On the viscosity of sodium poly(styrene sulphonate), a flexible polyelectrolyte

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This paper concerns mainly the effect of the shear rate on the reduced viscosity of sodium poly(styrene sulphonate) (Na PSS) in salt-free solution. A maximum in reduced viscosity is obtained for a critical concentration attributed to a preferential intermolecular distance. This maximum seems to have the same origin as that observed by light or neutron scattering. Then, in excess of external salt, the viscosity of Na PSS is compared with that of polystyrene in organic solvent. The main difference between these two polymers is the large increase in the stiffness of the chain in the presence of ionic charge, causing large non-Newtonian behaviour of the polyelectrolyte when the polymer concentration increases even in 0.1 M NaCl.

INTRODUCTION

The viscosity of polyelectrolytes has been discussed for a long time and especially its behaviour corresponding to the dependence of the reduced viscosity (η_{red}) on the polymer concentration in the absence of external salt.

A large increase of η_{red} is generally observed when dilution increases and the intrinsic viscosity was often extrapolated using the Fuoss relation[1]. Considering the role of electroviscous effects, Pals and Hermans suggested adopting the iso-ionic dilution to determine the intrinsic viscosity $[\eta]$ at given ionic content[2].

Some authors described a maximum in the η_{red} values followed by a decrease of η_{red} when the polymer concentration goes to zero[3-8]. This effect was recently discussed by Ise and coworkers[9]; previously, the maximum was also attributed to polymer adsorption on the capillary tube or to the presence of salt impurities. It was interpreted by Cohen et al.[5] using the mode–mode coupling approximation to the hydrodynamics of charged Brownian spheres.

The role of the external salt (concentration c_s) is very important in the intrinsic viscosity of flexible polyelectrolyte. It is generally admitted that:

$$[\eta]_{c_s} = [\eta]_\infty + S c_s^{-1/2} \qquad (1)$$

in which $[\eta]_\infty$ is the intrinsic viscosity extrapolated to infinite ionic strength and S, the slope of the dependence of $[\eta]_{c_s}$ with $c_s^{-1/2}$, is related to the stiffness of the molecule considering the treatment of Odijk[10]. Desbrières estimated $[\eta]$ of Na poly(styrene sulphonate) as a function of c_s and determined an intrinsic persistence length ($L_p = 20$ Å) from extrapolation to infinite ionic

strength[11] using the following relation proposed by Odijk[10]:

$$[\eta]_{c_s} = [\eta]_\infty \left(\frac{L_t}{L_p}\right)^{3/2} \alpha_\eta^3 \frac{\Phi_s}{\Phi_\infty} \qquad (2)$$

Here L_t is the total persistence length with $L_t = L_p + L_e$ and L_e the electrostatic contribution; α_η is the expansion factor and Φ the Flory term in the two conditions considered. The large variation of $[\eta]_{c_s}$ is directly related to the large contribution of the electrostatic term in L_t ($L_e > L_p$ as soon as $c_s < 0.016$ N).

From Odijk, scaling relations for semidilute polyelectrolyte solutions were given and different structures were described depending on the polymer concentration[12].

The effect of shear rate on the reduced viscosity is still under discussion; some data were recently described by Ise[9].

In this paper, the viscometric behaviour of Na poly(styrene sulphonate) (Na PSS) was investigated in the absence and presence of external salt to point out the role of electrostatic effects and the effect of shear rate. For that purpose, the behaviour of Na PSS with and without salt was compared with that of a sample of polystyrene in toluene.

EXPERIMENTAL

A sample of polystyrene (PS) obtained by anionic polymerization was characterized by gel permeation chromatography; $\bar{M}_w$ and $\bar{M}_n$ are respectively 1.318×10^6 (degree of polymerization $\overline{DP}_w = 13\,200$) and $995\,000$. Its intrinsic viscosity at 25°C was determined in toluene at
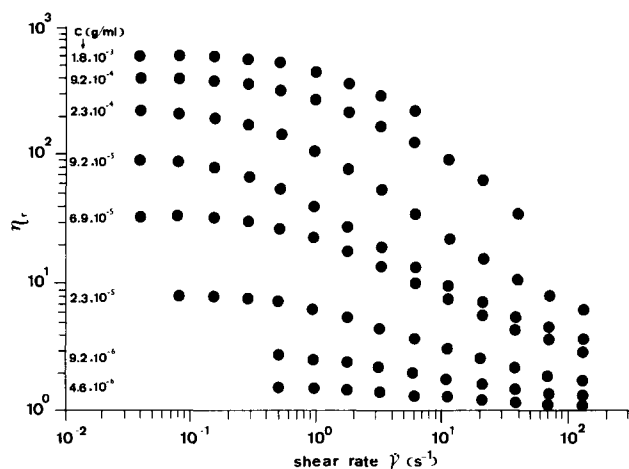
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Figure 1 Relative viscosity as a function of the shear rate ($\dot{\gamma}$) for Na PSS in water for different polymer concentrations expressed in g ml^{-1}
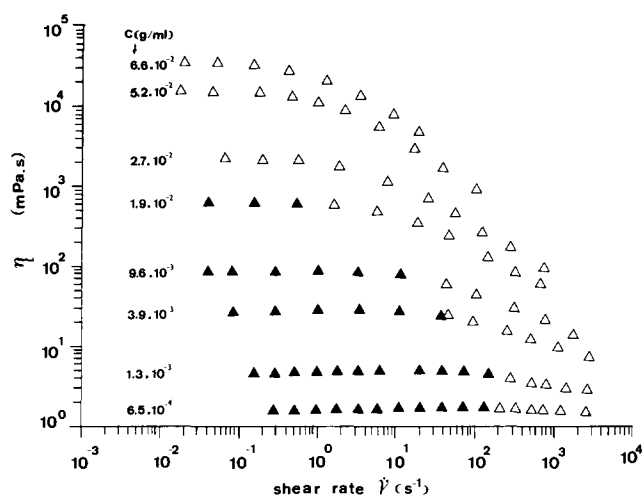

Figure 2 Viscosity as a function of the shear rate ($\dot{\gamma}$) for Na PSS in 0.1 M NaCl. Concentrations expressed in g ml^{-1}. Instrument: (▲) Low Shear 30; (△) Carri-Med

low shear rate: $[\eta] = 295$ ml g^{-1}. The polymer concentration used in this study varies from 0.2 to 200 g l^{-1}.

The Na PSS from Interscience (lot 20h-65) was purified by centrifugation (2 h at 20 000g) of a solution of Na PSS in pure water at 1 g l^{-1} and filtration through a 0.45 μm Sartorius membrane. Then Na PSS was precipitated with ethanol (final ethanol/water content equal to 50% v/v), after NaCl addition (6 g l^{-1}). The Na PSS was washed with ethanol–water mixtures up to 100% in ethanol in order to remove the excess salt. The Na PSS powder was dried for 48 h at 30°C under vacuum.

The average degree of sulphonation was found to be equal to 0.91 by pH-metric titration of the acidic form obtained through a cation-exchange resin (IR-120 H, Prolabo). Absence of NaCl was tested from potentiometric titration. The weight-average molecular weight $\bar{M}_w$ was determined by light scattering in 0.1 M NaCl; $\bar{M}_w = 2 \times 10^6$ using dn/d$c = 0.207$ ($\overline{DP}_w \approx 9700$); the intrinsic viscosity in 0.1 M NaCl was found to be 1400 ml g^{-1}. The polymer concentrations investigated in 0.1 M NaCl were 0.182 up to 65 g l^{-1}. In water, the polymer concentration varied from 1.38×10^{-3} to 1.8 g l^{-1}. Aqueous Na PSS solutions in the absence of salt were prepared from bidistilled water in a quartz apparatus.

Viscosity was measured with a Low Shear 30 equipment from Contraves at 25 ± 0.1°C (10^{-2} s$^{-1} < \dot{\gamma} < 128$ s^{-1}) and a Carri-Med Cs rheometer equipped with the Rheo 1000 system and the 4-3 software. Different geometries were used (double cylindrical cylinders: $R_1 = 20$ mm, $R_2 = 20.38$ mm, $R_3 = 21.96$ mm, $R_4 = 22.38$ mm and $h = 20.5$ mm; cone: 6 cm diameter, 4° cone angle). The shear stress varied depending upon the geometry used from 0.005 to 90 N m^{-2}, and the approximate shear rate from 10^{-1} to 2000 s^{-1} depending on experimental conditions.

RESULTS AND DISCUSSION

Viscosity as a function of shear rate and polymer concentration

The experimental data are given in *Figures 1* and *2* for Na PSS in water and Na PSS in 0.1 M NaCl respectively. In the range of $\dot{\gamma}$ and concentrations investigated, no shear-rate dependence was observed with PS even if the molecular weight is in the same range as Na PSS. On the contrary, large effects were obtained on Na PSS in NaCl and H$_2$O. In water, the Newtonian plateau becomes larger when the polymer concentration increases, which is related to the screening of the electrostatic effects; the non-Newtonian effects observed in the presence of external salt are related to the larger stiffness of poly(styrene sulphonate) compared with that of polystyrene and are also reflected by the higher intrinsic viscosity. The shear-rate effect may also come from interchain interactions in the semidilute regime.

The values of viscosity obtained in pure water and given in *Figure 1* were used to plot *Figure 3*, corresponding to η_{red} as a function of polymer concentration. These curves pass through a sharp maximum for $c = 1.4 \times 10^{-4}$ g ml^{-1} independent of the molecular weight. This result agrees qualitatively with previous data given in the literature. Compared with the recent data from Ise[9], the range of shear rates covered is larger here and the maximum much more significant.
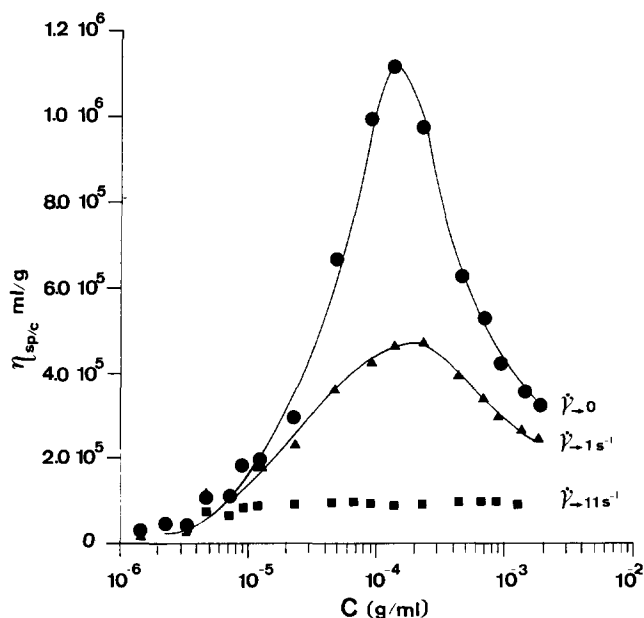

Figure 3 Reduced viscosity of Na PSS in water for different shear rates as a function of polymer concentration

Table 1

c_{max} (g ml^{-1})	d (Å)	q_{max} (Å^{-1})	q_{max}[a] (Å^{-1})
1.4×10^{-4}	1070	5.9×10^{-3}	6×10^{-3}
9×10^{-4}	420	1.5×10^{-2}	1.32×10^{-2}

[a] Estimated values from Figure 4 in ref. 14

A maximum is also described by Cohen et al.[5] but for a lower polymer concentration ($\sim 5 \times 10^{-6}$ g ml^{-1}).

Figure 3 demonstrates that the maximum is very sensitive to the shear-rate condition. The position is slightly modified by $\dot{\gamma}$ and the amplitude decreases with $\dot{\gamma}$. Over $\dot{\gamma} = 11$ s^{-1} the maximum is suppressed. As the peak observed by Cohen et al.[5] may not be observed in our experiments owing to a lack of sensitivity of the viscometer in this domain of viscosities and, on the other hand, as Cohen et al.[5] cannot obtain the peak shown in *Figure 3* owing to the high shear rate adopted (600 s^{-1}), the maximum observed by Cohen et al.[5] and that described here are different. It leads one to suppose that at least two maxima exist in the variation of the reduced viscosity of Na PSS solutions, in the absence of salt, as a function of polymer concentration.

In the presence of 2×10^{-4} N NaCl, the maximum is displaced to $c = 0.9$ g l^{-1} and the height of the peak decreases largely (($\eta_{sp/c})_{max} = 92\,497$ ml g^{-1}).

The peak observed for the reduced viscosity in the range of low polymer concentration and very low ionic content was described by Cohen et al.[5] as a correlation hole effect[13]. Cohen et al. suggest comparing it with the maximum also found by quasielastic light scattering experiments on dilute solutions[14] or by neutron scattering in the semidilute regime[15]. This peak corresponds to a preferential distance in solution controls by the Debye screening length K^{-1}.

From values obtained for the critical concentrations of the maximum in viscosity, it is possible to calculate the critical inter-rod spacing (d) and then the corresponding scattering wavevector q_{max}:

$$\frac{d}{2} = \left(\frac{c_{max}N\pi b}{m_0}\right)^{-1/2} \quad \text{and} \quad q_{max} = \frac{2\pi}{d}$$

where m_0 is the monomeric mass (196), b is the monomeric length (2.5 Å) and N is the Avogadro number. The values found are given in *Table 1*.

These values are in very good agreement with the dependence of q_{max} with $c^{-1/2}$ found by light and neutron scattering[14]; viscosity completes the range of experiments covered by the other techniques. This seems to confirm the origin of the maximum of viscosity and our interpretation.

The results given in *Figure 1* show that no power law is observed in the non-Newtonian regime. The viscosity decreases when $\dot{\gamma}$ increases, with an inflection; the maximum slopes are given in *Figure 4* as a function of polymer concentration. The absolute values of the slopes pass through a maximum in the same range as η_{red} ($\dot{\gamma} = 0$), demonstrating the larger effect of the shear rate in this range of polymer concentration. This maximum may correspond to an electrostatic network for the critical polymer concentration followed by its disruption due to the screening of electrostatic repulsions when ionic content increases. This slope $|n|$ for a given polymer

concentration is much larger in water than in salt, as shown in *Figure 4*, due to large interchain interactions.

In 0.1 M NaCl, the Newtonian plateau is limited by a critical shear rate $\dot{\gamma}_r$ decreasing when the polymer concentration increases; the dependence of $\dot{\gamma}_r$ as a function of the polymer concentration is given in *Figure 5*; the slope of the curves given in *Figure 2* in the non-Newtonian regime are given in *Figure 6*.

In excess of salt, the behaviour of the Na PSS looks like that of a neutral polymer. First, from *Figure 5*, $\dot{\gamma}_r$ is constant in the dilute regime up to $c \sim 2$ g l^{-1}. This polymer concentration corresponds to an overlap parameter $c[\eta] = 3$, larger than 1 as usually admitted. This value is also larger than 1.3 found on polysac-
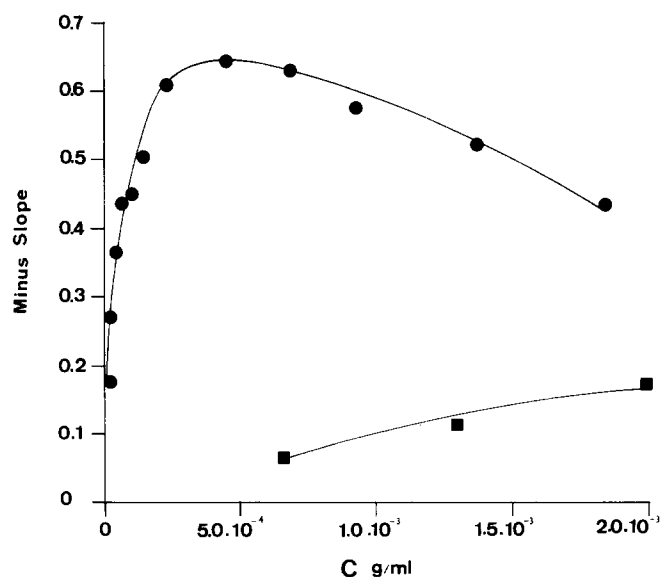

Figure 4 Maximum slope of $\eta_r(\dot{\gamma})$ (experimental values in *Figure 1*) as a function of the polymer concentration: (●) Na PSS in H$_2$O; (■) Na PSS in 0.1 M NaCl
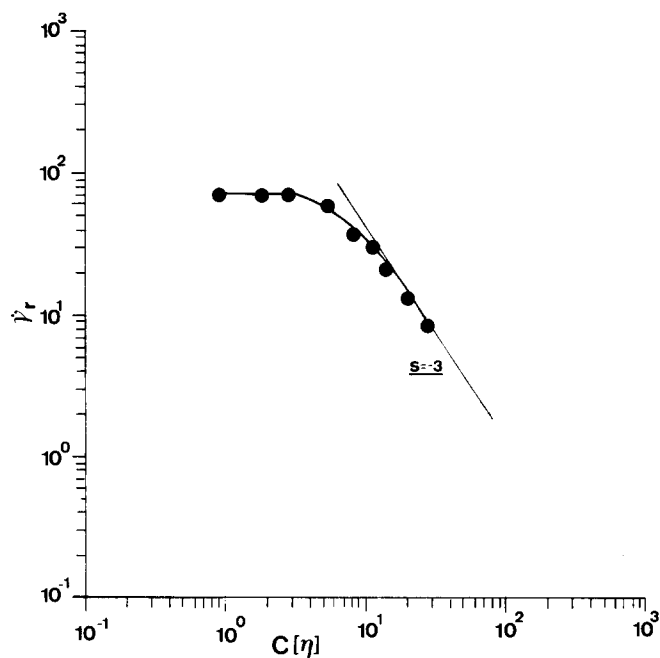

Figure 5 Variation of $\dot{\gamma}_r$ (shear rate of transition between Newtonian and non-Newtonian regime) as a function of the polymer concentration (experimental values in *Figure 2*) expressed as the overlap parameter $c[\eta]$
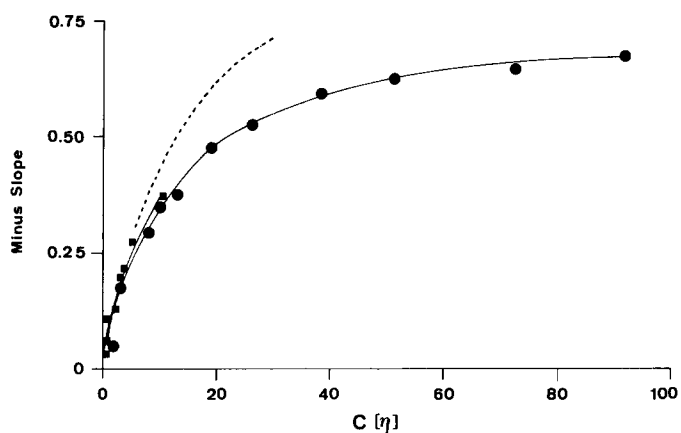
Figure 6 Exponent of the power law $\eta \sim \dot{\gamma}^n$ in the non-Newtonian regime as a function of the polymer concentration (experimental data in *Figure 2*) expressed as the overlap parameter $c[\eta]$: ($\bullet$) Na PSS/0.1 M NaCl; ($\blacksquare$) Na PSS/1 M NaCl; (----) data from Graessley[18] on PS
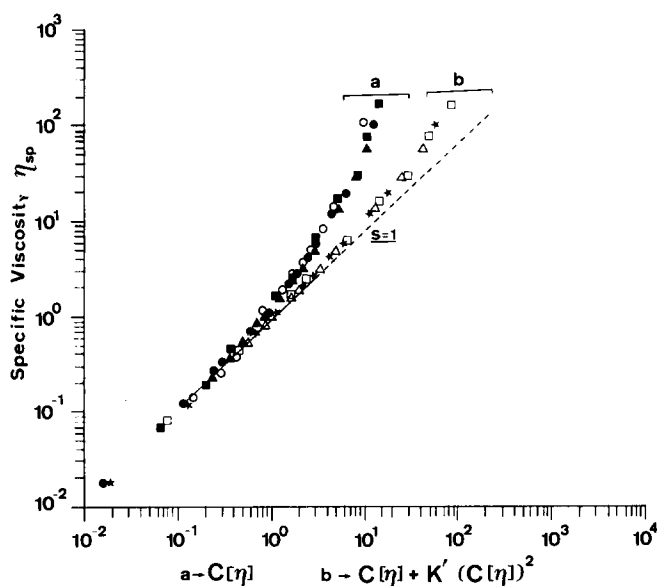

Figure 7 Specific viscosity in the Newtonian plateau as a function of the overlap parameter: (a) $c[\eta]$ and (b) $c[\eta] + k'(c[\eta])^2$: (a) ($\blacktriangle$) Na PSS in 0.1 M NaCl, ($\blacksquare$) Na PSS in 1 M NaCl, ($\bullet$) PS in toluene, ($\bigcirc$) PS from literature[19]; (b) ($\triangle$) Na PSS in 0.1 M NaCl, ($\square$) Na PSS in 1 M NaCl, ($*$) PS in toluene

charides, which are generally semiflexible polymers[16,17]. For large $c[\eta]$ the slope goes to -3.

The absolute value of the slope $|n|$ (*Figure 6*) increases with polymer concentration as predicted by Graessley but going to 0.7, reflecting the electrostatic long-range interactions; this value is lower than given for PS (limit $|n| = 0.818$)[18].

Specific viscosity as a function of the overlap parameter

The specific viscosity is directly related to the overlap parameter $c[\eta]$ as previously discussed[16]; the experimental values obtained for Na PSS in 0.1 M and 1 M NaCl and for PS in toluene, in the Newtonian plateau, are given in *Figure 7*. The results are compared with that obtained by Kulicke and Kniewske[19] on a PS in the same range of $c[\eta]$. Agreement with our results is good.

Our data for PS and Na PSS give the same curve when

η_{sp} is represented as a function of $c[\eta] + k'(c[\eta])^2$ up to 10^2. The different polymers behave in the same way. Especially, the Huggins relation is followed by Na PSS and PS up to $c[\eta] \sim 3$ as found previously (*Figure 5*) as a limit of the dilute domain (linear part of curve (b), with a slope equal to 1). It appears that, in the Newtonian regime, there is no large difference between the neutral polymer (PS) and its derivative (Na PSS) in a salt excess from a qualitative point of view.

CONCLUSIONS

The aim of this paper was to discuss the original behaviour of the viscosity of polyelectrolytes in aqueous solutions. Large shear-rate effects were observed compared to the behaviour of the corresponding neutral polymer even in excess of added salts. In the absence of external salt, the reduced viscosity determined in the Newtonian plateau passes through a sharp maximum for a critical concentration which may correspond to an electrostatic lattice. It does not correspond to that given in the literature and especially that discussed by Cohen et al.[5]. This maximum was not observed in light scattering owing to technical conditions (i.e. too large wavelength), but its position demonstrates that it has the same origin as the peak found from light and neutron scattering. The critical concentration of this maximum determined from viscometry is equal to $0.14 \, \mathrm{g \, l^{-1}}$ independent of the molecular weight in the absence of salt; it increases when external salt is added. The height of this peak is very sensitive to the shear rate adopted for measurements. In the presence of NaCl over 0.1 M a transition from dilute to semidilute regime is obtained for $c[\eta] \sim 3$, much larger than usually predicted, but which seems to characterize a flexible polymer.

The shear-rate effect is more important on Na PSS than on PS even in the same range of molecular weight; this is due to the larger stiffness of the polyelectrolyte compared with the neutral polymer and to electrostatic interchain exclusion.

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