Small-angle scattering by polyelectrolyte solutions: Interpretation of molecular weight dependence of the scattering peak position

J. Pleštil* and Yu. M. Ostanevich
Joint Institute of Nuclear Research, Dubna, USSR

and D. Hlavatá and K. Dušek
Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Prague 6, Czechoslovakia

The variation in small-angle scattering curves of aqueous solutions of sodium poly(styrene sulphonate) with molecular weight is, in contrast to the original paper by Ise *et al.*, interpereted as the result of differences in the single-chain scattering factors. Structural models of polyelectrolyte solutions are briefly discussed.

(Keywords: polyelectrolyte solution; sodium poly(styrene sulphonate); small-angle scattering; interference function; conformation)

INTRODUCTION

Small-angle scattering curves of salt-free polyelectrolyte solutions have a broad maximum, the position of which depends mainly on the polyelectrolyte concentration and charge density.

To explain the occurrence of this maximum, various structural models have been proposed. A cylindrical model[1-3] assumed the existence of a local parallel arrangement of polyions. De Gennes and coworkers[4] suggested an isotropic model assuming partially flexible chains oriented randomly. The model proposed by Ise and Okubo[5] supposed that the maximum on the scattering curves arises due to the three-dimensional ordering of polymer coils.

It has been observed recently[6,7] that the position of the maximum on the scattering curves is influenced also by the molecular weight of the polymer. It is shifted towards smaller values of momentum transfer h ($h = 4\pi/\lambda \sin\theta$, where 2θ is the scattering angle, λ is the wavelength) with increasing molecular weight, which seems to support the validity of the ordered-coils model. The theoretical inter-polyion distances calculated on the basis of the model are, however, too large compared with the experimental ones estimated using the Bragg equation ($D_{th}/D_{exp} \simeq 2$). In order to explain this discrepancy, Ise *et al.* suppose a two-state structure, in which the ordered regions coexist with the disordered ones. Such a structure is believed to be caused by attractive interaction of polyions.

In recently published work Ise *et al.*[7] reported the results of a small-angle X-ray scattering investigation of sodium poly(styrene sulphonate) aqueous solutions. Their results again confirmed the molecular weight dependence of scattering behaviour. They compared the D_{exp} values obtained at a given number concentration for

different molecular weights and stated that D_{exp} decreases with increasing M_w. In the framework of their model they explain this dependence by the enhancement of attraction with increasing valency of polyions.

The aim of this paper is to propose an alternative interpretation of the M_w dependence of the scattering peak position.

SCATTERING CURVES

Small-angle X-ray scattering (SAXS) data of sodium poly(styrene sulphonate) solutions (NaPSS) are taken from the work of Ise *et al.*[7] The weight-average molecular weight, M_w, and polydispersity index, M_w/M_n, were 4600, 18 000, 74 000, 780 000 and 1.07, 1.14, 1.17, 2.1, respectively. For the description of experimental conditions and procedures we refer the reader to the original paper.

The curves of NaPSS samples of various M_w ($c = 0.04$ g cm^{-3}) possess the following features (*Figure 1*):

(a) For $h \gtrsim 0.12$ Å^{-1}, the scattering intensity does not depend on M_w.

(b) For $h \lesssim 0.12$ Å^{-1}, the intensity increases with increasing M_w.

(c) The scattering peak is shifted towards smaller values of h with increase in M_w.

(d) For $M_w \gtrsim 10^5$, the scattering intensity ceases to be sensitive to M_w.

In *Figure 2*, the normalized scattering intensity, I/c, for the NaPSS sample of $M_w = 74\,000$ is plotted for several concentrations. We can see that I/c varies with the concentration in the inner part of the scattering curve only. At higher h ($h \gtrsim 1.2 h_{max}$, h_{max} being the position of the scattering maximum), the I/c curve coincides with curves obtained for any lower concentration.

In order to explain these properties of the NaPSS scattering curves, we describe the theoretical scattering functions.

*On leave from the Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague 6, Czechoslovakia
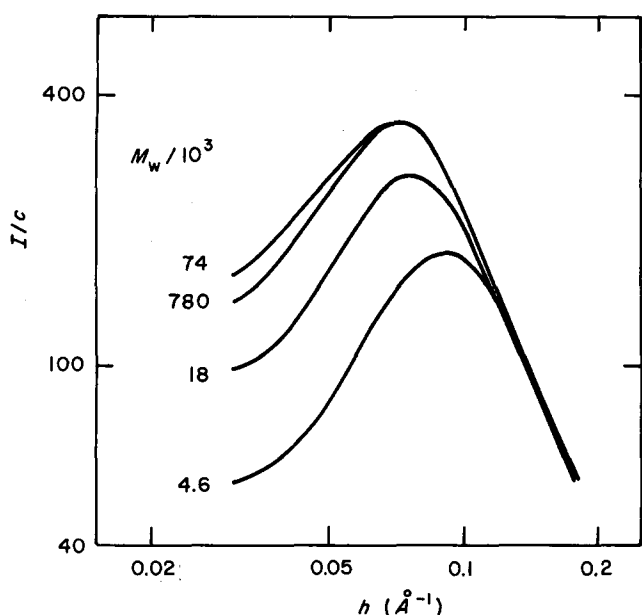
Figure 1 Variation in SAXS of NaPSS with molecular weight. Numbers of curves denote weight-average molecular weights. Polymer concentration $c = 0.04 \, \text{g cm}^{-3}$. Data taken from Ise et al.[7]

For an assembly of N interacting particles, the scattering curve can be described by

$$I(h) = N\langle F^2(h)\rangle B(h) = I_1(h)B(h) \qquad (1)$$

where $\langle F^2(h)\rangle$ is the scattering amplitude of the particle and $B(h)$ is an interference function. For systems without long-range ordering and at sufficiently large values of the argument, $B(h) = 1$, and the scattering intensity for these h values is equal to the single-particle scattering function, $I_1(h)$. If the position of the particle does not affect the probability of its various orientations, we have for the interference function[8]:

$$B(h) = 1 + f(h)P(h) \qquad (2)$$

where the function $P(h)$ is given by the positions of particles, and the function $f(h) \equiv \langle F(h)\rangle^2/\langle F^2(h)\rangle$ depends on the shape of particles and on the correlations between their orientations.

Let us now mention some properties of the scattering factor, $I_1(h)$, of the chain molecule.

For the analysis of single-chain scattering, the Debye equation[9] is widely used:

$$I_1(h) = AM(2/x^2)(e^{-x} + x - 1) \qquad (3)$$

where $x = h^2 R^2$, R is the radius of gyration, M is the molecular weight and A may be considered as constant for our purposes. The Debye equation describes the angular dependence of scattering by a Gaussian coil. Experimental curves are in agreement with this equation up to $h \simeq 0.1 \, \text{Å}^{-1}$ despite the fact that the basic assumptions on which the Debye equation rests fail for $h \gtrsim 0.03 \, \text{Å}^{-1}$. This is probably due to mutual compensation of departures from these assumptions[10].

For $hR < 1$, equation (1) simplifies to the Guinier approximation of the scattering curve, which holds regardless of the particle shape[11]:

$$I_1(h) = AM \exp(-h^2 R^2/3) \qquad (4)$$

For $hR > 3$, equation (3) can be replaced by

$$I_1(h) = AM(2/h^2 R^2) \qquad (5)$$

Considering the proportionality $R^2 \sim M$, we can see that in the range of h given above the scattering intensity of a Gaussian chain does not depend on molecular weight.

For sufficiently great values of h, the scattering factor describes the rodlike behaviour of the molecules:

$$I_1(h) = AM_L\pi \exp(-h^2 R_c^2/2)/h \qquad (6)$$

where M_L is the mass per unit length, R_c is the radius of gyration of the chain cross-section, and A is the same constant as in equation (3). A comparison between equations (4) and (6) leads to the relationship between the extrapolated intensities in the form:

$$I_1(0) = (M/M_L\pi)(I_1(h)h)_0 \qquad (7)$$

which enables one to estimate $I_1(0)$ using the data from the tail of the scattering curve.

From the transition point (h^*) between the $1/h^2$ and $1/h$ branches of the scattering curve, the persistence length can be calculated[12] as

$$a = 2.3/h^* \qquad (8)$$

The radius of gyration is connected with the persistence length by the relation[13]

$$R^2 = a^2\left[\frac{L}{3a} - 1 + \frac{2a}{L}\left(1 - \frac{a}{L}(1 - e^{-L/a})\right)\right] \qquad (9)$$

where $L = M/M_L$ is the length of the macromolecule.

Now let us come back to the experimental scattering curves.

The insensitivity of the normalized intensities I/c to the polyelectrolyte concentration for $h \gtrsim 1.2 h_{max}$ (*Figure 2*) reveals that $B(h) = 1$ in this region, i.e. the experimental intensity is proportional to the single-chain scattering factor.

As regards the molecular weight dependence of scattering (*Figure 1*), we believe that all the above-mentioned features can be explained by the molecular weight dependence of the single-chain scattering factor.

At high values of h, rodlike behaviour is expected (equation (6)) and the scattering intensity is practically the same for all M_w values. From the Guinier plot of the cross-section scattering factor $I(h)h$ (*Figure 3*), the radius of gyration of the cross-section, $R_c = 8.5 \pm 0.4 \, \text{Å}$, and the extrapolated intensity $(I(h)h/c)_0 = 28 \pm 2$ were determined. Using equation (7), we calculated the scattering intensity, $I_1(0)$, for the hypothetical case without the interference effect. For the samples of $M_w = 4600$, 18 000, 74 000 and 780 000 the values of $I_1(0)/c$ were estimated to be 500, 1950, 8000 and 84 000 respectively, in the same units as in *Figure 1*. In the light of these values it seems to be understandable why the observed intensity increases and the peak is shifted towards smaller angles with increasing M_w.

For low molecular weight samples, the inner part of the experimental scattering curves is not far from the Guinier region, and the single-chain scattering factor, I_1, increases with increasing M_w. For higher M_w, however, this part of
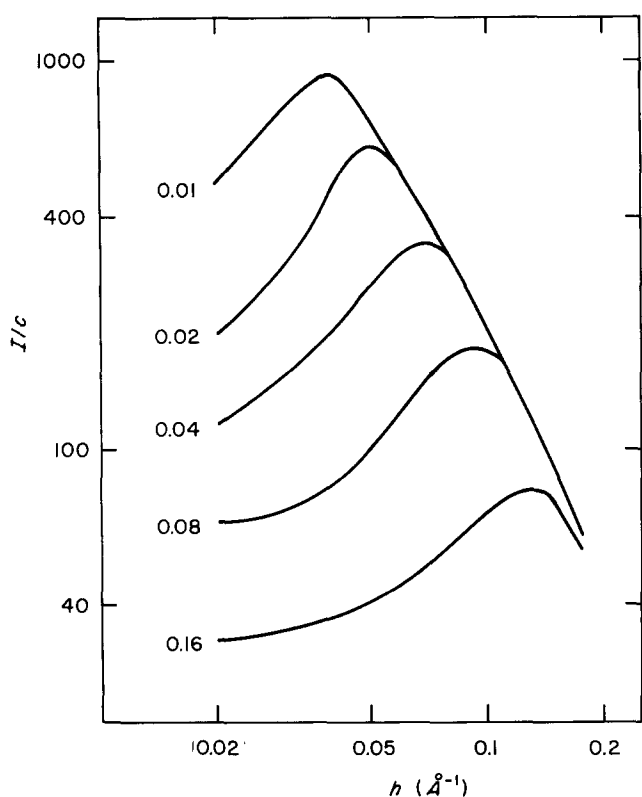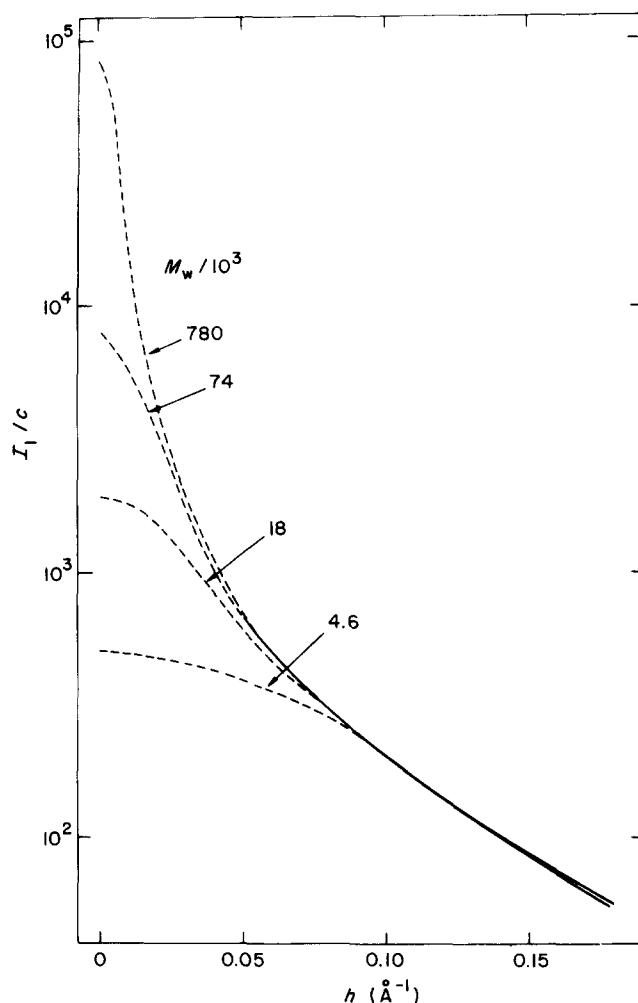
Figure 2 Variation in SAXS of NaPSS with concentration. Numbers on curves denote polymer concentrations. Molecular weight $M_w = 74\,000$. Data taken from Ise et al.[7]
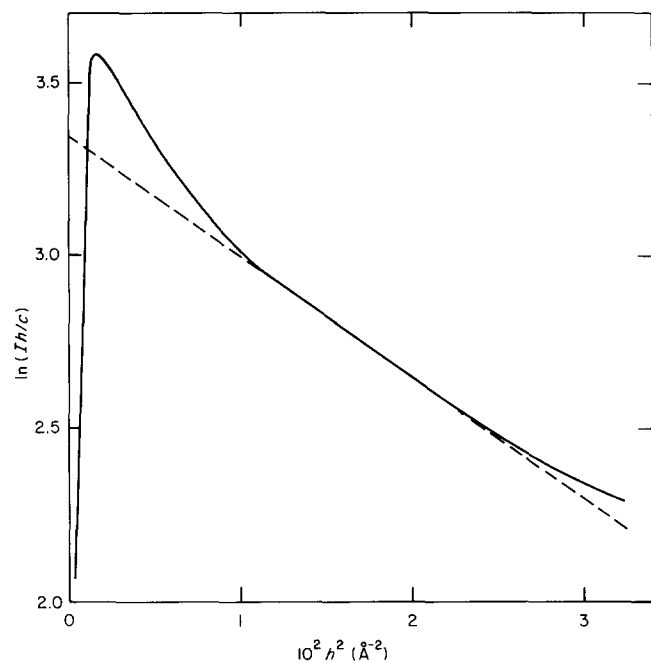
Figure 3 Guinier plot of cross-section factor of NaPSS. $M_w = 74\,000$, $c = 0.01\,\mathrm{g\,cm^{-3}}$

Figure 4 Single-chain scattering functions of NaPSS. Numbers on curves denote weight-average molecular weights. Full curves, experimental intensities; broken curves, extrapolation according to equation (4) ($M_w = 4.6 \times 10^3$, see *Figure 5*) or equation (3) ($M_w = 18 \times 10^3$, 74×10^3 and 780×10^3)

SINGLE-SCATTERING CURVES

Information about the arrangement of macroions is involved in the interference function $B(h)$. For the determination of the course of this function, the single-chain scattering factor, $I_1(h)$, must be known. As a rule, it is practically impossible to evaluate $I_1(h)$ for strongly interacting macroions from the SAXS curves. However, we believe that the data discussed here are informative enough to enable such an evaluation to be made with satisfactory reliability.

Our determination of the single-macroion scattering factor is based on the properties of the experimental scattering curves given above.

For $h \geqslant 1.2h$ (h_{max} being the peak position for the lowest concentration used) we suppose $I_1(h)$ to be equal to the experimental scattering intensity $I(h)$. The respective parts of the $I_1(h)$ curves are shown by full curves in *Figure 4*.

In the inner part ($h \leqslant 1.2h_{max}$), $I_1(h)$ was approximated by the formula (3) or (4). This part is shown by broken curves in *Figure 4*.

The Guinier approximation has been used for the sample of lowest M_w only. From the Guinier plot (*Figure 5*) we obtained the radius of gyration $R = 16.7\,\text{Å}$, and the extrapolated intensity, $I_1(0)/c = 520$, for this sample. The latter value is in close agreement with the value

the scattering curve corresponds to the $1/h^2$ region (equation (5)), where the scattering is not influenced by M_w in the case of a Gaussian coil. For the polyelectrolyte chain, departures from the Gaussian behaviour can be expected; nevertheless, we suppose that the insensitivity of $I_1(h)$ to M_w will be preserved.

Hence, all the features of the experimental scattering curves mentioned above can be, at least qualitatively, explained by the properties of the single-chain scattering function $I_1(h)$.
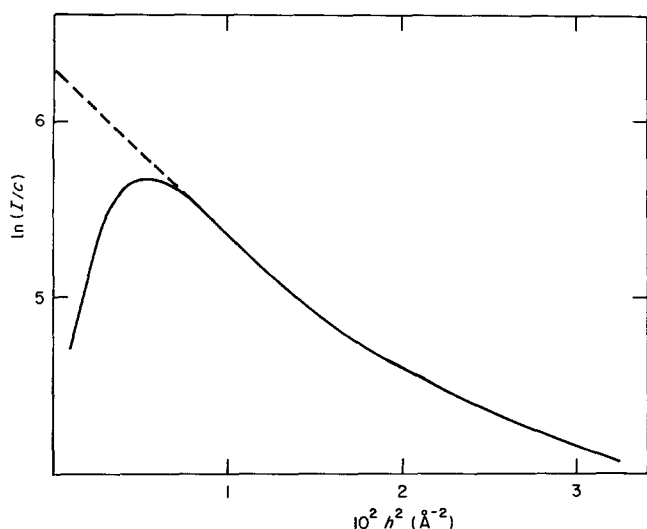
Figure 5 Guinier plot of SAXS intensity of NaPSS. $M_w = 4600$, $c = 0.02$ g cm^{-3}

Table 1 Radii of gyration^a (Å) of NaPSS

M_w	R_D	R_a	R_G	R_{rod}
4.6×10^3			16.7	18.2
18×10^3	44	38		64
74×10^3	95	90		259
780×10^3	297	308		2372

^{a} Radii of gyration have been obtained as follows:

R_D fitting of SAXS data to the Debye function (equation (3))

R_a calculated according to equation (9) using the persistence length $a = 30$ Å

R_G from the Guinier plot (*Figure 5*, equation (4))

R_{rod} calculated assuming a fully stretched conformation of macroions

$I_1(0)/c = 500$ estimated on the basis of the cross-section scattering curve and molecular weight.

For samples of higher M_w we employed the Debye equation (3). Taking into account the values of $I_1(0)/c$ estimated using equation (7), and supposing the Debye function to be equal to the experimental scattering intensity at $h = 1.2h_{max}$, the values of both parameters in equation (1) can be determined. Of these, the radius of gyration is of interest. Its values are summarized in *Table 1*.

As an alternative way of determining the radius of gyration we calculated this quantity from the persistence length according to equation (9). The transition point, h^*, between the $1/h^2$ and $1/h$ branches cannot be determined precisely in our case, because we have reliable data in the $1/h$ branch only. Nevertheless, from departures from $1/h$ behaviour (*Figure 3*) we estimated the transition point as 0.08 Å^{-1} and the corresponding persistence length as being about 30 Å. This value leads to the radii of gyration, R_a, shown in *Table 1*.

The radii of gyration given in the last column of *Table 1* were obtained by assuming the chains to be fully extended $(R_{rod}^2 = L^2/12 + R_c^2)$.

The quantity R_G, which was obtained from the Guinier plot, is the Z-average radius of gyration. The other values of R given in *Table 1* correspond to a system of identical molecules with molecular weight equal to the weight-average M_w.

In the dilute regime $(C < C^* = M/NL^3$, N being the Avogadro number) a fully extended conformation of the

polyion is expected[4]. Such a situation occurred for the sample with $M = 4600$, where the critical concentration C^* is 0.044 g cm^{-3}. In fact, the experimentally determined radius of gyration, R_G, is in good accord with the value of R_{rod} for this sample. Moreover, R_G might be slightly underestimated, because it has been determined from that part of the scattering curve where $hR_G = 1.5$–2.

The radii of gyration (R_D) obtained by fitting the scattering intensities at two points $(h = 0$ and $h = 1.2h_{max})$ to the Debye function can be compared with the values based on the persistence length (R_a). Satisfactory agreement between these two quantities justifies to some extent the procedure used here for the determination of the single-chain scattering factor.

INTERFERENCE FUNCTIONS

The interference functions were obtained by dividing the experimental scattering curves by the single-chain scattering function, $I_1(h)$, determined in the previous section. The resulting $B(h)$ curves (*Figures 6* and *7*) increase monotonically from low values at small angles to $B(h) = 1$ at larger angles. No maximum, which would indicate some preferential interparticle distance, is observed. Such behaviour can be explained using the idea of the correlation hole effect[14].

Because of a repulsive interaction between polyelectrolyte segments, we can assume that the probability of finding two segments at a distance much shorter than the average intersegment distance is small. In other words, each segment is surrounded by a region (correlation hole) that is virtually excluded to other charged segments. The corresponding pair distribution
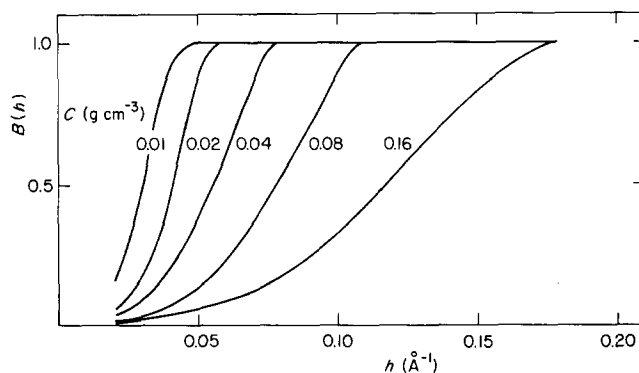

Figure 6 Variation of interference function of NaPSS with polymer concentration. Numbers on curves denote polymer concentrations. $M_w = 74\,000$
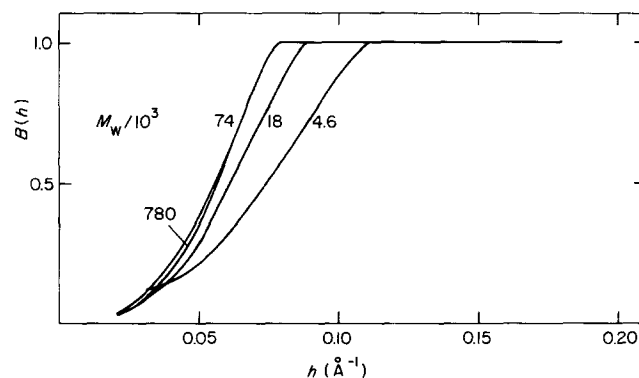

Figure 7 Variation of interference function of NaPSS with molecular weight. Numbers on curves denote weight-average molecular weights. Polymer concentration $c = 0.04$ g cm^{-3}

function of segments leads to the interference function being qualitatively similar to those shown in *Figures 6* and *7* given by Benmouna *et al.*[15]

Analysis of the data given in *Figure 6* shows that the concentration dependence of the interference function can be described by a universal function of $hc^{-\alpha}$. For the sample of $M_w = 74\,000$, the exponent is 0.45 in the concentration range 0.01–0.08 g cm^{-3}. For the most concentrated solution ($c = 0.16$ g cm^{-3}) $\alpha = 0.49$ must be used in order to make the interference curve fit those for lower concentrations. A similar universal function can also be found for the other molecular weights. The value of the exponent α has been found to be 0.45 and 0.49 for the samples of $M_w = 18\,000$ and 4600, respectively, always in the concentration range 0.02–0.04 g cm^{-3}.

It is tempting to interpret values of α close to 0.5 as evidence of a two-dimensional character of the polyelectrolyte structure. This argument might be true if the function $f(h)$ from equation (2) did not depend on h in the region where $B(h) \neq 1$. This condition is met exactly for particles of spherical symmetry and for systems with parallel ordering. It is hardly the case for chain polyions in solution. It can be shown, however, that for rodlike particles $f(h)$ is very close to unity (>0.95) for $hL < 4$ (L being the rod length), regardless of the degree of orientation. For the sample with $M_w = 4600$ the length of the polyion can be estimated as 50 Å. Hence, for $h \lesssim 0.1$ Å^{-1} we can expect $f(h)$ to be practically independent of h and the interference function is in this case affected by the position of polyions only and not by their orientations.

Figure 7 shows that the interference function depends on molecular weight. For nonspherical scattering objects, such behaviour is not surprising. We believe that the M_w dependence of $B(h)$ can be accounted for by the M_w influence on the factor $f(h)$. For the sake of illustration, we calculated the interference functions of random coils consisting of rodlike segments for various segment lengths. The formulae given by Koyama[16] have been used. *Figure 8* shows that the calculated $B(h)$ curves vary with increasing segment length in a similar way as the experimental curves do with an increase in M_w.

In our opinion, variation of the position of the scattering maximum with molecular weight does not imply changes in the macroion distribution in space. The molecular weight affects the position of the maximum

Figure 8 Theoretical interference functions $B(h) = 1 - f(h)\exp(-h^2 R_0^2/4)$ of random coils consisting of rodlike interacting segments. Numbers on curves denote lengths of segments. Characteristic distance of segment interaction $R_0 = 20$ Å (see Koyama[16])

only through factors connected mainly with the single-chain characteristics ($\langle F(h)\rangle^2$, $\langle F^2(h)\rangle$).

CONCLUDING REMARKS

It has been shown here that the molecular weight dependence of the scattering peak position can be explained without assuming a three-dimensional ordering of macroions. Admitting for a moment that there exists some characteristic distance in the structure of polyelectrolyte solutions, this distance cannot be identified with that between the centres of gravity of linear macroions. Possible exceptions correspond to those instances where this distance is much larger than the size of macroions. The molecular weights and concentrations employed in the scattering experiments, however, are usually too high to fulfil such a condition. Therefore, it is not necessary to compare the experimental characteristic distances with the theoretical ones based on the number concentration of macroions, which led to the suggestion of the three-dimensional two-state structure model[6]. This analysis shows that an alternative explanation is possible.

In the preceding papers[17,18] we employed the modified cylindrical model for the interpretation of small-angle scattering data of polyelectrolytes. The model assumes that the solution consists of randomly oriented domains, inside which polyion segments are situated parallel to each other. This model fails to explain the molecular weight dependence of the interference function, because we have $f(h) = 1$ for parallel segments. Hence, the assumption of a strictly parallel ordering must be dropped. This fact, of course, does rule out some correlation in the orientations of spatially neighbouring segments. The question now arises whether such a correlation does exist or whether the structure is completely irregular and can be described by the isotropic model of de Gennes *et al.*[4] This question is not easy to answer. The reason is that the scattering curve of long segments with a correlation of orientations is very similar to that of randomly oriented shorter segments.

SUMMARY

According to Ise *et al.*, the maximum on small-angle X-ray scattering (SAXS) curves of polyelectrolyte solutions is ascribed to interference on the three-dimensional lattice of polymer coils; this finding is supported by a variation of the maximum with molecular weight. In this paper another interpretation of Ise's SAXS data for poly(styrene sulphonate) is proposed.

The scattering curve $I(h)$ can be described as the product of the single-particle scattering factor $I_1(h)$ and interference function $B(h)$. By constructing the $I_1(h)$ function using a combination of the Debye equation and that part of the measured curve for $h \gtrsim 1.2h_{max}$, (h_{max} being the position of the maximum) where $I_1(h) \simeq I(h)$, the $B(h)$ function is evaluated. The interference function increases monotonically with increasing h up to $B(h) = 1$; no maximum indicating some preferential interparticle distance is observed. It is shown that variation of the maximum on the $I(h)$ curves can be explained by the properties of $I_1(h)$ only.

The radii of gyration obtained by fitting the intensities at $h = 1$ and $h = 1.2h_{max}$ to the Debye function and those obtained on the basis of persistence length from the
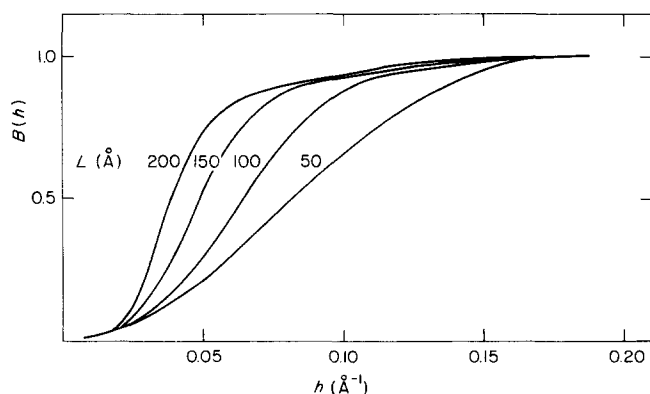
scattering curve are in good agreement, which justifies to some extent the procedure used.

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