Synthesis and rheological properties of low charge density polyampholytes in nonaqueous solvents

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The synthesis and rheological properties of a family of styrene-based polyampholytes are described. These polymers are composed mainly of styrene with relatively low levels of 4-vinylpyridine (4VP) and zinc neutralized sulphonated styrene (Zn-SS). Although these materials resemble in some instances the homogeneously-charged sulphonated polystyrene ionomers, marked differences in solution properties are noted. For example, in a single component nonaqueous solvent (such as xylene), the ampholytic ionomers are completely soluble, while the sulphonated ionomer requires the use of soluble polar cosolvents. Moreover, viscosity measurements over a broad shear rate range shows that these polyampholytes are effective viscosifiers possessing pronounced dilatant characteristics. This interesting behaviour can be varied over a broad shear gradient through minor changes in the polymer structure. The results show that through the interactions of 4VP and Zn-SS, a degree of control over physical properties is established which is not readily attained in other ionomeric materials. In an attempt to understand this particular rheological behaviour, an equation is proposed which summarizes on a molecular level the observed shear thickening behaviour. In its derivation, it is assumed that due to the shear gradient, intramolecular associations are transformed into intermolecular linkages. If the lifetime of these associations are longer than the relaxation time of the chain, an increase in the apparent molecular weight of the polymer will occur resulting in a rise in the viscosity of the polymer solution. Further implications of this equation are discussed with regard to associating-type polymer solutions.

(Keywords: polyampholytes; infra/intramolecular associations; coordination chemistry; shear thickening; nonaqueous solvents)

INTRODUCTION

Ionomers are a distinct class of polymers containing relatively few ionic groups (typically <10 mole%) on a polymer chain. Although it is widely recognized that the introduction of these ionic groups onto the polymer chain results in marked changes in its solid state properties[1-4], relatively little effort has focused on the dilute solution behaviour of these materials until recently. This lack of information is due, in part, to the limited solubility of ionomers in conventional solvents at ordinary temperatures caused by crystallinity effects or to the strong intra- and intermolecular ionic associations present in these systems. Interestingly, these ionic groups, specifically metal neutralized sulphonate groups, associate through secondary, noncovalent interactions with other polar molecules such as amines or alcohols. Through these specific interactions, the viscometric studies in both dilute and semidilute solution have been investigated[5-10]. This solubilization phenomena has been rationalized[5] in terms of a polymer–alcohol equilibrium in which the alcohol and associated polymer is postulated to be in equilibrium with a strongly solvated species. For complete elimination of the ionic associations, higher levels than the 'stoichiometric amount' of alcohol are required, indicating that the equilibria favours the associated ionic groups.

More recently, several publications[6,9] have described the dilute and semidilute viscosity behaviour of sulphonated polystyrene in a number of organic solvents.

These materials display unusual solution behaviour which can be investigated in different solvents ranging from those of low polarity, i.e. tetrahydrofuran up to highly polar solvents, i.e. dimethylformamide. Utilizing the sodium salt as a model system, it was observed that the solution behaviour in low polar solvents is consistent with the properties observed in the previously described mixed solvent systems where ion pair interactions dominate behaviour. Contrary to these results, dissociation of the sodium counterion from the vicinity of the chain occurs in polar solvents ($\varepsilon > 35$) resulting in a classical polyelectrolyte behaviour as the polymer concentration is reduced. Therefore, ion pair associations and polyelectrolyte behaviour are distinctly dependent on the dielectric constant of the solvent, and on the specific interaction energy between the ionic group and the solvent. In all of these studies, the ionomers possess a homogeneous ionic charge, i.e. typically sulphonate-containing ionomers.

It has been recognized[11-20], however, that polymers containing both anionic and cationic groups exhibit complex solution behaviour. Although both water soluble[11-19] and nonaqueous solvent[20] soluble polyampholytes have been synthesized, the major thrust has been directed to understanding and utilizing the water soluble materials. In striking contrast to conventional polyelectrolytes, these latter polymers become more soluble as the ionic strength of the solution is increased. This is undoubtedly due to the favourable interaction of

the polyampholytes with the dissolved inorganic salts. More recently[21], a new family of acrylamide based polyampholytes were synthesized containing a non-stoichiometric amount of anionic and cationic monomer units. Unlike the previously published work, these ampholytic ionomers possess relatively low charge density and display solution properties not readily attainable in conventional polyelectrolytes or in highly-charged polyampholytes. For example, at certain specific molecular compositions, these ampholytic ionomers display rheological behaviour that remains approximately invariant to large increases in the ionic strength of the solution.

In this paper, we describe the synthesis and rheological properties of a family of ampholytic ionomers capable of dissolving in single component hydrocarbon solvents. These polymeric materials are composed of styrene as a neutral monomer copolymerized with relatively low levels of 4-vinylpyridine (4VP) and styrene sulphonate (SS). The latter monomer units are typically associated with transition metal ions which interact with 4VP via a coordination-type chemistry. The strength of this interaction and the resultant solution properties are a strong function of the nature of this counterion. If the SS units are left unneutralized, then the anticipated acid–base interactions dominate solution behaviour. Furthermore, the behaviour of these ampholytic ionomers are compared to the homogeneously-charged sulphonated polystyrene associated with the identical metal counterion. As expected, markedly different solubility behaviour and viscometric properties (especially as the shear rate is varied) are observed. Moreover, the results show that 'addition' of interacting monomer units along an ionomer chain establishes a marked degree of control over solution properties not readily attained in the homogeneously charged materials or in nonionic polymers.

EXPERIMENTAL

The ampholytic ionomer was synthesized by sulphonating the preformed styrene-4-vinylpyridine copolymer. This particular synthesis procedure allows for a direct comparison of the physical properties of the nonionic copolymer with the same polymer containing relatively low levels of sulphonate groups. The following emulsion copolymerization procedure was generally utilized in the preparation of the styrene-4VP copolymer. Freshly distilled styrene (50 g) and 4-vinylpyridine (2.66 g) were added to a four necked reaction flask containing distilled water (120 ml), sodium laurylsulphate (3.2 g) and potassium persulphate (0.2 g). The molecular weight of the copolymer was modified with the addition of dodecylthiol (0.05 g). The solution was thoroughly mixed with an air driven stirrer and

continually purged with either nitrogen or argon gas. After approximately 60 min, the temperature of the mixture was elevated to 50°C and the reaction was permitted to proceed for 24 h. A sharp exotherm was noted in all emulsion copolymerizations usually within 30 min after heating began. This observation indicates that the polymerization was complete within that time period. The copolymer was subsequently isolated from the reaction mixture with the addition of excess amounts of acetone. The precipitated material was further washed with a large excess of acetone. The copolymer was vacuum dried for 48 h at 75°C. Nitrogen content of the copolymers was determined by Carlo Erba Strumentazione-Nitrogen Analyzer 1500 instrument and was used to calculate the 4VP content. In this specific example, the copolymer contained 0.68 wt% nitrogen which corresponds to 7.8 mol% 4VP.

The preparation of the zinc neutralized sulphonated styrene–styrene-4VP ampholytic ionomer was as follows: 10.0 g of the previously prepared styrene-4VP copolymer was dissolved in 100 ml of 1,2-dichloroethane. The solution was subsequently heated to 50°C, and the appropriate amount of acetylsulphate was added, in this instance, 11.25 mmol of acetic anhydride and 7.25 mmol of concentrated sulphuric acid. The solution was stirred for 60 min at 50°C, and the reaction terminated by the addition of methanol (9.0 ml). Then, 17.4 meq. of zinc acetate (dissolved in methanol and water) was added with vigorous agitation to completely neutralize all sulphonic acid present. The solution was filtered and the polymer was isolated as the zinc salt by steam stripping. The sulphonated copolymer was vacuum dried for 24 h at 80°C. The sulphur content of the polymer was determined by Dietert sulphur analysis and was used to calculate the sulphonate content. Again, in this specific example, the sulphonate copolymer containing 2.4 mol% sulphonate moieties, i.e. approximately 2.4 styrene monomer units out of 100 monomer units were modified through the sulphonation reaction. *Tables 1* and *2* detail the specific characterization data on the ampholytic ionomers used throughout this study.

The polymer solutions were prepared in stoppered volumetric flasks using conventional magnetic stirrers for

Table 2 Composition of the styrene-based ampholytic ionomers[a] (variable counterion)

Designation-counterion	4-Vinylpyridine level (mol %)	Sulphonation level (mol %)
110	2.1	0.0
110-H	2.1	1.8
110-Zn	2.1	1.8
110-Ni	2.1	1.8
110-Cd	2.1	1.8
110-Na	2.1	1.8

[a] Viscosity average molecular weight is $519\,000\,\mathrm{g\,mol^{-1}}$

Table 1 Composition of the styrene-based ampholytic ionomers (zinc counterion)

Designation	Nitrogen content (wt%)	Sulphur content (wt%)	4VP level (mol %)	Sulphonation level (mol %)	Molecular weight[a] (10^{-3})
44B	0.65	0.72	4.8	2.4	519
44A	1.2	0.59	9.0	2.0	590
106C	0.34	0.57	2.5	1.9	698
48CS	0.23	0.45	1.7	1.5	716

[a] Based on the viscosity average of the nonionic copolymer in xylene

agitation. The polymer was weighed into the flask to an accuracy of 1.0 mg. The solvents used in this study were xylene with and without alcohol (normally methanol or oleyl alcohol).

Reduced viscosities at concentrations typically less than $0.5 \, g \, dl^{-1}$ were measured with a standard Ubbelohde capillary viscometer placed into a temperature controlled water bath (25°C). The solutions were temperature equilibrated for approximately 15 min prior to viscosity measurement. The measurement was repeated several times (typically three measurements) until reproducible flow rate times were obtained.

All viscosity measurements pertaining to solutions having concentrations greater than $0.5 \, g \, dl^{-1}$ were performed on a Brookfield viscometer (Model LVT) utilizing a UL adapter for low viscosity solutions and various size spindles for the higher viscosity measurements. Unless otherwise specified, the viscosity values reported correspond to 12 RPM at 25°C.

Shear rate dependent measurements were performed on a Haake Rotovisco rotational viscometer. The viscosity at low shear rates (up to $300 \, s^{-1}$) and high shear rates (up to $25 \, 000 \, s^{-1}$) were measured on the CV 100 model and M500 model, respectively, using couette cells with the appropriate gaps.

RESULTS AND DISCUSSION

Solubility behaviour

The solubility characteristics in xylene of several representative ampholytic ionomers are presented in *Table 3*. As a point for comparison, data on the solubility of several sulphonated polystyrene (SPS) ionomers are included. A close examination of the data confirms that the 4-vinylpyridine moiety situated along the chain backbone has a very favourable influence on the solubility behaviour. For instance, even at relatively low sulphonate levels, it is not possible to solubilize the SPS ionomers in a single component solvent without 4VP being present. As described earlier, a greater than stoichiometric amount of a polar cosolvent, such as alcohols or amines, are necessary for complete dissolution of the SPS ionomers[5]. Therefore, in some respects, the 4VP is acting as a chemically bounded cosolvent; at least with regard to the sodium neutralized 'polyampholyte' where strong dipolar interactions control solution properties. It is interesting to note that at higher sulphonation levels, the sodium neutralized materials are insoluble unless significantly higher levels of 4VP are incorporated into the ionomer structure.

Turning our attention to the zinc neutralized polyampholyte, we observe that solubility occurs over a broad sulphonation range only if the level of 4VP is

Table 3 Solubility characteristics in xylene of zinc and sodium neutralized sulphonated polystyrene (SPS) ionomers and their ampholytic ionomer analogues

Polymer	Sulphonation level (mol %)	4VP level (mol %)	Solubility[a]
SPS(Na)	1.7	0.0	insoluble
Na-'polyampholyte'	1.6	2.1	soluble
SPS(Zn)	2.6	0.0	insoluble
Zn-polyampholyte	2.4	4.8	soluble

[a] Solubility observations are based on 0.5 g polymer/100 ml solvent under vigorous agitation at room temperature

approximately equal to or larger than the sulphonate level on a molar basis. Interestingly, it is known[22] that the average stoichiometry of zinc–poly(vinylpyridine) complexes are similar to the known crystalline monomeric vinylpyridine complexes—with three exceptions. These former complexes were highly crosslinked by the transition metal, no trace of crystallinity was observed, and no polymer complex of stoichiometry approximating that of the monomer complex (four coordinated vinylpyridines) was obtained. The average stoichiometry of the zinc–poly(vinylpyridine) complex was two pyridine rings coordinated to the transition metal. It is quite unlikely for the ampholytic ionomers to possess this particular stoichiometry due to the constraints imposed on the zinc atom by the sulphonate group. That is, since the sulphonate group occupies one coordination site, only one vinylpyridine unit can interact in a favourable manner. However, it may be still difficult for all the groups to coordinate with each other due to the steric constraints imposed on these groups by the chain itself. This effect should become increasingly prominent at low, but approximately equivalent molar ratios of interacting groups. As we will presently observe, this effect can have a pronounced effect on solution properties. This behaviour is in marked contrast to the nontransition metal neutralized ionomers where significantly higher 4VP concentrations are required for solubilization.

Throughout the remainder of this paper, we will focus our attention on the behaviour of the transition metal ion neutralized polyampholytes and show how rather modest changes in polymer structure brings about dramatic changes in solution rheology.

Dilute solution behaviour

There is clearly a large number of structural variations that can be synthesized with styrene, 4-vinylpyridine and styrene sulphonate. Additional variability arises since the latter monomer can be modified via association with any of the transition metal ions. In this work the level of sulphonation remains relatively invariant (1.5–3 mol%), but the level of 4VP is varied up to about 10 mol% (see *Table 1*). Within this range of sulphonation and base level, the more general solution characteristics of these materials can be observed. That is, the influence of both intra- and intermolecular associations via ionic interactions appear to have the most pronounced influence on the solution rheology. A typical example of these effects are presented in *Figure 1* where the reduced viscosity of three polyampholytes and their nonionic precursors are plotted against polymer concentration in a single component organic solvent. The polymer concentration was varied so as to span both the dilute and semidilute regimes. Even though the viscosity average molecular weight is not a constant (see *Table 1*), marked differences are noted in a direct comparison of the nonionic copolymer with its ampholytic ionomer counterpart.

In the dilute solution, defined in qualitative terms as the concentration at which the ampholytic ionomer has a reduced viscosity below its nonionic precursor, the hydrodynamic volume of the polyampholyte is reduced to a more significant extent at the lower levels of 4VP. Contrary to expectations, the polyampholyte containing 9.0 mol% 4VP has an intrinsic viscosity in close
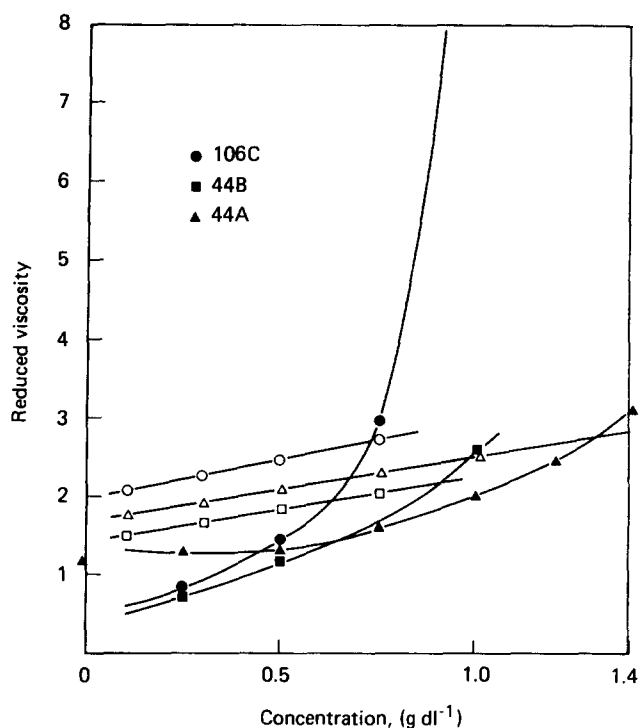
Figure 1 Reduced viscosity–polymer concentration behaviour of three ampholytic ionomers (denoted by solid symbols) and their corresponding nonionic parents (denoted by the identical, but open symbols)

approximation to its nonionic precursor. Furthermore, the polyampholyte containing the least amount of 4VP approaches more rapidly the chain overlap region and subsequently forms a very viscous, gel-like fluid at markedly lower polymer levels. Although the molecular weights of these materials differ by about 35%, the controlling molecular parameter, to a first approximation, is the 4VP level. These particular viscometric measurements (and quasielastic light scattering measurements) confirm that as the level of the basic moiety is increased, the hydrodynamic volume of the polyampholyte is observed to closely approach its nonionic counterpart. These results parallel previous observations of sulphonated ionomers in dilute solution at low 4VP levels. That is, the hydrodynamic volume monotonically decreases with increasing levels of sulphonation. This is a rather common structural feature of the sulphonated ionomers in nonpolar solvents[7,9]. It may indicate that these intraionic linkages are not related in a stoichiometrically specific fashion and, therefore, substantially more than two ionic groups can participate in a linkage point. This would qualitatively account for the continual decrease in the ionomer chain dimensions.

Contrary to these observations more specific structures are expected to be produced in the ampholytes since the zinc counterion interacts with essentially one 4VP moiety. That is, it is highly probable that as the level of 4VP is increased (and sulphonation level remains invariant), nearest neighbours interactions will become increasingly dominant. In turn, increasingly fewer of the segments of the coil will become perturbed resulting in a coil size which increasingly approaches the nonionic copolymer. *Figure 2* shows these effects on the coil dimension in highly schematic form. In qualitative terms, the closer the interacting groups become, the smaller the 'loops' become and as a consequence, will have a diminishing influence on

chain dimensions. Clearly, these effects distinguish the ampholytic ionomers from the homogeneously-charged sulphonated ionomers.

As the polyampholyte concentration is increased, the data show that, contrary to expectations, the most expanded coil requires a higher concentration to approach the equivalent reduced viscosity as its nonionic counterpart. Again, this result is in striking contrast with the sulphonated ionomers[7,9], but it is undoubtedly due to the inability of all zinc ions to interact in a 1:1 stoichiometric fashion with a 4VP group. As a result, the remaining unassociated groups are able to intermolecularly interact, causing large changes in the reduced viscosity as is observed. These results (and other measurements to be published in the near furture) do show that minor modifications in structure produce large changes in rheological properties.

At this point it is instructive to detail the strength of these intra- and intermolecular ionic associations since these results are useful in showing the relative ease to which the ratio of intra–interionic associations can be manipulated. Typical results are shown in *Figure 3* where the reduced viscosity of a polyampholyte (48CS) and its nonionic counterpart is compared in both xylene and xylene/alcohol solutions. The polymer concentration was again varied so as to span the dilute and semidilute solution regimes. Not surprisingly, the nonionic polymer is unaffected by the rather low level of a 'weak' alcohol. In contrast, the alcohol weakens the intramolecular associations (i.e. at concentrations below the crossover point) allowing the coil dimensions to expand and approach the intrinsic viscosity of the nonionic polymer. However, since intermolecular associations dominate solution behaviour above the crossover point resulting in an increase in the 'apparent' molecular weight of the polymer; a decrease in solution viscosity is observed as the alcohol level is increased. These results parallel previous detailed measurements in mixed solvents by Lundberg and Makowski[5]. In their studies, temperature and low shear rate measurements ($<100\,\mathrm{s}^{-1}$) data were also presented. Although temperature produced dramatic changes in viscosity, the shear rate data appeared Newtonian. However, as we will see, a distinguishing characteristic of these associating polymers, in general, is the ability to modify the relative population of the intra- to intermolecular associations via changes in shear rate. In order to observe these effects, the shear rate range was extended up to $25\,000\,\mathrm{s}^{-1}$.
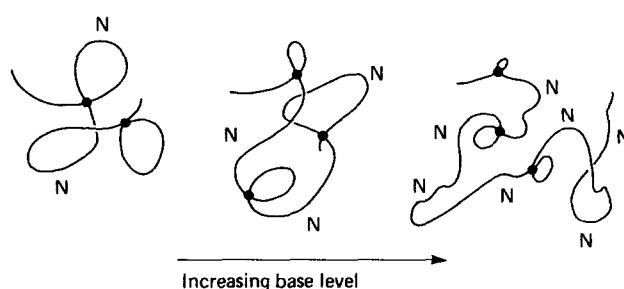

Increasing base level

Figure 2 Highly schematic drawing showing the influence of the base (4-vinylpyridine) concentration on the coil dimensions of polyampholytes in a dilute solution. It is assumed that the sulphonation level is a constant. Each (●) represents a single zinc ion (Z)/4-vinylpyridine (N) association
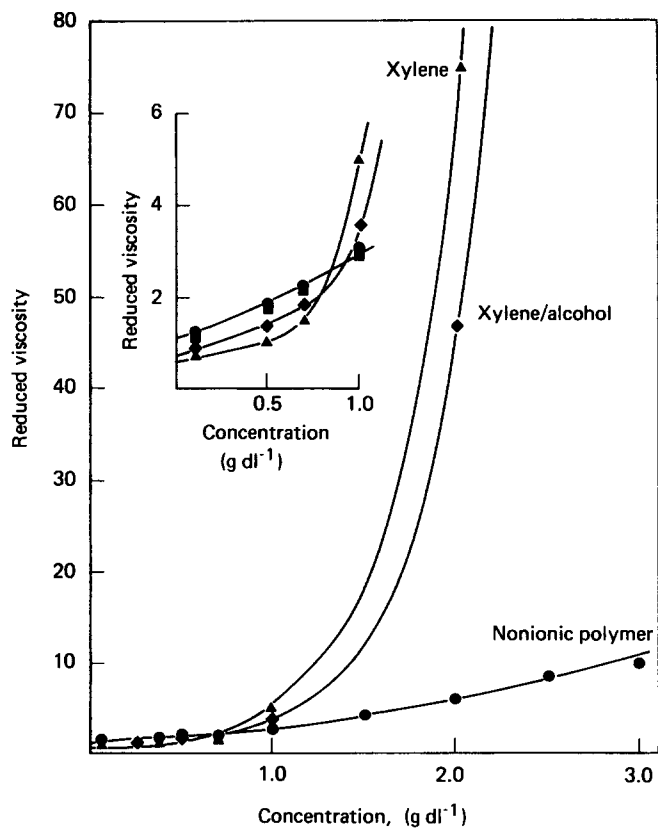
Figure 3 Reduced viscosity plotted against polymer concentration of a polyampholyte (48CS) [and its nonionic counterpart in xylene] in xylene/alcohol (1% oleyl alcohol by weight) solutions. The insert shows the reduced viscosity–concentration behaviour below the point where the polyampholyte curves meet the nonionic polymer data, i.e. the dilute solution regime. The addition of alcohol to the nonionic copolymer does not affect the reduced viscosity at this alcohol level

'stronger' alcohol is used (for example, methanol) at somewhat higher concentrations. A larger concentration of a 'weaker' alcohol is also effective (see *Figure 5*). Therefore, these dilute solutions results confirm that the shear thickening phenomena is primarily due to the ability of a shear field to modify and subsequently increase the ratio of inter- to intramolecular ionic associations. As a result, these increased associations enhance the apparent molecular weight of the ampholytic ionomer and viscosity. Apparently, the zinc ion-4VP interactions are sufficiently strong and numerous that a gel-like state is achieved. Furthermore, it is not surprising that since the strength of these associations are weakened by alcohol,
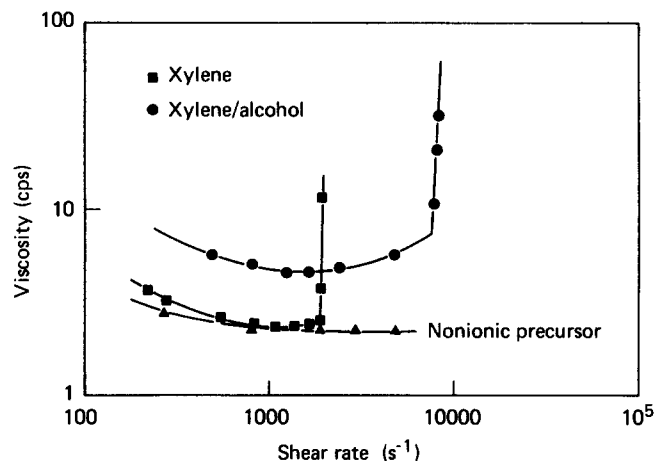

Figure 4 Viscosity–shear rate curves of xylene and xylene–alcohol (1% oleyl alcohol by weight) solutions containing the polyampholyte (48CS) in the vicinity of the overlap concentration, g dl^{-1} (see *Figure 3* for further details)
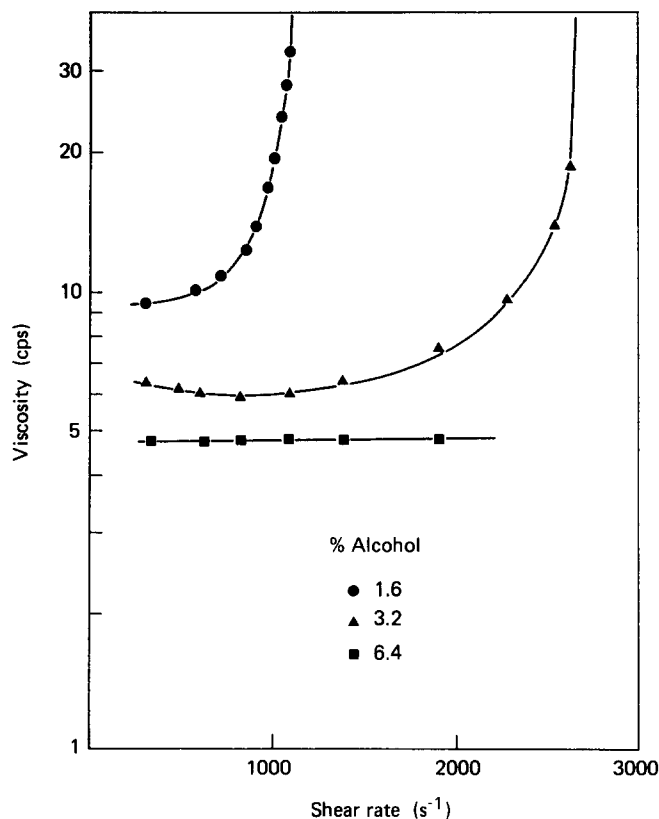
Viscosity–shear rate profiles

Figure 4 presents typical viscosity–shear rate data on solutions containing the polyampholyte 48CS. Even though the sulphonation reaction does not change the molecular weight of these polyampholytes [as indicated by the extrapolation of the reduced viscosity curves to zero concentration at modest levels of alcohol (not shown)], it is quite clear that the ionic associations have a marked influence on the shear rate behaviour. While the nonionic precursor behaves in the anticipated shear thinning manner, the polyampholyte in xylene shows a .shear thinning regime, followed by a modest shear thickening and ultimately reaching a gel-like state. One distinguishing characteristic of this system is the complete reversibility of this phenomena. Interestingly, the addition of alcohol produces a two-fold increase in viscosity in the shear thinning region. This is followed by a broadened shear thickening region, again leading to a gel-like state at higher shear rates.

In this concentration range, the polymer coil, for the most part, can be assumed to be individualized entities with relatively little intermolecular interactions capable of influencing the solution properties. Therefore, as detailed earlier, it is not surprising that the viscosity rises with the addition of a polar cosolvent. Moreover, the alcohol does not completely prohibit the ability of these systems to shear thicken. Experiments have shown that shear thinning will occur over the entire shear rate range if a

Figure 5 Viscosity–shear rate behaviour of the polyampholyte (48CS) in a number of xylene–oleyl alcohol solutions. Polymer concentration is 1 g dl^{-1}

higher shear rates, in general, are required to achieve the highly viscous, gel state.

Further clarification of this shear thickening phenomena is possible by increasing the distance between associating groups via simple dilution. These results are shown in *Figure 6*. The viscosity–shear rate data confirm that significantly higher shear rates are necessary at lower polymer concentration to achieve the shear thickening region. That is, the highly individualized polyampholyte coils needed to be more highly distorted for the interionic linkages to be effective. This can only be achieved through higher shear rates, as observed.

As anticipated, decreasing the distance between coils by advancing the polymer concentration into the semidilute region produces a shear thickening region at rather low shear rates (*Figure 7*) in xylene. That is, only modest distortions of the coil dimensions are required to markedly increase the level of the intermolecular associations. Interestingly, addition of alcohol to these solutions reduces the overall viscosity of the solution, but again does substantially prohibit the ability of the ampholytic ionomer from shear thickening. This lowering of the solution viscosity in the semidilute region parallels the results given in *Figure 3*.

It should be noted that this is a rather atypical rheological behaviour of macromolecules in solution, and we believe these are the first such observations in a single component solvent containing a lightly sulphonated
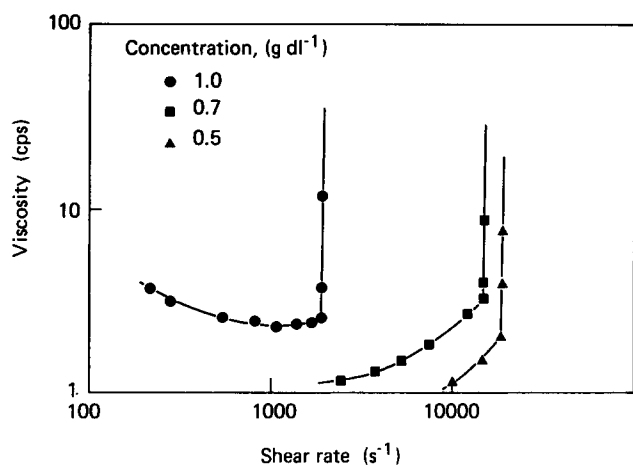
Figure 6 Viscosity–shear rate behaviour as a function of polymer concentration (48CS) in xylene solutions
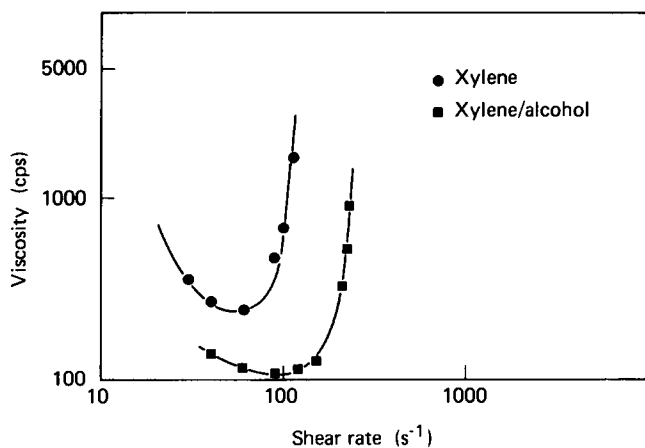
Figure 7 Viscosity–shear rate profiles of the polyampholyte (48CS) in xylene and xylene–alcohol (1% oleyl alcohol by weight) solutions above the overlap concentration, 2 g dl^{-1} (see *Figure 3* for further details)

ampholytic ionomer. It is anticipated, however, that these results are quite general with regard to ionically associating polymers, although shear thickening and other time dependent solution properties have been investigated in a number of other solution systems. These studies have included polymers in very viscous organic solvents[23-29] (examples: polybutene in polybutene oils and polystyrene in Aroclor), aqueous solvents (examples: polymethylacrylic acid and poly(vinyl alcohol)–borate complexes) and nonaqueous low viscosity solvents[32-33] (examples: polyisobutylene in tetraline solutions and polymethylmethacrylate in cyclohexanone). In most of these studies, specific molecular mechanisms were advanced to explain the occurrence of the time and gradient dependent shear thickening phenomena. Included are the large scale network type associations through the conversion of intra- and intermolecular bonding as observed in the ampholytic ionomers.

Peterlin[25] has theoretically predicted that shear thickening can arise even with nonpolar macromolecules in completely nonpolar solvents. According to the theory, the randomly coiled chains will collide and interpenetrate each other more often and effectively when the shear gradient is higher and the coils are of high molecular weight. The resultant entanglements will have a significantly enhanced lifetime if the viscosity of the solvent is increased. Therefore, if the entanglement lifetime is sufficiently large, the growth of large entangled aggregates will pursue. These aggregates can eventually lead to large network formation which gradually enhances the viscosity of the solution. Although the resistance of the coil to rapid changes in shape, i.e. the internal viscosity, is rather high in low viscosity fluids, the viscous forces in a high viscosity solvent can overcome the chain inertia producing facile deformation of the chain. Thus, the optimum conditions for finding the 'upturn effect' are low shear gradients, high molecular weight polymers and high viscosity solvents. The low shear gradients are necessary in order to prevent rapid degradation of the high molecular weight polymer. In marked contrast to this behaviour, it is apparent that even though the internal viscosity of the polyampholytes in dilute solution is undoubtedly higher than its nonionic counterpart in nonpolar solvents, the shear gradient is still able to effectively couple with the chain resulting in an increase in interionic linkages. This is due to the unique ability of these charged macromolecules to effectively interact with each other under shear in even low viscosity solvents producing substantial increases in their effective molecular weight. In turn, the frictional forces of the solvent will become more efficiently 'coupled' with the chains producing progressively larger chain extensions. As a result, more intramolecular associations will become available for interacting with other polymer chains. The production of the first few initial intermolecular associations are crucial for effective shear thickening; that is, these associations should be both strong, possess lifetimes longer than the relaxation time of the polymer coil, and are not inhibited from forming intermolecular associations through steric hinderance effects within the polymer structure itself.

Modification of polyampholyte structure—4VP level

Figures 8–10 show the viscosity–shear rate data on a series of polyampholytes in xylene where the
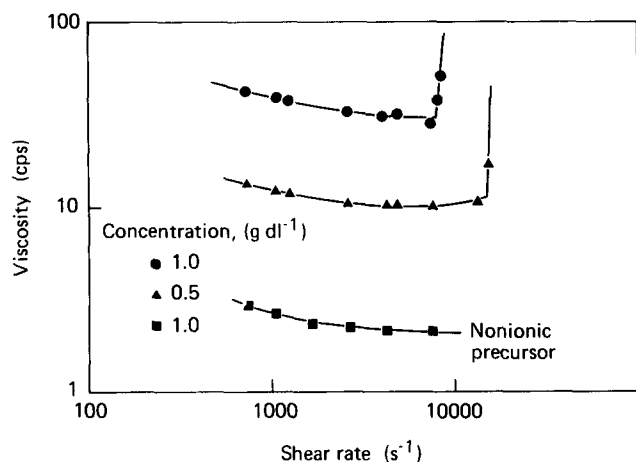
Figure 8 Viscosity–shear rate behaviour as a function of polyampholyte (106C) concentration in xylene solutions. 4-vinylpyridine level is 2.5 mol%
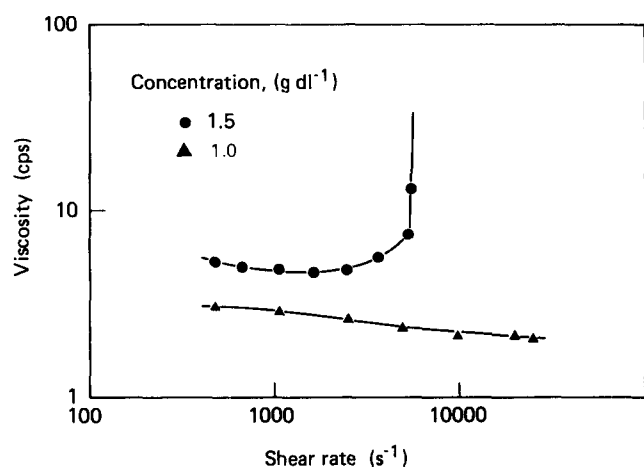

Figure 9 Viscosity–shear rate behaviour as a function of polyampholyte (44B) concentration in xylene solutions. 4-vinylpyridine level is 4.8 mol%

sulphonation level remains relatively invariant, while the 4VP level is varied. (The reader is again referred to *Figure 1* for the reduced viscosity—concentration data of these solutions.) *Figure 8* shows the anticipated shear rate behaviour of these ampholytic ionomers. At low shear gradients, the typical thinning characteristics are observed, followed by the dramatic viscosity upturn into a highly viscous state. Again shear thickening occurs below (but near the crossover point) and, of course, above the crossover point. However, approximately doubling the 4NVP level inhibits the thickening ability until concentrations well above the crossover point is reached (*Figure 9*). Complete elimination of shear thickening is noted at even higher base levels over the shear rate range studied (*Figure 10*). However, we do anticipate that shear thickening behaviour will be observed at significantly higher shear gradients in these latter solutions. In any event, it is apparent that the low viscosity fluid can effectively perturb the hydrodynamic volume of the polyampholyte to such an extent as to allow for the formation of interionic associations. As the distance between the intra-associated groups is decreased, this 'coupling' between the shear gradient and polymer chain is also decreased. In quite qualitative terms, this effect could be due, in part, to the inability of the gradient to effectively 'open' up increasingly 'smaller loops' (see

Figure 2) until much higher shear rates are reached. In the near future, we will report on the rheological properties of polyampholytes containing higher 4VP levels over a broader shear rate range.

Counterion effects

In the previous discussion, we focused on the ampholytic ionomers containing the zinc counterion for the most part. It is of interest, however, to examine the effect of counterion structure since it is expected that the strength of the counterion-4VP linkage will have a marked effect on the rheological properties. *Table 2* lists a number of these polyampholytes used in this study. These materials were formed from the identical sulphonation synthesis route and subsequently small aliquots were neutralized with the appropriate metal acetate. *Figure 11* shows some of the preliminary viscosity–shear rate profiles in xylene at a polymer concentration above the overlap concentration. Although the interpretation of these results is complicated by the level of intraionic
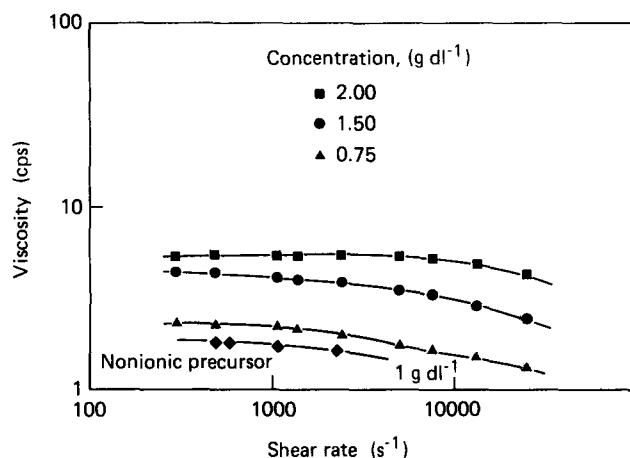

Figure 10 Viscosity–shear rate behaviour as a function of polyampholyte (44A) concentration in xylene solutions. 4-vinylpyridine level is 9.0 mol%
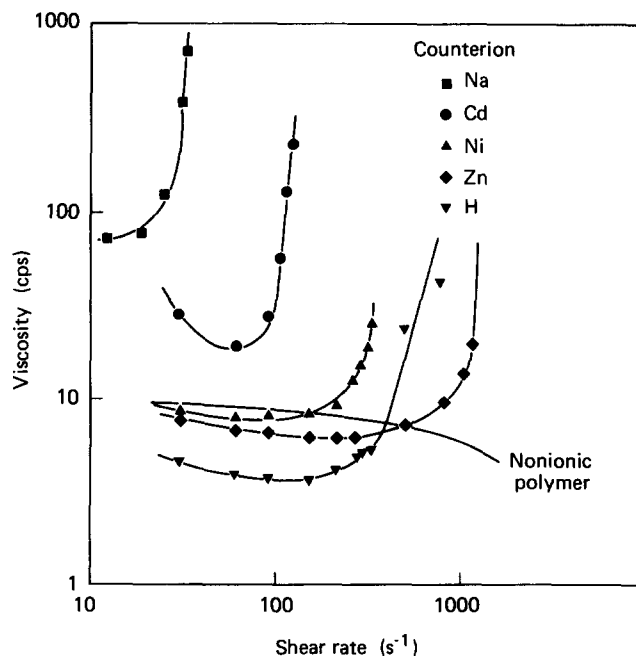

Figure 11 Viscosity as a function of shear rate of xylene solutions containing polyampholytes (110) associated with a variety of counterions. Polymer concentration is 1 g dl^{-1}

linkages, it is still possible to observe the specific influence of the counterion structure on properties in a qualitative manner. As the strength of the 4VP-counterion associations becomes more intense (Na < Cd < Ni < Zn < H), it appears that the intrinsic viscosity is moderately reduced and that higher polymer concentrations are necessary to crossover the reduced viscosity–concentration curve of the nonionic parent. However, the shear thickening behaviour is found to be directly related to the strength of the association. As expected, temperature has the least effect on polyampholyte solution properties if the strength of the association is large (see *Figure 12*). Apparently there is little change in the level of intra-interionic associations in the polymer solution system even up to temperatures approaching 120°C.

General considerations on shear thickening in dilute associating polymer systems

It is interesting to note that the shear thickening phenomena and other time dependent rheological properties occur not only in polymer solutions but also in colloidal solutions[34-36]. In a majority of these latter studies, the changes in solution properties were related to a change in the state of particle aggregation as the shear gradient is increased. For example, Gillespie predicted[36] that this phenomena in colloidal systems is due to enhanced structural links which tend to increase with shear. As a result, the viscosity will increase if the lifetime of the link is longer than the average relaxation time of the system. Extension of this theory[36] to associating polymers, i.e. polyampholytes, details in a somewhat quantitative manner, the shear thickening phenomena
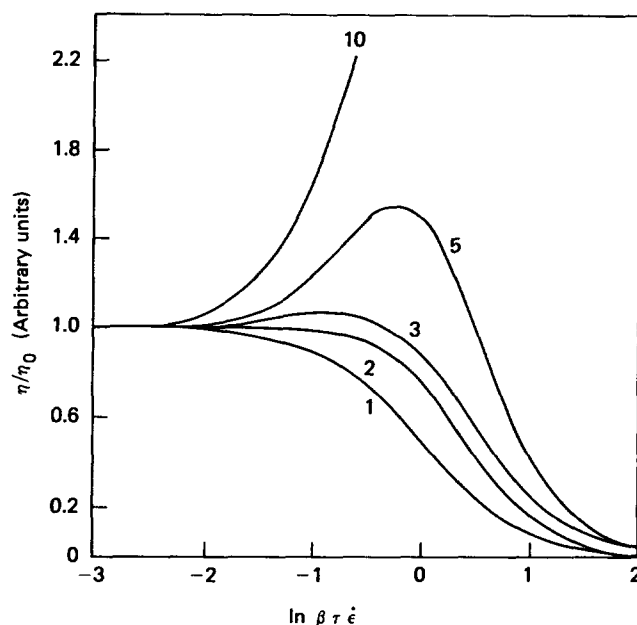
Figure 13 Graph of equation (1) from text. Each curve represents an increasing level of intermolecular associations, C_A

described in this paper. Equation (1) summarizes the analysis

$$\frac{\eta}{\eta_0} \sim \frac{1 + C_A(\beta\tau\dot{\varepsilon})}{(1 + \beta\tau\dot{\varepsilon})} \quad (1)$$

η is the viscosity at a specific shear rate $\dot{\varepsilon}$, η_0 is the viscosity extrapolated to zero shear rate, C_A is the number of intermolecular associations per molecule, β is the rate constant for the shear induced intermolecular association rupture, and τ is the average relaxation time of the coil. In a dilute solution, τ is assumed to be related to a Zimm-type[38] relaxation mode. However, this relaxation mode will, undoubtedly, be perturbed by the strong intramolecular associations. As of the present time, the exact nature of these effects are largely unknown, but experiments are proceeding (i.e. pure elongation flow-birefringence measurements) to clarify these specific effects on the internal dynamics of these polymers.

Figure 13 shows a plot of equation (1) with each curve corresponding to a different value of C_A. It is immediately apparent that shear thickening begins to occur after approximately two intermolecular associations are formed. Moreover, the extent of shear thickening is markedly enhanced as the level of these associations are increased. Furthermore, after about seven such intermolecular links form, the viscosity begins to rise in an exponential manner which parallels in some ways the previous experimental results.

A detailed comparison between the experimental and theoretical results are complicated by several unknown quantities: that is the exact number, strength and lifetime of these ionic associations. However, this theory still provides some guidelines on the effect of polymer structure on the shear thickening phenomena. For example, if the level or strength of the intermolecular associations are weakened to such an extent that the lifetime of these links are reduced, a maximum in the shear thickening curve should result as opposed to an exponential rise to a gel-like state. Experimentally this effect can be observed in the SPS ionomer solutions.
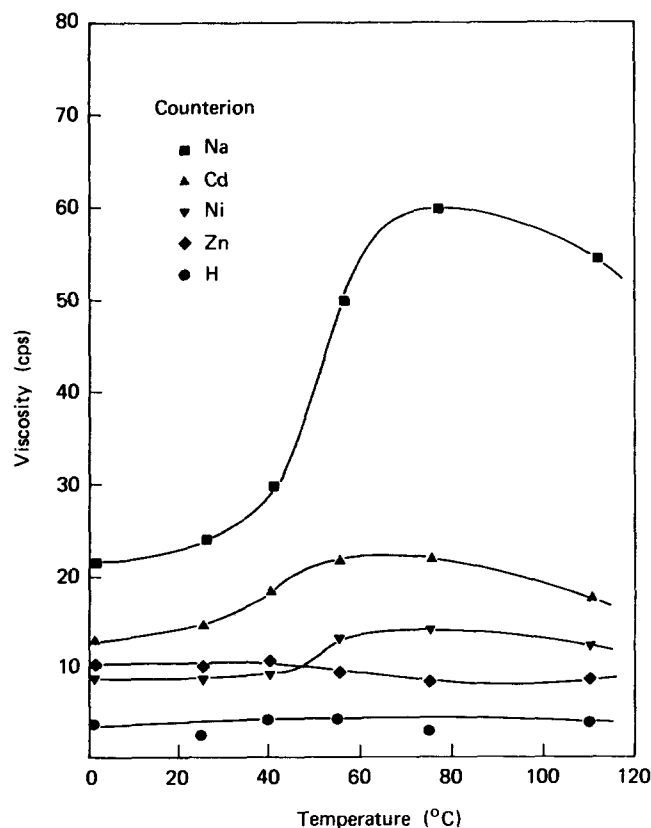
Figure 12 Viscosity as a function of temperature of xylene solutions containing a polyampholyte (110) associated with a variety of counterions. Polymer concentration is 1 g dl^{-1}. Shear rate: 1 s^{-1}

Figure 14 shows the viscosity-shear rate curves of a zinc neutralized sulphonated polystyrene (in xylene/alcohol solutions) in which the level of sulphonation closely approximates the sulphonate in the ampholytic ionomers. Only after the polymer concentration is above about 2.0 g dl^{-1} does the anticipated exponential rise in the viscosity occur. This concentration is above the overlap region which could be indicative that the associations in these materials are weaker than those found in the polyampholytes due, undoubtedly, to the presence of the polar cosolvent.

Further lowering of the sulphonation level at the identical alcohol concentration results in a maximum in the viscosity-shear rate curve (see *Figure 15*) which is in general agreement with equation (1).

Experiments are presently being carried out on 'model' ionomers (monodispersed sulphonated polystyrenes) in polar and nonpolar solvents in order to further clarify the interrelationship between molecular structure and their physical properties, such as the shear thickening phenomena.

Finally, extensive theoretical work[39] concerned with the mechanism of chain extension in an elongational flow field has shown that at critical strain rate ($\dot{\varepsilon}_c$), the polymer chain is rapidly extended. This relationship is given by:

$$\dot{\varepsilon}_c \tau \approx 1 \qquad (2)$$

Substitution of equation (2) into equation (1) predicts that the controlling factors in the rheological properties at full chain extension are the number and the rate constant for shear induced rupture of the intermolecular associations, i.e.

$$\frac{\eta}{\eta_0} \sim \frac{1 + C_A \beta}{(1 + \beta)^2} \qquad (3)$$

This result is quite reasonable since at full chain extension, the number of intermolecular links are at their maximum
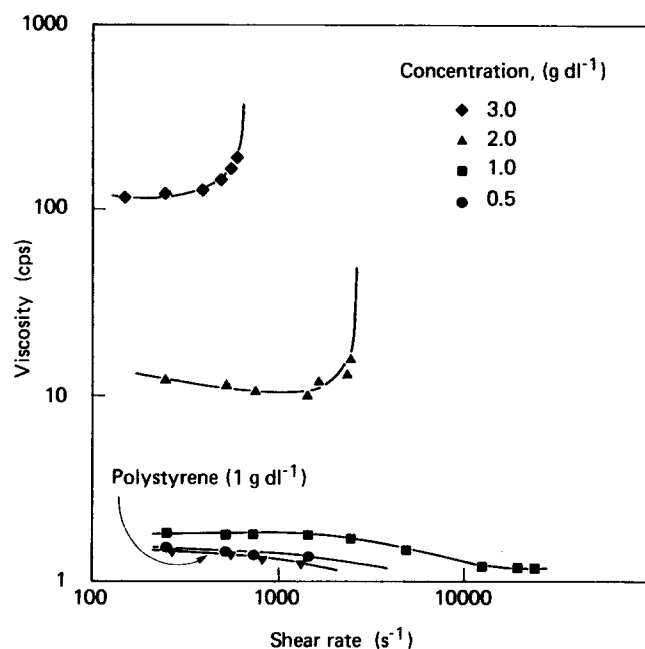

Figure 14   Viscosity as a function of shear rate of xylene–alcohol (4% by weight oleyl alcohol) solutions containing a 2.6 mol% zinc neutralized sulphonated polystyrene and its nonionic counterpart
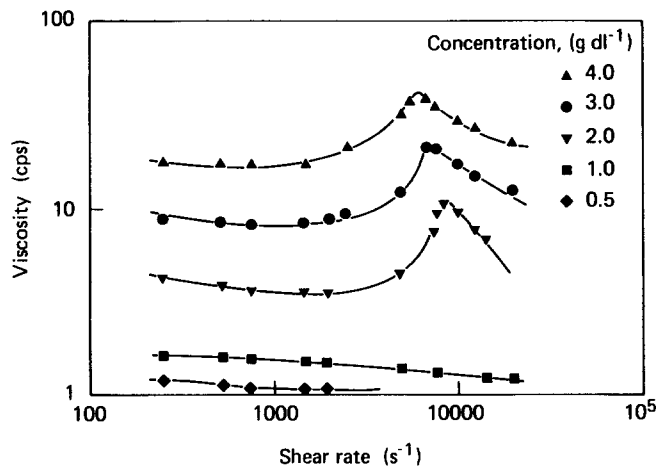

Figure 15   Viscosity as a function of shear rate of xylene–alcohol (4% by weight oleyl alcohol) solutions containing a 0.95 mol% zinc neutralized sulphonated polystyrene

extent possible and only their number and their corresponding average lifetime should control rheological properties. Moreover, the theory predicts that an increase in the solvent viscosity (η_s) and/or molecular weight ($M^{1.5}$) should have a favourable effect on the magnitude of the shear thickening phenomena. In general, temperature will decrease these interesting rheological characteristics. These results parallel both the experimental results and theoretical predictions of Peterlin *et al.*[25] and the recent theoretical treatment of the shear thickening phenomena by Witten and Cohen[40]. The implications and derivation of equation (1) will be published at a later date[37].

CONCLUSION

The rheological properties of dilute and semidilute solutions containing ampholytic ionomers were investigated. These polyampholytes are composed of styrene (major component), transition metal neutralized sulphonated styrene and 4-vinylpyridine. The viscometric properties were measured since these measurements are sensitive to changes in both the hydrodynamic volume of the individual chains in dilute solutions and the effects of the degree of association between interacting chains in the semidilute region. The results show that in dilute solution, the metal ions preferentially interact with 4VP in an approximately one-to-one stoichiometric manner. Increasing the distance between these two groups prohibits complete coordination. As a result, the reduced viscosity–concentration behaviour is markedly different than if higher levels of 4VP are present along the chain. Therefore, the shear thickening behaviour and other rheological properties can be manipulated through these relatively modest structural changes. Our results further show that the rheological behaviour are markedly influenced by changing polymer concentration, alcohol level and the nature of the counterion associated with the sulphonate group.

Finally, we note that it is possible to understand in a semi-quantitative manner, the shear thickening phenomena associated with the sulphonated ionomers and the ampholytic ionomers. In a shear field the initial intramolecular ionic associations are loosened to such a degree as to allow for the formation of intermolecular ionic links. Consequently, the apparent molecular weight

is increased and the viscosity correspondingly rises. A controlling factor, as indicated in the analysis, is the link lifetime. If the link lifetime is substantial, the exponential rise in visocsity is observed; however, if the link lifetime is lessened, i.e. attractive strength is reduced, then the shear gradient will eventually break the association. A maximum in the viscosity–shear rate curve will result. These conclusions are in quantitative agreement with the rheological measurements. Furthermore these results are useful as a basis for interpreting similar measurements on 'model' associating polymers under a variety of experimental conditions where the so-called 'universal' solution characteristics may be observed.

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