Synthesis, solution viscosity and interfacial properties of random copolymers spanning a broad range of anionic character

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The synthesis, solution rheology and surface properties of a family of copolymers composed of styrene and sodium-2-acrylamido-2-methylpropane sulphonate (Na-AMPS) are described. These copolymers were prepared containing a broad range of sulphonate groups in order to explore the effect that these anionic groups have on solution properties in solvents with widely differing dielectric constants. In non-polar solvents, ionomer behaviour is observed where ion-pair interactions and their related associative effects dominate solution rheology. Typically, copolymers containing less than about 10 mol % anionic charge are soluble in these particular solvents. However, improved solubilization occurs with solvents of higher dielectric constant, as indicated by the pronounced polyelectrolyte effect. The specific properties of these copolymers are typical of polyelectrolytes in general. 'Bridging' these two general classes of phenomena (and polymeric materials), i.e. associative and polyelectrolyte, is the pronounced surface activity in water (for example) of those random copolymers of 'intermediate' compositions. Specifically, copolymers composed of approximately 1:1 molar ratio of lipophilic monomer (styrene) to hydrophilic monomer (Na-AMPS) exhibit this behaviour. Therefore, a distinguishing characteristic of these copolymers is their ability to control the rheology and surface properties of a large variety of fluids simply by modifying the ratio of non-ionic to ionic monomer units within the structure of the polymer chain.

(Keywords: random copolymer; anionic groups; associative behaviour; polyelectrolyte effect; surface activity)

INTRODUCTION

It is widely recognized that polymeric materials are especially effective in controlling the rheology of fluid systems. Rather broad control is achievable due to the long contour length of the polymer chains and their unique ability to entangle with each other. This is especially valid if the degree of polymerization is high. In these instances, relatively low levels of polymer are required to establish the appropriate rheological characteristics.

In recent years low levels of ionic groups have been introduced into a variety of polymer chains, resulting in substantial change in non-aqueous solution properties[1-5]. The results of these studies clearly show that these ionic moieties establish a degree of control over fluid properties not easily achieved with their non-ionic precursors or with other non-ionically interacting chains. These property changes are due to the ability of these ionic groups to form microphase-separated regions containing either multiplets or higher-order aggregates of the ionic materials (i.e. low dielectric bulk systems)[6,7] or interionic associations in dilute and semi-dilute non-polar solutions. A direct consequence of these strong interchain interactions is, for example, exceptional thickening behaviour at or above the chain overlap concentration as compared to its non-associating counterpart and a marked viscosity increase within specific shear rate ranges.

In aqueous solutions, however, solubility considerations dictate either that the chain backbone itself is water-soluble or that all monomer units of a wholly hydrocarbon-solvent-soluble chain are functionalized with ionic units, i.e. polyelectrolytes. These latter materials are extremely useful in a variety of applications owing, in part, to their ability to viscosify effectively low-ionic-strength aqueous solutions at low polymer concentrations. It is well known[8] that at these low polymer levels an upturn in the reduced viscosity is observed which is generally attributed to the ionization of the ionic groups attached to the chain backbone. Repulsive interactions force the chain to expand, causing the rise in viscosity at low dilutions.

In this paper, we report our results on the synthesis, solubility, rheology and surface properties of copolymers of styrene with sodium-2-acrylamido-2-methylpropane sulphonate (STAMPS copolymers) spanning a very broad range of anionic character. Typically, the sulphonation range is between 0 and 70 mol% sulphonate content. Furthermore, the purpose of this work is to 'connect' the well known rheological properties of water-soluble ion-containing polyelectrolytes with its low-charge counterparts (ionomers) which, as previously noted, are soluble in both non-polar and polar non-aqueous solvents. It is clearly shown that solubility, rheology and, interestingly, surface properties are markedly different than the above-mentioned polymers within specific sulphonation levels. Moreover, the data show that these anionically charged copolymers permit a wide degree of control over the rheological properties in solution not readily attained in non-ionic polymeric materials.

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EXPERIMENTAL

The copolymers of styrene with sodium-2-acrylamido-2-methylpropane sulphonate (Na-AMPS) (***Figure 1***) were prepared by direct polymerization of the styrene and Na-AMPS monomers (*M*) with a free-radical initiator (*I*) in dimethylformamide. The value of $M/I^{1/2}$ is 10.0 in all the copolymerizations described here. A representative example of a polymerization is described as follows.

A solution of styrene and Na-AMPS is dimethylformamide (DMF) was stirred for approximately 2 h under an argon gas blanket at room temperature. Typical monomer concentrations were 30.0 g (0.288 moles) of styrene, 4.44 g (0.015 moles) Na-AMPS dissolved in 34.44 g DMF. The initiator, azobisisobutyronitrile (AIBN), was subsequently added (4.37 g, 0.026 moles) and the solution temperature adjusted to 55°C. The temperature was controlled continually throughout the polymerization (i.e. 18–24 h). In all cases, the temperature did not exceed 60°C. Also the solution was stirred continually during the reaction and kept flooded with dried argon gas. Subsequently, the copolymer was precipitated from DMF with hot isopropanol (35–40°C), filtered at elevated temperature and dried in a vacuum oven at 25°C for 24 h. The conversion was 80.1%. Sulphur content was determined by Dietert sulphur analysis and was used to calculate the sulphonate or Na-AMPS content. In this specific procedure the sulphonate content was 4.1 mol% (1.16 wt% sulphur). The compositions of the STAMPS copolymers described in this study are presented in *Table 1*.

The AMPS free acid monomer was kindly supplied by the Lubrizol Chemical Corporation and was neutralized with a stoichiometric amount of sodium hydroxide in water. After 1 h, the neutralized product was isolated and then used directly in the above-described polymerization procedure.

Solubility (1 g dl^{-1}) of the STAMPS copolymers listed in *Table 1* was observed in a wide variety of solvents covering a broad range of dielectric constants. The specific solvents are listed in *Table 2*.

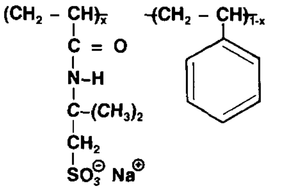

Figure 1 General structure of the copolymers of styrene with sodium-2-acrylamido-2-methylpropane sulphonate (STAMPS)

Table 1 Composition of the copolymers of styrene (M_1) with sodium-2-acrylamido-2-methylpropane sulphonate (M_2)

Designation	Feed ratio (M_1:M_2)	Conversion (%)	Sulphur (wt%)	Sulphonate content (mol%)	M_1 in copolymer (mol%)
13615-48P	95:5	80.1	1.16	4.1	95.9
13615-49P	90:10	67.0	2.33	8.3	91.7
13615-50P	80:20	73.7	4.24	16.5	83.5
13615-51P	70:30	78.2	6.76	29.8	70.2
13615-52P	60:40	76.5	7.82	36.9	63.1
13615-53P	50:50	62.3	8.70	42.8	57.2
13615-54P	40:60	58.4	9.25	47.1	52.9
12736-74A	30:70	78.8	10.10	55.0	45.0
13615-63P[a]	30:70	87.3	11.38	66.7	33.3
12736-74B	20:80	58.6	10.45	57.7	42.3

[a] Polymerization solvent: methylformamide

Table 2 Dielectric properties of the solvents used in this study

Solvent	Dielectric constant
Xylene	2.3
Tetrahydrofuran (THF)	7.6
Methanol	32.6
Dimethylformamide (DMF)	36.7
Water	78.5
Formamide	109.0
Methylformamide	190.0

Low shear rate viscosity measurements (25°C) were performed on a Contraves Low Shear 30 instrument with the low shear rate data extrapolated to zero-shear-rate conditions or on a standard Ubbelohde viscometer in a temperature-controlled water bath (25°C). The solutions were thermally equilibrated for approximately 20 min prior to the appropriate flow-rate measurements.

Surface tension was measured with a Fisher model 215 Autotensiomat surface-tension analyser, which is based on the de Nuoy ring principle. The surface-tension analyser employs a strain-sensitive wire that is fixed at one end to a balance beam and at the other end to a transducer, which provides a force proportional to the surface tension as the ring is pulled out of the liquid. The typical output of the analyser is the pulling force on the ring as a function of the ring displacement from the liquid surface.

The absolute surface tension is the maximum output with a small correction, which depends on the size of the ring, the diameter of the wire, the densities of the phases and the curvature of the detached liquid interface. If the solution is not elastic, the detachment of the solution from the ring is abrupt. However, if the solution is elastic, the surface may be deformable. In this case, the typical trace shows that the surface can be significantly displaced vertically above the free liquid surface. We term this quantity the 'extension length', which is expressed in height above the free liquid surface.

RESULTS AND DISCUSSION

Reactivity ratio/polymer composition studies

The monomer feed ratios and the resultant STAMPS copolymer compositions are determined from sulphur elemental analysis (*Table 1*). *Figure 2* shows the copolymer composition as a function of monomer feed composition for the copolymerization of Na-AMPS with styrene in DMF (open circles). The filled circle represents the copolymerization of the monomers in a medium of higher dielectric constant, i.e. methylformamide. In addition, the broken line represents the ideal random copolymerization conditions. An analysis of these data by the Fineman–Ross method[9] shows that the product of the reactivity ratios is less than 1.0, which strongly indicates that the copolymer possesses a random tendency in the copolymerization reaction. The prerequisite for this behaviour is that the reactivity of the polymer radical is determined solely by the end monomer unit. Furthermore, it is found that the copolymer composition point where deviations occur is at approximately 40 mol% Na-AMPS in the monomer feed. It is at this point in the compositional space that the polymer product is marginally less random in nature. A close examination of the copolymerization indicates that the copolymer at these high Na-AMPS levels became rather insoluble in DMF. Increasing the dielectric constant of the solvent enhances the solubility of the copolymer, resulting in a completely random copolymer composition. This result is presented in *Figure 2*, where the filled circle represents the addition of 70 mol% Na-AMPS in the monomer feed. In methylformamide, an essentially random copolymer structure is obtained, while in DMF, a less random structure is formed.

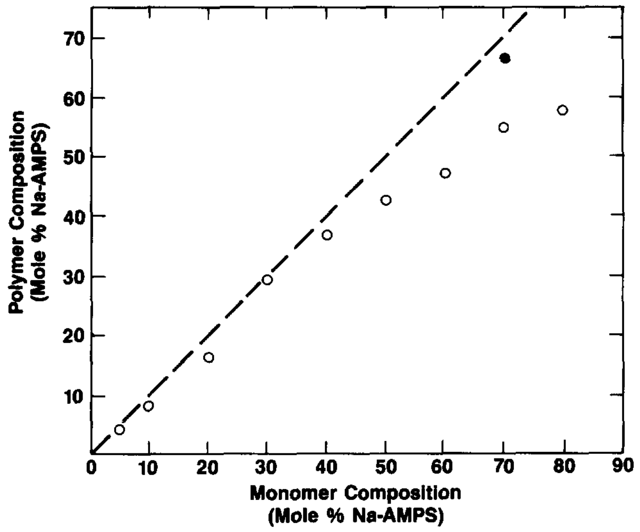

Figure 2 Copolymer composition as a function of monomer feed composition for the copolymerization of styrene with Na-AMPS

Solubility

Solubility observations were carried out on all copolymers listed in *Table 1*. The results of our visual observations at 1 g dl^{-1} polymer concentration in solvents spanning a wide range of dielectric constants (*Table 2*) are presented in *Table 3*. A close examination of the data reveals complex solution behaviour due, to a first approximation, to the dielectric constant (ε) of the solvent. In low-ε solvents, only the lowest Na-AMPS containing copolymers are soluble (see also *Figure 3*). This is undoubtedly due to the inability of the lower-ε solvents to solubilize the sodium-neutralized sulphonate groups, which are known to be soluble in higher-polarity solvents, such as water. From our extensive rheological measurements, these copolymers behave as conventional ionomers[2,3] in these low-ε solvents. For example, addition of a polar cosolvent such as methanol

Table 3 Solubility behaviour of the copolymers of styrene with sodium-2-acrylamido-2-methylpropane sulphonate (1 g dl^{-1})[a]

Sulphonate content (mol%)	Solvent						
	Xylene	THF	Methanol	DMF	Water	Formamide	Methylformamide
4.1	S	S	I	S	I	I	I
8.3	S	S	I	S	I	P	H
16.5	I	I	S	S	I	P	S
29.8	I	I	S	S	I	S	S
36.9	I	I	S	S	G	S	S
42.8	I	I	S	P	S	S	S
47.1	I	I	S	S	S	S	S
55.0	I	I	S	P	S	S	S
66.7	I	I	S	P	S	S	S
57.7	I	I	S	P	S	S	S

[a] S Soluble
H Soluble with a turbid appearance but no gross separation
P Partial solubility
G Insoluble, forms a gel or semi-solid mass
I Insoluble, gross separation into distinct phases which separate rapidly on standing after agitation

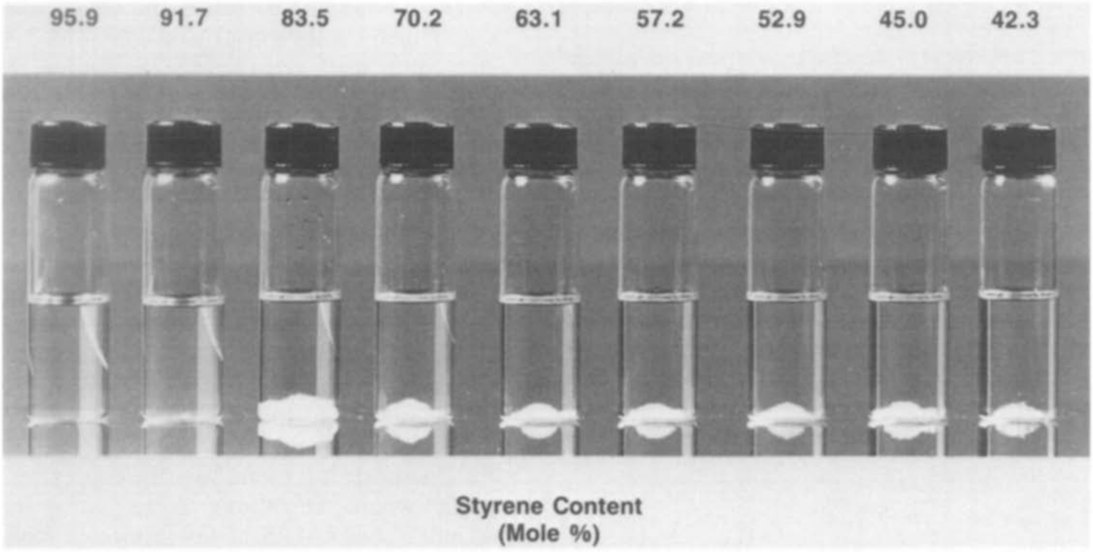

Figure 3 Photograph detailing the solubility of the family of styrene–Na-AMPS copolymers in xylene. Copolymer concentration is 1.0 g dl^{-1}

preferentially solvates the ionic groups permitting solubilization of the high Na-AMPS copolymers. Eventually, a limit is reached in the addition of methanol to these solutions since these polar solvents are also a non-solvent for the styrene component of the copolymer. In these studies visually clear and homogeneous solutions are obtained up to about the 16 mol % sulphonation level.

Increasing the ε value (methanol: 32.6) permits solubilization to occur at the higher Na-AMPS contents, i.e. 16.5 to 66.7 mol % (*Figure 4*). Clearly, this indicates the marked preference of the higher ionic character copolymers for a more polar solvent environment even with relatively high styrene content.

Interestingly, DMF is a polar solvent capable of also solubilizing polystyrene. As a result, this solvent is able to solubilize the STAMPS copolymers over the complete compositional range. At the $1\,g\,dl^{-1}$ concentration that was our standard throughout this study, it was observed that only partial solubility was attained at the highest Na-AMPS levels (*Figure 5*). Complete solubilization of all copolymers occurs, however, at about $0.5\,g\,dl^{-1}$.

Finally, it is noted that, at dielectric constants approaching that of water or higher, solubility occurs only at the higher sulphonation levels. Again this is attributed to the inability of these solvents to solubilize high-styrene-content copolymers. A typical example of these results is presented in *Figure 6*, which shows that an intermediate swollen gel phase exists between the insoluble and the soluble regions in the phase behaviour of these copolymers. Similar behaviour is found in both formamide and methylformamide solvents.

Rheological behaviour

Recently in the course of studies on the behaviour of lightly sulphonated polystyrene[3], it was noted that depending on the solvent polarity either a polyelectrolyte effect or an associative-type phenomenon controlled the solution viscosity. Those solvents of high ε favour higher levels of ionization of the metal sulphonate groups and therefore contributed directly to polyelectrolyte behaviour. The controlling mechanism for this phenomenon arises because the fully ionized anionic groups chemically attached to the polymer chain repel each other in dilute solution. As a result, the hydrodynamic radius of the chain increases, producing

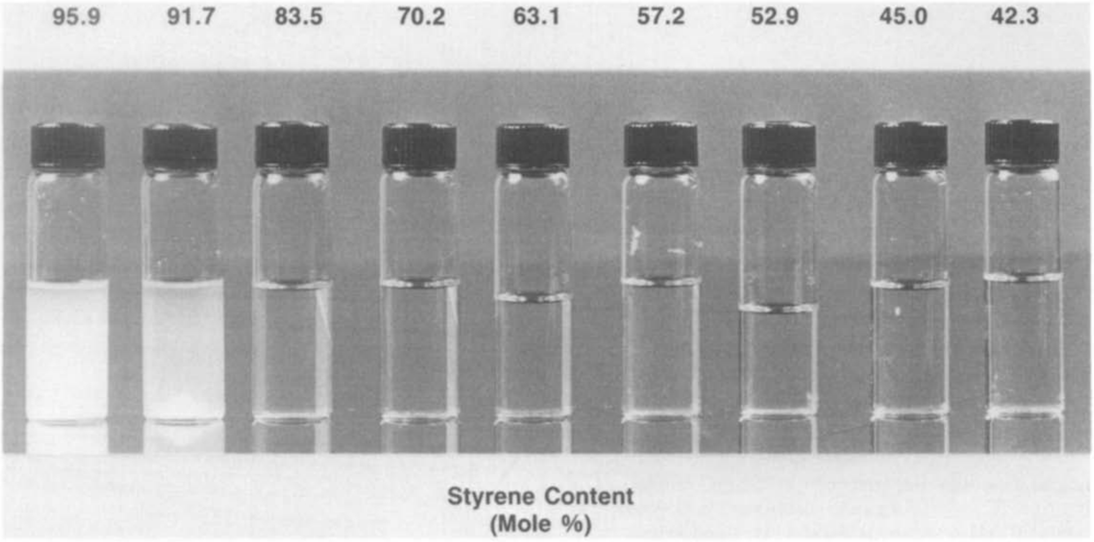

Figure 4 Photograph detailing the solubility of the family of styrene–Na-AMPS copolymers in methanol. Copolymer concentration is $1.0\,g\,dl^{-1}$

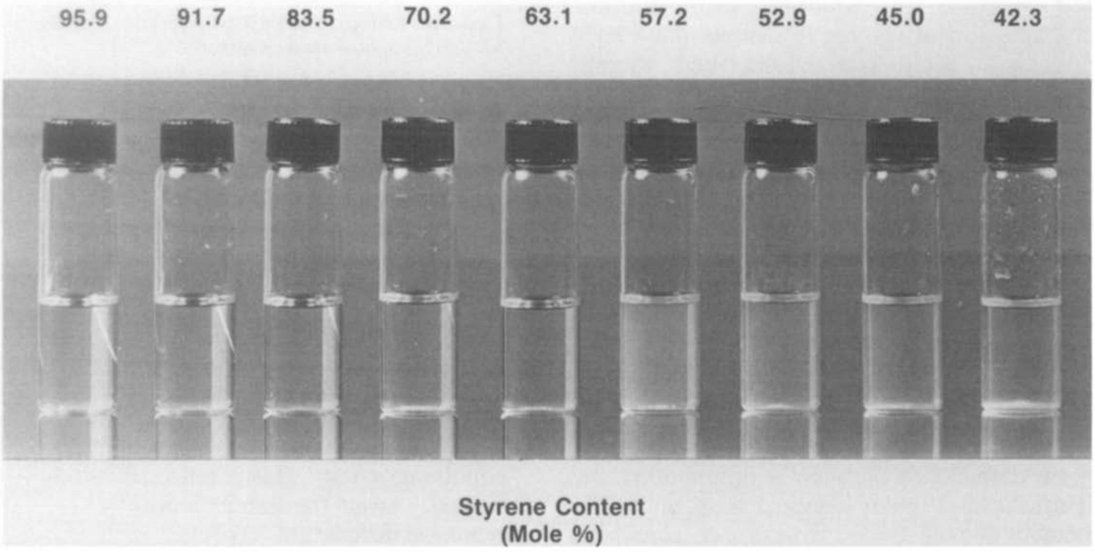

Figure 5 Photograph detailing the solubility of the family of styrene–Na-AMPS copolymers in dimethylformamide. Copolymer concentration is $1.0\,g\,dl^{-1}$

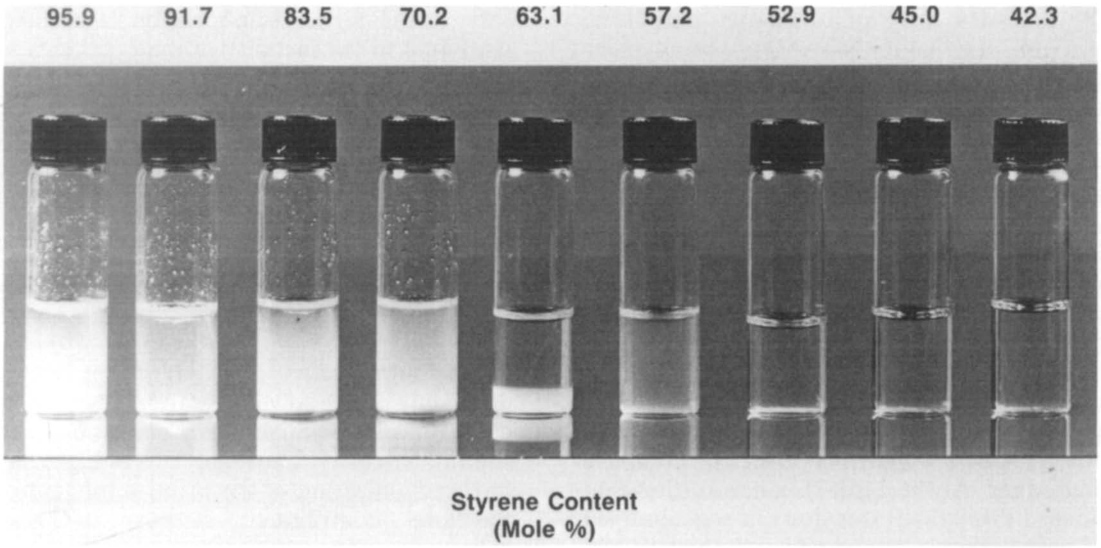

Figure 6 Photograph detailing the solubility of the family of styrene–Na-AMPS copolymers in water. Copolymer concentration is 1.0 g dl^{-1}

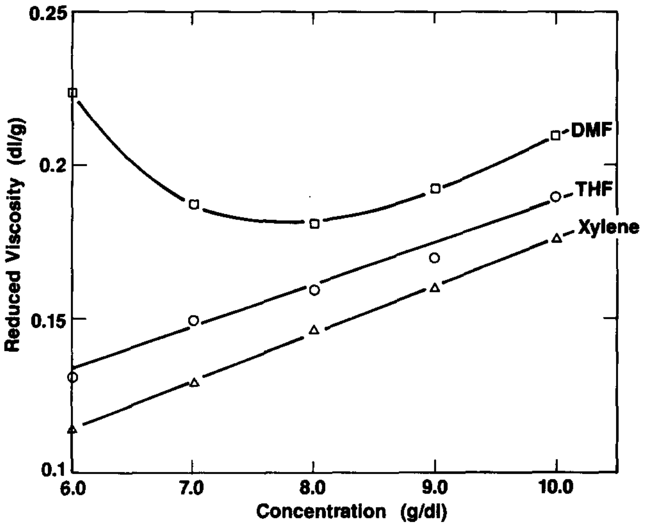

Figure 7 Reduced viscosity–polymer concentration profiles of a 4.1 mol% Na-AMPS – 95.9 mol% styrene copolymer in dimethylformamide (DMF), tetrahydrofuran (THF) and xylene

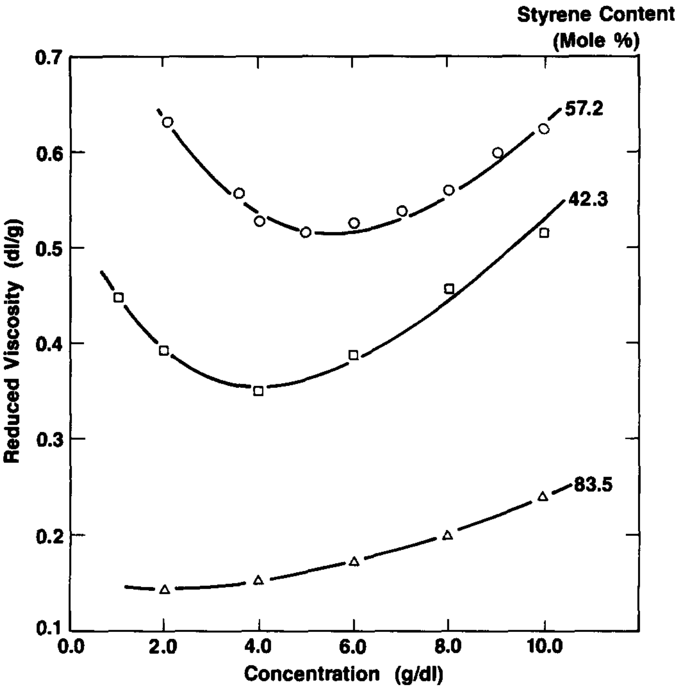

Figure 8 Reduced viscosity–polymer concentration profiles of several STAMPS copolymers in methanol

the marked increase in viscosity with dilution. Interestingly, addition of soluble low-molecular-weight salts shields these ionic interactions, and thereby eliminates the polyelectrolyte effect. Alternatively, lowering the dielectric constant of the solvent medium essentially results in the formation of ion pairs and again 'shielding' effects dominate dilute solution behaviour of lightly sulphonated polystyrene in a low-dielectric medium.

As anticipated, similar solution characteristics are found in lightly sulphonated STAMPS copolymers. *Figure 7* illustrates an example of this behaviour, where the reduced viscosity–concentration relationship of the 4.1 mol% Na-AMPS copolymer is shown in both polar (DMF) and non-polar (THF, xylene) solvents. In the latter solvent, polyelectrolyte behaviour is not observed, and, in fact, the data closely parallel the unfunctionalized polystyrene synthesized under identical conditions. The reduced viscosity of polystyrene is, however, somewhat lower than that of its sulphonated counterpart. This behaviour is entirely consistent with the associative phenomena found in other ionomers previously described. On the contrary, this ionomer in DMF exhibits a marked upsweep in the reduced viscosity and is clearly a manifestation of polyelectrolyte behaviour.

As noted previously, methanol is capable of solubilizing these copolymers at sulphonate levels above 10 mol%. An example of the reduced viscosity–concentration profiles of these materials is shown in *Figure 8*. If it is assumed that the average molecular weights are approximately identical, then it is apparent that the higher sulphonate contents permit a larger expansion in the hydrodynamic radius of the copolymer chain. This is reflected in the higher reduced viscosity over the same concentration range. Higher repulsive forces are expected with the larger anionic charge density. Furthermore, ion-pair associations appear to dominate behaviour in methanol at the

16.5 mol% Na-AMPS level. Therefore, as expected, insolubility occurs at even lower sulphonate levels.

Similar polyelectrolyte behaviour is observed in water (*Figure 9*), where there is an upsweep in the reduced viscosity at low polymer concentrations at all sulphonate levels where solubility occurs. It is noteworthy that the reduced viscosities have increased by about an order of magnitude from those in methanol. This again is correlated to a very strong polyelectrolyte effect. It is interesting to note that the well known hydrophobic effect[10] is not strongly operative. This effect is attributed to the squeezing out of solution of the more hydrocarbon-like sequences (in this instance, the styrene units). Consequently, a gel-like structure forms, promoting a large viscosity increase. Although the exact mechanism for this dramatic viscosity rise still remains to be resolved in detail, it is apparent that the hydrophobic effect does not impede the expansion of the copolymer chain due to the polyelectrolyte effect.

Shielding of the sulphonate groups in these copolymers occurs with addition of low-molecular-weight salts, as illustrated in *Figure 10*. Again, the addition of relatively low levels of sodium chloride produces a substantial reduction in the reduced viscosity–polymer concentration profiles. This extreme sensitivity to low-ionic-strength environments may be due to both an enhancement in the hydrophobic effect and the screening of the anionic charges. Both mechanisms operating together will cause a reduction in the reduced viscosity in this rather dilute concentration range. It is instructive that dissolving these copolymers in solvents of even larger dielectric constant than water changes the concentration region where the polyelectrolyte effect occurs. In fact, an overall reduction in the reduced viscosity is noted over the identical concentration range (*Figure 11*). In general, the higher the styrene content, the lower is the reduced viscosity. This can be attributed to the extreme insolubility of the styrene component preventing any measurable change in the hydrodynamic radius due to the repulsion of the ionized sulphonate groups. Even though the data in *Figures 9* and *11* span the identical polymer concentration range, a polyelectrolyte effect is not found in formamide at lower polymer levels.

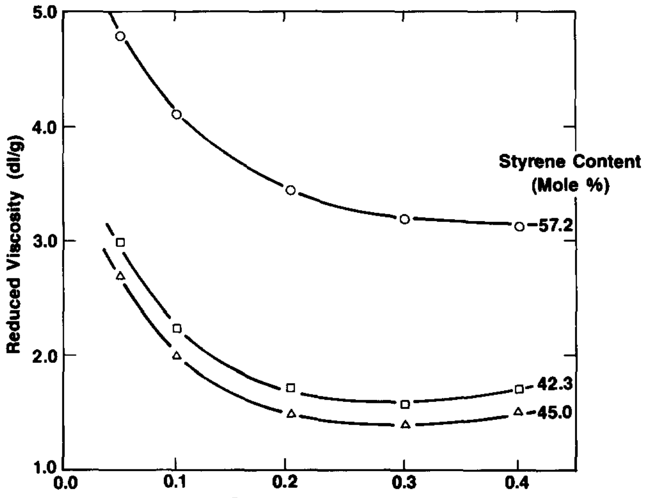

Figure 9 Reduced viscosity–polymer concentration profiles of several STAMPS copolymers in water

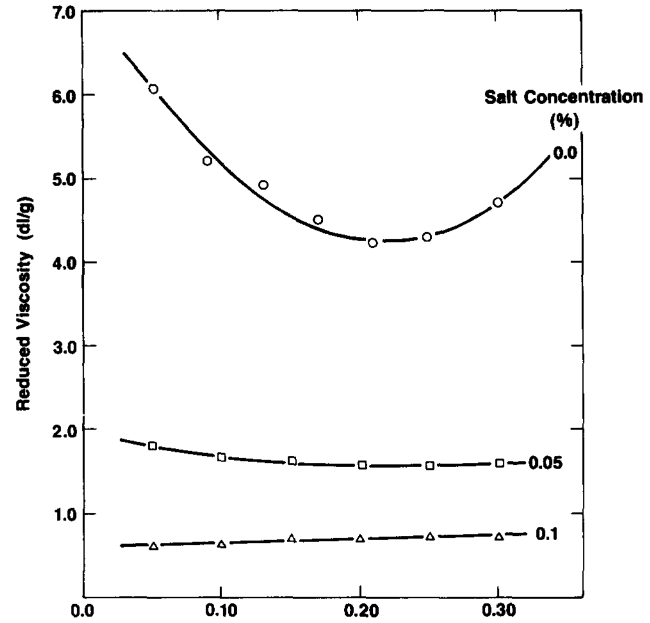

Figure 10 Reduced viscosity–polymer concentration profiles of a 47.1 mol% Na-AMPS – 52.9 mol% styrene copolymer in fresh and salt (sodium chloride) water

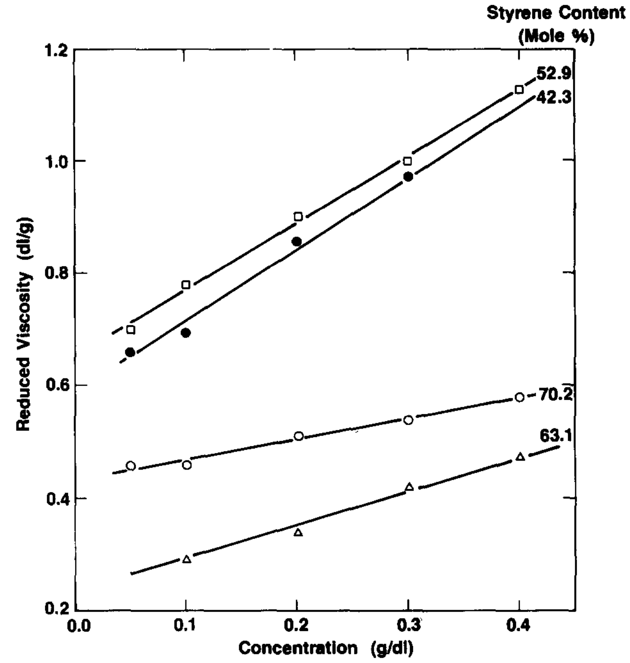

Figure 11 Reduced viscosity–polymer concentration profiles of several STAMPS copolymers in formamide

Air–liquid interface properties

It is a well known phenomenon that the surface tension of water can be substantially reduced with the solubilization of surfactants[11] and triblock copolymers[12,13], for example. In the most general case, these materials have different solubilities towards the dissolved solvent within the same molecule. When an adsorbed surfactant molecule orients itself in such a way at the air–liquid interface, the hydrophilic end embeds itself into the aqueous phase while the hydrocarbon tail orients itself outside of the liquid. This orientation mechanism results in a substantial lowering of the surface tension. This rather simplified model of interfacial tension becomes more complicated in the case of polymeric

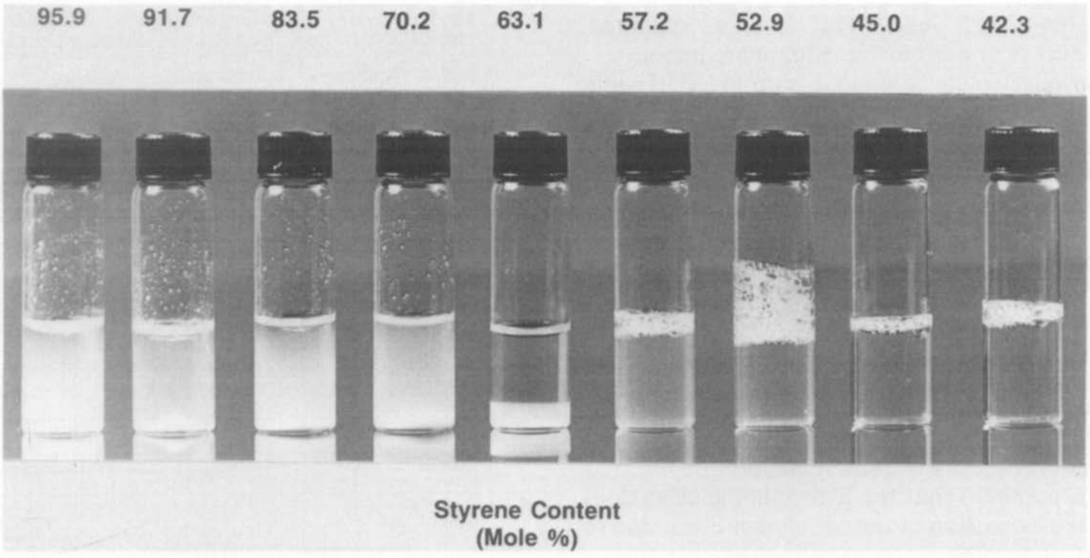

Figure 12 Photograph detailing the solubility and surface activity of the family of styrene–Na-AMPS copolymers in water. Copolymer concentration is 1.0 g dl^{-1}

surface-active agents. The 'head group' in the triblock copolymers in some particular instances is the end block, while the middle block is the water-insoluble component. The lowering of the surface tension is the result of the water-soluble blocks protruding into the aqueous phase, whereas the central block lies almost flat on the water surface[13]. If, however, the hydrophilic and lipophilic sites are distributed randomly along the chain backbone as in the STAMPS copolymers, the surface tension of water is still affected. The first observation of the lowering of the surface tension is the marked persistence of foam after vigorous agitation of the solution. An example of this behaviour is presented in *Figure 12* where the aqueous solutions of *Figure 6* were shaken and subsequently permitted to remain undisturbed for 5 min. Apparently the copolymer is lowering the surface tension of water. In more quantitative terms, the specific details, the surface-tension reduction over a wide polymer concentration for these four copolymers are shown in *Figure 13*. Even though the polyelectrolyte effect undoubtedly influences these results, several conclusions can be reached. The first is the existence of a critical micelle concentration (*CMC*) for these copolymers between 5.0 and 10.0 g dl^{-1} concentration. The second conclusion is that the surface-tension lowering occurs at approximately a molar ratio of one hydrophilic (Na-AMPS) to one lipophilic (styrene) unit. These surface-tension values are significantly lower than for the triblock copolymers of Takahashi *et al.*[12], for example. Lastly, it is observed that the aqueous surface possesses rather elastic properties comparable to the surface gelation phenomena previously found in lightly sulphonated polystyrene in dimethylsulphoxide[14]. The extension lengths shown in *Figure 13* clearly confirm that this phenomenon is a direct function of the lipophile composition within the copolymer chain. The largest differences occur within the *CMC* regime. Only a small effect is noted at the 42.3 mol % styrene level. The purpose of these measurements is to suggest that polymer solutions in contact with an adsorbing interface may experience a surface gelation, i.e. the adsorbed layer may be in the semi-dilute or semi-concentrated regime while the bulk solution maintains a vanishing shear viscosity.

These observations are further summarized in *Figure 14*, where the surface tension and extension length data

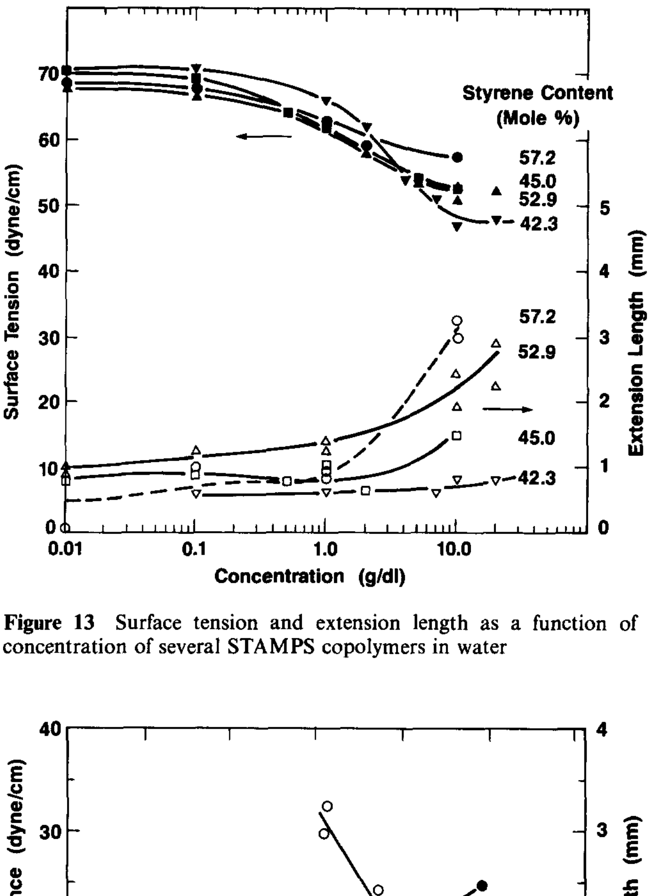

Figure 13 Surface tension and extension length as a function of concentration of several STAMPS copolymers in water

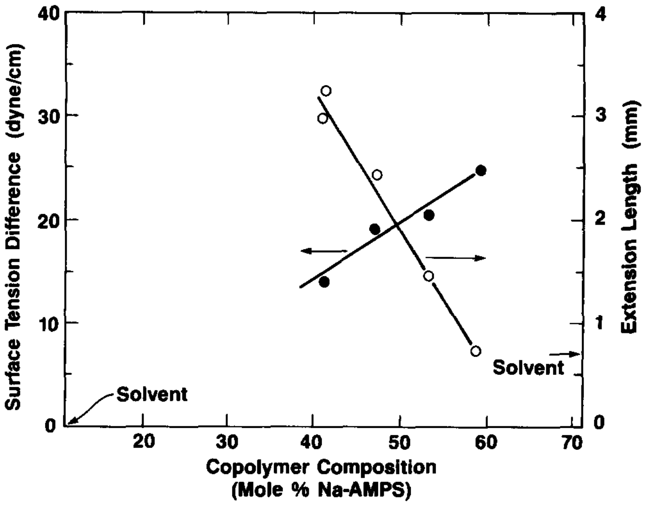

Figure 14 Surface tension and extension length as a function of copolymer composition in water at 10.0 g dl^{-1} concentrates

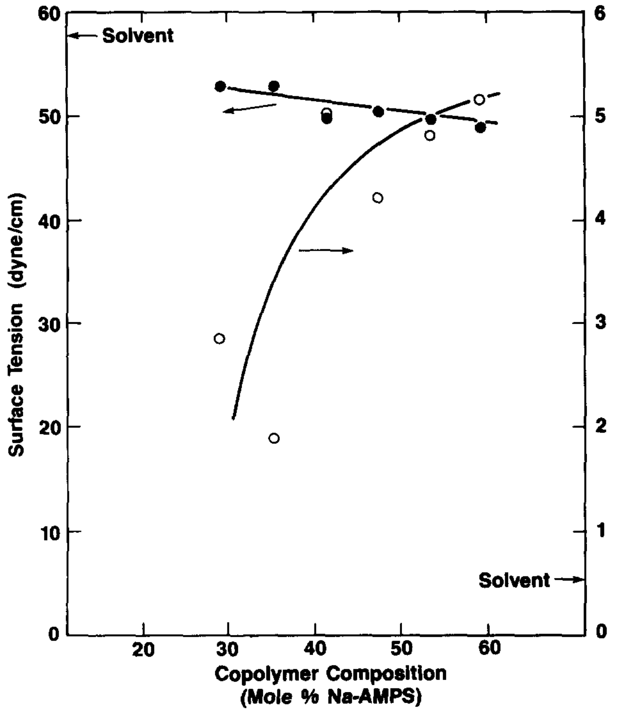

Figure 15 Surface tension and extension length as a function of copolymer composition in formamide at 10.0 g dl^{-1} concentration

are compared with those of water as a function of sulphonate content at 10.0 g dl^{-1} (i.e. above the *CMC*). It is observed that the reduction in the surface tension is directly related to the Na-AMPS level, while the increase in the extension length is directly related to the styrene content. Similar extension-length results are found in the more polar solvents except that very little lowering of the surface tension occurs (*Figure 15*).

CONCLUSIONS

The solubility, solution and surface properties of a family of copolymers of styrene with sodium-2-acrylamido-2-methylpropane sulphonate were studied. A distinguishing characteristic of these materials is the wide range of the sulphonate component present in the copolymer composition. At low sulphonate contents the ion pairs or ion-pair associations dominate solution rheology and solubility in the more non-polar solvents. Increasing the dielectric constant produces a marked increase in solubility of these copolymers over a wide range of anionic character. In most of these more polar solvents, a polyelectrolyte effect dominates the dilute solution rheology. This effect is due to the repulsive forces of the chemically bound sulphonate groups as the counterion is ionized. Reduction in the reduced viscosity is found with the addition of soluble low-molecular-weight salts. Furthermore, marked surface-tension reductions are found in aqueous solutions in the 'intermediate' sulphonate compositions. These measurements show that these copolymers in the range of about 40.0 to 60.0 mol% Na-AMPS behave as polymeric surfactants. These results are summarized in *Figure 16*, where superimposed on *Figure 2* is the solubility and surface behaviour (in water) of the extensively evaluated sulphonate copolymers. Finally, these studies clearly show that these copolymers are capable of expressing the associative phenomena of typical non-polar ionomer solutions, the polyelectrolyte effect of fully charged polymers in water (and in polar non-aqueous solvents) and polymeric surfactant behaviour (and surface gelation) in aqueous solutions, simply by adjusting the ratio of hydrophilic groups (Na-AMPS) to lipophilic units (styrene) in a random fashion along the chain backbone.

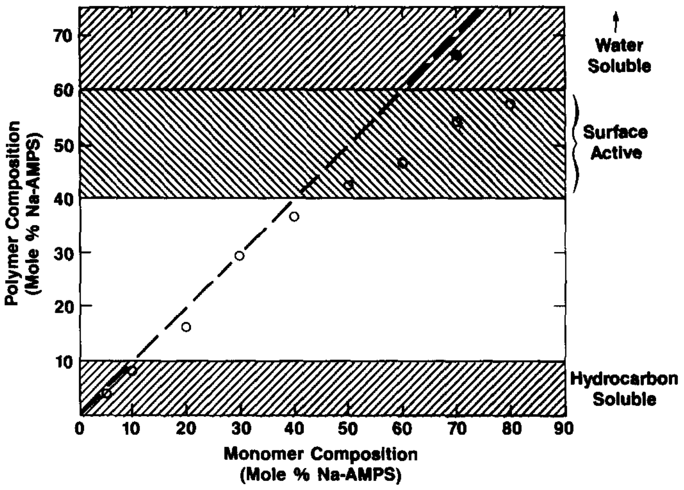

Figure 16 A general summary of the solution and surface behaviour of the STAMPS copolymers as a function of polymer composition and monomer feed composition

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