Water-soluble copolymers: 27. Synthesis and aqueous solution behaviour of associative acrylamide/*N*-alkylacrylamide copolymers

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Copolymers of acrylamide (AM) and *N*-alkylacrylamides have been prepared by micellar copolymerization in aqueous solution utilizing sodium dodecyl sulphate as a surfactant and potassium persulphate as the initiator. Synthesis, characterization, and copolymerization of the *N*-alkylacrylamide monomers with eight, ten and twelve carbons on the alkyl substituent are described. Rheological properties have been studied as a function of polymer concentration, electrolyte concentration, temperature and shear rate. A remarkable increase in apparent viscosity observed at low mole fractions of the *N*-alkylacrylamide in the copolymer occurs at a critical concentration which is a function of length of the alkyl chain in the monomer and copolymer molecular weight. Viscosity behaviour is interpreted in terms of a concentration dependent model involving interchain hydrophobic associations in aqueous solutions.

(Keywords: Acrylamide copolymers; micellar copolymerization; viscosity)

INTRODUCTION

Extensive studies in our laboratories over the past few years have been focused on tailoring macromolecules which in aqueous electrolyte solutions can maintain or increase viscosity[1–22]. Such polymers are of interest in a number of important commercial applications such as enhanced oil recovery, drag reduction, flocculation and super absorbency. In this paper we describe our work on the *N*-alkylacrylamide–acrylamide associative copolymers which form ordered domains in aqueous solutions. Effects of polymer concentration, salt, temperature and shear stress on rheological behaviour are reported in detail. While observations of 'hydrophobic' associations of this type have long been recognized for biopolymers and more recently utilized in coatings formulations[23–25], the relationships between molecular structure and rheological behaviour are poorly understood. Our main objective is to develop such relationships by studying carefully prepared and characterized polymers utilizing techniques including low angle laser light scattering, quasielectric light scattering, size exclusion chromatography, ^{13}C n.m.r., *FT*i.r., elemental analysis, fluorescence spectroscopy, and rheometry.

EXPERIMENTAL

Synthesis of N*-alkylacrylamide monomers*

The alkylacrylamides were prepared as follows. A 500 ml, four-necked flask was equipped with a thermometer, mechanical stirrer, N_2 inlet and addition funnel. After purging with N_2, the *N*-n-alkylamine (0.11 mol) and triethylamine (0.12 mol) were dissolved in 100 ml tetrahydrofuran (THF) and placed in the flask. The solution was then cooled to 0°C. Acryloyl chloride (0.11 mol) was dissolved in 100 ml THF and then slowly added to the reaction flask over a period of 2.5 h at such a rate that the temperature did not exceed 5°C. The resulting mixture was stirred at 10°C for 2 h. Following filtration of triethylamine hydrochloride and evaporation of THF, the crude product was twice recrystallized from acetone at −25°C[26,27]. The products were characterized by elemental analysis, melting point, *FT*i.r., ^{13}C n.m.r., and gas chromatography. Monomer characterization data are listed in *Table 1*. Typical *FT*i.r. and ^{13}C n.m.r. spectra can be seen in *Figures 1* and *2*, respectively.

*Synthesis of acrylamide-*N*-n-alkylacrylamide copolymers*

The copolymers of acrylamide with *N*-alkylacrylamide were prepared by micellar copolymerization using

Table 1 Characterization of *N*-alkylacrylamides

	Elemental analysis						
	Calculated			Observed			
Monomer	C	H	N	C	H	N	Melting point (°C)
octylAAm	72.08	11.68	7.64	71.87	11.39	7.67	33.5–34.5
decylAAm	73.88	11.92	6.63	73.88	11.80	6.60	45.0–46.0
dodecylAAm	75.25	12.21	5.85	75.16	12.14	5.89	55.5–56.5

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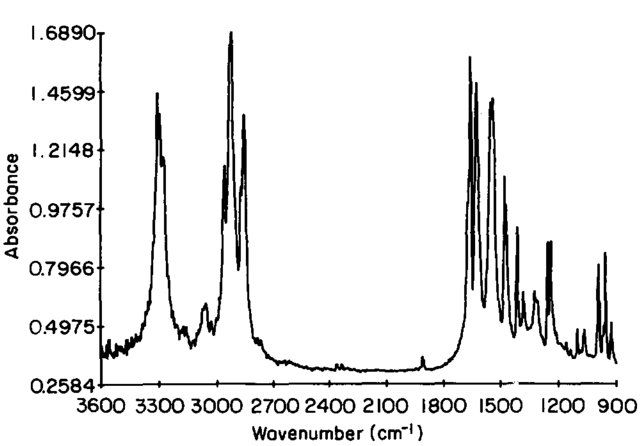


Figure 1 *FT*i.r. spectrum of *N*-n-decylacrylamide

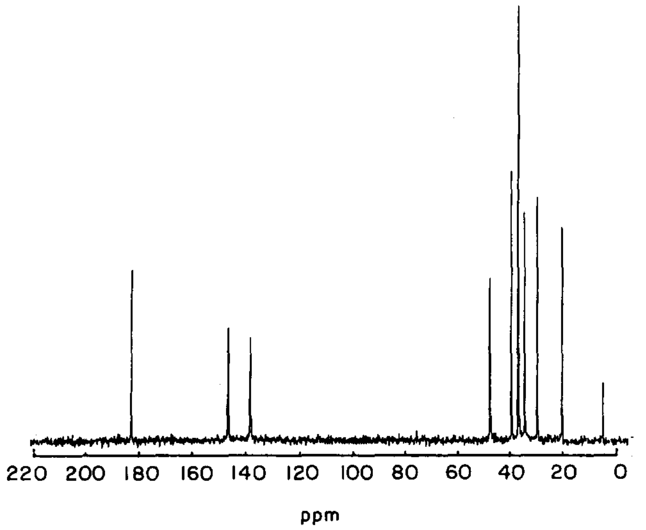


Figure 2 ^{13}C n.m.r. spectrum of *N*-n-dodecylacrylamide

sodium dodecyl sulphate as the surfactant and potassium persulphate as the free radical initiator[26]. A typical example of a micellar copolymerization is as follows. A one litre, three-necked flask was equipped with a mechanical stirrer, reflux condenser and gas inlet. After the flask was purged with nitrogen for half an hour, 15.85 g (0.055 mol) sodium dodecyl sulphate, 14.76 g (0.208 mol) acrylamide (twice recrystallized), 0.33 g (1.57×10^{-3} mol) *N*-n-decylacrylamide and 470.7 g (26.15 mol) deaerated water were added to the reaction flask. Within 10–15 min a homogeneous, water-clear mixture resulted.

The solution was then heated to 50°C and 0.01 g (3.70×10^{-5} mol) of potassium persulphate initiator was added. The reaction was allowed to proceed for 3 h, after which the mixture was cooled and diluted with an equivalent volume of water. Acetone was then slowly added while stirring to precipitate the copolymer. The polymer was washed with acetone twice and dried under reduced pressure at room temperature for 5 h. The 'dry' polymer was redissolved in water, dialysed against pure water, then freeze-dried. A 10–15% weight loss due to surfactant was observed after dialysis. Elemental analysis confirmed the absence of surfactant in the dialysed copolymer.

The copolymers used in this study are listed in *Table 2*. The composition of the copolymers could not be calculated by elemental analysis since the amount of *N*-alkylacrylamide incorporated in the copolymer was small, well below the accurate limit of instrumental detection.

Elemental analysis

Elemental analysis to determine carbon, hydrogen, nitrogen and sulphur content was conducted by MHW Laboratories of Phoenix, Arizona.

Solution viscosity determinations

Stock polymer solutions were prepared by dissolving lyophilized polymer in water or aqueous NaCl solution. Solution viscosities of the associative polymers were determined using a Contraves (LS-30) low shear rotational rheometer at shear rates ranging from 1.28 to 94.5 s^{-1}. All viscosities were measured at temperatures in the range 25–55°C and salt (NaCl and $CaCl_2$) concentrations in the range of 0–0.855 M. These studies were conducted in the absence of surfactant, with the exception of the study of the effects of surfactants on the solution viscosity.

RESULTS AND DISCUSSION

Conceptual model

The properties of copolymers containing hydrophobic groups along the polymer backbone can be quite surprising. For example, in the copolymers of this study, incorporation of only a small mole percent (< 1) of the C-10, *N*-alkylacrylamide monomer yields systems with greatly enhanced viscosities at concentrations above a critical value.

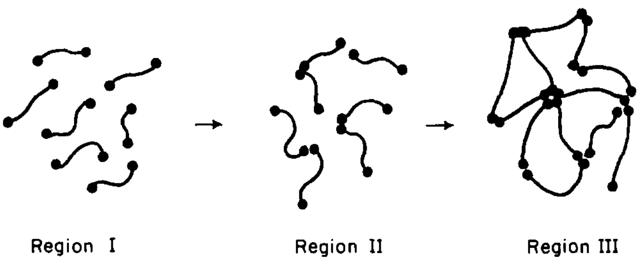
The method of polymerization obviously affects solution properties. In the micellar copolymerization described in the experimental section of this paper, we suggest that the hydrophobic monomers are probably polymerized in a blocky fashion since they should tend to aggregate in the interior of the micellar domain, away from the aqueous phase. Support for this proposal comes from two observations. First, no enhancement of solution properties is realized for copolymerization via homogeneous solution polymerization involving a common solvent. This type of polymerization would probably be random since the reactivities of the monomers should be similar.

A second source of support comes from preliminary studies in our laboratories using pyrene as a fluorescence

Table 2 Reaction parameters and solubility properties[a]

Sample name	Monomer feed ratio	Water solubility	Percent conversion
C-8–0.25	99.75/0.25	soluble	33.5
C-8–0.50	99.50/0.50	soluble	35.5
C-8–0.75	99.25/0.75	soluble	36.1
C-10–0.25	99.75/0.25	soluble	33.7
C-10–0.50	99.50/0.50	soluble	35.6
C-10–0.75	99.25/0.75	soluble	36.5
C-12–0.25	99.75/0.25	soluble	28.6
C-12–0.50	99.50/0.50	insoluble	31.4
C-12–0.75	99.25/0.75	insoluble	31.3

[a] Total monomer concentration = 0.44 M; sodium dodecyl sulphate concentration = 0.12 M; $[K_2S_2O_8] = 7.86 \times 10^{-5}$ M; $T = 50$°C



Scheme 1 Conceptual model for association of hydrophobic copolymers in aqueous solutions

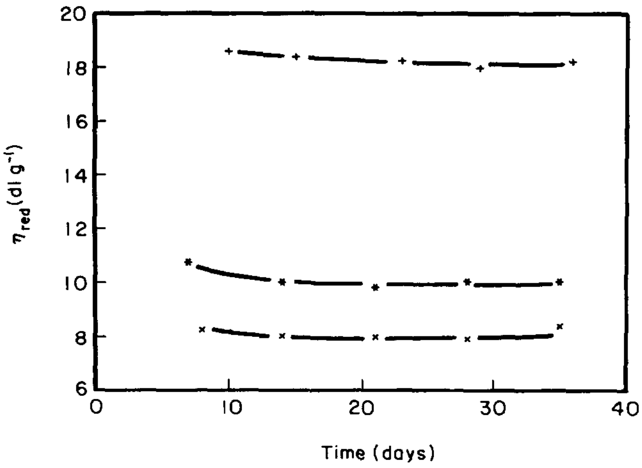


Figure 3 Ageing effect for copolymers of acrylamide with octylacrylamide in water at 25°C. ×, C-8 AAm–0.25; *, C-8 AAm–0.50; +, C-8 AAm–0.75

probe of solution ordering[28,29]. A concentration dependence on apparent viscosity is preceded by a rapid increase in pyrene fluorescence lifetimes. At present we interpret these results in terms of a model presented in *Scheme 1*. At low concentration the hydrophobic groups on separate polymer chains have little interaction. The large pyrene probe is not protected from the aqueous environment or from added ions such as the bromide anion; therefore, fluorescence quenching is relatively rapid. As the polymer concentration increases, hydrophobic domain ordering becomes important. Fluorescence lifetimes of the probe increase and quenching constants for added bromide ions are low. Interestingly, the rapid increase in the fluorescence lifetime occurs at a concentration well below that observed for the eventual viscosity increase. Although domain ordering may be well advanced at lower concentration, the eventual bridging of domains leading to a network apparently occurs at a much higher concentration.

Further fluorescence studies based on the synthetic models in this research will be reported in a subsequent paper in this series. It is recognized that major modifications of the conceptual model are likely as hydrophobe distribution, concentration, domain size and probe size are examined in additional experiments.

Ageing effects

Water-soluble copolymers, especially those with hydrophobic substitution, often exhibit time-dependent reorganization in solution. In order to properly assess the effects of polymer composition, shear rate, temperature and added electrolytes on solution behaviour, ageing studies were first conducted.

Figure 3 shows the ageing effect for copolymers of acrylamide with octylacrylamide in pure water at 25°C. The viscosity was measured after filtration of the solutions using a 5.0 μm filter (VWR Scientific Co.). The values of the abscissa represent the number of days since the copolymers were placed into water. The reduced viscosities of the copolymers decreased slightly with time.

Figure 4 shows the ageing effect for the copolymers of acrylamide with decylacrylamide and dodecylacrylamide in pure water at 25°C. The copolymers required greater times for redissolution as the mol% of decylacrylamide increased. Initially, the copolymer of acrylamide with 0.75 mol% decylacrylamide (C-10–0.75) (in the feed) had a lower reduced viscosity than the copolymer of acrylamide with 0.50 mol% decylacrylamide (C-10–0.50). However, the C-10–0.75 copolymer displayed a greater reduced viscosity than the C-10–0.5 copolymer and essentially a constant viscosity after three to four weeks.

The reduced viscosities of the copolymers of acrylamide with 0.25 mol% decylacrylamide (C-10–0.25), (C-10–0.50), and 0.25 mol% dodecylacrylamide (C-12–0.25) decreased only slightly with time. All subsequent viscosity measurements were conducted after a time interval of at least one month from solution preparation in order to allow solution equilibration.

Effects of polymer composition

Figure 5 shows the concentration dependence of the solution viscosity for copolymers of acrylamide with octylacrylamide of different mole ratios in 0.342 M NaCl solution. The viscosities were measured at a shear rate of 1.28 s^{-1} at 25°C. The concentration dependence of viscosity for these copolymers increases with increasing octylacrylamide content. The C-8–0.75 copolymer showed a significantly greater dependence of the viscosity on concentration than the other two copolymers.

Figures 6 and *7* show the concentration dependence of the solution viscosity for copolymers of acrylamide with decylacrylamide in 0.342 M NaCl solution and in water, respectively. In both cases, almost the same solution behaviour was observed. The concentration dependence

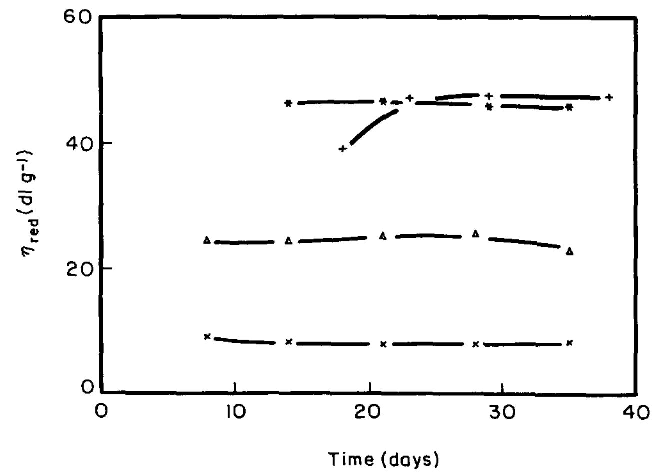


Figure 4 Ageing effect for copolymers of acrylamide with decylacrylamide and dodecylacrylamide in water at 25°C. ×, C-10–0.25; *, C-10–0.50; +, C-10–0.75; △, C-12–0.25

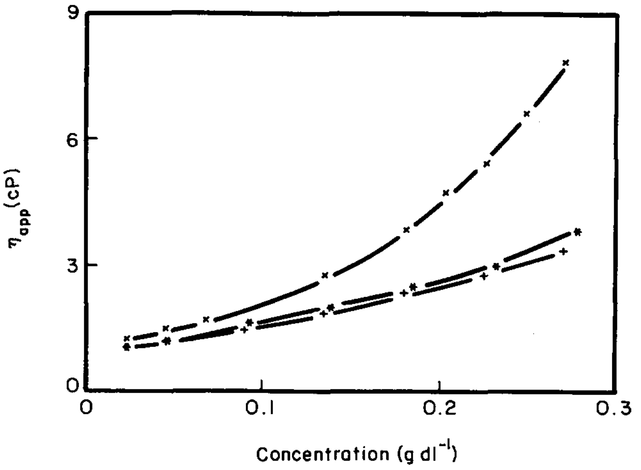


Figure 5 Effect of copolymer concentration on the apparent viscosity of copolymers of acrylamide with octylacrylamide in 0.342 M NaCl at 25°C and a shear rate of $1.28\,s^{-1}$. ×, C-8–0.75; *, C-8–0.50; +, C-8–0.25

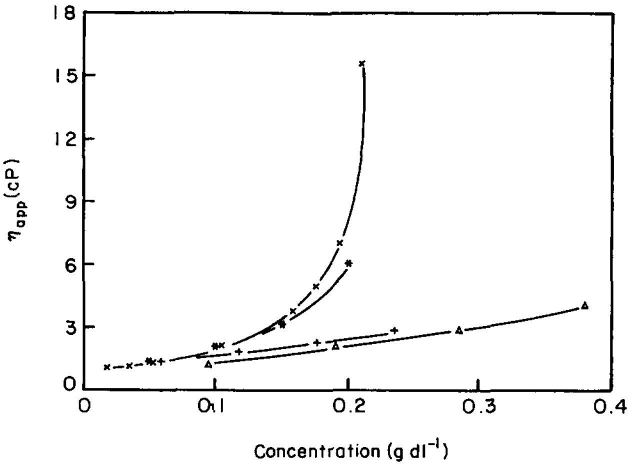


Figure 6 Effect of copolymer concentration on the apparent viscosity of copolymers of acrylamide with decylacrylamide in 0.342 M NaCl at 25°C and a shear rate of $1.28\,s^{-1}$. ×, C-10–0.75; *, C-10–0.50; +, C-10–0.25; △, PAAm

of the viscosity became greater as the decylacrylamide content in the copolymer increased. A dramatic increase in solution viscosity was observed at about $0.15\,g\,dl^{-1}$ for the C-10–0.75 copolymer. For comparison, the concentration dependence of the viscosity for a polyacrylamide sample which was prepared under the same experimental conditions as the associative copolymers is also shown in *Figures 6* and *7*.

The overlap concentration (C^*) of polyacrylamide and the C-10–0.25 copolymer could not be clearly observed in the concentration range investigated. The remarkable increase of the viscosity of the C-10–0.75 copolymer is attributed to the strong interchain associations.

Figure 8 displays comparisons of the viscosity dependence on concentration for copolymers of acrylamide with 0.25 mol% *N*-alkylacrylamide in 0.342 M NaCl solution at 25°C. The C-8–0.25 and C-10–0.25 copolymers showed almost the same concentration dependence, whereas the C-12–0.25 copolymer displayed a greater dependence of the viscosity on concentration than the other two copolymers.

Figures 9 and *10* show comparisons of the viscosity

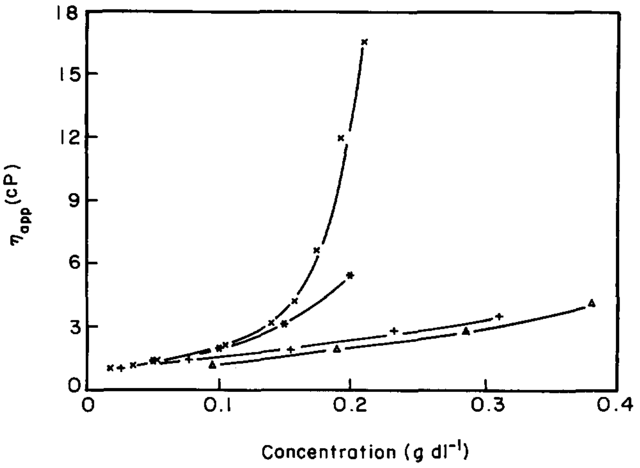


Figure 7 Effect of copolymer concentration on the apparent viscosity of copolymers of acrylamide with decylacrylamide in water at 25°C and a shear rate of $1.28\,s^{-1}$. ×, C-10–0.75; *, C-10–0.50; +, C-10–0.25; △, PAAm

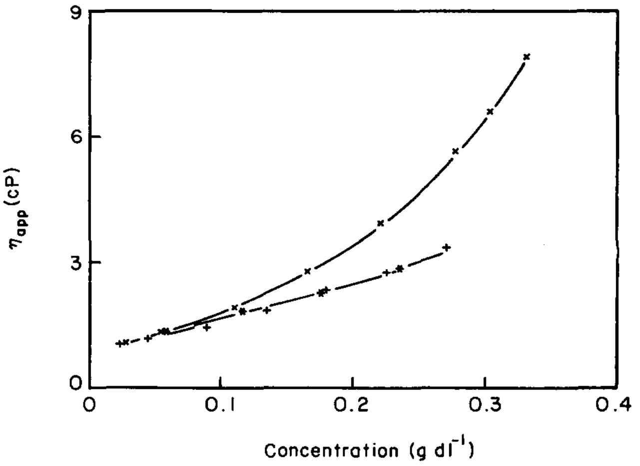


Figure 8 Effect of copolymer concentration on the apparent viscosity of copolymers of acrylamide with 0.25 mol% n-alkylacrylamides in 0.342 M NaCl at 25°C and a shear rate of $1.28\,s^{-1}$. ×, C-12–0.25; *, C-10–0.25; +, C-8–0.25

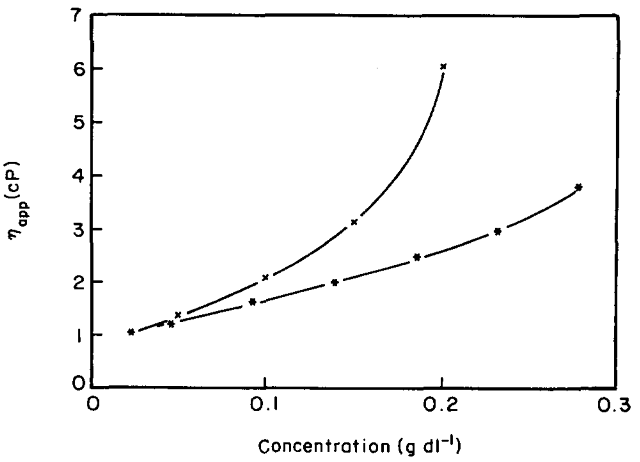


Figure 9 Effect of copolymer concentration on the apparent viscosity of copolymers of acrylamide with 0.50 mol% n-alkylacrylamides in 0.342 M NaCl at 25°C and a shear rate of $1.28\,s^{-1}$. ×, C-10–0.50; *, C-8–0.50

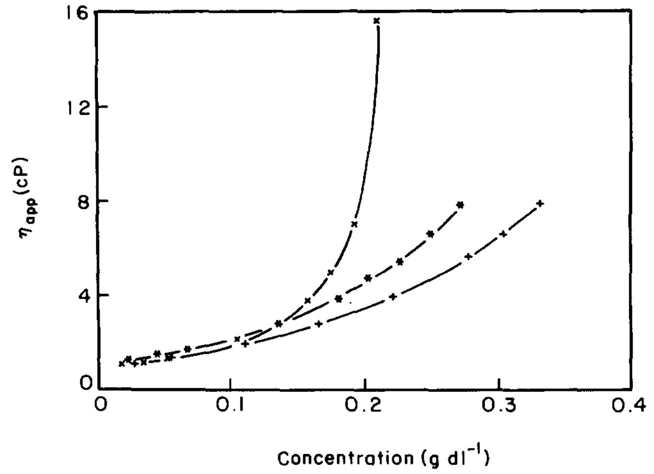


Figure 10 Effect of copolymer concentration on the apparent viscosity of copolymers of acrylamide with 0.75 and 0.25 mol% n-alkylacrylamides in 0.342 M NaCl at 25°C and a shear rate of 1.28 s^{-1}. ×, C-10–0.75; *, C-8–0.75; +, C-12–0.25

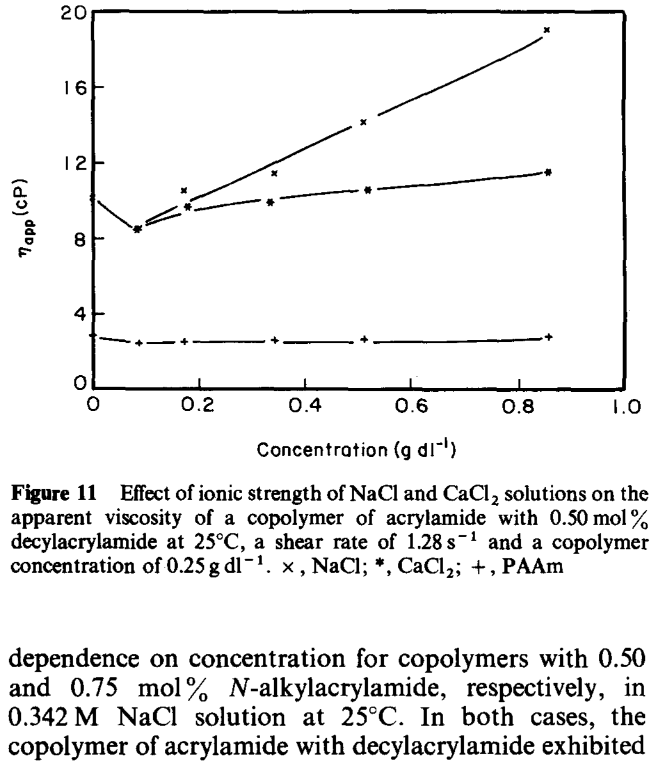


Figure 11 Effect of ionic strength of NaCl and $CaCl_2$ solutions on the apparent viscosity of a copolymer of acrylamide with 0.50 mol% decylacrylamide at 25°C, a shear rate of 1.28 s^{-1} and a copolymer concentration of 0.25 g dl^{-1}. ×, NaCl; *, $CaCl_2$; +, PAAm

dependence on concentration for copolymers with 0.50 and 0.75 mol% *N*-alkylacrylamide, respectively, in 0.342 M NaCl solution at 25°C. In both cases, the copolymer of acrylamide with decylacrylamide exhibited a greater dependence on concentration than the copolymer of acrylamide with octylacrylamide. The C-12–0.25 copolymer displayed a lower concentration dependence than the C-8–0.75 and C-10–0.75 copolymers (*Figure 10*). Interchain association increases with increasing content of *N*-alkylacrylamide in the copolymer and with increasing hydrophobicity of the *N*-alkylacrylamide.

Effects of additives on the viscosity

NaCl. The effect of salt on the viscosity of the polymer solution was investigated using the C-10–0.50 copolymer and homopolyacrylamide (*Figure 11*). The viscosity of the C-10–0.50 copolymer solution increased with increasing NaCl concentration except at an ionic strength of 0.086 M. In contrast, the viscosity of the polyacrylamide solution was essentially invariant with changes in ionic strength (NaCl). These results suggest that intermolecular association is favoured by the addition of salt. The same phenomenon was observed for the C-10–0.75 copolymer. A similar effect has been reported for a polysoap by Strauss and coworkers[30].

Surfactant. The effect of nonionic and anionic surfactants on the viscosity of the copolymer solutions was investigated using the C-10–0.50 copolymer (*Figure 12*). The viscosity of the polymer solution decreased remarkably upon addition of nonionic or anionic surfactant. Further addition of surfactant yielded no change in the apparent viscosity. Obviously the surfactant disrupts the interchain association. Apparently, the added free surfactant generates non-crosslinking, micelle-like associations with individual hydrophobic segments, thereby suppressing the intermolecular association of two or more hydrophobic domains from different polymers. *Figure 12* also shows that the viscosity of a polymer solution in the presence of anionic surfactant is slightly higher than that in the presence of nonionic surfactant. The addition of ionic species has already been shown to cause an increase in viscosity due to enhanced ordering of hydrophobic domains (*Figure 11*).

Effects of temperature

In order to assess the effect of temperature on the solution behaviour of hydrophobically modified acrylamide copolymers, the apparent viscosity of the C-10–0.75 copolymer was measured at four temperatures and at different shear rates (*Figure 13*). The apparent viscosities of the copolymers decrease with increasing temperature at constant shear rate due to the decrease in solvent viscosity. *Figure 14* shows the reduced viscosity versus shear rate plots at different temperatures for the C-10–0.75 copolymer. The reduced viscosity of this copolymer increases with increasing temperature at the same shear rate.

Figure 15 shows the reduced viscosity versus temperature plots for the C-10–0.75 copolymer and polyacrylamide at a shear rate of 1.28 s^{-1}. The reduced viscosity of the C-10–0.75 copolymer increases with increasing temperature, whereas the reduced viscosity of

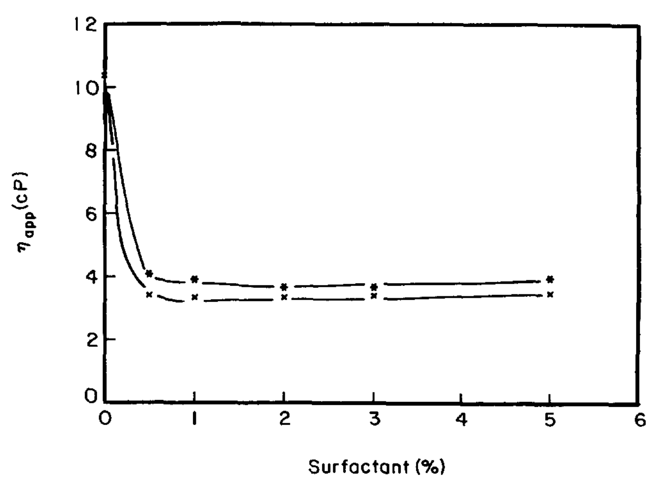


Figure 12 Effect of surfactant concentration on the apparent viscosity of a copolymer of acrylamide with 0.50 mol% decylacrylamide at 25°C, a shear rate of 1.28 s^{-1} and a copolymer concentration of 0.25 g dl^{-1}. ×, Sodium dodecyl sulphate; *, octylphenol ethoxylate

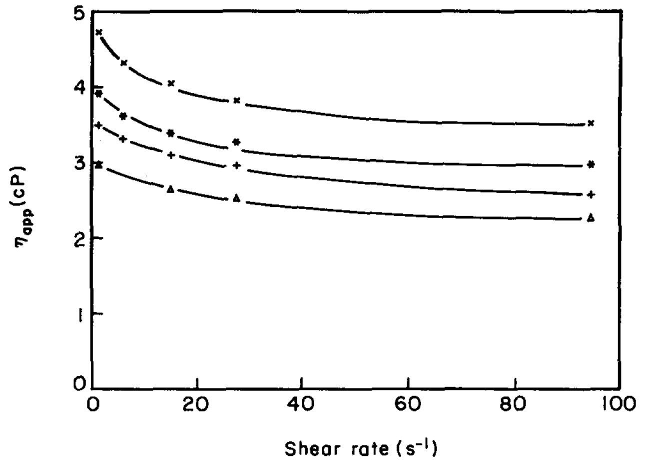


Figure 13 Effect of shear rate on the apparent viscosity of a copolymer of acrylamide with 0.75 mol% decylacrylamide in 0.342 M NaCl at a copolymer concentration of 0.19 g dl^{-1} and temperatures of: ×, 25°C; *, 35°C; +, 45°C; △, 55°C

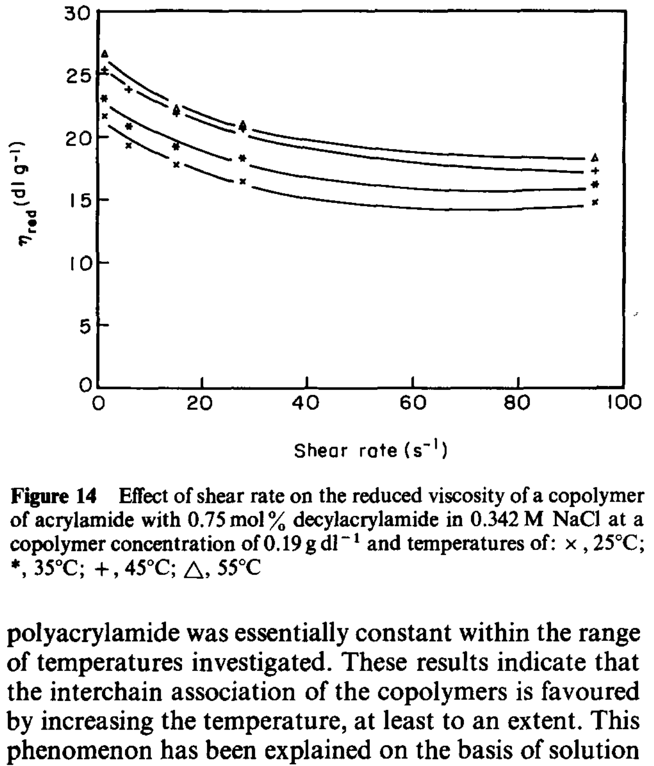


Figure 14 Effect of shear rate on the reduced viscosity of a copolymer of acrylamide with 0.75 mol% decylacrylamide in 0.342 M NaCl at a copolymer concentration of 0.19 g dl^{-1} and temperatures of: ×, 25°C; *, 35°C; +, 45°C; △, 55°C

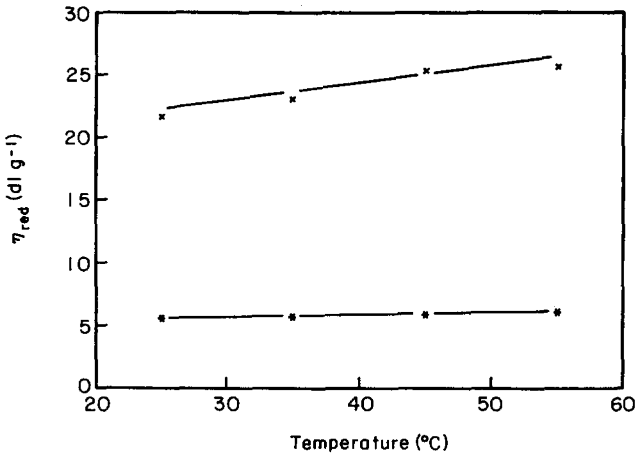


Figure 15 Effect of temperature on the reduced viscosity of polyacrylamide and a copolymer of acrylamide and with 0.75 mol% decylacrylamide and in 0.342 M NaCl at a copolymer concentration of 0.19 g dl^{-1} and a shear rate of 1.28 s^{-1}. ×, C-10–0.75; *, polyacrylamide

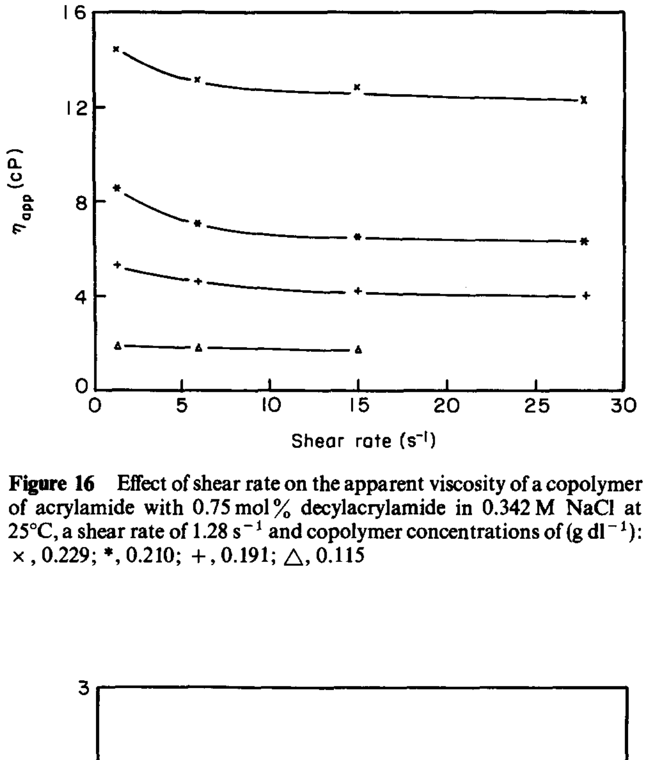


Figure 16 Effect of shear rate on the apparent viscosity of a copolymer of acrylamide with 0.75 mol% decylacrylamide in 0.342 M NaCl at 25°C, a shear rate of 1.28 s^{-1} and copolymer concentrations of (g dl^{-1}): ×, 0.229; *, 0.210; +, 0.191; △, 0.115

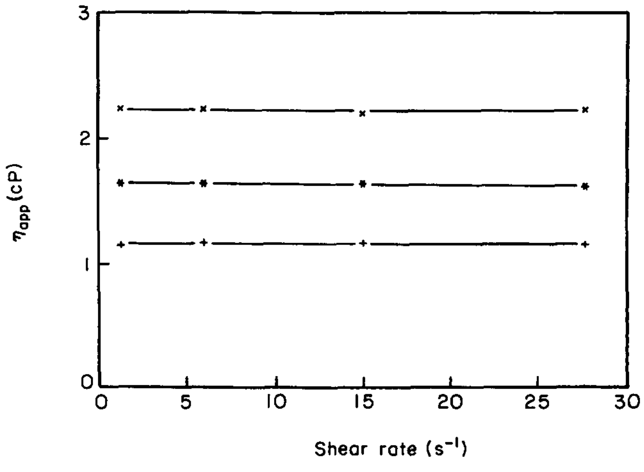


Figure 17 Effect of shear rate on the apparent viscosity of polyacrylamide in 0.342 M NaCl at 25°C, a shear rate of 1.28 s^{-1} and polymer concentrations of (g dl^{-1}): ×, 0.216; *, 0.130; +, 0.043

polyacrylamide was essentially constant within the range of temperatures investigated. These results indicate that the interchain association of the copolymers is favoured by increasing the temperature, at least to an extent. This phenomenon has been explained on the basis of solution thermodynamics[31]. Hydrophobic hydration is exothermic while hydrophobe–hydrophobe interaction is endothermic.

Effects of shear rate

Figures 16 and *17* show the apparent viscosity versus shear rate for the C-10–0.75 copolymer and polyacrylamide, respectively, at different polymer concentrations in 0.342 M NaCl at 25°C. The apparent viscosity of the C-10–0.75 copolymer decreases with increasing shear rate, whereas the apparent viscosity of polyacrylamide is not affected by increases in shear rate over the polymer concentration range investigated. *Figure 16* also shows that the pseudoplastic behaviour increases with increasing polymer concentration. This phenomenon is evident in *Figure 18* in which the apparent viscosity is plotted versus concentration for C-10–0.75 at shear rates of 1.28 and 94.5 s^{-1}. The high viscosity of

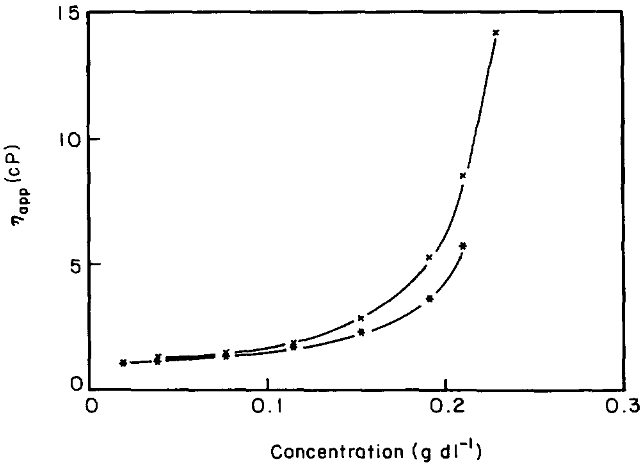


Figure 18 Effect of copolymer concentration on the apparent viscosity of a copolymer of acrylamide with 0.75 mol % decylacrylamide in water at 25°C and shear rates of: ×, 1.28 s^{-1}, *, 94.5 s^{-1}

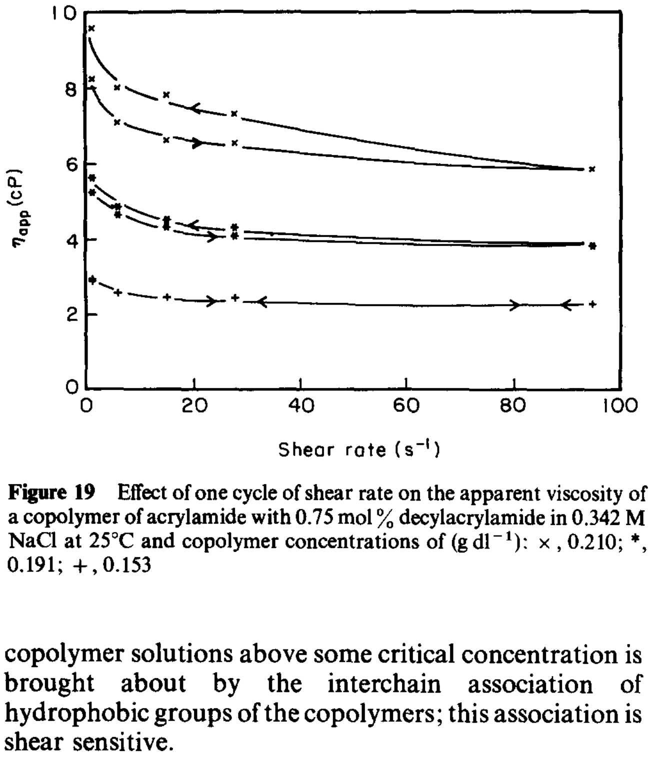


Figure 19 Effect of one cycle of shear rate on the apparent viscosity of a copolymer of acrylamide with 0.75 mol % decylacrylamide in 0.342 M NaCl at 25°C and copolymer concentrations of (g dl^{-1}): ×, 0.210; *, 0.191; +, 0.153

copolymer solutions above some critical concentration is brought about by the interchain association of hydrophobic groups of the copolymers; this association is shear sensitive.

In *Figure 19* the apparent viscosity of the C-10–0.75 copolymer as a function of increasing, then decreasing shear rates was investigated. Three polymer concentrations were studied. Initially the viscosity was measured as the shear rate was increased to greater values. Immediately following the measurement at 94.5 s^{-1}, the shear rate was sequentially decreased with intermittent measurements. Surprisingly, the solution viscosities are greater at each shear rate along the decreasing portion of the shear rate curve than along the increasing portion. This figure also shows that the degree of increase of the viscosity as a function of shear history is dependent on polymer concentration. To confirm this phenomenon in detail, the viscosity of the C-10–0.75 copolymer was measured through two cycles of increasing and then, decreasing shear rates (*Figure 20*). The apparent viscosities in the second cycle of shear rate are larger than the viscosities obtained at corresponding shear rates in the first cycle. The same phenomenon is observed with the C-10–0.50 copolymer, although the degree of the viscosity increase is small.

The results imply that not only do associations recover immediately after the application of shear, but also the associations are enhanced by the application of shear. An explanation of this peculiar behaviour may be that the viscosity increase is a result of an increase in order of the hydrophobic domains induced by the application of shear. Thus, the hydrophobic domains are enhanced by groups which had not participated in the intermolecular association before the application of shear.

The viscosity of the C-10–0.50 copolymer was also measured in the presence of nonionic surfactant at increasing and decreasing shear rates. As mentioned previously, a dramatic reduction in viscosity is observed upon addition of surfactant. There also is no viscosity dependence on shear in the presence of nonionic surfactant. Likewise, a viscosity increase is not observed at decreasing values of shear rate; i.e. the polymer behaved like polyacrylamide. Therefore, interchain associations are completely disrupted by the addition of surfactant.

Effects of molecular weight

In *Figure 21* the reduced viscosity is plotted against concentration for C-10–0.50 copolymers of varying molecular weights. The copolymers were prepared via micellar copolymerization by varying the initiator concentration and reaction temperature. The degree of upsweep of the viscosity at some critical polymer concentration becomes greater as the molecular weight increases. This indicates that the attainment of interchain associations depends on molecular weight as well as the hydrophobic character of the comonomer. A polyacrylamide sample prepared under the same conditions as the C-10–0.50 copolymer has a molecular weight of about 1.2×10^6 g mol^{-1} as determined from its intrinsic viscosity via the Mark–Houwink–Sakurada relationship[32].

Intrinsic viscosity and Huggins parameter for an acrylamide–N-alkylacrylamide copolymer

The intrinsic viscosities of the copolymers, $[\eta]$, and their Huggins parameters, k', were determined by

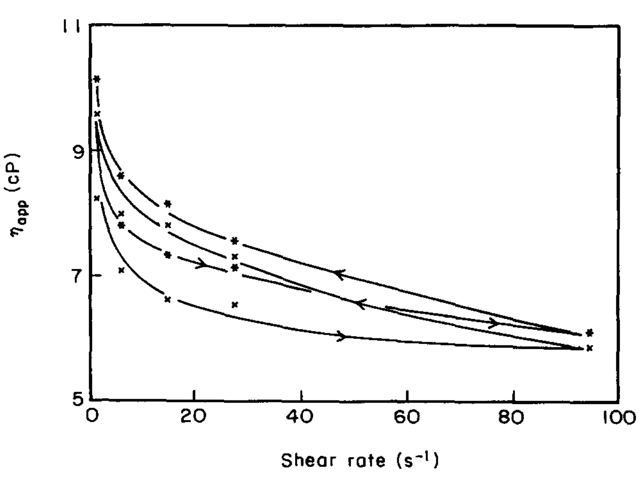


Figure 20 Effect of two cycles of shear rate on the apparent viscosity of a copolymer of acrylamide with 0.75 mol % decylacrylamide in 0.342 M NaCl at 25°C and a copolymer concentration of 0.210 g dl^{-1}. ×, First cycle; *, second cycle

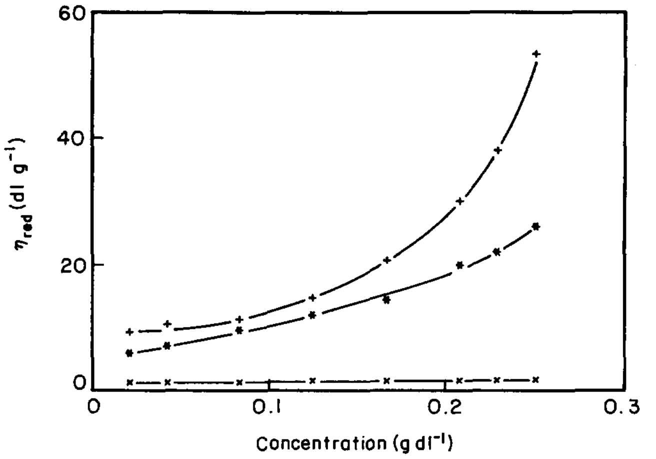


Figure 21 Effect of copolymer concentration on the reduced viscosity of copolymers of acrylamide with 0.50 mol % decylacrylamide of various molecular weights in 0.342 M NaCl at 25°C and a shear rate of 1.28 s^{-1}. ×, 50°C, 45 min, KPS 0.10 g; *, 50°C, 3 h, KPS 0.01 g; +, 30°C, 24 h, KPS 0.01 g

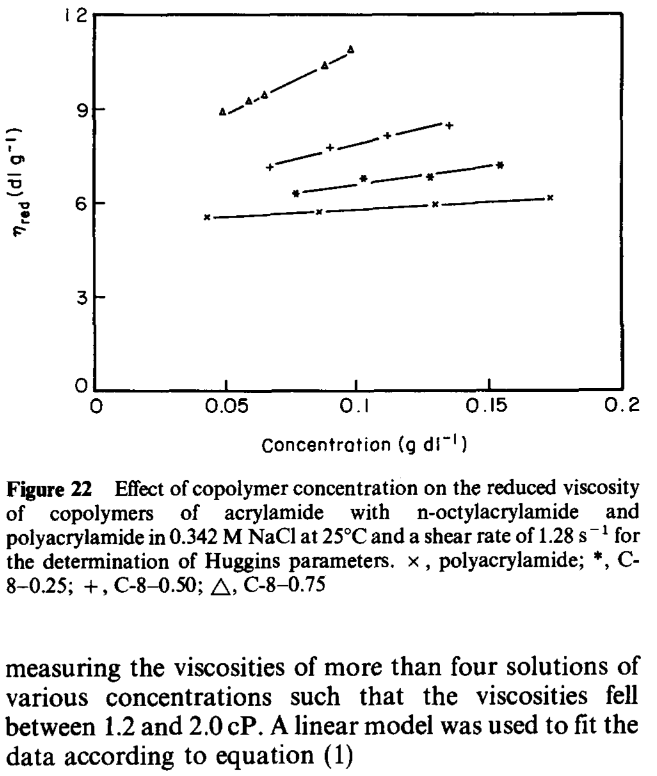


Figure 22 Effect of copolymer concentration on the reduced viscosity of copolymers of acrylamide with n-octylacrylamide and polyacrylamide in 0.342 M NaCl at 25°C and a shear rate of 1.28 s^{-1} for the determination of Huggins parameters. ×, polyacrylamide; *, C-8-0.25; +, C-8-0.50; △, C-8-0.75

measuring the viscosities of more than four solutions of various concentrations such that the viscosities fell between 1.2 and 2.0 cP. A linear model was used to fit the data according to equation (1)

$$\frac{\eta-\eta_0}{\eta_0 C}=[\eta]+K'[\eta]^2 C \qquad (1)$$

where C is the concentration of polymer in g dl^{-1} and η_0 is the viscosity of the solvent.

Figure 22 shows the reduced viscosity versus concentration plots for copolymers of acrylamide with octylacrylamide. *Table 3* lists the intrinsic viscosity and Huggins parameters obtained by use of equation (1). The Huggins parameter increases with increasing octylacrylamide content in the copolymers. The intrinsic viscosities of the copolymers increase slightly with increasing hydrophobic content.

Strauss and coworkers reported that Huggins constant increases with increasing dodecyl content for copolymers of vinyl-*N*-ethyl and vinyldodecyl pyridinium bromide[30]. These results indicate that, for hydrophobically modified polymers, the tendency for the macromolecules to form intermolecular associations may be reflected by increases in the Huggins constant. However, it should be pointed out that a theoretical interpretation of the Huggins constant values may have little use in dilute solutions in which ordering occurs.

Table 3 Intrinsic viscosities and Huggins parameters for AAm–octylAAm copolymers

Monomer feed ratio, AAM/octylAAm	Intrinsic viscosity	Huggins parameter
100/0	5.32	0.17
99.75/0.25	5.56	0.34
99.50/0.50	5.94	0.54
99.25/0.75	6.92	0.84

CONCLUSIONS

The concentration dependence of the viscosity of the hydrophobically modified acrylamide copolymers under investigation increases with increasing hydrophobicity. Solution viscosities of the hydrophobically modified acrylamide copolymers increase with the addition of salt (NaCl, $CaCl_2$). A decrease in the viscosity is observed upon the addition of surfactant. Interchain association of hydrophobic groups is favoured by increasing temperatures in the range of 25 to 55°C. An increase in molecular weight enhances intermolecular association, as evidenced by a lowering of the onset values and an increase in the rate of upsweep of viscosity with concentration. For specific microstructures, interchain association may be enhanced to an extent by first subjecting the solutions to low shear stress. The viscosity increase of hydrophobically modified acrylamide copolymers at a critical concentration compared to non-modified acrylamide of the same molecular weight is clearly due to the interchain association of hydrophobic groups at a critical polymer concentration. Although the rheological data are consistent with the proposed conceptual model, further studies will be necessary to elucidate the precise nature of these interactions.

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REFERENCES

1 McCormick, C. L. and Chen, G. S. *J. Polym. Sci., Polym. Chem. Edn* 1982, **20**, 817
2 McCormick, C. L., Chen, G. S. and Hutchinson, B. H. Jr. *J. Appl. Polym. Sci.* 1982, **27**, 3103
3 Neidlinger, H. H., Chen, G. S. and McCormick, C. L. *J. Appl. Polym. Sci.* 1984, **29**, 713
4 McCormick, C. L. and Park, L. S. *J. Polym. Sci., Polym. Chem. Edn* 1984, **22**, 49
5 McCormick, C. L. and Chen, G. S. *J. Polym. Sci., Polym. Chem. Edn* 1984, **22**, 3633
6 McCormick, C. L. and Chen, G. S. *J. Polym. Sci., Polym. Chem. Edn* 1984, **22**, 3649
7 McCormick, C. L. and Park, L. S. *J. Appl. Polym. Sci.* 1985, **30**, 45

8 McCormick, C. L. and Blackmon, K. P. *J. Polym. Sci., Polym. Chem. Edn* 1986, **24**, 2635

9 McCormick, C. L., Blackmon, K. P. and Elliott, D. L. *J. Polym. Sci., Polym. Chem. Edn.* 1986, **24**, 2619

10 McCormick, C. L. and Elliott, D. L. *Macromolecules* 1986, **19**, 542

11 Hutchinson, B. H. and McCormick, C. L. *Polymer* 1986, **27**, 623

12 McCormick, C. L., Hutchinson, B. H. and Morgan, S. E. *Makromol. Chem.* 1987, **188**, 357

13 McCormick, C. L. and Blackmon, K. P. *Macromolecules* 1986, **19**, 1512

14 McCormick, C. L., Elliott, D. L. and Blackmon, K. P. *Macromolecules* 1986, **19**, 1516

15 McCormick, C. L. and Blackmon, K. P. *J. Macromol. Sci.* (*A*), *Chem.* 1986, **25**, 1451

16 McCormick, C. L., Blackmon, K. P. and Elliott, D. L. *J. Macromol. Sci.* (*A*), *Chem.* 1986, **23**, 1469

17 McCormick, C. L. and Blackmon, K. P. *Polymer* 1986, **27**, 1971

18 McCormick, C. L., Blackmon, K. P. and Elliott, D. L. *Polymer* 1986, **27**, 1976

19 McCormick, C. L. and Blackmon, K. P. *Angew. Makromol. Chem.* 1986, **144**, 73

20 McCormick, C. L., Blackmon, K. P. and Elliott, D. L. *Angew. Makromol. Chem.* 1986, **144**, 87

21 McCormick, C. L. and Elliott, D. L. *J. Polym. Sci., Polym. Chem. Edn.* 1986, **A25**, 1329

22 McCormick, C. L. and Blackmon, K. P. US Patent 4 584 358 (1986)

23 S. Evani, US Patent 4 432 881 (1984)

24 Hoy, K. L. and Hoy, R. C. US Patent 4 426 485 (1984)

25 Landoll, L. M. US Patent 4 288 277 (1980)

26 Turner, S. R., Siano, D. B. and Bock, J. US Patent 4 520 182 (1985)

27 Emmons, W. D. and Stevens, T. E. US Patent 4 395 524 (1983)

28 McCormick, C. L. and Johnson, C. B. *Polym. Mater. Sci. Eng.* 1986, **55**, 366

29 McCormick, C. L., Lundy, C. E., Hoyle, C. E. and Clark, M. D. *Macromolecules* submitted

30 Strauss, J. P., Gershfel, N. L. and Crook, E. H. *J. Phys. Chem.* 1956, **60**, 577

31 Molyneaux, P. 'Water-Soluble Polymers: Properties and Behavior', CRC Press, Boca Raton, 1984, Vol. 1, p. 7

32 Brandrup, J. and Immergut, E. H. (Eds) 'Polymer Handbook' 2nd edn, Wiley Interscience, New York, 1975, p. IV-1