Rheology of dilute polyelectrolyte solutions

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The flow properties of polyelectrolyte solutions have been studied using narrow molecular weight polystyrene sulphonate (PSS) samples of different molecular weight. In salt-free solutions the viscosity behaviour was characteristically dependent on the molecular weight of the polyelectrolyte. For low molecular weight samples the simple classical behaviour was observed, the reduced viscosity of the solution increasing sharply on dilution. The shear dependence of viscosity was low in general, but increased on dilution in parallel with the increase of reduced viscosity. For high molecular weights the reduced viscosity reached a maximum on dilution, followed by a rapid decrease on further dilution of the solutions. The viscosity was strongly shear-dependent and approached infinity at low shearing stresses. At low concentrations the reduced viscosity of HPSS solutions was markedly higher than that of NaPSS solutions, the difference vanishing at higher concentrations. These findings indicate that the viscosity behaviour of salt-free polyelectrolyte solutions is essentially determined by strong electrostatic interactions between highly expanded polyion chains, with the possible formation of ordered quasicrystalline structures in dilute solutions.

(**Keywords: polyelectrolyte solutions; polystyrene sulphonates; shear-dependent viscosity; ordered structures**)

INTRODUCTION

A number of recent investigations have been concerned with the rheology of polyelectrolyte solutions[1–7] and charged colloidal suspensions[8–10]. In the case of colloids, such as latex suspensions, considerable progress has been made in understanding these phenomena. Under certain conditions such suspensions can withstand low shearing stresses, and exhibit pronounced shear thinning effects under steady flow conditions. In general, these phenomena occur in concentrated suspensions at low ionic strength, and are due to long-range repulsive electrostatic interactions between the suspended particles. The situation is more complex in polyelectrolyte solutions, since factors like chain conformation, orientation of the chains and entanglement between different chains are likely to affect the flow properties of these solutions.

However, a link between the behaviour of polyelectrolytes and charged colloidal suspensions may be anticipated, because the interparticle interactions are similar, favouring the formation of ordered equilibrium structures. Whenever thermodynamically stable ordered structures are formed, energy is dissipated when the structure is deformed or dispersed, leading to enhanced viscosity at low shearing stresses. There may even exist a threshold in the activation energy for flow, appearing as a yield stress in the stress–strain relationship. There is evidence for the formation of such ordered structures in charged latex suspensions under low ionic strength conditions[10–13]. On the other hand, very little is known about the structure of salt-free polyelectrolyte solutions. Rheological studies of these solutions are therefore essential, as they provide clues to understanding the properties of these systems. In the present investigation the flow behaviour of salt-free polyelectrolyte solutions was studied in the low concentration and low shearing stress limit. The measurements were carried out with well characterized samples of polystyrene sulphonate (PSS) polyelectrolytes, covering a wide range of molecular weights.

EXPERIMENTAL

Materials

The polystyrene sulphonic acid (HPSS) samples were prepared[14] from narrow molecular weight polystyrene (PS) (from Pressure Chem. Comp., Pittsburgh, USA) by sulphonating PS dissolved in cyclohexane with concentrated (95–97%) sulphuric acid, in the presence of P_2O_5. To ascertain that the sulphonation was carried out under non-degrading conditions the intrinsic viscosity of the NaPSS samples were determined in 0.2 M NaCl solutions and correlated with the molecular weight of the samples. The latter were obtained from the nominal molecular weights of the PS samples. The degree of substitution was checked and was found to be unity in all cases. For two samples the molecular weight of NaPSS was determined by light scattering, and was found to agree with the computed M_w values. The results are shown in *Figure 1* and demonstrate that the sulphonation was essentially non-degrading (with the possible exception of the highest molecular weight sample, where a slight degradation may have taken place). The resulting Mark–Houwink–Sakurada equations for NaPSS in 0.2 M NaCl at 25°C are:

$$[\eta] = 1.28 \times 10^{-3}\, M^{0.89}\ \mathrm{ml\ g^{-1}} \qquad (1)$$

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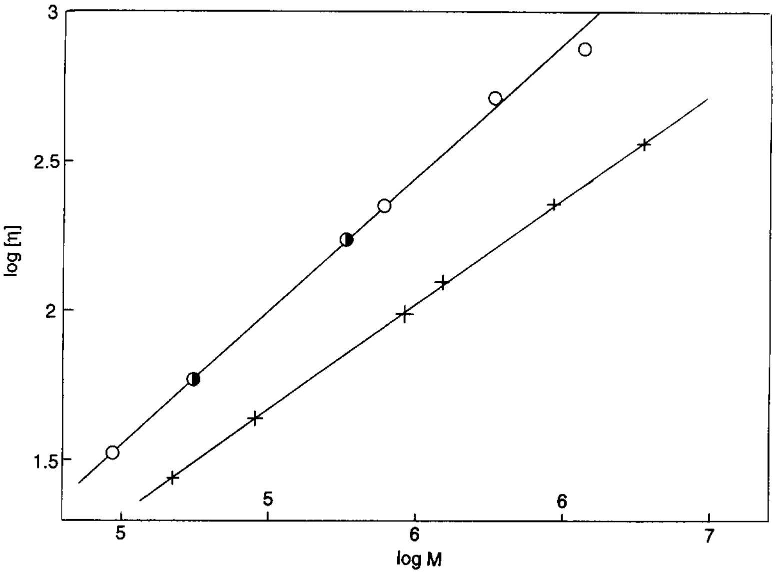

Figure 1 Double logarithmic plot of intrinsic viscosity $[\eta]$ *versus* molecular weight (M): ○, NaPSS in 0.2 M NaCl solutions; +, PS in toluene; ◐, M determined by light scattering

Table 1 Data for the polystyrene sulphonate samples

Sample	$M_w \times 10^{-3}$ of parent PS	$M_w \times 10^{-3}$ of NaPSS	$[\eta]$ (ml g^{-1}) of NaPSS in 0.2 M NaCl
PSS_{48}	47.5	94	33.7
PS_{90}	90	178	58.8
PSS_{290}	290	574	174
PSS_{390}	390	772	227
PSS_{929}	929	1840	528
PSS_{1860}	1860	3680	768

and for PS in toluene at 25°C:

$$[\eta] = 13.2 \times 10^{-3}\ M^{0.71}\ \text{ml g}^{-1} \qquad (2)$$

Data about the samples are listed in *Table 1*.

The pure HPSS stock solution was obtained by dialysing the crude polyacid solution against distilled water, until the electrolytic conductivity of the latter remained unchanged. The NaPSS stock solution was obtained by neutralizing an aliquot of the HPSS solution with an equivalent amount of NaOH. The water used to prepare the solutions had an electrolytic conductivity in the range $(0.4\text{–}0.6) \times 10^{-4}\,\Omega^{-1}\,\text{m}^{-1}$.

Viscosity measurements

All viscosity measurements were carried out in capillary viscometers at 25°C. Measurements in the 0.2 M NaCl solutions, where the viscosity was Newtonian, were carried out in an Ostwald viscometer at a shearing stress of 1.25 Pa at the capillary wall (velocity gradient for water $1400\,\text{s}^{-1}$). For studies of the shear dependence of viscosity in salt-free solutions, a specially designed viscometer[15] was used. The capillary of the viscometer had a diameter of 0.56 mm and a length of 593 mm. The measurements could be carried out with a continuously varying driving-head, in the range 2–180 mm. The corresponding shear stress at the capillary wall was $(4.62\text{–}415.4) \times 10^{-3}$ Pa for water. During the measurements the solution in the viscometer was kept under a nitrogen atmosphere.

In the case of shear-dependent viscous flow it is necessary to apply the Weissenberg correction[16,17] in order to obtain the true viscosity of the solution. At the capillary wall we have the relation:

$$\tau = \eta^* q^* = \frac{pR}{2L} \qquad (3)$$

where τ is the shearing stress, η^* and q^* are the apparent viscosity and apparent velocity gradient, respectively, p is the driving pressure, R the radius of the capillary and L its length. The apparent viscosity is obtained from the Poiseuille law:

$$\eta^* = \pi R^4 p / 8LQ \qquad (4)$$

where Q is the volume flow.

The Weissenberg correction determines the true viscosity η at the capillary wall and is usually written in the form:

$$\eta = \eta^* Z \qquad (5)$$

$$q = q^*/Z \qquad (6)$$

where the correcting factor Z is

$$Z = \frac{4}{3 + (\text{d} \ln Q / \text{d} \ln p)} \qquad (7)$$

This equation may be rearranged in a more convenient form. Taking the logarithmic derivative of equation (4) we obtain:

$$\frac{\text{d} \ln \eta^*}{\text{d} \ln p} = 1 - \frac{\text{d} \ln Q}{\text{d} \ln p} = 1 - \frac{\text{d} \ln Q}{\text{d} \ln \tau} \qquad (8)$$

Thus

$$Z = \frac{4}{4 - (\text{d} \ln \eta^* / \text{d} \ln \tau)} \qquad (9)$$

Obviously all relevant information to determine η is inherent in the functional dependence of η^* on the shearing stress τ (alternatively the pressure difference p, or the driving-head h). Hence, it is more appropriate to use the shearing stress (rather than the velocity gradient) as the independent variable characterizing the shear dependence of viscosity. That dependence is usually expressed in the form of a power series[18]. For the specific viscosity we have:

$$\eta_{sp} = \eta_{sp}^0\left(1 + \sum_i a_i \tau^i\right) \qquad (10)$$

where η_{sp}^0 is the zero-shear specific viscosity, and the coefficients a_i are measures of the shear dependence. However, this representation is useful only when the zero-shear viscosity can be determined, and then only in a range close to the origin. Since these conditions are not fulfilled in the present investigation we use an alternative measure of the shear dependence, θ, defined as the shear-stress-induced relative change of specific viscosity. Thus:

$$\theta = -\frac{1}{\eta_{sp}}\frac{d\eta_{sp}}{d\tau} = -\frac{d\ln\eta_{sp}}{d\tau} \qquad (11)$$

the negative sign indicating that the effect is shear thinning.

The parameter θ represents an objective measure of the shear dependence and can be used over the entire range of shearing stress covered by the experiments. It may be related to the coefficients a_i in equation (10) in the limit of vanishing shearing stress. When the limiting shear dependence is linear we have:

$$\theta = -a_1 \qquad (12)$$

and when it is quadratic, we have:

$$\theta = -2a_2\tau \qquad (13)$$

The viscosity was represented as plots of $1/\eta_{sp}$ against τ. The advantage of this representation is that the variables are confined to a finite space. When the viscosity tends to infinity the curve

$$1/\eta_{sp} = f(\tau) \qquad (14)$$

tends to zero, and intersects the positive τ-axis in case there is a yield stress. The parameter θ may be directly determined from such a plot. Taking the derivative of equation (14) we obtain:

$$\theta = \eta_{sp}\frac{df}{d\tau} \qquad (15)$$

Some typical plots of $1/\eta_{sp}$ against the shearing stress (expressed in terms of the driving-head h) are shown in *Figure 2*. The curves were linear over a wide range of shearing stress, but in general the curves changed direction at low shearing stresses. For low molecular weight samples the curves intersected the $1/\eta_{sp}$ axis at a finite positive value, allowing the determination of the zero-shear viscosity by extrapolation. For the two highest molecular weight samples the extrapolated curves intersected the positive τ-axis, or passed through the origin, indicating the possible existence of a yield stress, or an infinite zero-shear viscosity. To obtain a definite value for the low-shear viscosity of these samples, the viscosity was determined at the shear stress $\tau = 23.1 \times 10^{-3}$ Pa ($h = 10$ mm) by interpolation. For the low molecular weight samples this viscosity value was practically equal to the zero-shear viscosity.

RESULTS AND DISCUSSION

The results of the viscosity measurements are depicted in *Figures 3–8*, where the concentration dependence of the reduced viscosity ($\eta_{red} = \eta_{sp}/c$) for the different samples is reproduced. For sample PSS$_{90}$ the behaviour

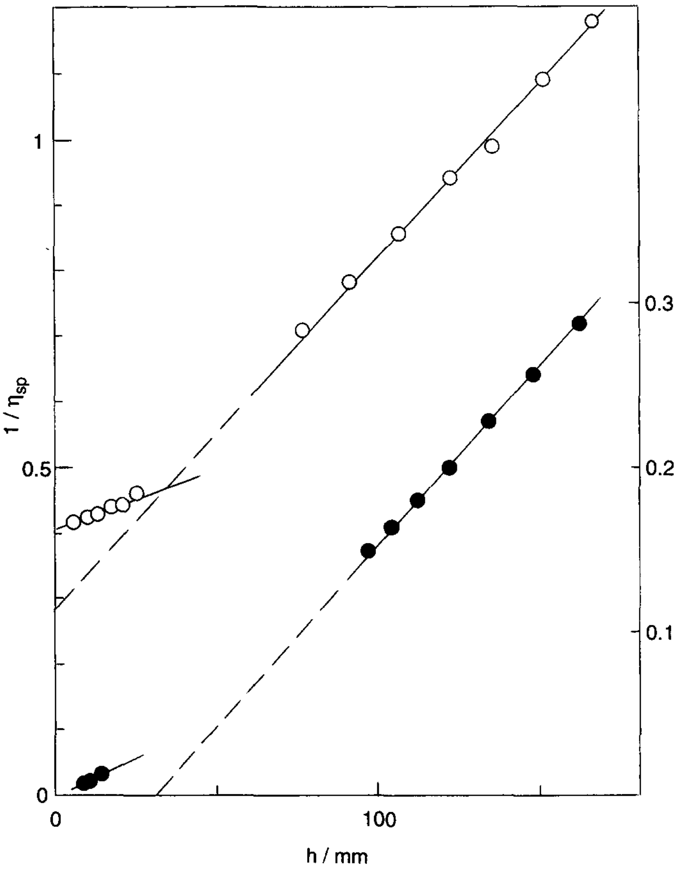

Figure 2 Plots of $1/\eta_{sp}$ *versus* the driving-head h in salt-free solutions: ○, NaPSS$_{390}$, $C = 16.34 \times 10^{-6}$ g ml^{-1}; ●, NaPSS$_{1860}$, $C = 23.10 \times 10^{-6}$ g ml^{-1}

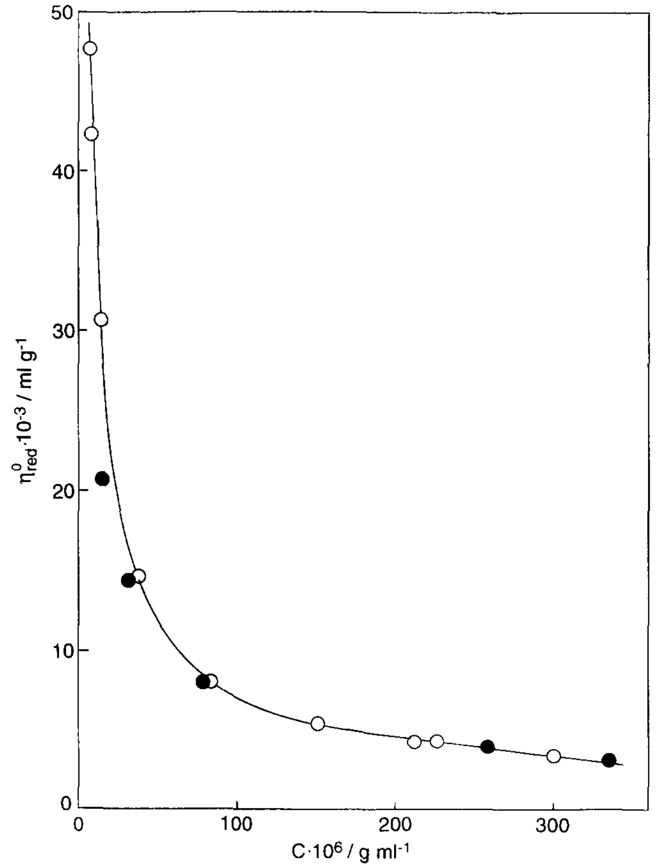

Figure 3 Concentration dependence of zero-shear reduced viscosity: ○, HPSS$_{90}$; ●, NaPSS$_{90}$

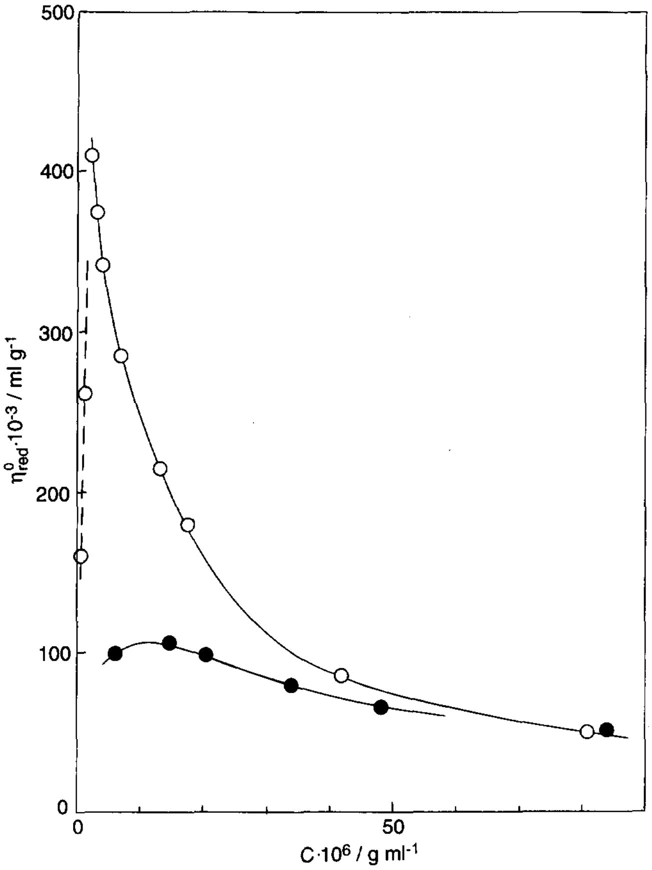

Figure 4 Concentration dependence of zero-shear reduced viscosity: ○, $HPSS_{290}$; ●, $NaPSS_{290}$

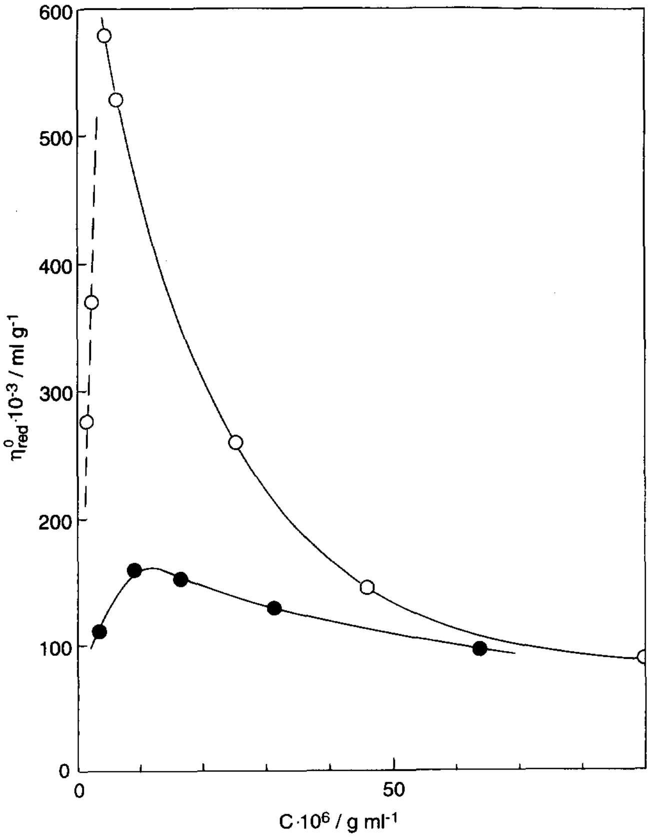

Figure 5 Concentration dependence of zero-shear reduced viscosity: ○, $HPSS_{390}$; ●, $NaPSS_{390}$

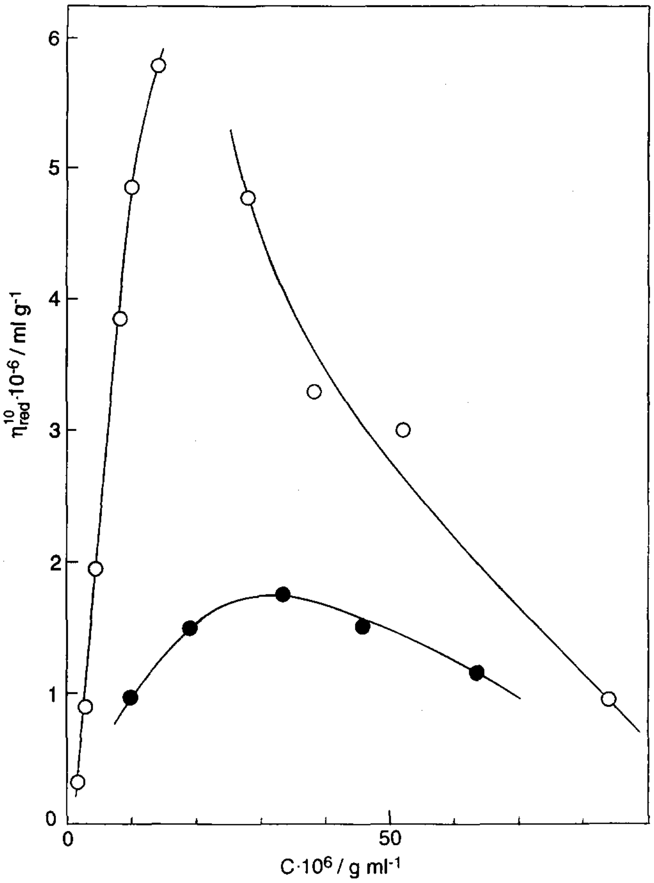

Figure 6 Concentration dependence of the reduced viscosity at $h = 10$ mm: ○, $HPSS_{929}$; ●, $NaPSS_{929}$

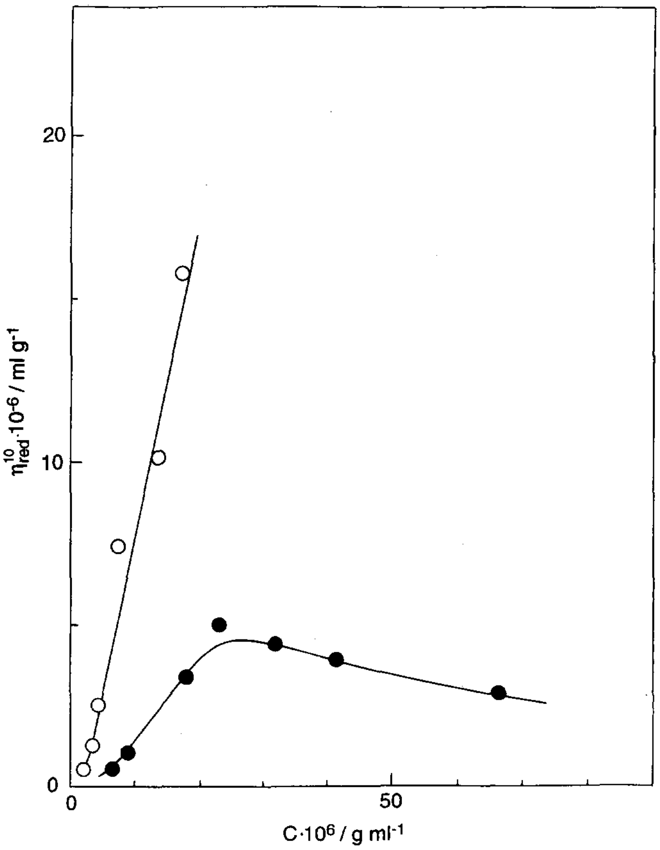

Figure 7 Concentration dependence of the reduced viscosity at $h = 10$ mm: ○, $HPSS_{1860}$; ●, $NaPSS_{1860}$

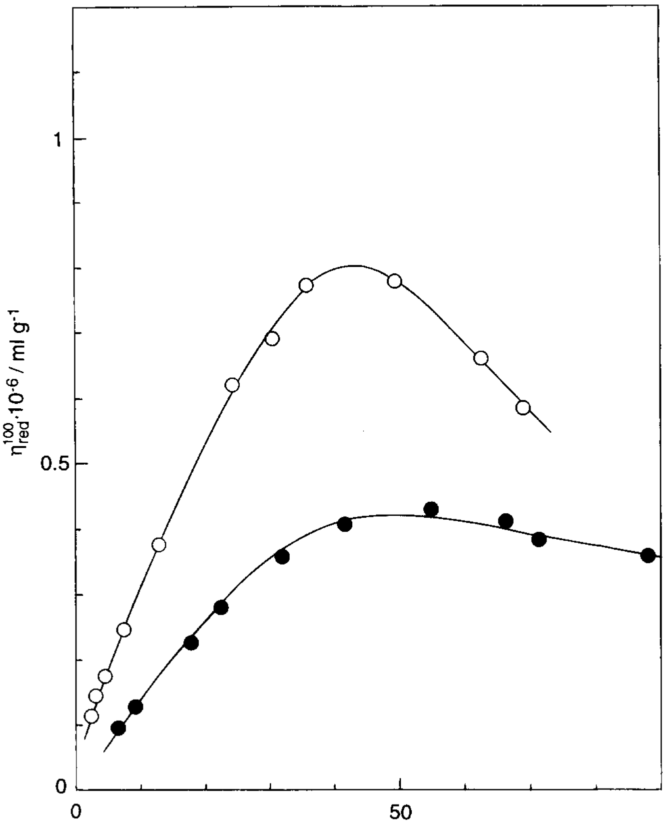

Figure 8 Concentration dependence of the reduced viscosity at $h = 100$ mm: ○, $HPSS_{1860}$; ●, $NaPSS_{1860}$

follows the description by Fuoss[19], the reduced viscosity apparently increasing without limit on dilution. For the higher molecular weight samples the increase is followed by a rapid decrease at very low concentrations[20–23]. The decrease probably remains undetected in the lowest molecular weight sample, since in this case measurements could not be performed at sufficiently low concentrations, owing to the comparatively low viscosity of these solutions. The maximum, which is very sharp for the low molecular weight samples, becomes flattened out at higher molecular weights, where it likewise is shifted towards higher concentrations. The rapid increase in reduced viscosity is generally attributed to the electrostatic expansion of the polyions. However, this intramolecular electrostatic effect is accompanied by intermolecular electrostatic interactions between similarly charged polyions. Although the effect of these interactions is not completely understood, they probably play a significant role in the rheological behaviour of polyelectrolyte solutions.

An important clue is the pronounced difference in viscosity between HPSS and NaPSS solutions. This effect was first observed by Butler *et al.*[24], who found that PSS in the acid form has a higher reduced viscosity than the corresponding alkali salt. In the present investigation it was found that the difference vanishes at higher concentrations, whereas it becomes pronounced in dilute solutions, near to the maximum of the viscosity curve. Since HPSS is a strong acid, it has the same charge density as NaPSS and therefore no difference in the electrostatic expansion of the polyion is expected. Differences in short-range interactions, such as hydrophobic interactions or hydrogen bonding between sulphonate groups, can also be ruled out as a possible cause for the effect, since the difference vanishes at high concentrations, where such interactions would become dominant. Thus, there remain the long-range electrostatic interactions between the polyions, which become important in dilute polyelectrolyte solutions under salt-free conditions.

These interactions are very sensitive to the presence of traces of salt and in this respect a difference between polyacid and polysalt solutions can be established. A solution of polyacid in water represents a pure two-component system. In these solutions the self-ionization of water is suppressed and therefore practically no co-ions are present in the solution. On the other hand, NaPSS solutions can hydrolyse. Even though NaPSS derives from a strong acid, ion exchange can take place between the Na^+ counterion atmosphere and water, resulting in the formation of small amounts of NaOH. These solutions are therefore not perfectly salt free. The effect of hydrolysis becomes more important when the solutions are diluted. This explains why the difference between HPSS and NaPSS is most pronounced in dilute solutions, near to the maximum of the reduced viscosity curve.

The viscosity of salt-free polyelectrolyte solutions is characterized by an extreme shear dependence. This dependence, embodied in the parameter θ, in general varies with the shearing stress. In the linear range of the viscosity curve equation (14), where $df/d\tau$ is constant, θ is a hyperbolic function of the shearing stress. In *Figure 9*, θ values for the different samples, determined at a fixed shearing stress of $\tau = 0.231$ Pa ($h = 100$ mm), are depicted as functions of concentration. We find a close correlation between θ and the reduced viscosity. For the lowest molecular weight sample the shear dependence is barely noticeable at high concentrations, but it

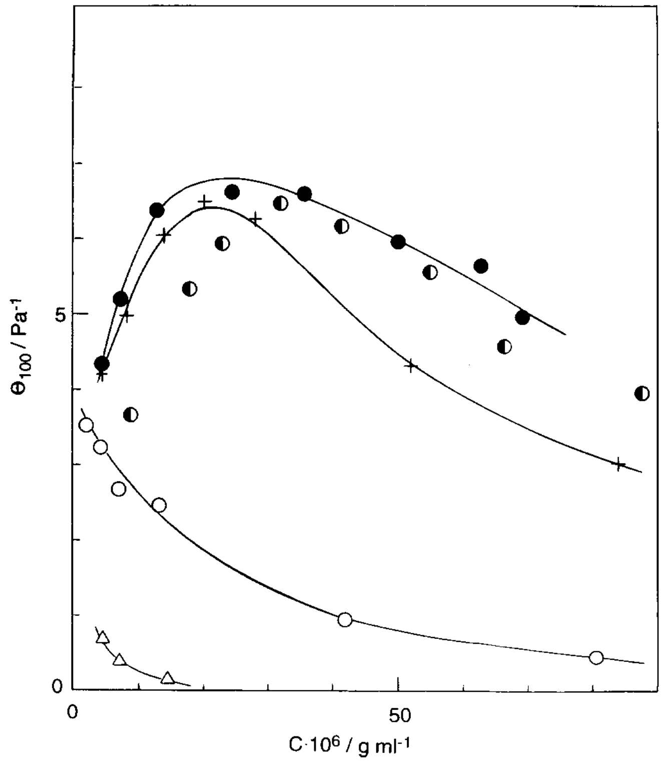

Figure 9 Concentration dependence of the parameter θ at $h = 100$ mm: △, $HPSS_{90}$; ○, $HPSS_{290}$; +, $HPSS_{929}$; ●, $HPSS_{1860}$; ◐, $NaPSS_{1860}$

experiences a substantial increase in the region characterized by polyion expansion. For the high molecular weight samples the maximum in the viscosity curve is reproduced in the concentration dependence of θ. Also, essentially no difference between the θ values for HPSS and the corresponding NaPSS samples is observed.

The viscosity measurements with NaPSS in 0.2 M NaCl solutions indicate a behaviour similar to that of flexible neutral polymers. The viscosity is shear-independent and the intrinsic viscosity can be determined by extrapolation according to Huggins equation. However, the exponent $a = 0.89$ in the Mark–Houwink–Sakurada equation is considerably higher than the recommended literature value[25], indicating that the polyelectrolyte has an extended chain conformation even at fairly high salt concentrations. In salt-free solutions the pronounced shear dependence and the rapid decrease of reduced viscosity in very dilute solutions does not allow an accurate determination of zero-shear intrinsic viscosity. The frictional properties, and hence the conformation of an isolated polyelectrolyte molecule, therefore remain undetermined.

Interest is focused, instead, on the region at the maximum of the reduced viscosity curve. The very high peak value of the reduced viscosity at the maximum, which is several orders of magnitude higher than the theoretical intrinsic viscosity of a comparable rod-like molecule[26], and its sudden decline on further dilution of the solutions, suggest the collapse of a structure upheld by intermolecular interactions. For stiff rod-like polyions a long-range ordered structure, with the polyions arranged equidistantly and in parallel, is energetically favourable[27]. However, for flexible polyelectrolytes such a structure is unlikely, since the long-range order would be destroyed by fluctuations in the polyion conformation. A more likely structure therefore involves locally ordered crystalline regions, alternating with amorphous regions of lower order. The crystalline regions would be oriented at random under equilibrium conditions, making the solutions macroscopically isotropic. Under low shear conditions the ordered regions tend to 'cross-link' the polyion matrix, which would explain the very high viscosity of the solutions at low shearing stresses. At high shear conditions, the structure is destroyed and the viscosity deteriorates.

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