Small-angle scattering by polyelectrolyte solutions. Hydration and conformation of poly(methacrylic acid)

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Hydration and conformation of poly(methacrylic acid) in D_2O ($c = 0.036$ g cm^{-3}), neutralized by NaOD or LiOD, was studied by combination of neutron and X-ray small-angle scattering in the whole range of the degree of neutralization, α. Differences in the radii of gyration of polyion cross-section determined from the X-ray and neutron data indicate the existence of a monomolecular hydration shell, the density of which for $\alpha = 1$ is about 10% higher than that of bulk water. Condensation of counterions on the polymer chain, increasing with α, has been proved. Persistence length is about 8 Å for $\alpha \leqslant 0.2$, increases up to 12 Å for $\alpha \simeq 0.2$–0.5 and then remains constant.

INTRODUCTION

Polyelectrolytes are macromolecules that contain groups ionizable under certain conditions. Charges that arise on the macromolecule significantly affect both its own conformation and the structure of the solvent in its vicinity. An investigation of these factors is of considerable importance for the understanding of the properties and functions of polyelectrolytes. Small-angle X-ray and neutron scattering are appropriate methods for such studies, as they allow determination of structural characteristics of macroions, as these methods are at the same time sensitive to their solvation and interaction with counterions[1–4].

This study presents the results of an investigation of aqueous solutions of poly(methacrylic acid) at various degrees of neutralization by means of small-angle X-ray (SAXS) and neutron (SANS) scattering. Compared with an earlier paper[2], the measurement range of scattering curves has been extended to $h = 0.5$ Å^{-1}, which makes possible the determination of characteristics that describe the structure of solution on the scale of several monomer units.

EXPERIMENTAL

Samples

Poly(methacrylic acid) (PMA) with $M_w = 51\,000$, polymerized as described in detail previously[5], was dissolved in D_2O and neutralized with carbonate-free hydroxides LiOD and NaOD. The PMA concentration in all samples was $c = 0.036$ g cm^{-3}.

Small-angle X-ray scattering (SAXS)

The scattering curves were measured with a Kratky camera. The experimental conditions and corrections of scattering data have been described earlier[5]. The differential scattering cross-section (in cm^{-1}) was calculated from the corrected intensities, I, using the relation

$$\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}(h) = \frac{a}{\tilde{I}_L K_L T d} I$$

in which $h = (4\pi/\lambda)\sin\theta$ is the modulus of the scattering vector, λ is the radiation wavelength, 2θ is the scattering angle, a is the sample–detector distance, d and T respectively are the thickness and transmission of the sample, $\tilde{I}_L$ is the intensity of radiation scattered from the standard sample LUPOLEN[6], and K_L is the calibration constant.

Small-angle neutron scattering (SANS)

The measurement was made with the time-of-flight small-angle spectrometer[7] at the IBR-2 pulse reactor[8] at the Joint Institute for Nuclear Research, Dubna. Two sets of data were recorded for each sample: (1) scattering from the sample alone (I_S), (2) scattering from the sample and from the vanadium standard placed in the primary beam between the sample and detector (I_{SV}).

The differential scattering cross-section per unit volume of the sample is, then,

$$\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}(h) = \frac{I_S}{I_{SV} - I_S} \frac{\Omega_V}{\Omega_S} \frac{T_V d_V}{d} \left(\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}\right)_V$$

where Ω_S and Ω_V are solid angles at which the detector is seen from the position of the sample and from the position

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of the standard, respectively, T_V, d_V and $(d\Sigma/d\Omega)_V$ are the transmission, thickness and differential scattering cross-section of the vanadium standard, respectively. The contribution of incoherent scattering was estimated by means of scattering measurements on D_2O/H_2O mixtures containing the same number of protons as the tested samples.

RESULTS AND DISCUSSION

Scattering curves

Figure 1 shows the SAXS and SANS curves of poly(methacrylic acid) in D_2O neutralized with LiOD for various degrees of neutralization, α. Similar scattering curves were also obtained for solutions neutralized with NaOD. At $\alpha = 0$ the scattering intensities decrease monotonically with increasing scattering vector, h. At $\alpha > 0$ the curves have a maximum that is a result of electrostatic interactions between the polyions[5].

With increasing α neutron intensities decrease, while for the X-radiation (at least at high h) the opposite trend is observed. Such behaviour is a consequence of the existence of a hydration layer that surrounds the polyion and inside which water molecules are arranged more closely than in ordinary water[2].

Measurements of SANS curves of mixtures of deuterated and normal molecules make it possible to extract scattering functions corresponding to intra- and interparticle interferences[9-11]. The results of such measurements for PMA solutions[12,13] demonstrate that the interparticle interference provides a negative contribution to the intensity. With increasing h the absolute value of this contribution decreases, and for $h \gtrsim 1.2\, h_{max}$ (h_{max} is the position of the maximum) it can be neglected. Hence, at large h the observed intensity is equal to the scattering function of the individual polyions.

In this paper structure parameters that correspond to the length of several monomer units are discussed. Because the scattering curve is sensitive to these parameters only in the region of large h, this part of the scattering curve can be used instead of the form factor for their evaluation.

For sufficiently high h, the scattering from a linear macromolecule is the same as from a system of rods. The scattering curve can thus be written as[14]

$$\frac{d\Sigma}{d\Omega}(h) = (M_L c(\Delta b)^2 \pi/N_A)\exp(-R_c^2 h^2/2)/h \qquad (1)$$

$$\text{for } 2/L_p < h < 1/R_c$$

where M_L is the chain mass per unit length (g mol^{-1} cm^{-1}), c is the polymer concentration (g cm^{-3}), $\Delta b = b - \bar{V}\rho$ is the excess of scattering amplitude (cm g^{-1}), $\bar{V}$ is the partial volume of the polymer (cm^3 g^{-1}), ρ is the scattering density of the solvent (cm^{-2}), R_c is the radius of gyration of the chain cross-section, N_A is the Avogadro number and L_p is the persistence length.
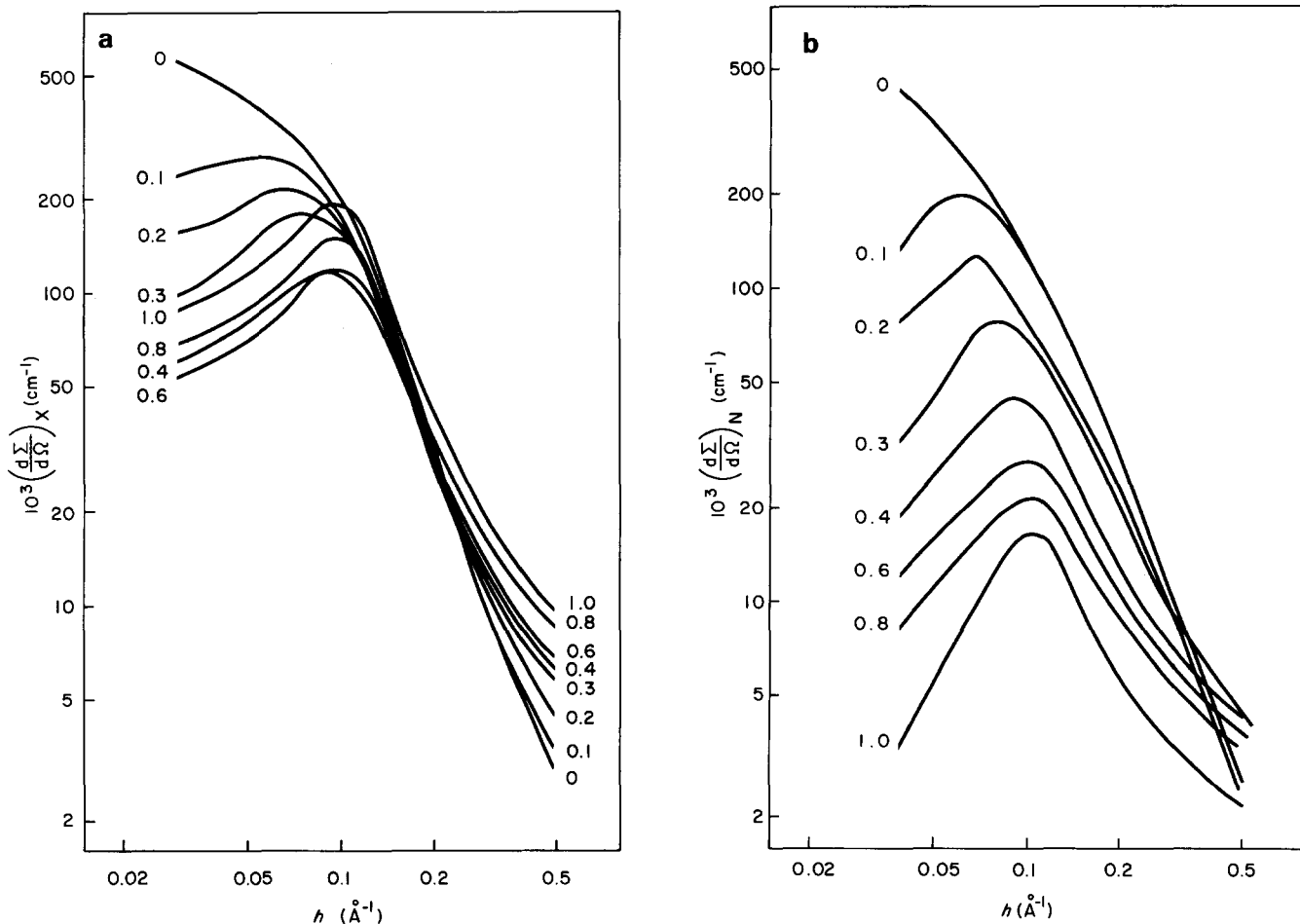

Figure 1 Neutron (a) and X-ray (b) small-angle scattering curves of PMA solutions in D_2O ($c = 0.036$ g cm^{-3}, counterion Li$^+$). Numbers denote the degree of neutralization

The persistence length characterizes chain stiffness. It can be determined from the position of the transition point (h^+) from the region where the behaviour of the scattering curve is that characteristic for coils ($I \sim h^{-\omega}$, $\omega = 2$ for gaussian coils, $\omega = 5/3$ for expanded coils) into a region with the rod-like behaviour of the chain (equation (1)). For short chains ($L \lesssim 10^2 L_p$), the relation[15]

$$L_p = 2.3/h^+ \qquad (2)$$

can be used.

Using relation (1), it is possible to determine parameters of the cross-section of the chain (M_L, R_c) in those cases where the radius of gyration of the cross-section is small compared with the persistence length ($2R_c < L_p$). An analysis of the data shows that such condition is satisfied only for a radius of gyration of the cross-section determined by means of SANS (R_{cN}). For the X-radiation, the radius of gyration of the cross-section is much larger than R_{cN}, and relation (1) cannot be directly used for the interpretation of SAXS data. Therefore the following procedure was used. First, by means of relation (1) and the SANS curves, the cross-section radius of gyration R_{cN} and the extrapolated intensity ($h \times d\Sigma/d\Omega)_N^{h \to 0}$ were determined. The corresponding values for X-radiation were then determined from the Guinier plot of the ratio of X-ray and neutron intensities (*Figure 2*), using the relation

$$\left(\frac{d\Sigma}{d\Omega}\right)_X \bigg/ \left(\frac{d\Sigma}{d\Omega}\right)_N = \frac{(\Delta b)_X^2}{(\Delta b)_N^2} \exp(-(R_{cX}^2 - R_{cN}^2)h^2/2) \qquad (3)$$

The application of the above relation for $h < 2/L_p$ also is based on the assumption that deviations of the scattering curve from the behaviour described by (1) in this region are independent of contrast.

Hydration of polyions, binding of counterions

Figure 3 and *Table 1* show the radii of gyration of the PMA chain cross-section with Na^+ and Li^+ counterions as a function of the degree of neutralization. When comparing the X-ray (R_{cX}) and neutron (R_{cN}) radii, one
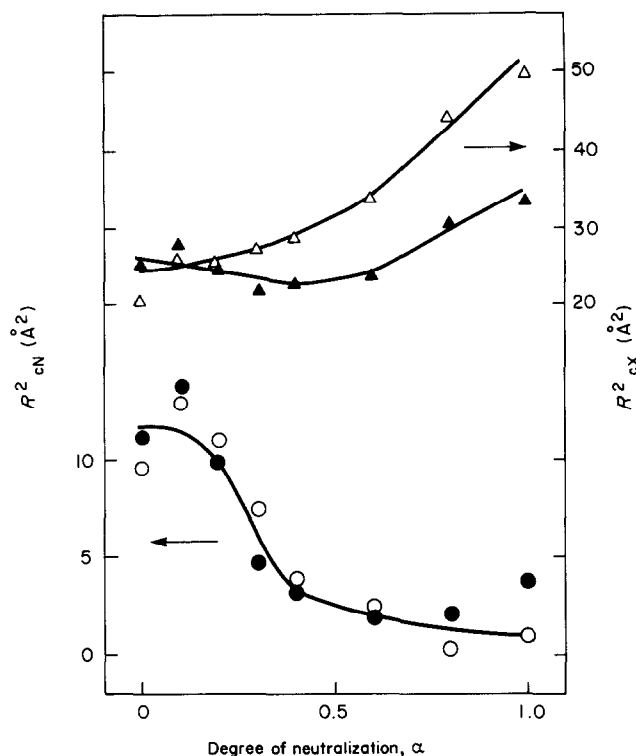
Figure 3 ($\triangle$, $\blacktriangle$) X-ray (R_{cX}) and ($\bigcirc$, $\bullet$) neutron (R_{cN} radii of gyration of the cross-section of the PMA chain in D_2O in relation to the degree of neutralization; ($\triangle$, $\bigcirc$) Na^+ counterions, ($\blacktriangle$, $\bullet$) Li^+ counterions

can see that R_{cX} is always larger than R_{cN}. With increasing degree of neutralization R_{cX} increases, while R_{cN} decreases. These findings can be explained by the hydration of polyions. In the neighbourhood of polyions a hydration layer is formed inside which the water structure differs from that of normal water. The excess of scattering amplitude of PMA in D_2O is positive for X-radiation and negative for neutrons. The behaviour of R_{cX} and R_{cN} described here indicates that the excess of scattering amplitude of the hydration layer must be positive both for the X-radiation and for neutrons. This means that the water density in the hydration shell is higher than that of normal water. The same conclusion can be made also on the basis of the density or refractivity measurements[16]. Unlike these measurements, which yield only hydration-induced volume changes that characterize the whole solution, scattering methods may provide information also on the dimensions of the hydration layer.

At low degrees of neutralization ($\alpha < 0.3$) the R_{cX} values for Na^+ and Li^+ do not differ from each other to any important degree, but at higher α the R_{cX} values for Na^+ are distinctly larger. The same can be said about extrapolated intensities ($hd\Sigma/d\Omega)_X^{h \to 0}$. The sensitivity of parameters, determined from SAXS curves, to counterion type may be interpreted as proof of the localization of a proportion of counterions in the vicinity of macroions. To estimate the proportion thus bound, it is advantageous to use the ratio of SAXS and SANS differential cross-sections extrapolated to $h \to 0$ which, according to equation (3), is equal to the ratio of the squares of excess of scattering amplitudes. In this way we eliminate the effect of the parameter M_L (equation (1)), the value of which depends on the conformation of the polyion. Moreover, this ratio was determined more exactly in our case ($\pm 15\%$) than were the individual extrapolated intensities ($\pm 25\%$). This apparent paradox arises because the accuracy of
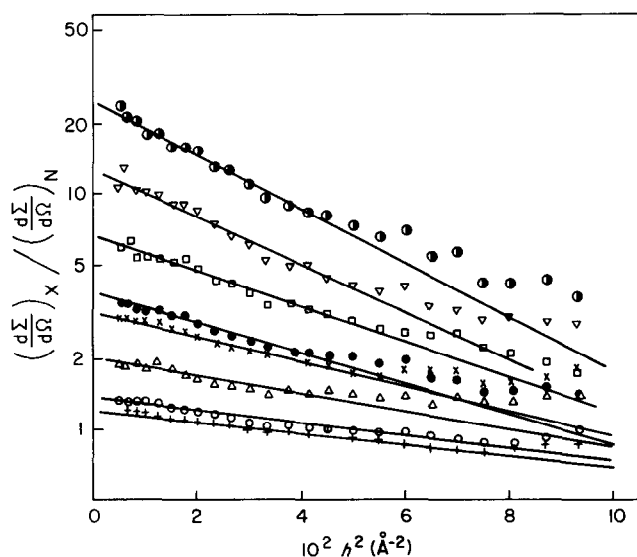
Figure 2 Guinier plot of the ratio of X-ray and neutron scattering intensities of PMA solutions in D_2O, counterion Na^+. Degree of neutralization, α: ($+$) 0.0; ($\bigcirc$) 0.1; ($\triangle$) 0.2; ($\times$) 0.3; ($\bullet$) 0.4; ($\square$) 0.6; ($\triangledown$) 0.8; ($\oplus$) 1.0

Table 1 X-ray (R_{cX}) and neutron (R_{cN}) radii of gyration of the cross-section of the PMA chain in D_2O, extrapolated neutron and X-ray intensities, number of bound counterions B per monomer unit (equation (5)) and persistence length L_p (equation (2), *Figure 5*) as a function of the degree of neutralization α with counterions Na^+ and Li^+

α	R_{cX} (Å)	R_{cN} (Å)	$10^5(cm^{-2})\left(h\frac{d\Sigma}{d\Omega}\right)^{h\to 0}_X$	$10^5(cm^{-2})\left(h\frac{d\Sigma}{d\Omega}\right)^{h\to 0}_N$	B^a	L_p (Å)
Neutralization with Na^+						
0.0	4.5	3.1	6.2	5.2	(0.07)	7.9
0.1	5.1	3.6	7.9	5.6	0.04	7.8
0.2	5.1	3.4	7.3	3.8	0.05	7.8
0.3	5.3	2.8	8.2	2.6	0.15	8.8
0.4	5.4	1.9	9.9	2.5	0.15	10.2
0.6	5.8	1.6	14.8	2.3	0.18	11.9
0.8	6.7	0.4	20.5	1.6	0.30	12.0
1.0	7.1	1.0	31.0	1.2	0.42	12.2
Neutralization with Li^+						
0.0	5.1	3.3	6.9	5.1	(0.26)	7.9
0.1	5.3	3.7	8.3	5.5	0.15	8.2
0.2	5.0	3.2	7.5	3.7	0.15	8.2
0.3	4.7	2.2	7.0	3.5	−0.11	8.8
0.4	4.7	1.8	7.9	2.7	0.04	10.5
0.6	4.8	1.4	9.7	2.1	0.07	12.7
0.8	5.6	1.5	13.6	2.0	0.02	12.7
1.0	5.8	2.0	17.8	1.3	0.29	12.6

^{a}Error in B values ± 0.1 (Na^+), ± 0.2 (Li^+)

extrapolated intensities for the X-radiation and for neutrons depends on the accuracy of data in the tail of SANS curves ($h = 0.3$–0.5 Å^{-1}), where the intensity-to-background ratio is very unfavourable ($\simeq 5\%$), while the extrapolated ratio of intensities was determined from more exact data at lower h ($\lesssim 0.2$ Å^{-1}).

Figure 4 shows the ratio of excess of scattering amplitudes $|(\Delta b)_X/(\Delta b)_N|$ for Na^+ and Li^+ counterions, along with the values calculated assuming that only hydrated polyions, and not counterions, contribute to the scattering. The latter values are based on the partial volume of PMA at $\alpha = 0$ (59.3 cm^3 mol^{-1})[17] and volume changes related to its neutralization, as reported by Ikegami[16]. At low α (< 0.3) the experimental values of $|(\Delta b)_X/(\Delta b)_N|$ for both counterions equal the theoretical ones within the limits of experimental error. At larger α deviations can be observed, especially for Na^+ counterions.

Considering the contribution of bound counterions, the excess of scattering amplitude can be written as

$$\Delta b = \Delta b^{mono} + B\Delta b^{ion} \qquad (4)$$

where B is the number of bound counterions per monomer unit and Δb^{mono} and Δb^{ion} are excess of scattering amplitudes of the monomer unit and counterion (in cm mol^{-1}). By denoting $C = ((d\Sigma/d\Omega)_X/(d\Sigma/d\Omega)_N)^{1/2}_{h\to 0} = |(\Delta b)_X/(\Delta b)_N|$, we obtain, bearing in mind that for PMA in D_2O $(\Delta b)_N < 0$,

$$B = -[C(\Delta b)^{mono}_N + (\Delta b)^{mono}_X]/[C(\Delta b)^{ion}_N + (\Delta b)^{ion}_X] \qquad (5)$$

In calculating the excess of scattering amplitude of counterions, the partial volume was taken as $V = -7$ cm^3 mol^{-1} (ref. 18), which is valid for infinite dilution. The acutal partial volume will probably be somewhat larger, which means that the estimates of the numbers of bound counterions (*Table 1*) are low. The non-zero B values obtained for samples without counterions ($\alpha = 0$) illustrate the uncertainty of this method of determination of the number of bound counterions. The
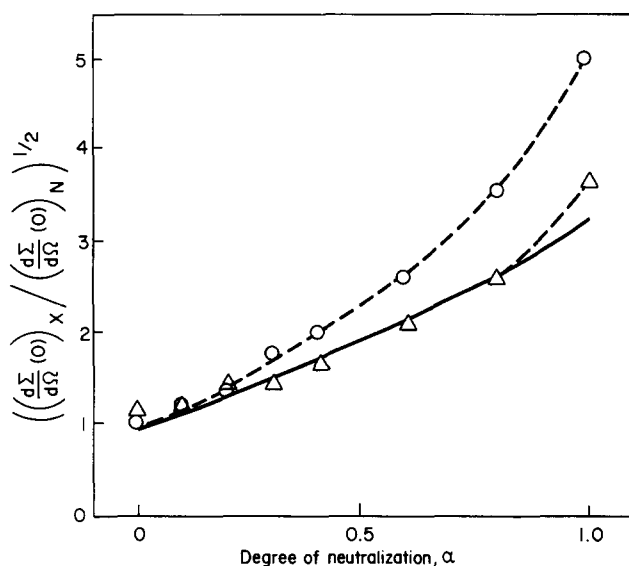

Figure 4 (-----), dependence of the extrapolated ratio of X-ray and neutron intensities on the degree of neutralization for PMA in D_2O. (———), dependence calculated using the partial volume of PMA[16,17] irrespective of the condensation of counterions. ($\bigcirc$) Na^+; ($\triangle$) Li^+

uncertainty of B values is rather considerable, especially in the case of Li^+ counterions, so that these values are not usefully discussed in greater detail in the light of theoretical results based on the equation of Poisson and Boltzmann[19,20] or the condensation theory of Oosawa[21] and Manning[22]. It is noted that in order to interpret the scattering curves of polyelectrolytes on an absolute scale, counterions should also be considered.

According to the data of Ikegami[16], the neutralization of PMA by NaOH is accompanied by volume change that corresponds to an increase in the number of water molecules in the hydration shell per one monomer unit by a factor of 1.1 compared with the same volume of normal water. Our scattering data are in agreement with this result, if it is allowed that near the polyion there is an increased concentration of counterions compared with

the average concentration. An attempt will now be made to estimate the size of the hydration shell in which this change in density takes place.

The radius of gyration of the cross-section is approximated by[23]

$$R_c^2 = fR_{cp}^2 + (1 - f)R_{ci}^2 \qquad (6)$$

where R_{cp} and R_{ci} are the respective radii of gyration of the hydrated polyion and of the shell containing bound counterions and $f = \Delta b^{mono}/\Delta b$. Assume that the structure of the chain and its surrounds is the same for Na^+ as for Li^+ counterions. Using relation (6) together with the experimental values of $R_{cx}(Na^+)$ and $R_{cx}(Li^+)$, it is then possible to determine the radii of gyration R_{cp} and R_{ci} for $\alpha \geqslant 0.4$. The radius of gyration of the hydrated chain, R_{cp}, for these α values is very close to R_{cx} for Li^+ counterions (cf. *Tables 1* and *2*). The more so may such agreement be expected at low α. Hence, we may regard the $R_{cx}(Li^+)$ values as a good approximation of the radius of gyration of the hydrated chain in the whole range of α. It can be shown similarly that the SANS cross-section radii of gyration of the hydrated chain may be approximated by the $R_{cN}(Li^+)$ values.

In order to assess dimensions of the hydrated chain, it is necessary to use a model of the chain cross-section, here the two-phase model (dry polymer + hydration shell) with radii of gyration R_1 and R_2. Assuming that their centres coincide, an equation analogous to (6) can be used to relate the experimental radii of gyration to R_1 and R_2. Now, however, the fraction f denotes the ratio of excess of scattering amplitudes of the bare and hydrated polyion, $\Delta b^{bare}/\Delta b^{hydr}$. Supposing, furthermore, that the radii R_1 and R_2 are the same for X-rays as for neutrons, both radii can be determined from the $R_{cx}(Li^+)$ and $R_{cN}(Li^+)$ values:

$$R_2^2 = R_{cX}^2 + \frac{f_X}{f_N - f_X}(R_{cX}^2 - R_{cN}^2) \qquad (7a)$$

$$R_1^2 = R_2^2 - \frac{1}{f_N - f_X}(R_{cX}^2 - R_{cN}^2) \qquad (7b)$$

The radius of the hydrated chain, r_H, can be then written as

$$r_H^2 = R_2^2 + \sqrt{R_2^2 - (2A_1/\pi)(R_2^2 - R_1^2)} \qquad (8)$$

where A_1 is the cross-sectional area of the dry polyion.

In order to calculate Δb^{bare}, the intrinsic volume of polyion, V_{int} (or, more precisely, the volume from which solvent is excluded) must be known. However, this quantity is not accessible experimentally. From the partial volume and macroscopic density of unionised PMA, V_{int} is estimated to lie between 0.70 and 0.76 cm^3 g^{-1}. The radii R_1, R_2 and r_H calculated on the assumption $V_{int} = 0.73$ cm^3 g^{-1} are given in *Table 2*. Uncertainty in V_{int} leads to an uncertainty in R_2 and r_H, especially at low degrees of neutralization. However, with increasing α the sensitivity of R_2 and r_H to V_{int} is greatly reduced. For illustration possible deviations (%) of r_H, associated with the uncertainty in V_{int} at several degrees of neutralization, are: $+90$, $-20(\alpha = 0)$; $+30$, $-12(\alpha = 0.1)$; $+11$, $-7(\alpha = 0.4)$; $+3$, $-2(\alpha = 1.0)$.

Thus, at higher degrees of neutralization ($\alpha \geqslant 0.4$) the radii have been determined with a reasonable accuracy.

Table 2 Cross-sectional radii of gyration of the hydrated polyion R_{cp} (equation (6)), shell containing bound counterions R_{ci} (equation (7)), bare polyion R_1 (equation (7b)), hydration shell R_2 (equation (7b)) and radius of the cross-secton of hydrated polyion r_H (equation (8))

α	R_{cp} (Å)	R_{ci} (Å)	R_1 (Å)	R_2 (Å)	r_H (Å)
0.0	—	—	4.1	8.9	12.1
0.1	—	—	4.5	7.6	10.3
0.2	—	—	4.1	6.8	9.2
0.3	—	—	3.6	6.4	8.5
0.4	4.8	9.1	3.6	6.2	8.1
0.6	5.3	8.9	3.8	5.9	7.8
0.8	5.8	10.2	4.5	6.5	8.8
1.0	6.2	10.0	4.9	6.5	8.8

The cross-sectional radius of gyration of the bare polyion is $R_1 = 4.1 \pm 0.5$ Å (*Table 2*). As could be expected, this value is significantly larger than that obtained on the assumption of a circular homogeneous cross-section (2.6 Å).

Using the dimensional characteristics given above, it is possible to derive the following idealized structure of the surroundings of a fully ionized PMA chain ($\alpha = 1$). The PMA chain is enveloped by a monomolecular shell of hydration water (outer radius = 8.8 Å) that contains ~ 18 molecules of water per one monomer unit of PMA. The density of hydration water is higher than that of normal water by $\sim 8\%$. The characteristic distance of bound counterions from the centre of the polyion is 10 Å.

Persistence length

The persistence length was determined from neutron scattering curves using relation (2). To make visible the transition point h^+, the scattering intensity multiplied by $h^2 \exp(h^2 R_{cN}^2/2)$ was plotted as a function of h (*Figure 5*). The exponential factor eliminates the effect of the chain cross-section on the scattering curve.

The persistence length is closely related to the unperturbed chain dimensions. For sufficiently long chains ($L \gg L_p$) the unperturbed radius of gyration is $R_0^2 = L_p L/3$, where L is the contour length of the chain. The same quantity may also be expressed by means of the characteristic ratio C_∞ as $R_0^2 = C_\infty nl^2/6$, where n is the number of bonds each of length l. Hence, obviously, the characteristic ratio is proportional to the persistence length: $C_\infty = (2L/nl^2)L_p$. The proportionality constant $2L/nl^2$ for PMA is 1.07 Å^{-1}.

Figure 6 shows persistence lengths and C_∞ values as a function of degree of neutralization. The differences between the results for Na^+ and Li^+ counterions are not important (cf. *Table 1*). At low α ($\leqslant 0.2$), L_p is constant ($\simeq 8$ Å). For $\alpha > 0.2$, L_p increases and at $\alpha \simeq 0.5$ becomes $L_p \simeq 12$ Å; this value remains constant with increasing α. This behaviour is in agreement with the dependence of C_∞ on α calculated by Davenport and Wright[24] from the conformation energies, and also with the unperturbed dimensions determined from the viscosity data of Katchalsky and Eisenberg[25], and of Noda *et al.*[26] (cf. ref. 24).

The persistence length is given by interactions of several adjacent monomer units. Its constant value for $\alpha \leqslant 0.2$ may therefore be explained by the fact that at low charge density the probability of occurrence in the polymer chain of two or more adjoining charged monomer units is small, and consequently, electrostatic interactions only
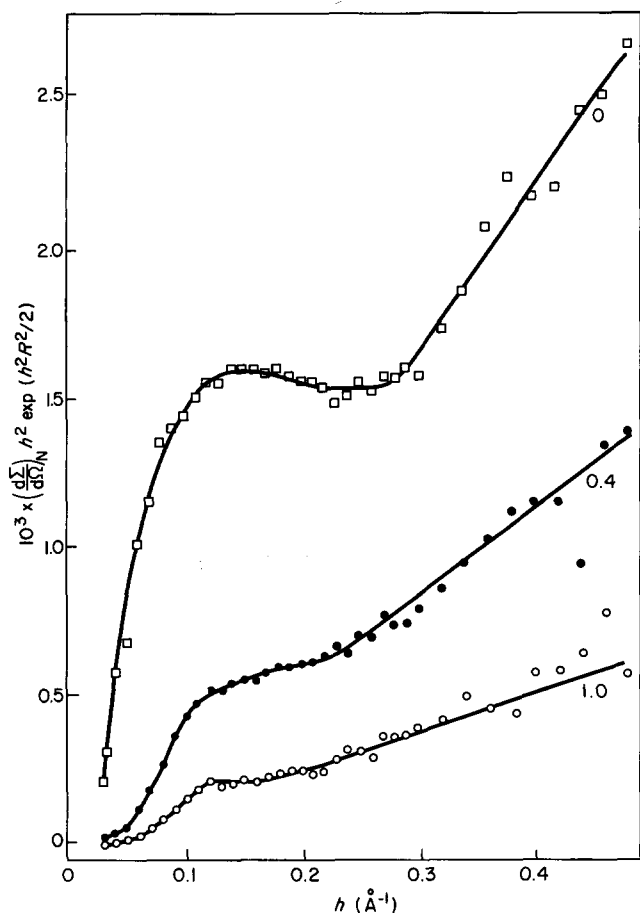
Figure 5 Examples of Kratky plot used in the determination of the persistence length of PMA $(c = 0.036\,\text{g cm}^{-3}$, counterion Na^+). (+) $\alpha = 0$; (●) $\alpha = 0.4$; (○) $\alpha = 1.0$

Figure 6 Dependence of the persistence length, L_p, and characteristic ratio, C_∞, on the degree of neutralization of PMA: (○) Na^+ counterions; (●) Li^+ counterions

weakly influence local chain structure; in this range the persistence length of the polyion is virtually equal to that of the corresponding neutral chain (L_{p0}).

At increased charge density, interactions between charged neighbouring monomer units become operative, and the persistence length is increased by the contribution associated with electrostatic interactions (L_{pe}).

At high degrees of neutralization the charge density on the polyion does not increase any more with increasing α owing to counterion condensation; as a consequence, the persistence length also remains unchanged.

It is of interest to compare the electrostatic persistence length with the value obtained by the theory of Odijk[27]. For polyelectrolytes without salt, Odijk has derived the relation

$$L_{pe} = (16\pi Qm)^{-1}\lambda c^{-1} \tag{9}$$

where Q is the Bjerrum length, m is the length of the monomer unit, $\lambda = Q/A$ is the charge parameter, A is the mean distance between neighbouring charged groups and c is the concentration of the monomer units. According to the condensation theory of Oosawa[21] and Manning[22], at high charge densities a proportion of counterions condense, so that λ remains unity. For the solution studied $(c = 0.036\,\text{g cm}^{-3} = 2.5 \times 10^{-4}$ monomer $\text{Å}^{-3})$ and using $Q = 7\,\text{Å}$ and $m = 2.5\,\text{Å}$, an electrostatic
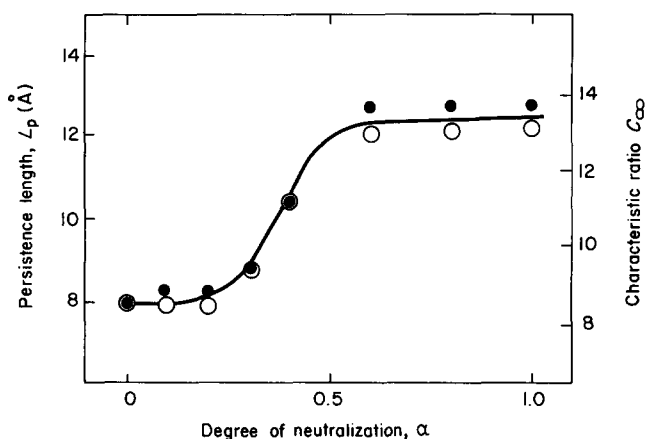
contribution was obtained to the persistence length $L_{pe} = 4.6\,\text{Å}$; this value is in a very good agreement with the experimental values for $\alpha = 1$, viz. $4.7\,\text{Å}$ (Li) and $4.3\,\text{Å}$ (Na).

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