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Viscosity and scattering of very weakly charged polyelectrolytes

Gilbert Weill

Institut C. Sadron (CRM-EAHP) – CNRS and Université L. Pasteur 6, rue Boussingault, 67083 Strasbourg Cedex (France)

Abstract

Careful examination of the concentration range where both intrinsic viscosity and light scattering show a polyelectrolyte effect, even for singly charged halato-telechelic ionomers in DMF, together with the neutron scattering results at higher concentration show that weakly charged polymers may be a very useful tool to understand the complicated effects of coulombic interaction in polyelectrolyte solutions. A theoretical framework is given for a systematic study of such weakly charged polymers. The current state of understanding is presented of the properties of solutions of strong polyelectrolytes and of charged rigid particles. Finally it is shown how the transposition to weak polyelectrolytes solutions sheds light on the respective contributions of intra- and intermolecular interactions.

Keywords: Polyelectrolytes; Viscosity; Light and neutron scattering; Halato-telechelic ionomers; Sulfonated polystyrene

1. Introduction

Interest in solutions of very weak polyelectrolytes has developed in the recent years for several different purposes:

- to check up to which charge they present the characteristic behaviour of polyelectrolytes, in salt free solutions, and to better understand the intra or intermolecular origin of this behaviour, in particular the uprise of the relative viscosity $\eta_{sp/c}$, the low scattering intensity at $q = 0$ and the presence of a peak in the total structure factor $S_T(q)$ [1]
- to study the new transitions which can be expected below the θ point of the parent uncharged polymer due to the competition between the attractive Van der Waals and repulsive coulombic excluded volume interaction [2]
- to study the onset of aggregation with the decreasing polarity of good solvents of the parent uncharged polymer, as models for the clustering of the ionic groups in ionomers [3].

As a result a number of significative results have now been published which can be quantitatively used to achieve the first purpose.

In what follows we first recall a few results from the literature. We then present the current state of understanding of the properties of solutions of strong polyelectrolytes and of charged rigid particles. Finally we show how the transposition to weak polyelectrolytes solutions sheds light on the respective contributions of intra- and intermolecular interactions.

2. Experimental results on weakly charged polyelectrolytes

2.1 *Water solutions of segmented polyethylene oxide (PEO)*

Figures 1 and 2 reproduce the concentration dependence of the intrinsic viscosity and q depen-

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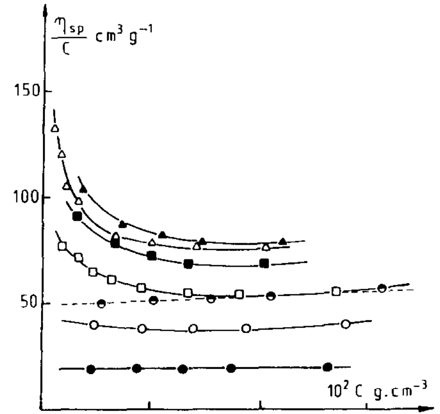

Fig. 1. Reduced viscosities (η_{sp}/c) versus PEO concentration (c) of the segmented PEO with increasing $\bar{n}$ in the absence of added salt $\bar{n} = 2.8$ (●); 6.3 (○); 7.7 (□); 10.1 (■); 12.1 (△); 13.9 (▲); 7.2 unfractionated (○). Lines are merely for reader's convenience.

dent structure factor of segmented polyethylene oxide according to ref. [4]. These polymers have been obtained by condensation of α, ω diol polyethylene oxide (M $\simeq$ 2000) with pyromellitic anhydride at exact stoechiometry and fractionated. The polymers therefore contain a number $\bar{n}$ of PEO sequences separated by hinges carrying two charges, with a total charge $Z = 2(\bar{n} - 1)$ or on average 1 charge per $\simeq$ 75 C–C bonds. It is clearly seen in Fig. 1 that below $c_p \simeq 1.5\ 10^{-2}$ g/l η_{sp}/c shows a rapid increase for $\bar{n} > 6$–7 and that even at higher concentrations η_{sp}/c remains significantly higher than for the uncharged polymer of similar length ($[\eta] = 2.4\ 10^{-2} M^{0.7}$). Figure 2 shows that below a polymer concentration c of 1.5 10^{-2} g/l the reduced structure factor $S_T(q)/c$M for the sample with $\bar{n} = 10$ is much depressed as compared to the single particle structure factor $P(q)$

$$P(q) = \frac{2}{q^2 R_G^2}\left(q^2 R_G^2 - 1 + e^{q^2 R_G^2}\right)$$

where the radius of gyration $R_G = 40$ Å has been calculated from the characteristic ratio at infinite dilution for PEO, $C_\infty \simeq 4$. It presents a weak maximum whose position shifts toward lower q and higher intensity as c decreases. Although less pronounced these two effects are similar to that encountered in strong polyelectrolytes (with essentially 1 charge per 2 C–C bonds).

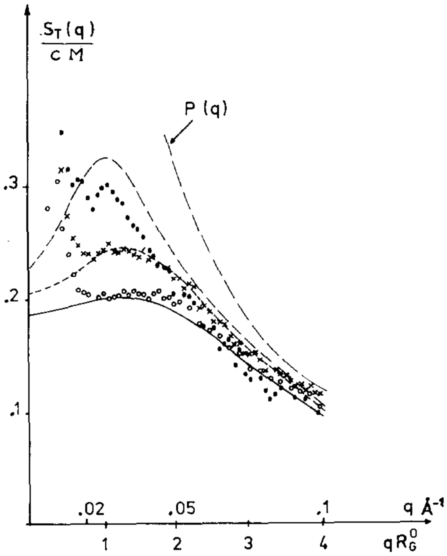

Fig. 2. Normalized reduced structure factor $S_T(q)/c$M of salt free solutions of segmented PEO $\bar{n} = 10.1$ for three different PEO concentrations $c = 15.4$ g/l (○); 9.2 g/l (×); 3. 1 g/l (●). Lines are theoretical fits (see text).

2.2 Weakly sulfonated polystyrene (PS) in DMF

Even if the charges are less regularly distributed, the results obtained on these systems allow to observe the effect of the increasing charge density [5–7]. Figure 3 gives the concentration dependence of the inverse reduced intensity $K c\mathrm{M}/R(q)$ at $q \ll R_G^{-1}$ as observed by light scattering [5], and stresses the fact the rise of the reduced viscosity [7] takes place in a concentration range where the reduced structure factor at $q = 0$ increases from a nearly constant value at higher c to its value 1 at infinite dilution. The neutron scattering data of Fig. 4 redrawn from Fig. 7 of ref. [8] (unfortunately observed on a sample with $M \simeq 1/10$ of that of Fig. 3) show that in the concentration range where the reduced structure factor at $q = 0$ is highly depressed, one observes indeed a maximum in its q dependence.

These observations fit with the previous one and emphasize the relation between the rise in reduced viscosity and the very dilute regime observed by light scattering.

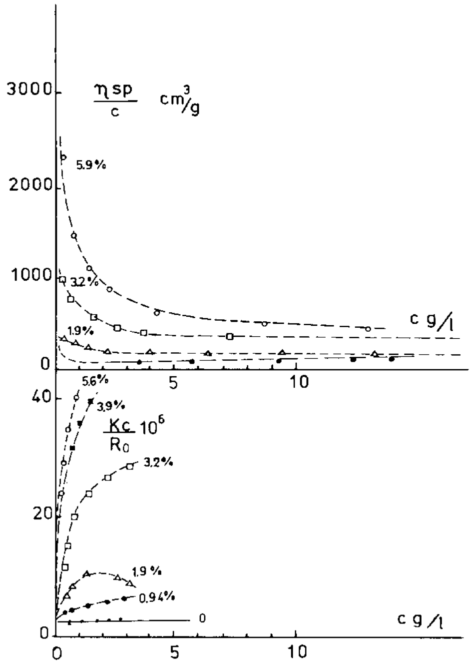

Fig. 3. Reduced viscosities and reduced inverse $q \simeq 0$ light scattering of sulfonated PS (M = 400.000) with different degrees of sulfonation in DMF. The points are redrawn on a same concentration scale from refs. [5] and [7].

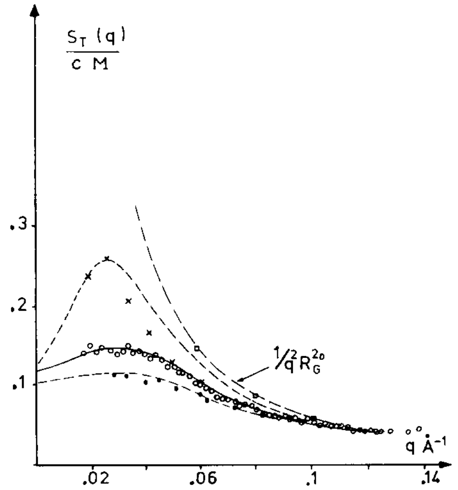

Fig. 4. Normalized reduced structure factor $S_I(q)/c$M of 8% sulfonated PS (M ≃ 50.000) in DMF c = 40 g/l (□; 20 g/l (○); 5 g/l (×). Points are redrawn from ref. [8]. Lines are theoretical fits (see text).

2.3 Halato-telechelic ionomers in DMF

Jerôme et al. have synthesized halato-telechelic polymers with charges at both or only one end, and the viscosity and light scattering of these systems have been studied by Hara et al. [9,10]. The results, as redrawn from the Figures of refs. [9] and [10] show that one charge per macromolecule is sufficient to induce the low c rise of η_{sp}/c and that again, this behaviour takes place in the concentration range where light scattering indicates a very dilute regime (Figs. 5 and 6).

3. Theoretical models for the viscosity and scattering of polyelectrolyte systems

3.1 Viscosity

The characteristic behaviour of the reduced viscosity $\eta_{sp/c}$ has been first related to the increased moleculecular dimensions resulting in strong polyelectrolytes from the intramolecular coulombic repulsions. They result in a local stiffening (electrostatic contribution to the persistence length) and in an increased excluded volume interaction between the locally rigid segments taken as cylinders with an effective diameter κ^{-1} [11,12]. At very low concentrations the molecule is expected to be fully stretched. It has, however, been observed [13] that at very low concentration the reduced viscosity presents a maximum and then decays to much smaller values. This behaviour can also be found in dilute solutions of rigid spherical particles such as charged latex [14]. Transposition of the theory developed by Hess and Klein in this latter case to chain polyelectrolytes by Cohen et al. [15] lead to an expression of the form

$$\eta_{sp} \propto R_H l_B^2 c_{p0}^2 Z^2/\kappa^3 \tag{1}$$

where R_H is the hydrodynamic radius of the chain, c_{p0} the concentration in polyion, Z the number of charges per polyion and κ the Debye Screening length resulting from the polyelectrolyte counterions and added salt counterions and co-ions

$$\kappa^2 \propto l_B([c_p] + 2[c_s]) \tag{2}$$

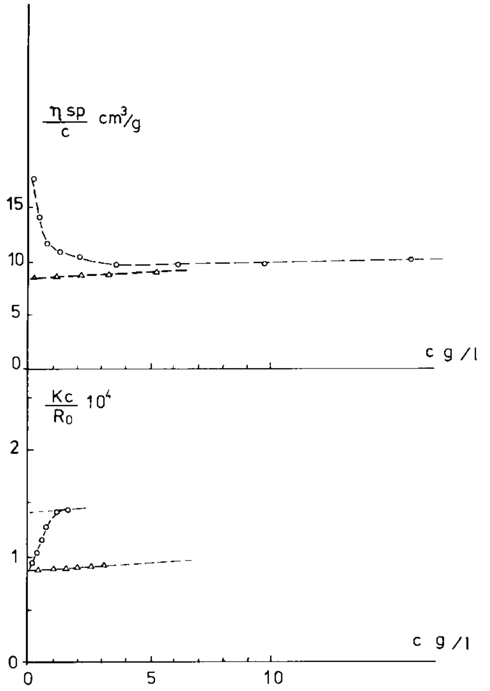

Fig. 5. Reduced viscosity and reduced inverse $q = 0$ light scattering of dihalato-telechelic PS (M ≃ 12.000) in DMF. The points are redrawn on the same concentration scale from ref. [9].

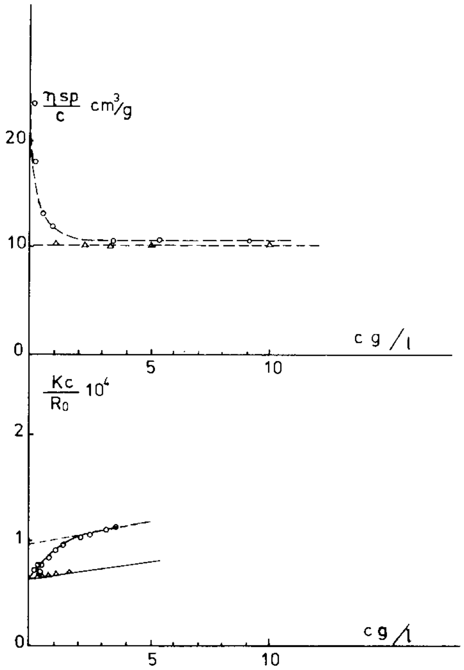

Fig. 6. Reduced viscosity and reduced inverse q ≃ 0 light scattering of monohalato-telechelic PS (M ≃ 15.000) in DMF. The points are redrawn on the same concentration scale from ref. [10].

where l_B is the Bjerrum length and $[c_p] = [c_{p0}]Z$ is the molar concentration in counterions and $[c_s]$ the molar concentration in added salt. Relation (1) becomes

$$\frac{\eta_{sp}}{c} \simeq \frac{[c_p]}{\left([c_p] + 2[c_s]\right)^{3/2}} \tag{3}$$

from which one derives the position of the maximum at $[c_p]/[c_s] = 4$ in excellent agreement with experiment. Relation (1) also predicts correctly the $c_p^{-1/2}$ dependence of the reduced viscosity in salt free solutions. One should not that in this theory:

- the deformation of the chain enters through R_H which can still vary with concentration with an extent dependent on Z for non-fully stretched chains
- in relation (1) Z^2 replaces the original factor Z^4 appearing for weakly charged spheres in the theory of Hess and Klein [14]

3.2 Scattering

The low scattering of solutions of strongly charged macromolecules is known for a long time and related to the small osmotic compressibility brought about by the presence of counterions with an osmotic coefficient ϕ

$$\pi = \frac{1}{\mathrm{M}}(1 + \phi Z)c \tag{4}$$

where M is the molecular weight and Z the charge of the polyelectrolyte. Here $\phi < 1$ and tends to 1 at extreme dilution but decays rapidly with increasing concentration with a decreasing slope so that

$$\frac{\partial \pi}{\partial c} = \frac{1}{\mathrm{M}}\left[1 + \left(\phi + c\frac{\partial \phi}{\partial c}\right)Z\right] \tag{5}$$

The term in parenthesis tends to zero at vanishing concentration but increases with increasing concentration, so that the reduced scattered intensity I/c which is proportional to $(\partial\pi/\partial c)^{-1}$ decreases.

For that reason it has long ago been suggested [16] that the decrease of I/c in pure water can be understood in terms of the scattering by spheres with a concentration dependent effective diameter. For such a solution of hard spheres the total scattering factor $S_T(q)$ is a product of a single particle structure factor $P(q)$ and a solution structure factor $S(q)$ due to the excluded volume or "correlation hole" effect

$$\begin{aligned} S_{\mathrm{T}}(q) &= c\mathrm{M}[P(q)S(q)] \\ &= c\mathrm{M}\left(P(q,D)\left[1+\frac{4\pi ND^3a}{3\mathrm{M}}\frac{J_1(qD_0)}{qD_0}c\right]\right) \end{aligned} \tag{6}$$

where D and D_0 are the real and effective diameter, respectively.

Interpretation of the results of Fig. 4 according to that relation in ref. [9] has led to a variation of D_0 at vanishingly low c and constant M linear in Z. This phenomenological theory carries however no prediction for the variation of D_0 with c, M and Z. Since $P(q)$ and $S(q)$ are respectively a monotonously decreasing or increasing function of q a peak in S_T is expected but it is not clear whether the calculation can be applied with $P(q)$ the chain structure factor and D_0 the diameter of an arbitrary overall correlation hole.

A more exact calculation can be carried out in the frame work of the random phase approximation developed for the calculation of the scattering of solutions of chain molecules with excluded volume [17] which gives

$$\frac{nN^2}{S_{\mathrm{T}}(q)} = \frac{1}{P(q)} + v \tag{7}$$

where v is the excluded volume per chain segment, N the number of segments per chain and n the number density of chains.

It has been suggested [18,19] that relation (7) can account for the scattering of charged chains provided that v, which is q independent as the Fourier transform of a short-range interaction δ-function, is taken as the Fourier transform of a direct correlation function $c(r)$ based on a Debye-Hückel potential

$$c(r) = \exp^{-v(r)/RT} \simeq 1 - \frac{\mathrm{e}^2}{4\pi\epsilon_0\epsilon_{\mathrm{r}}kT}\frac{\mathrm{e}^{-\kappa r}}{r}$$

with the result [20]

$$\frac{nN^2}{S_{\mathrm{T}}(q)} = \frac{1}{P(q)} + \frac{4\pi l_{\mathrm{B}}f^2}{q^2+\kappa^2} \tag{8}$$

where l_B is the Bjerrum length $\mathrm{e}^2/4\pi\epsilon_0\epsilon_{\mathrm{r}}kT$ and f the fraction of segments carrying a charge. Inserting the possibility of a simultaneous q independent excluded volume parameter on uncharged segments, and writing relation (8) in terms of the usual experimental quantities c, M and A_2, one has

$$S_{\mathrm{T}}(q) = c\mathrm{M}\frac{P(q)}{1+\left(2A_2\mathrm{M}c+\dfrac{4\pi l_{\mathrm{B}}f'^2N\mathrm{M}c}{q^2+\kappa^2}\right)P(\theta)} \tag{9}$$

where N is Avogadro number and f' the fraction of charge per unit mass.

The use of relation (9) is limited by the uncertainties in the concentration dependence of $P(q)$ resulting from the change in persistence length and overall radius of gyration, and in the evaluation of the screening length κ^{-1} where both the counterions and the charges carried by the chain may contribute. Both problems may be better understood in the case of very weakly charged polyelectrolytes. In any case it is interesting to remark that if κ^2 is proportional to c in salt-free solutions, the last term in the denominator of relation (i) is constant so that the reduced scattered intensity at $q=0$ $(P(q)=1))$ should be nearly independent of the concentration (but for the small $2A_2Mc$ term).

3.3 Conformation and screening in solutions of very weakly charged polyelectrolytes

According to De Gennes [21] and Kokhlov [22], we define very weakly charged polyelectrolytes as polymers where f is small enough for a blob description of the chain. The blobs retain locally their gaussian character but coulombic interaction between blobs lead to a progressive alignment. Following Kokhlov we define the number g of charges in a blob of size D by the two conditions:

$$\frac{g^2\mathrm{e}^2}{4\pi\epsilon_0\epsilon_r D} = kT \text{ or } D \simeq g^2 l_{\mathrm{B}} \tag{10}$$

(the bare repulsion between adjacent blobs is of the order kT)

$$D^2 = gf^{-1}b^2 \tag{11}$$

(the blob is gaussian).

The chain of blobs is characterized by a persistence length. Its variation with concentration can be evaluated by transposition to the chain of blobs of the calculation of Odijk [18] and Fixman [19] for the electrostatic contribution to the persistence length in strongly charged polyelectrolytes

$$l_p = \frac{D}{2} + \frac{l_B}{4\kappa^2 D^2} h(\kappa L)$$

$$= l_B\left(\frac{g^2}{2} + \frac{1}{4\kappa D^2} h(n\kappa D)\right) \tag{12}$$

According to Kokhlov [22] the screening in dilute solutions should be attributed to the counterions only while in semi-dilute solutions the charge z carried by a volume of dimension ζ, where ζ is the correlation length, could act as a z-valent coion.

4. Discussion of the experimental results

Our first step will be the interpretation of the scattering data reported in Fig. 2 and Fig. 4 at the light of relation (9). As mentioned, if one assumes that κ^2 is proportional to the polymer concentration through

$$\kappa^2 = 4\pi l_B cNf',k \tag{13}$$

where k depends on the contribution of the polymer charges ($k = 1$ for screening by the counterions only), one can rewrite relation (9), with $f'M = Z$ the number of charges carried by one polyelectrolyte molecule

$$S_T(q) = cM\frac{P(q)}{1 + \left(2A_2M_c + \frac{Z}{k}\frac{1}{1 + q^2/\kappa^2}\right)P(q)} \tag{14}$$

from which one has

$$S_T(0) = cM\frac{1}{1 + 2A_2Mc + Z/k} \tag{15}$$

Moreover for very weakly charged polyelectrolytes which are locally described by a gaussian blob model $P(q)$ can be described asymptotically at high q by

$$P(q) = \frac{2}{1 + q^2R_G^{02}}$$

where R_G^0 is the unperturbed radius of gyration of the parent uncharged polymer in θ conditions.

If $P(q)$ can be described by such an expression (with eventually an increased value of R_G^2) in the range of q where $S_T(q)$ presents a maximum we obtain for the position of the maximum

$$q^{*2} = \left(\frac{2Z}{k}\frac{\kappa^2}{R_G^2}\right)^{1/2} - \kappa^2 \tag{17}$$

The neutron scattering results in the references and from which Figs. 2 and 4 have been redrawn are given in arbitrary units and no light scattering results leading to an absolute value of $S(0)$, i.e. of Z/k are available on the same samples. We know, however, Z, A_2 and R_G^{02} as measured on the uncharged polymers. We have then been able to fit the data to absolute values using the fact that $S(q)$ tends to $P(q)$ at large qR_G^0 and then derive from the low q behaviour a value of Z/k and a value of κ^2. These two quantities have been adjusted separately and κ^2 has been supposed proportional to the polymer concentration. The fits given in Figs. 2 and 4 have been obtained with the following values.

Segmented PEO

$Z = 18 \quad A_2 = 1.8\ 10^{-3} \quad R_G = 40$ Å

$\kappa^2 = 20\ 10^{-4}$ Å^{-2} for $c = 15$ g/l

corresponding to $k = 3$, i.e. both the counterion and the divalent charged hinges contribute to the screening. This value of k would lead to $Z/k = 12$ (due to divalent nature of the charges on the hinges) while the fit requires $Z/k = 3$ which is not fully consistent).

On another hand it has been found necessary to use for $c = 3\ 10^{-3}$ g/cm^3 a slightly higher value of $R_G = 50$ Å to reproduce the position and the intensity of the maximum. This is very consistent with the increase in persistence length calculated with relation (12) for $\kappa^2 = 4\ 10^{-4}\ \text{Å}^{-2}$.

Sulfonated polystyrene (8 %)

$$\mathrm{M} = 50000 \quad Z \simeq 36 \quad A_2 = 3.8\ 10^{-4} \quad R_G^0 \simeq 60\ \text{Å}$$

$$\kappa^2 = 30\ 10^{-4} \quad \text{for } c = 40\ \text{g/l}$$

corresponding to $k = 2$ i.e. both the counterions and the individual monovalent charged groups of the polymer contribute to the screening but as before this value would lead to $Z/n = 18$ while the fit requires $Z/k = 7$.

The fit is rather satisfactory. We have not found useful to modify R_G^0 with decreasing concentration. The authors of ref. (7) have extracted $P(q)$ from experiments using mixtures of deuterated and undeuterated chains and claim a very large increase of R_G from the initial slope. The values of $P(q)$ in the range of q of interest seem, however, much less affected and moreover should be interpreted using the asymptotic expression of $P(q)$ leading to $R_G \simeq 70$ Å at 40 g/l and $R_G \simeq 80$ Å at 5 g/l. One should also remark that most of the points used to define the initial slope are for values of $q < 0.010\ \text{Å}^{-1}$ while the scattering factors are reported for $q > 0.015\ \text{Å}^{-1}$ and begin to show at the lowest q the classical increased scattering which is also found in this q-range in the segmented PEO system. That it can be suppressed is clearly shown on the light scattering results shown in Figs. (3), (4) and (5).

It is clear from these results that above a given concentration the inverse reduced scattered intensity Kc/I varies only slightly with concentration in good agreement with relation (15)

$$\frac{Kc}{I} \propto 1 + Z/k + 2A_2\mathrm{M}c$$

The value of Z/k is easily derived for the halato-telechelic polymers (Figs. 5 and 6) where the light scattering experiments have been carried out in a large enough range of concentration. We find $Z/k \simeq 0.5$ for the monohalato-telechelic polymer, and $Z/k \simeq 2/3$ for the dihalato-telechelic polymer.

This is apparently consistent with the chain charges contributing as respectively a monovalent and a divalent ion to the screening. The data for the weakly sulfonated polystyrene in Fig. (3) do not reach the range of concentrations where the neutron scattering experiments are performed. It is therefore not possible to specify how Z/k varies as a function of the degree of ionisation, but a proportionality with Z ($k \simeq$ constant) does not seem inconsistent.

We can now ask whether relation (9) can be extended to explain the decay of Kc/I towards its limiting value $1/\mathrm{M}$ at lower concentration. The simplest possibility would be that κ^2 tends with decreasing concentration towards a limiting value arising from a residual salt content. The last term in the denominator of relation (9) would then become proportional to c and account for an additional coulombic contribution to the second virial coefficient, proportional to f'^2. This is, however, totally inconsistent with the rise in the reduced viscosity which takes place in the same concentration range. Indeed neither an explanation in terms of single chain expansion (which is in any case irrelevant for the halato-telechelic polymers) nor in terms of screened coulombic interaction between chains (since κ^2 becomes constant in relation (1)) is possible.

To try and solve this paradox, let us remind that relation (9) derived from RPA holds in a mean field situation, that is in a situation of coil overlap, where the system can be considered as uniform at large enough scale. If we compare the concentration range where the neutron scattering experiments have been performed and for which Kc/I becomes only slightly function of concentration, they could all be indeed in the region of sufficient coil overlap (taking in account their expansion with decreasing concentration) where $c \simeq [\eta]^{-1}$. The experiments carried out with halato-telechelic polymers, however, seem, to prove that relation (9) could hold till concentrations much smaller than coil overlap (but we do not have results at much higher concentration). One is in anyway led to the idea that κ^2 *has not reached a limiting value* imposed by the residual salt, where η_{sp}/c should, from relation (1), have passed a maximum, but continues to decrease with concentration and that it is relation (9) which becomes inappropriate. This may be due to the fact that a mean field approximation becomes irrelevant, in the same way as in the Flory–Huggins theory, the molecular weight independent A_2 must be corrected in dilute conditions to take into account the large fluctuations at low concentrations. The situation is then much better accounted for by a hard-sphere model. An improved version of the effective hard-sphere model using a Debye-Hückel potential above the mean radius of the molecule [23] could be a reasonable approximation provided that one evaluates the distribution of counterions inside (which renormalizes Z) and outside (which fixes κ^2) of the coil. This can be done in a crude way by using the two states model of Oosawa for the calculation of the osmotic coefficient [24]. The experiments reported so far are not systematic enough to test such a model, and in particular the effect of varying M at fixed charge Z, or the charge Z at fixed M, on the viscosity, light scattering and neutron scattering results. Such a systematic study seems however desirable at the light of the preceeding remarks. Halato-telechelic PS with variable M and weakly sulfonated PS with both variable M and degree of sulfonation in solution in DMF seem very well suited for such a study.

Conclusion

A careful examination of the concentration range where both intrinsic viscosity and light scattering show a polyelectrolyte effect, even for singly charged halato-telechelic ionomers in DMF, together with the neutron scattering results at higher concentration show that weakly charged polymers may be a very useful tool to understand the complicated effects of coulombic interaction in polyelectrolyte solutions. A theoretical framework has been given for a systematic study of such weakly charged polymers.

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