polymer papers

The behaviour of polyelectrolyte solutions in elongational flow; the determination of conformational relaxation times (with an Appendix of an anomalous adsorption effect)

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The elongational flow method for determining conformational relaxation times of macromolecules (τ) in solution, based on the determination of the critical strain rate to induce the coil→stretch transition has been described previously for neutral polystyrene (PS) solution. In the present work it is applied to a polyelectrolyte, the Na$^+$ salt of polystyrene sulphonate (NaPSS), which is available in monodisperse form in several molecular weights. It was found that, in highly dilute solutions in the absence of added salt, τ is up to three orders of magnitude larger than for neutral PS indicating a more expanded and/or more permeable chain conformation. The existence of a critical strain rate plus the observed quadratic molecular-weight (*M*) dependence suggest a free-draining coil at these low salt concentrations. On adding salt, a drastic and sharp decrease in τ, followed, thereafter, by a more gentle decrease on addition of further salt, is interpreted as a transition to a more collapsed non-free-draining coil behaviour, which is then retained. On raising and subsequently lowering of pH, τ increases and decreases in a reversible manner with a small hysteresis corresponding to the overall increase in salt concentration. Exchanging Na$^+$ or Ca^{++} decreases τ drastically, from which a stiffer and more compact molecular conformation, assigned to intramolecular ionic bridging, is inferred. However, the same dependence on ionic strength of added salt is otherwise observed. For divalent salt forms, τ increases with polymer concentration until gelation occurs, indicating intermolecular ionic bridging. Many of the observed effects are in qualitative agreement with the accepted picture of polyelectrolyte behaviour, such as the pH-dependency of τ. However, some aspects provide a more detailed picture, for example, the quadratic-dependency of τ on *M* at low ionic strengths and the transition-like collapse of the coil to a non-free-draining state with increasing ionic strength. Other effects such as the competition between inter- and intramolecular linking with Ca^{++} appear to be new. All these illustrate the power of the method at this initial stage. In addition, extraordinarily tenacious adhesion of the molecules to the glass walls of the channel into which they enter in an oriented state was observed and attributed to a previously unrealizable degree of multiple attachment of the chain when fully stretched out, resulting in drastic consequences for subsequent flow behaviour.

Keywords Elongational flow birefringence; polyelectrolyte; conformational relaxation time; adsorption; polystyrene sulphonate; molecular expansion

INTRODUCTION

The behaviour of polyelectrolyte molecules in solution has been for many years a subject attracting considerable theoretical attention[1–8]. Much of the work has been based on the interpretation of viscosity data and to a lesser extent on light and quite recently neutron scattering results. To this we now have a new technique to add arising essentially from our attempts to extend flexible, neutral molecules in dilute solution. This, as we now find, can be applied to polyelectrolytes. Since there are relatively few independent experimental probes of the solution behaviour of polyelectrolyte molecules, this application should be significant even if it merely fulfilled a corroborative role; as will be apparent it shows promise of providing much more.

The technique in question consists of creating a purely elongational flow-field by means of opposed jets or cross-slots[9,10] as shown in *Figure 1*. The geometry produces a null point in velocity at the centre of the gap and an elongational flow field is produced along the central axis as the solution accelerates towards the two jets entrances or exit channels. A *rod*-like molecule in such a flow-field will tend to align parallel to the flow, the degree of alignment, as measured by birefringence, increases continuously with increasing strain rate, $\dot{\varepsilon}$, as illustrated in *Figure 2*(*a*).

Theories on the behaviour of a *flexible* molecule in such a flow field predict that the molecule will extend almost completely from its random-coil state at a critical elongational strain rate, $\dot{\varepsilon}_c$, as illustrated in *Figure 2*(*b*). This is the so called coil→stretch transition setting in when

$$\dot{\varepsilon}_c \tau = 1$$

where τ is the relaxation time associated with this transition (see e.g. ref. 14). Our previous works on flexible

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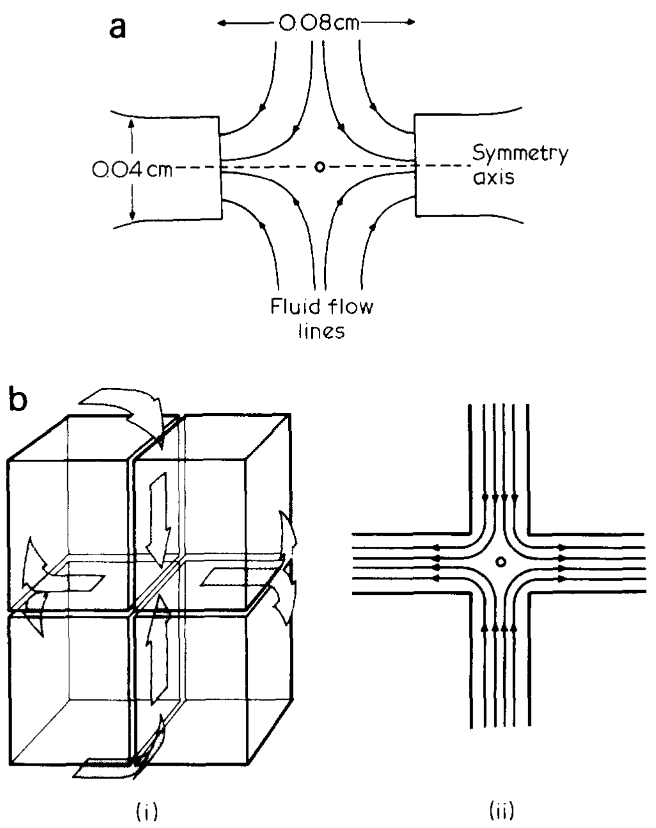

Figure 1 Diagrams of flow systems used for the study of elongational flow induced chain extension. (a) Schematics of impinging suction jets producing uniaxial elongational flow (b) Cross-slot device producing a planar elongational flow field (i) perspective view (ii) idealised flow field in the slots. The extension of the chains is diagnosed by observing the appearance of a birefringent line appearing at a critical strain rate ($\dot{\varepsilon}_c$) highly localized along the central axis passing through the stagnation point (O). This line is the broken line in (a) and along the outgoing axis in (ii) of (b)

chains using this device have shown[9,10] that $\dot{\varepsilon}_c$, hence τ, could be directly determined by registering the $\dot{\varepsilon}$ value where birefringence sets in within the localized region along the centre line or axis of the flow system (for the origin of and significance of localization see refs. 11–14). When monodisperse neutral polystyrene (PS) was used the onset of birefringence occurred in a narrow range of $\dot{\varepsilon}$ thus allowing determination of $\dot{\varepsilon}_c$ and through it τ[9]. Both the absolute value of τ and its observed molecular weight dependence ($\tau \propto M^{1.5}$) conformed to expectations for a non-free-draining model indicating that it is the relaxation time associated with a non-free-draining coil which governs the chain extension. It should be emphasized that τ is the relaxation time associated with the mechanical response of the random coil molecule to a small deformation, not that of the time required for the molecule to go from the random coil to the extended state. Physically this means that it is the first stage of the deformation which is the rate determining factor: once the chain starts to extend the process will 'run away'.

Having had considerable success with neutral PS we felt that we were in possession of a remarkably simple and powerful tool to study chain extension and corresponding relaxation times in other systems. We chose polyelectrolytes as a next step for three reasons:

(1) Polyelectrolytes are important materials in polymer science (both synthetic and biological) deserving study for their own sake and particularly when a new approach promises to be in sight.

(2) The study on neutral PS required monodisperse material in the high molecular weight range for it to be fruitful and practicable. Closely equivalent polyelectrolytic materials are available in the form of polystyrene sulphonates(PSS). Therefore, our previous experience[9] merely had to be transferred to a material which was chemically identical as regards chain backbone but having charged groups on the otherwise identical side groups.

(3) We wanted to explore the effect of chain rigidity. Neutral PS being a highly flexible molecule we wanted to go over to increasingly stiffer chains. Polyelectrolytes provide such an opportunity in addition to permitting chain flexibility to be varied within wide limits by controlling the charge neutralization of the ionic groups along the chain.

Polyelectrolyte molecules can take up various random coil configurations over a wide range of coil expansion depending on the environment and the net charge on the molecule, and at extremely high charge the rod-like limit is expected to be reached. The work to be described here will be concerned with the dependence of coil dimensions and coil geometry, on the ionic strength (as influenced by added salt concentration) of the solution, on pH, and on the valency of the counterion. The chain extending behaviour of the molecule was followed through measurements of $\dot{\varepsilon}_c$, $(1/\tau)$, and its molecular weight dependence.

EXPERIMENTAL

The experimental methods of creating the extensional flow fields capable of extending polyelectrolyte molecules of molecular weights such as were commercially available, consisted of opposed jets and cross-slots, described in detail elsewhere (see e.g. ref. 9) and reproduced schematically in *Figure 1*. As already stated the extension of the molecules was followed by observing the development of the birefringence. $\dot{\varepsilon}_c$ itself could be readily detected visually by the sudden appearance of the birefringence. In addition electronic recording of intensity was used, in the first place to have an objective record of this onset of birefringence and secondly to follow the further development of the birefringence beyond $\dot{\varepsilon}_c$ (in which respect there were considerable differences between the neutral PS and PSS) (see *Figure 3*).

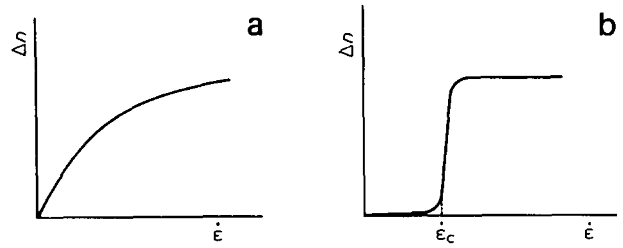

Figure 2 Schematic representation of the differing responses of (a) rod-like and (b) flexible macromolecules to the orienting effect of elongational flow. The diagrams represent the orientation, expressed as birefringence Δn (the quantity being measured in these experiments) as a function of strain rate ($\dot{\varepsilon}$). In the case of (b) chain extension sets in suddenly at a critical strain rate $\dot{\varepsilon}_c$. Actual examples for (a) are shown in refs. 13 and 19, for (b) in refs. 9, 10, 13 and 20

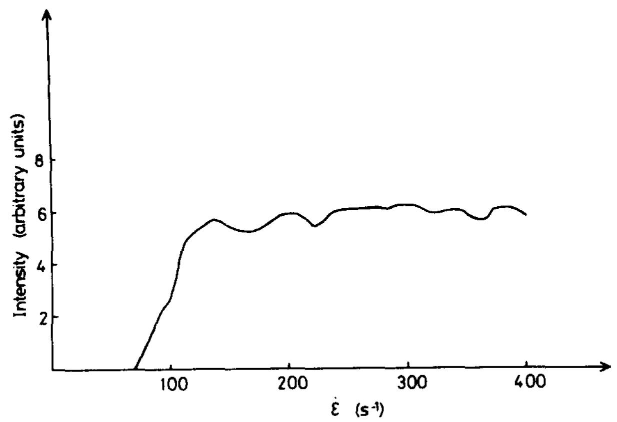

Figure 3 Plot of the measured intensity of the localized birefringent line *versus* flow rate, showing a step-like increase in intensity with increasing flow rate for a 0.1% solution of PSS ($\bar{M}_w = 1.06 \times 10^6$) in a 0.0005M NaCl solution, i.e. in region I of *Figure 5*

The polyelectrolytes used were PSS supplied in the form of sodium salt by Pressure Chemical Company. The highest molecular weights available were used. These were in descending order $\bar{M}_w = 1.06 \times 10^6$, $\bar{M}_w = 6.9 \times 10^5$, $\bar{M}_w = 3.54 \times 10^5$ and $\bar{M}_w = 1.77 \times 10^5$. The polydispersity index as given the suppliers was around $\bar{M}_w/\bar{M}_n = 1.10$ for the different samples.

Special care was needed in the preparation of the solutions. The polymers were first dialysed against pure water to remove excess salt. In some experiments the monovalent sodium counterion was exchanged for divalent calcium. Solutions of 0.1% concentration in pure water were made from the resulting polymer. Measurements of τ ($\tau = 1/\dot{\varepsilon}_c$) were carried out repeatedly in the same apparatus over a period of days, and it was found that τ values obtained were not identical in the repeated runs but decreased systematically with the time elapsed after the preparation of the solution. Eventually after 2–3 days a constant value was reached, a value which depended on the molecular weight (*Figure 4*). To reduce the chance of mechanical degradation, as little flow as possible was used in these measurements of τ. After three days the solutions were freeze dried, redissolved in pure water and τ measured again over the following three days. The time dependence of τ in dissolving and its final value were found to be reproducible, indicating that degradation was not a problem nor the reason for the decrease in τ with time from the start of dissolving. As will be mentioned again in the discussion this time dependence of τ is interpreted as the gradual break-up of molecular aggregates in the dissolution process. Clearly at least three days are needed to completely dissolve the polymer. For all measurements to be reported the NaPSS concentrations was held at 0.1%. Variation of polymer concentration would have been desirable, but owing to externally imposed time limitation could not be encompassed within this study.

The ionic strength of a 0.1% solution of NaPSS ($\bar{M}_w = 1.06 \times 10^6$) was increased by adding NaCl to a maximum concentration of about 0.06 molar. Measurements of τ were made at several added-salt concentrations. The measurements were repeated on the polymer for which the sodium had been exchanged for calcium and $CaCl_2$ added to increase ionic strength.

The investigation of the pH dependence of τ was again carried out on a 0.1% solution of NaPSS of $\bar{M}_w = 1.06 \times 10^6$ with 0.017 molar added NaCl. The pH of the solution was increased by adding NaOH and then decreased by the addition of HCl.

All materials used were kindly analysed for us at the School of Chemistry, Bristol, with a view to assessing the degree of sulphonation.

RESULTS

As for neutral PS a localised birefringent line was observed at strain rates above a certain critical value. Even if in general, this line was seen less bright and its boundaries more diffuse, particularly for solutions with high added salt concentration, than had been observed for dilute solutions of neutral PS, there was little difficulty in identifying $\dot{\varepsilon}_c$ visually, and it could be registered electronically (*Figure 3*)*.

Figure 4 shows the time dependence of τ for 0.1% solutions of NaPSS of $\bar{M}_w = 6.9 \times 10^5$, 3.54×10^5 and 1.77×10^5 in water, already referred to in the previous section, leading to the conclusion that at least three days should be allowed for complete dissolution of molecular aggregates. The observed dependence of τ on ionic strength for both the sodium and calcium salt is shown in *Figure 5* for a 0.1% solution of polymer with $\bar{M}_w = 1.06 \times 10^6$. Taking the sodium salt first, three distinct regions can be identified. I, a high relaxation time at very low salt concentration decreasing steeply with increasing salt concentration. II, a huge drop in τ which is practically discontinuous at a critical NaCl concentration. III, slowly decreasing τ at higher concentration beyond the drop. The Ca salt follows the same pattern although fewer points are available (these experiments were carried out later, just before the present programme had to terminate). However, here the τ values were one to two orders of magnitude smaller, and the τ vs. salt concentration curve was shifted to lower salt concentration; this will be apparent when bringing the two scales, one for each salt, along the abscissa at the top of the diagram into coincidence.

Because of the limited strain rate that could be realized

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* Having shown that a critical $\dot{\varepsilon}_c$ value is identifiable, the main purpose of these experiments, a few additional observations and qualifications will be listed. *Figure 3* shows that after the sudden initial step the orientation (as expressed by the intensity measured) continues to rise gently with increasing $\dot{\varepsilon}_c$. This is opposed to the flattening off at a maximum corresponding to the stretched out chain for neutral PS[9] (in fact with PS this plateau was often followed by an unexplained decrease initially attributable to degradation; more recently a reorientation of the sidegroups is suspected instead or in addition to such an effect[18]). Although the birefringence was not measured as such, the effect may be due to the fact that the line was also observed to broaden, hence the actual birefringence associated with the increasing total intensity may remain unaltered and correspond to that of the fully stretched out chain as in PS. Alternatively, the continuing rise beyond the step may mean that the chain is not in its fully stretched state at $\dot{\varepsilon}_c$. Without the actual numerical value of the retardation the two alternatives cannot be distinguished. (Even in the knowledge of such a value the existence or otherwise of full chain extension could not be ascertained as the birefringence due to completely stretched out PSS would be practically unknown.) Incidentally, the shape of *Figure 3* is not unique: while the position of the step is reproducible in a given system, its relative size and that of the subsequent rise could be different in different runs. Thus steps larger than shown by *Figure 3*, which is for a very low salt concentration of 0.0005 molar, have been obtained.

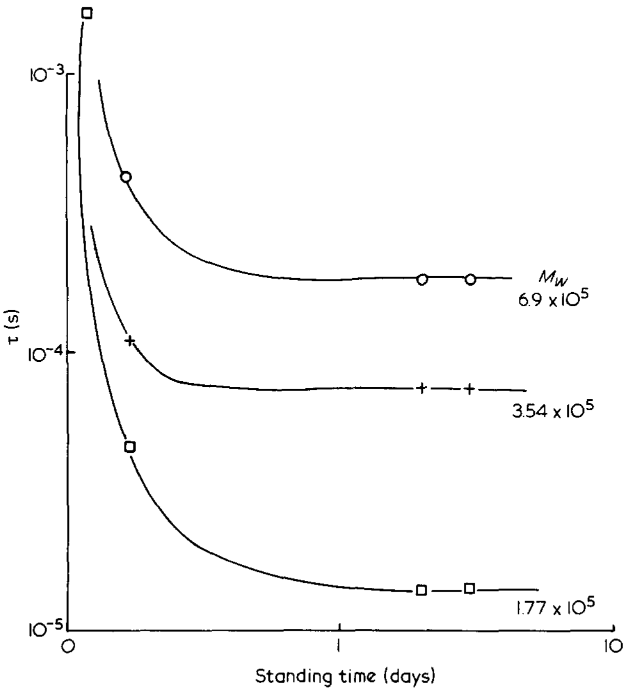

Figure 4 A plot on log scales of relaxation time, τ, *versus* time in solution for polystyrene sulphonates, PSS, of $\bar{M}_w = 6.9\times10^5$. 3.54×10^5 and 1.77×10^5 (mean error of points $\pm10\%$)

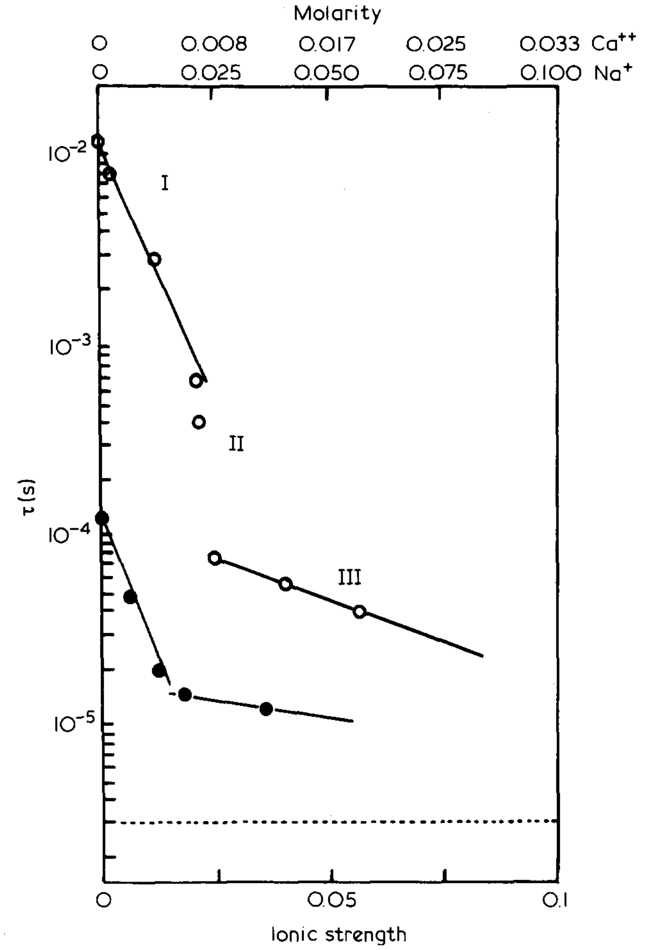

Figure 5 Plots of the log of relaxation time, τ, *versus* ionic strength of added NaCl (○) and $CaCl_2$ (●). Abscissa scales showing the corresponding molarity for these added salts are also included on the top. The broken line indicates the relaxation time expected for a polystyrene molecule of the same degree of polymerization as that of the polystyrene sulphonate used, and in a solvent of the same viscosity

in the present apparatus ($\dot{\varepsilon} \sim 10^5\ s^{-1}$) relaxation times less than about 2×10^{-5} s could not be measured. The horizontal broken line in *Figure 5* shows the relaxation time expected for neutral PS (i.e. uncharged flexible chain) having the same number of repeat units (the difference in the viscosities of the different solvents having been taken into account).

The pH dependence of τ for a 0.1% solution of NaPSS ($\bar{M}_w = 1.06\times10^6$) in a 0.017 molar NaCl solution is shown in *Figure 6*. τ increases with pH though the effect is not as great as can be brought about by changes in ionic strength. As can be seen a small hysteresis occurs on increasing and then decreasing the pH: this is due to an increase in ionic strength resulting from the salt produced in the neutralization by HCl of the added NaOH.

At low added salt concentrations (0.004 molar NaCl), i.e. in region I, it was possible to measure τ for all four samples within the $\dot{\varepsilon}$ range which could be spanned by our apparatus. In this way the effect of molecular weight on τ could be determined paralleling the corresponding study on neutral PS[9]. The results are plotted on log scales in *Figure 7*. The relaxation time was found to have a quadratic dependence on the molecular weight at this ionic strength. It was not possible to measure the molecular weight dependence of τ at high salt concentrations as the values of τ for the lower molecular weight polymers became too small (hence the $\dot{\varepsilon}_c$ values were beyond the range we could attain).

The microanalytical results showed the sulphonation to be 100%.

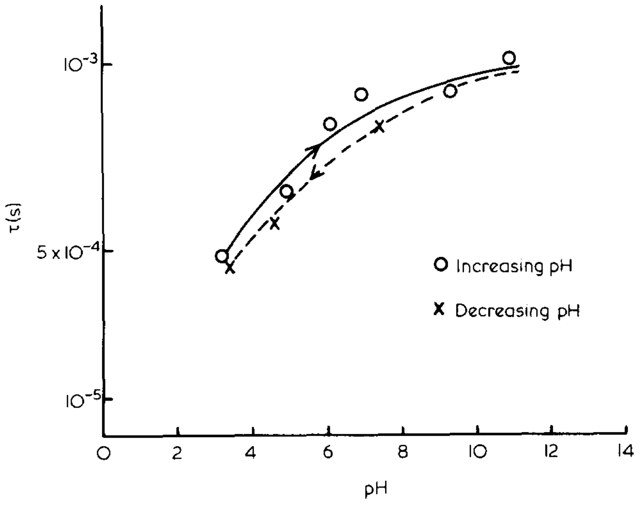

Figure 6 Plot of relaxation time, τ, *versus* pH for a 0.1% solution of NaPSS ($\bar{M}_w = 1.06\times10^6$) in 0.017 molar NaCl. The arrows indicate the path taken for the changes in pH

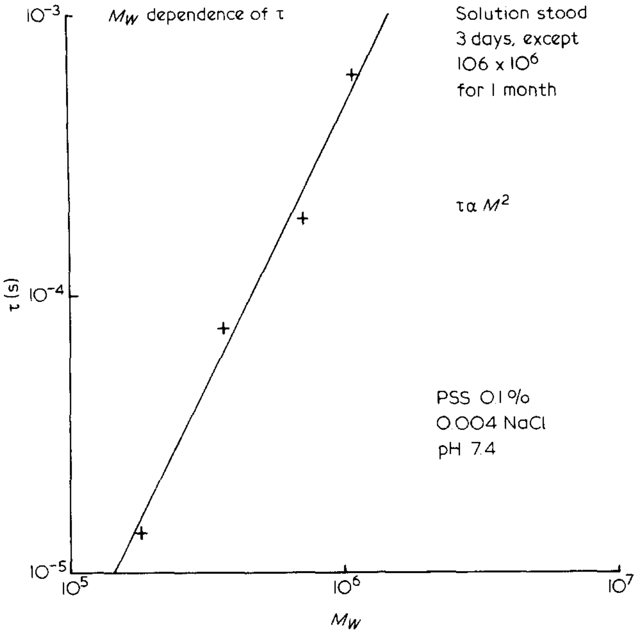

Figure 7 Plot of relaxation time, τ, *versus* molecular weight of PSS on log scales for a 0.1 % solution of NaPSS in 0.004 molar NaCl, i.e. in region I of *Figure 5*

DISCUSSION

By existing expectations from the theory of polyelectrolyte solutions, polyelectrolytes should be in a more or less expanded state as compared to the corresponding neutral chain, owing to mutual repulsion of adjacent charged groups along the chain. The exact state of expansion will depend on the degree of screening by the counterion in the solution, higher counterion concentrations allowing increasing contraction towards the random coil state adopted by the non-electrolytic counterpart of the same polymer. We would therefore expect a highly expanded state in the absence of added salt, with increasing contraction with added salt. This should be reflected by the configurational relaxation time, τ, as measured by our technique, through its response to elongational flow induced chain extension, the more expanded chain corresponding to larger and the more contracted chain to smaller τ values. It was one of the purposes of this work to test this behaviour, the results being represented by *Figure 5*.

At first glance we see that *Figure 5* reflects the broad expectations: a dramatic decrease of τ with added salt concentration. The details, however merit further attention. We see that all τ values are above that corresponding to non-polyelectrolytic PS of identical degree of polymerization (i.e. chain length) shown by the horizontal broken line. The value of $\tau = 4.38 \times 10^{-6}$ is extrapolated from the previously established relation $\tau \propto M^{1.5}$ for PS because such a low value of τ could not be measured directly owing to our limitations on $\dot{\varepsilon}$ (in view of the high degree of monodispersity we proceed to use the single symbol of M for molecular weight). In other words we could not go below $M = 2.0 \times 10^6$ for PS to achieve overlap with the PSS sample of highest M available used in *Figure 5*. Nevertheless the relation $\tau \propto M^{1.5}$ had been obeyed so accurately for PS samples[9] between $M = 2.0 \times 10^6$ and to $M = 2.0 \times 10^7$ (the highest M available), i.e. over an M range encompassing a variation of $10\times$, that we are reasonably confident that an extrapolation to lower molecular weights by a factor of 2 cannot be in serious error.

The behaviour of the molecule in the region of high monovalent counterion concentration is likely to approach that of neutral PS which, as established in our previous works, corresponds to that of a non-free-draining coil. The trend in region III clearly reflects this. We suggest therefore that region III already represents the non-free-draining regime, i.e. where most of the space encompassed by the coil itself can be regarded as a hydrodynamic sphere. The larger τ values (compared with PS) we attribute to a larger sphere diameter due to greater stiffness of the chain because of the presence of some intramolecular repulsion still present at the salt concentrations in question. Accordingly, the gentle rise of τ with decreasing salt concentration in region III would reflect the increasing diameter of the hydrodynamic sphere constituted by the otherwise non-free draining coil. We attribute the variation in τ with pH (*Figure 6*) to the same cause, i.e. to an expansion and contraction of the molecule. Again, increasing pH promotes dissociation leading to an increase in chain stiffening, hence larger τ, and to the reverse effect on decreasing pH, as in fact observed. This is qualitatively consistent with polyelectrolyte theory to which we now add some actual figures for τ. As already stated, the small departure from exact reversibility arises from an increase in salt concentration which occurs as alkali and acid is being progressively added to the same solution in order to change the pH.

Admittedly the assertion that in region III we have a non-free-draining coil would need to be verified by determining the M dependence of τ (as done for PS), but as already stated this could not be done with the realizable $\dot{\varepsilon}$ values for the M range of the materials available (the remedying of this insufficiency clearly remains a challenge for future experiments). The reality of this proposition is nevertheless clearly brought home by the sharp transition in τ represented by region II.

The change represented by region II is truly dramatic. To our knowledge such a sudden and huge transition has not been observed before neither is it anticipated, at least in this form, by theory. We consider therefore the present finding both novel and of importance.

Even without explicit theoretical back-up the transition in region II suggests a drastic change in molecular behaviour at this salt concentration. On the low-salt side of the transition, in region I, the relaxation times of the lower molecular-weight samples are now large enough to measure with the present apparatus, a point which is exploited to explore the molecular weight dependence of τ in this regime (*Figure 7*).

We know that the vastly increased τ in region I signifies a highly expanded chain conformation. If it remains a coil it must be of much increased dimension: in the limit the chain could even lose the coil character, and become rod like. Here the molecular weight dependence of τ provides the clue.

For coils we expect: $\tau \propto M^{1.5}$ in the non-free-draining case, as repeatedly referred to above and established for PS[9];* $\tau \propto M^{2.0}$ for the free-draining case (see e.g. ref. 15)

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* We are aware of the fact that in the theories the exponent of 1.5 is associated with the theta state which with the solvents we used (xylene, decalin) is not likely to pertain. Nevertheless, this exponent is a firm observational fact and provides us with a power law which we shall continue to associate with the essentially non-free-draining character of the coil.

and $\tau \propto M^3$ is an approximation for the rotational relaxation time of rods[16].

Figure 7 clearly shows a quadratic dependence, hence distinguishes between the three alternatives in favour of the free-draining coil. The physical picture seems reasonable, in fact self evident. As the coil expands owing to stiffening, hence extension of the segments constituting it, it would become permeable to the solvent which could thus more or less flow freely through it. The frictional forces now become directly proportional to the length of the chain, ($f \propto M^{1.0}$, f=frictional coefficient). In view of the fact that $\tau = f/K$, with K the elastic restoring force inversely proportional to M, then $\tau \propto M^{2.0}$ behaviour follows. That this permeable and highly expanded coil still possesses entropy elastic character is indicated by the existence of a critical $\dot{\varepsilon}_c$ value, i.e. by the step in the ε (strain, expressed as retardation or intensity in our experiment) vs. $\dot{\varepsilon}$ curve as shown in *Figure 3*. The same effect, i.e. the initial step in *Figure 3*, excludes the rod model on its own, i.e. without recourse to molecular weight dependence, as in the case of rods the birefringence should increase continuously with strain rate[12] (see *Figure 2a*).

With divalent calcium as the counterion the values of relaxation times were always lower than those obtained with sodium at the same normality. This indicates that the random coil molecule with added calcium responds to a lesser degree to the initial small deformation imposed on it (our interpretation of τ as assessed by our elongational flow method, i.e. by $\dot{\varepsilon}_c$—see Introduction) which implies smaller τ, hence by $\tau = f/K$, smaller frictional force and/or higher restoring force. This would be consistent with a greater compactness of the isolated molecule which would be understandable if the divalent calcium can link or build bridges between various parts of the *same* molecule in the dilute solutions in question where the molecules can be regarded as isolated. Such ionic bridges would increase K, the entropic restoring force constant, in all regions of the curve in *Figure 5*, in regime III in particular, where the non-free-draining character is assumed to prevail. In addition in this regime where the coil is not fully permeable (i.e. regime III), the equivalent hydrodynamic sphere, and thus the frictional coefficient would be smaller, reinforcing the effect of increasing K in the reduction of τ. It would also followed that owing to this intramolecular cross-linking at sufficiently high salt concentration τ might fall below that of non-electrolytic PS, a possibility which is at least suggested by *Figure 5*; the verification of this is clearly invited in future work.

For the higher valence counterions, the screening effect of the added ions will be greater for a given concentration of added salt, since the ionic strength, I, is given by $I = \frac{1}{2}\sum_i z_i^2 m_i$ where z_i and m_i are the valency and molarity of the i^{th} ion species, respectively. This means that behaviour which depends on the reduction of electrostatic repulsion along the polymer chain, that is, the collapse of the coil from an expanded state with increasing counterion concentration, should be observed at lower added salt concentration. This is seen in *Figure 5* when the data as a function of added salt concentration are compared. If compared as a function of ionic strength (bottom abscissa scale) the curves differ only by a vertical shift. It would be preferable to plot τ against total ionic strength of the solution, including the contribution of the polyelectrolyte, but the calculation of this contribution causes a serious problem. Use of the independent-monomer approximation may be appropriate at high added salt concentrations, but at lower salt concentrations, where the molecule is stiffer it is not valid, and in all cases the degree of dissociation must be known. The alternative approach taken here is to include only the contribution to the ionic strength from the added salt.

The above consideration relating to the effect of Ca^{++} ions in dilute polymer solutions raises the issue of the influence of the polymer concentration itself. Clearly on increasing the *polymer* concentration the onset of *inter*molecular ionic bridging should be expected. Indeed, increase in τ indicating an increase in effective chain dimensions with increasing polymer concentration while still in the true solution was observed. In fact, in a current phase of the work, due to J. A. Odell, a stage where macroscopically visible gelation sets in was attained on further increase of the concentration of polymer*, directly verifying the expectation of intermolecular bridging. Accordingly we have a situation where intra- and intermolecular ionic bridging compete with diametrically opposing effects on the resulting molecular dimension, which is directly registrable by our tests. This aspect of the work involving the effect of polymer concentration is clearly central, nevertheless it needs to be made more comprehensive, including a comparison with the corresponding behaviour with monovalent salts, before it can be reported on in specific detail. (In the work by J. A. Odell now in progress, the mechanical strength is being found to increase in the sequence Mg→Ca→Ba when these different bivalent counterions are compared. The implications are obvious from the decreasing solubilities of the corresponding simple ionic salts as known from basic inorganic chemistry.)

In conclusion, the configurational relaxation time, being an expression of chain conformation and chain stiffness, as assessed by our method based on the detection of critical strain rate in elongational flow, responds sensitively to all those variables which are anticipated from the basic behaviour of polyelectrolytes. Not only is this response in the expected direction, but its details, incompletely recorded as they may be at the present stage, offer a new and remarkably simple method for the study of the behaviour of the isolated polyelectrolyte molecule with the realistic promise of detecting and following their association as indicated in the final paragraph.

APPENDIX

A problem of experimentation; recognition of a novel adsorption effect

The prime purpose of this Appendix is to point out an experimental problem which has greatly hindered our own programme on the chain extending properties of elongational flow, an experience which we feel is our duty to pass on to would-be investigators taking up our method. As will be apparent, however, the problem presents itself through an extraordinary effect, which unexplained as it is, we feel is noteworthy in itself (with

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* Owing to the fact that materials of different origin, hence polydispersity, were used for these experiments the actual concentration values are not being quoted as they will not be comparable. Our objective here is merely to place the existence of the three stages of the sequence: coil contraction (compared to NaPSS), expansion of effective coil dimension and gelation with increasing *polymer* concentration in the presence of excess bivalent cation, on the map.

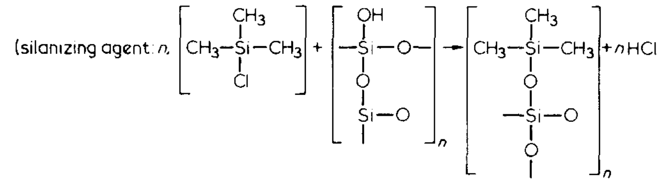
possibly far reaching consequences deserving a report in its own right). It is this dual purpose which is reflected by the title.

The experiments on the aqueous polyelectrolyte (PSS), the subject of the present paper, were originally a diversion in our studies on the elongation of uncharged non-polyelectrolytic chains, polystyrene (PS) in particular, in non-polar solvents. Our original intention was to use the same jet and slot systems interchangeably with PSS and PS. This we could not do and this is the practical problem we wish to draw attention to here, the first objective of this Appendix. The factual observation was that once the apparatus had been used with the aqueous polyelectrolyte it became unsuitable for similar experiments on PS in the usual organic solvents, because the sharp birefringent line at $\dot{\varepsilon}_c$, signalling chain extension, either did not appear or only in such broad ill-defined and unstable form that it could not be used for determining relaxation times even when the *identical* apparatus had been satisfactory for the purpose *before* the PSS solution was passed through it. No amount of cleaning (washing which included chromic acid, heating to temperatures below the softening of soda glass) could restore the usability of the jets or slots for the experimentation with PS, although it remained applicable for continued experimentation on PSS. The practical lesson, which we are anxious to convey here, is therefore the following: If experiments on both polyelectrolytes and non-polyelectrolytes are to be pursued by our method separate apparatus has to be used for each.

What has been said so far is a plain observational fact, which was to our detriment. Not only did it occur consistently but we could not (with one exception—see below) even avoid it. Apart from its nuisance value, the effect was so striking that it also raised our curiosity as regards its origin, and a few experiments were performed to track down its source which will be here transmitted.

In our attempts to make the apparatus, once used with PSS, usable again for PS (after all cleaning experiments failed) we replaced the various glass components with new unused ones, one by one. Not until fresh jets were applied was the initial capability of the apparatus restored. The implication is obvious: the jets became permanently modified by the PSS as diagnosed by the analogous subsequent experiment with PS. Two further important observations need adding. (1) Mere soaking the jets in PSS did not produce the modifying effect, unless the PSS solution was made to stream through the jets in an elongational flow mode, such as to stretch the chains. (2) PSS had no effect on subsequent experiments with PS in the blow mode, where (as is well established and understood) the orientation produced is manifest as a birefringent annular disc[17]. The important point in our opinion is that in the blow jet case this birefringent disc is confined to the space between the jets (ideally it is in its midplane) and does not extend into the jets.

Clearly both (1) and (2) above point to the fact that the PSS chains must be in a stretched out form within the jets themselves. Furthermore, in order to be able to modify the subsequent behaviour of the jets, the stretched out chains must become adsorbed. It follows from our experience that this adsorption must be extraordinarily tenacious for the chains to become unremovable, and by implication that only minute amounts of material can be involved. If adsorption is involved this should be sensitively influenced by the nature of the surface. This has been demonstrated by silanizing the surface of fresh, still unused jets.



$$\text{(silanizing agent: } n\text{)}\left[\mathrm{CH_3-\overset{CH_3}{\underset{Cl}{Si}}-CH_3}\right] + \left[\begin{matrix}\mathrm{-\overset{OH}{Si}-O-}\\ \mathrm{O}\\ \mathrm{Si-O}\end{matrix}\right]_n \rightarrow \left[\begin{matrix}\mathrm{CH_3-\overset{CH_3}{Si}-CH_3}\\ \mathrm{O}\\ \mathrm{-Si-O}\\ \mathrm{O}\end{matrix}\right]_n + n\mathrm{HCl}$$

The jets thus treated did not display any of the effects described: they remained usable for PS after experimentation with PSS.

This last experiment of course might provide a solution to our practical difficulties, which we had no opportunity to test and exploit further. Nevertheless even as it stands the observation demonstrates that adsorption must be involved.

Adsorption of polymers is an important and major topic in its own right. The usual adsorption studies, however, refer to the random coil under stationary conditions. The present experience, however, indicates that conditions can be quite different for adsorbtion of chains which adsorb in the virtually fully extended state, an issue which to our knowledge has never even been addressed in the past (understandably so, as full chain extension in solutions has only become possible through the present type of experiments). Qualitatively the trend inferred here is in line with expectations. Adsorption of polymers is known to be tenacious even in the random state owing to the possibility of multiple attachment points. If the chains are fully stretched out the number of potential contact points between polymer chain and solid interfaces will be enormously increased, hence enhancement of polymer retention may well be expected. Even so, without any quantitative feel for this enhancement, the actually observed persistence, in fact virtual permanence of the attachment of the chain to the solid, seems truly astonishing.

In the foregoing we made a reasonable case for the enhanced and practically permanent adsorption of polymer chains once brought in the fully extended state, and have drawn attention to this unexplored area of polymer behaviour. But it needs recalling that the whole effect has come to our notice, and in fact in a very forcible manner, through a hydrodynamic effect which so far has remained our only diagnostic tool of something having happened at all. Why an adsorbed layer of what can only correspond to a minute amount of polar material should affect the flow field of non-polar solution in such a drastic manner, and according to our observation extending as far as it has, 0.25 mm from the orifice into *open* solution, raises a hydrodynamic problem beyond our present comprehension. Whatever its origin it must be of significance wherever there is a combination of stretching flow in polymer solutions and solid surfaces, a situation which could arise in polymer hydrodynamics, whether in the laboratory, in technical installations, or living organisms.

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