Small-angle scattering from polyelectrolyte solutions: Dimensions of poly(methacrylic acid) chains in salt-free solutions

J. Pleštil*, Yu. M. Ostanevich and V. Yu. Bezzabotonov
Joint Institute for Nuclear Research, Laboratory of Neutron Physics, Dubna, USSR

and D. Hlavatá and J. Labský
Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06
Prague 6, Czechoslovakia
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The single-particle scattering function and the radius of gyration of the poly(methacrylic acid) (PMA) molecule have been obtained as a function of the degree of neutralization. A comparison of perturbed and unperturbed dimensions indicates that the expansion of PMA can be ascribed to the presence of charges alone. At a low degree of neutralization ($\beta \lesssim 0.2$), only long-range interactions contribute to the expansion. At higher β values, both long-range and short-range interactions are operative.

(Keywords: polyelectrolyte solution; poly(methacrylic acid); small-angle scattering; single-particle scattering function; conformation)

INTRODUCTION

Small-angle X-ray and neutron scattering experiments on salt-free polyelectrolyte solutions show the presence of a single broad maximum on scattering curves. This maximum is sometimes interpreted in terms of lattice-like models[1-4]. Such models usually assume (implicitly or explicitly) a particular conformation of macroions. Recent studies[5-8], however, favour the isotropic model proposed by de Gennes *et al.*[9], which does not assume either an ordered arrangement of macroions or their extreme conformations.

It is of importance to determine the single-macroion structure factor, because it not only provides information on macroion conformation but also makes it possible to study interparticle correlation. It has been shown by Williams *et al.*[10] that one can extract this factor by performing small-angle neutron scattering (SANS) measurements on mixtures of a normal and labelled (deuterated) polymer at a high concentration of both components. The method was later generalized by Akcasu *et al.*[11] and Benoit *et al.*[12].

The coherent intensity scattered from an incompressible solution of normal (H) and labelled (D) macromolecules can be written as[11,12]:

$$I(h) = (a_D - a_H)^2 c_D(1 - c_D)P(h) + (a_P - a_0)^2 S(h) \qquad (1)$$

where the scattering functions $P(h)$ and $S(h)$ come from intramolecular and both intra- and intermolecular interferences, respectively, $h = (4\pi/\lambda)\sin\theta$ is the modulus of the wavevector (with λ the wavelength and 2θ the scattering angle), and a_D, a_H and a_0 are the scattering lengths of the labelled monomer, normal monomer and solvent, respectively. The mean scattering length of monomer is $a_P = c_D a_D + (1 - c_D)a_H$, where c_D is the fraction of monomers that are deuterated. By choosing a_0 or c_D such that $a_P = a_0$, one can eliminate the second term in equation (1) and directly obtain the single-particle scattering function $P(h)$.

Equation (1) is valid if the two polymer species are identical except for their scattering lengths. It is rather difficult to meet this requirement. It seems probable, however, that the method can be successfully applied also to samples with modest differences in molecular weights of normal and deuterated polymers. Tangari *et al.*[13] analysed SANS curves for bulk polystyrene samples with mismatched molecular weights and were able to extract single-chain structure factors for specimens with mismatch ratio M_w^D/M_w^H between 0.3 and 1.9.

This paper presents a study of semidilute solutions of poly(methacrylic acid) (PMA) in the absence of salts. The structure factor and the radius of gyration of macroions have been obtained as a function of the degree of neutralization.

EXPERIMENTAL

Samples

Poly(methacrylic acid) ($M_w^H = 23\,000$, polydispersity index $u = M_w^H/M_n^H - 1 = 0.2$) and its deuterated homologue ($M_w^D = 19\,000$, $u = 0.5$) have been employed in this work. All solutions were prepared with D_2O, the counterion being Na^+. The solutions contained both protonated and deuterated PMA, the fraction of deuterated monomers being chosen so that the mean scattering length of the polymer was equal to that of the solvent ($a_P = a_0$). The fractions c_D were calculated as a function of the degree of neutralization, β, using partial volumes of un-ionized PMA[14], $\bar{V}_{PMA} = 59.3$ cm^3/mole monomoer, and of ionized PMA[15], $\bar{V}_{MPA} = 39.6$ cm^3/mole monomer. Condensation of the counterions was taken into account[16]. The

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* J.P. also works at the Institute of Macromolecular Chemistry, Prague.

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resultant c_D values varied from 0.29 (at $\beta = 1$) to 0.68 ($\beta = 0$). The scattering intensity of these samples is expected to be proportional to the average single-macroion structure factor.

The polymer concentration was 0.46 mole monomer/litre (0.04 g cm^{-3}) in most cases. For a fully neutralized solution ($\beta = 1$), the polymer concentration and the fraction of labelled polyions were varied.

SANS measurement

The measurements were carried out with the time-of-flight small-angle spectrometer[17] on the pulsed reactor IBR-2[18] at the Joint Institute for Nuclear Research in Dubna. The detector-to-sample distance was 11.13 m, and the primary beam was collimated to have a diameter 24 mm on the sample. Under these conditions, the observed wavevector modulus was in the range 0.015 to 0.2 Å^{-1} and the average number of thermal neutrons incident on the sample was 2×10^7 per second. The solution was placed in a 2 mm quartz cell. The incoherent contribution to the scattering was estimated by measuring the scattering from D_2O/H_2O mixtures containing the same number of protons as the solutions. For each sample, two sets of data were collected: (1) the scattering from the sample alone; (2) the scattering from the sample and from a vanadium standard placed between the sample and detector. These two data sets enable one to eliminate in a simple way the detector efficiency and any difference in transmission of the samples, and also to normalize the measured intensities to the incident spectrum.

RESULTS AND DISCUSSION

In order to assess to what extent the shape of the scattering curves is sensitive to the composition of the polymer mixture, the fraction of deuterated PMA, PMA(D), was varied for the fully neutralized sample (*Figure 1*). The scattering intensity of a completely deuterated ($c_D = 1$) and a nomral ($c_D = 0$) polymer shows the well known maximum. For $c_D = 0.2$–0.7, however, the scattered intensity decreases monotonically with increasing h, as expected for the single-macroion scattering function. As seen from *Figure 1*, the shape of the inner part of the scattering curves does not change significantly in a broad range of c_D. This rather surprising behaviour is in accord with equation (1). A more detailed analysis reveals that for samples with c_D between 0.1 and 0.7 the radius of gyration will not differ by more than 3% from the value obtained under the condition $a_P = a_0$ ($c_D = 0.29$).

The conditions of our experiment depart from ideal in several respects. The samples are not monodisperse and the molecular weights of the ordinary and labelled polymers are not matched too closely ($M_w^H/M_w^D = 1.2$). Furthermore, the Guinier range of scattering curves ($hR_z < 1$) is only marginally covered by the data for the samples under investigation. For these reasons, we fitted our data to the corrected Debye function[19]:

$$P(x) = \frac{2[x - 1 + (1 + ux)^{-1/u}]}{(1 + u)x^2} \tag{2}$$

where

$$x = R_z^2 h^2/(1 + 2u)$$

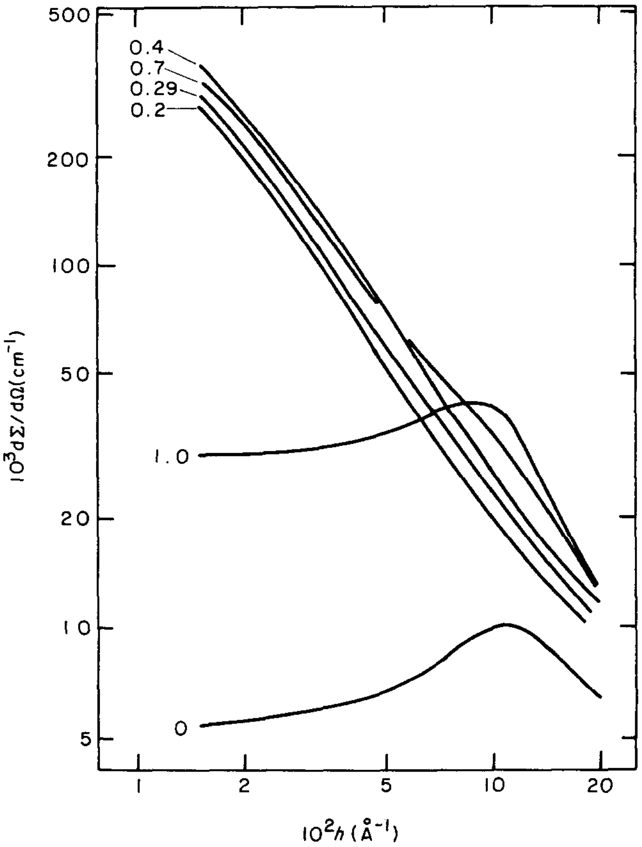

Figure 1 Variation of SANS curves of PMA(H)/PMA(D) mixtures (counterion Na$^+$, $\beta = 1$) in D_2O with the fraction of deuterated polymer, c_D. For $c_D = 0.29$, the mean scattering density of polymer matches that of solvent and pure single-macroion scattering is expected

and

$$u = M_w/M_n - 1$$

The value of R_z is related to the radius of gyration R_w of a chain with molecular weight M_w by[20]:

$$R_z^2 = R_w^2(1 + 2u)/(1 + u) \tag{3}$$

Formula (2) assumes Gaussian chains with a Schulz distribution of molecular weights. In the low h range ($hR < 4$) however, the scattering curve of the perturbed chain coincides with that of the unperturbed one[21]. Therefore, we believe that the Debye function could fit scattering data of polyelectrolytes reasonably well.

The polydispersity index u was calculated for each mixture and kept constant during the fitting process. Examples of data fitting are given in *Figure 2*. The z-average value of the radius of gyration R_z are reported in *Table 1* as a function of the degree of neutralization.

With increasing β, the radius of gyration of polyions increases and reaches a steady value near $\beta = 0.5$. The expansion is a result of electrostatic interactions between charged segments. The constancy of R_z at $\beta > 0.5$ can be explained by the condensation of counterions, which maintains a constant charge density of the polyion in this range.

Figure 2 shows scattering data of Na PMA ($\beta = 1$) at various concentrations. In the range between 0.01 and 0.04 g cm^{-3}, no significant concentration dependence of R_z is detected. This is not in accord with the results of

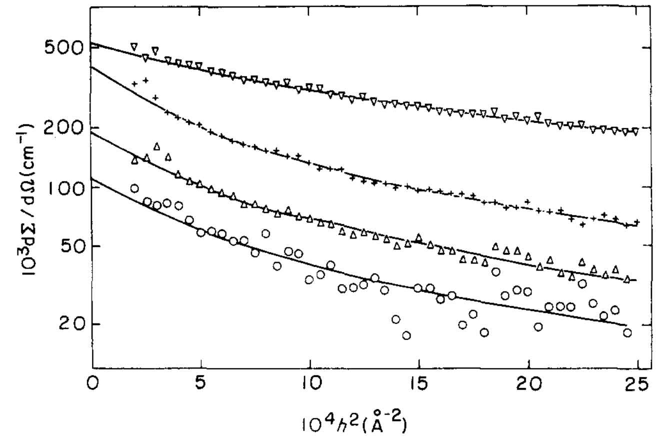

Figure 2 SANS data for mixtures of protonated and deuterated PMA in D_2O together with a corrected Debye function fit (equation (2)) (full curves): ▽, $\beta=0$, $c=0.04$ g cm^{-3} (the fitted value of R_z is 44.7 ± 0.5 Å); +, $\beta=1$, $c=0.04$ ($R_z=75.0\pm1.3$ Å); △, $\beta=1$, $c=0.02$ ($R_z=71\pm4$ Å); ○, $\beta=1$, $c=0.01$ ($R_z=70\pm8$ Å)

Table 1 Variation of single-polyion characteristics of PMA with the degree of neutralization β

β	R_z (Å)	R_w (Å)	L_p (Å)	R_{w0} (Å)	α_S	α_L	α_T
0.0	44.7	39.8	7.9	38.6	1.00	1.03	1.03
0.1	47.3	42.2	7.8	38.4	0.99	1.10	1.09
0.2	54.1	48.2	7.8	38.4	0.99	1.26	1.25
0.3	58.2	51.9	8.8	40.8	1.06	1.27	1.34
0.4	71.2	63.3	10.2	43.9	1.14	1.44	1.64
0.6	76.0	67.7	11.9	47.4	1.23	1.43	1.75
0.8	76.4	68.1	12.0	47.6	1.23	1.43	1.76
1.0	75.0	66.8	12.2	48.0	1.24	1.39	1.73

R_z was obtained by fitting equation (2) to scattering data
R_w was calculated from R_z according to equation (3)
L_p denotes the persistence length
R_{w0} is the unperturbed radius of gyration as determined using equation (5) with $L=590$ Å ($M=21\,000$)
Expansion coefficients α were calculated according to equations (4a)–(4c)

Moan *et al.*[22], who investigated solutions of unlabelled PMA with $M_w=13\,000$ and found the concentration dependence $R\sim c^{-0.30}$. Moreover, after corrections for polydispersity and the difference in M_w, our values of the radius of gyration are 20–40% lower than those reported by Moan *et al.*

As follows from a comparison of the observed radii of gyration with that of a fully stretched chain (~200 Å), even at the highest charge densities the conformation of polyions is far from that of fully extended ones in the above concentration range.

Both short-range and long-range interactions can contribute to the expansion of polyions. The following expansion coefficients can be defined:

$$\alpha_S = R_{w0}(\beta)/R_{w0}(\beta=0) \tag{4a}$$

$$\alpha_L = R_w(\beta)/R_{w0}(\beta) \tag{4b}$$

$$\alpha_T = R_w(\beta)/R_{w0}(\beta=0) \tag{4c}$$

where R_w and R_{w0} stand for the perturbed and the unperturbed radius of gyration, respectively. The coefficients α_S and α_L describe expansions attributable to short-range and long-range interactions, respectively; $\alpha_T(=\alpha_S\alpha_L)$ is the total expansion coefficient.

The radius of gyration of unperturbed coils can be calculated as[23]:

$$R_{w0}^2 = (L_pL/3)\left(1-\frac{3}{N}+\frac{6}{N^2}-\frac{6}{N^3}(1-e^{-N})\right) \tag{5}$$

where L_p is the persistence length, L is the contour length of the chain and $N=L/L_p$.

The values of the persistence length of PMA (*Table 1*) were obtained from the point of transition from coil scattering to rod scattering behaviour, h^*[24]:

$$L_p = 2.3/h^* \tag{6}$$

Experimental details of procedures will be described in a forthcoming paper[16].

The unperturbed radii R_{w0} were obtained by applying equation (5) with $L=590$ Å corresponding to $M_w=21\,000$. The latter value is a good approximation of the average molecular weights of PMA(H)/PMA(D) mixtures employed for the determination of R_z. The resultant unperturbed radii are in good agreement with those based on viscosity measurements[25–27]. The experimental radii of gyration R_z were corrected for polydispersity using equation (3) to give the radii R_w. Application of this relation (valid for Gaussian coils) to an expanded coil could lead to an error of about 2% in our case. The values of R_w and R_{w0} are shown in *Figure 3* and listed in *Table 1* together with the expansion coefficients based on these values.

For an un-ionized chain ($\beta=0$), the total expansion coefficient α_T is nearly 1 (see *Table 1* and *Figure 4*). This result leads to the conclusion that the expansion is exclusively due to the presence of charges for the investigated polyelectrolyte.

At $\beta\lesssim 0.2$, $\alpha_s=1$, and hence only long-range effects are operative ($\alpha_L>1$) in this range. This is quite natural, because at low charge densities the distances between charged monomers (along the chain) are large. In such a situation, the electrostatic interactions acting along the chain are weak and do not influence the local conformation of the backbone. An interaction of the charged monomers well separated along the chain can, of course, contribute to the expansion if the chain is flexible enough.

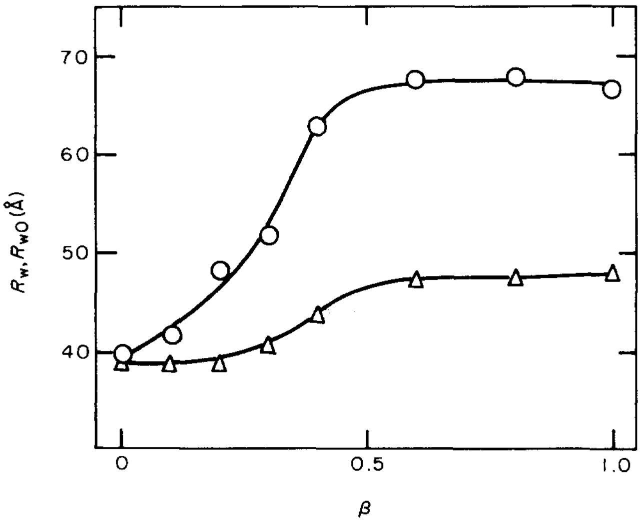

Figure 3 Variation of perturbed (○) and unperturbed (△) radii of gyration of PMA polyions with the degree of neutralization

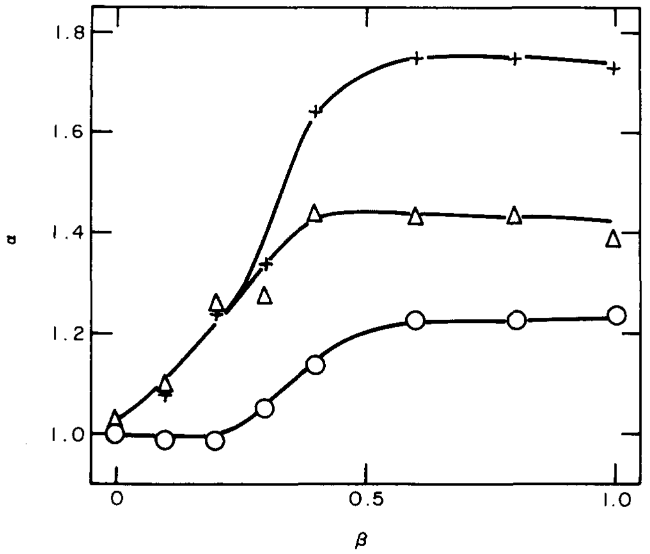

Figure 4 Variation of expansion coefficients α_T (+), α_L (△) and α_S (○) of PMA with the degree of neutralization

For $\beta \gtrsim 0.2$, the coefficient α_s starts to increase and reaches a steady value at $\beta \simeq 0.5$. For $\beta \gtrsim 0.5$, no dependence of the expansion coefficients on β is observed. This can be accounted for by the condensation of counterions. The charge density of polyions is stabilized, and so are the electrostatic interactions.

CONCLUSIONS

Dimensions of PMA polyions increase with increasing degree of neutralization for $\beta \lesssim 0.5$ and are constant beyond this range. In the concentration range examined ($c = 0.01$–$0.04\,\mathrm{g\,cm^{-3}}$), no changes of the radius of gyration are indicated. Its values are, at all β values, much smaller than that of a fully extended chain.

The expansion of polyions is attributable exclusively to the presence of charges. At low degrees of neutralization ($\beta \lesssim 0.2$) only the long-range interactions (excluded volume effect) contribute to the expansion.

The shape of the single-macroion structure factor as determined by the measurement of small-angle neutron scattering from mixtures of normal and labelled polymers is not very sensitive to departures from the ideal fraction of labelled species.

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