shown for copolymer S1.5 at three degrees of

Table 5 I_3/I_1 values as a function of temperature for various (co)polymer samples[a]

Temperature (°C)	S1.5(0)	S1.5(1)	S1.5(4)	PAM	HPAM
20	0.78	0.67	0.60	0.58	0.60
30	0.75	0.65	0.59	0.59	0.57
40	0.74	0.64	0.59	0.57	0.59
50	0.71	0.61	0.57	0.56	0.58

[a] Copolymer concentration = 1% (w/w)

hydrolysis. The data for a hydrolysed and a non-hydrolysed polyacrylamide are also given, for reference. Clearly, at this concentration, those copolymers which exhibit a certain degree of interchain hydrophobic associations (i.e. S1.5(0) and S1.5(1)) show a substantial loss of their reduced solution viscosities on increasing the temperature. In contrast, the two homopolymer samples and the copolymer at ≈40% hydrolysis (S1.5(4)) have essentially constant values of the viscosity with temperature. This suggests that an increase in temperature causes a rupture of the interchain liaisons between the hydrophobic groups while having a negligible effect on the individual chain dimensions. Fluorescence data for these samples as a function of temperature (*Table 5*) confirm the decrease of hydrophobic domains on increasing the temperature.

Data of the reduced viscosities as a function of temperature for samples S1.5(1) and S1.5(0) at various concentrations are given in *Figures 11* and *12*, respectively. For both samples, at concentrations of between 0.25% (w/w) and 1% (w/w), the temperature is seen to have a lessening effect on the reduced viscosities as the concentration is decreased. This may also be related to the number of interchain liaisons in solution. As was evidenced earlier (cf. *Figure 1* and *Table 4*), the number of interchain liaisons begins to contribute significantly to the solution viscosity at between 0.25% and 0.5% (w/w) copolymer concentration. The apparent viscosity for the non-hydrolysed copolymer (S1.5(0)) at 0.25% (w/w) concentration was, allowing for the differences in molecular weight, approximately equal to that of the homopolyacrylamide. Thus, while at 0.5% (w/w) a decrease in the reduced viscosity with increasing temperature is still observed, the data at 0.25% (w/w) were effectively invariant with temperature, suggesting an insignificant amount of interchain liaisons at all temperatures. Once again this result is supported with fluorescence data given in *Table 6*. It is interesting to note that, at an even lower concentration of 0.125% (w/w) for sample S1.5(0), the reduced viscosity was observed to rise with increasing temperature. This result agrees with the published data of McCormick *et al.*[7] for a comparable hydrophobically modified polyacrylamide at a solution concentration of 0.19% (w/w). The authors attributed this rise in viscosity to an increase in hydrophobic associations, based on thermodynamic considerations. They argued that the hydrophobic hydration is exothermic while hydrophobe–hydrophobe interaction is endothermic and hence favoured at higher temperatures. This is, however, contrary to the observed loss of hydrophobic liaisons at higher concentrations, which is supported by fluorescence data. Unfortunately, such fluorescence data are unavailable at these lower concentrations because the values of I_3/I_1 are not significantly different from that of the pure water case.

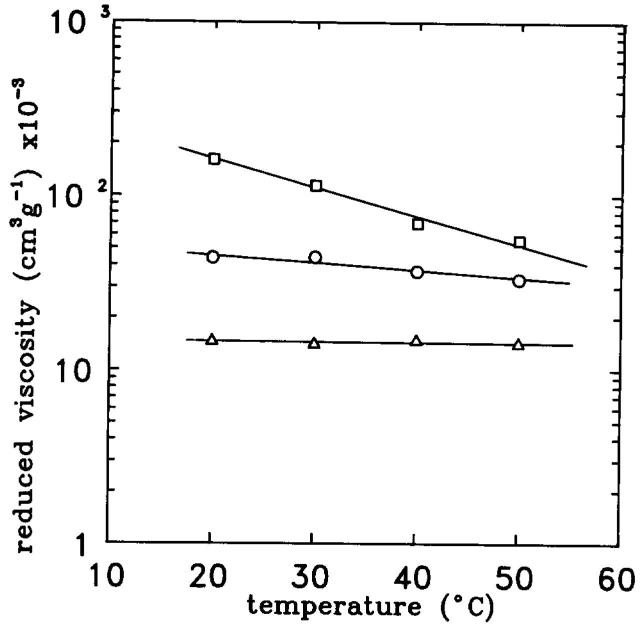

Figure 11 Effect of temperature on the reduced viscosities (log scale) of the hydrolysed copolymer sample S1.5(1) at three different concentrations (w/w): 1% (□); 0.5% (○); 0.25% (△). ($\dot{\gamma} = 0.5\,s^{-1}$)

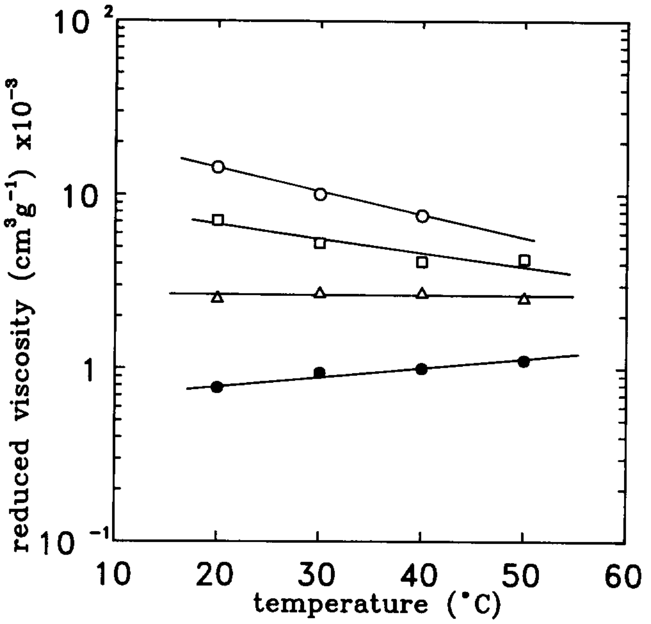

Figure 12 Effect of temperature on the reduced viscosities (log scale) of the non-hydrolysed copolymer sample S1.5(0) at four different concentrations (w/w): 1% (○); 0.5% (□); 0.25% (△); 0.125% (●). ($\dot{\gamma} = 0.5\,s^{-1}$)

Table 6 I_3/I_1 values for two copolymer samples as a function of temperature and concentration

	Copolymer concentration (wt%)					
	S1.5(0)			S1.5(1)		
Temperature (°C)	0.25	0.5	1.0	0.25	0.5	1.0
20	0.64	0.71	0.78	0.58	0.63	0.67
30	0.62	0.67	0.75	0.57	0.61	0.65
40	0.63	0.66	0.74	0.58	0.60	0.64
50	0.61	0.64	0.71	0.56	0.60	0.61

It has also been shown theoretically that, for a number of different associating copolymer systems, at concentrations of around or just above the critical overlap concentration, c^*, the number of interchain liaisons is insignificant relative to those of an intrachain nature[40–43]. While the values of c^* are not presently known for the copolymers investigated here or for those investigated by McCormick *et al.*[7], a value of between 0.1% and 0.2% may not be unreasonable based upon known data for a polyacrylamide of equivalent molecular weight[44]. Therefore, if the hydrophobic associations were of an essentially intrachain nature, the copolymer coil dimensions would be expected to diminish with any increase in the number of interactions. This would agree with the smaller intrinsic viscosities found for associating copolymers, compared with equivalent homopolymers, as a result of intrachain association[5,10]. However, both here and previously, at low copolymer concentrations, the reduced viscosity was seen to rise with increasing temperature. It seems more probable that this viscosity increase is in fact due to a decrease of the number of intrachain liaisons, which allows an expansion of the individual copolymer chains. At higher concentrations these changes in coil dimensions are masked by the more significant losses of interchain liaisons between the copolymers.

The effect of temperature on the reduced solution viscosities when salt is added to a hydrolysed copolymer sample (S1.5(1)) is shown in *Figure 13*. At each concentration of salt the viscosity response to increasing temperature was identical to that discussed above. The viscosity as a function of salt content, at each temperature, was also seen to behave in a similar manner to the data presented in a previous part of the discussion (*Figure 4*).

Data for the apparent viscosity as a function of shear rate, at the four temperatures examined, are given in *Figure 14* for a sample that, based on concentration data (*Figure 1* and *Table 4*), shows interchain liaisons at 20°C. Corresponding data for a homopolyacrylamide sample with no such hydrophobic liaisons at 20°C are given in *Figure 15*.

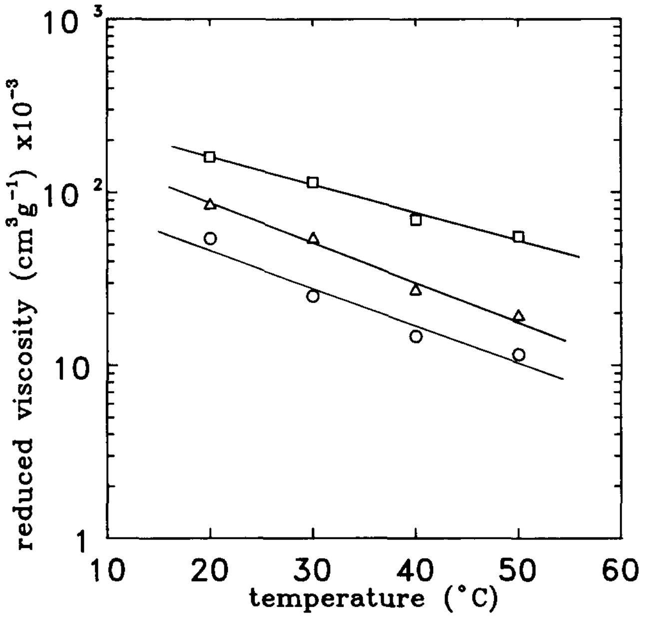

Figure 13 Effect of temperature on the reduced viscosities of copolymer sample S1.5(1) at three different salt molarities: 0 M (□); 0.4 M (○); 0.6 M (△). (Copolymer concentration = 1% (w/w); $\dot{\gamma} = 0.5\,s^{-1}$)

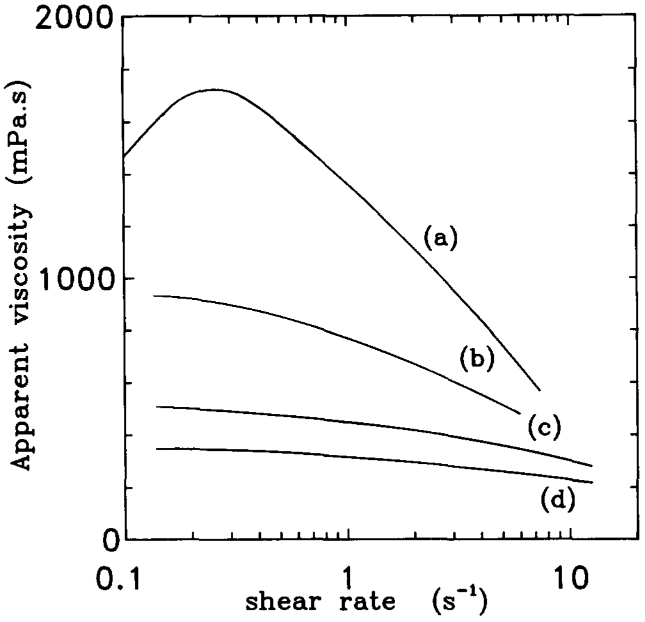

Figure 14 Effect of shear rate on the apparent viscosity for copolymer S1.5(1) at various temperatures: (a) 20°C; (b) 30°C; (c) 40°C; (d) 50°C. (Copolymer concentration = 1% (w/w))

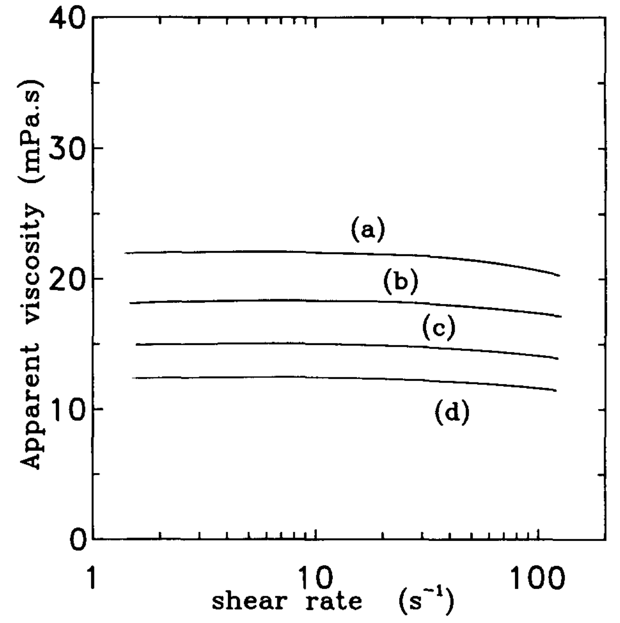

Figure 15 Effect of shear rate on the apparent viscosity for a homopolyacrylamide at various temperatures: (a) 20°C; (b) 30°C; (c) 40°C; (d) 50°C. (Polymer concentration = 1% (w/w))

The response of the apparent viscosity to increased shear rate, at 20°C, for the associating copolymer (*Figure 14*) is similar to that reported previously for similar copolymer systems[5,7,9,10,13,39]. The loss of viscosity at higher shear rates was attributed to the breakdown of interchain liaisons under a shear stress. For this sample, shear thickening was also seen at very low shear rates. This behaviour too has been reported previously[5,39,45], although definition of the conditions required in terms of copolymer concentration, hydrophobe content, etc., are not so well defined. It is clear, however, that the increased viscosities seen here for samples that are charged, but which can nonetheless interact hydrophobically, encourages this shear thickening. Previous studies by us[9,39] and others[7] on uncharged hydrophobically modified polyacrylamides in aqueous solution have failed to show any shear thickening behaviour in the absence of additives such as surfactants. However, a previous report by Bock *et al.*[5] on the same copolymers but at 18% hydrolysis of the acrylamide units did show shear thickening at low shear rates as observed here.

Clearly, increasing the temperature decreases the response of the copolymer solution viscosity to increased shear rate (*Figure 14*). Obviously, if the number of liaisons decreases upon increasing the temperature, then the number that will be broken on increasing the shear rate will also decrease. This result is supported by the data for the non-interacting polymer (*Figure 15*), where at all temperatures the response to increased shear rate is very limited.

Increases in temperature will, therefore, decrease both the solvent viscosity and the number of interchain liaisons, leading to marked decreases in the solution viscosities. The loss of interchain liaisons can be attributed to the increased solubility of the copolymers at elevated temperatures.

CONCLUSIONS

Interactions of hydrophobically modified copolymers based on acrylamide are very dependent on their microstructure. Increases in the size of the hydrophobically rich domains of the copolymer, at a constant level of hydrophobe, are directly related to an increase in hydrophobicity, and hence to an increased capability for aqueous viscosification due to hydrophobic interchain liaisons.

Partial hydrolysis of the water-soluble acrylamide blocks of the copolymers leads to an increased solubility of the copolymers and a consequent decrease in the numbers of hydrophobic liaisons. At the same time, the presence of charges causes an expansion in the copolymer chain dimensions. Up to a critical degree of hydrolysis, which is dependent on the hydrophobicity of the parent copolymers, the two effects of interchain liaisons and increased coil sizes can combine, giving very large increases in the solution viscosities. After this critical hydrolysis degree the viscosities are dependent solely on the electrolyte nature of the copolymer and, since all hydrophobic liaisons are effectively suppressed, the viscosity passes through a maximum.

Addition of salt to the copolymers, whether charged or uncharged, is seen to cause an increase in the solution viscosity after complete screening of the charges on the backbone. This is solely attributed to changes in the solubility of the hydrophobic groups.

When adding surfactant, all copolymers, whether or not they exhibited interchain liaisons in pure solution, were seen to exhibit a maximum in solution viscosity as a function of surfactant concentration. This maximum was always just below the surfactant c.m.c. and is attributed to the formation of mixed micelles with the hydrophobe.

Increases in the temperature were seen to lower solution viscosities owing to a loss of interchain liaisons caused by an increase in copolymer solubilities.

All the data suggest that the solution properties are very dependent on the microstructure-controlled hydrophobicity of any copolymer sample. However, complete structural analysis of such copolymers has yet to be achieved and so further work in this domain is required.

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