Small-angle scattering by polyelectrolyte solutions: Intermolecular correlation function of poly(methacrylic acid) in salt-free semidilute solutions

J. Pleštil*, D. Hlavatá† and J. Labský
Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Prague 6, Czechoslovakia

and Yu. M. Ostanevich and V. Yu. Bezzabotnov
Joint Institute for Nuclear Research, Dubna, USSR
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Intermolecular correlations in salt-free solutions of poly(methacrylic acid) neutralized by NaOD were investigated as a function of the degree of neutralization, α. At $\alpha = 0$, the relative concentration of monomer units belonging to foreign macromolecules at a distance r from a reference monomer unit, $g(r) = N(r)/\bar{N}$, is nearly equal to unity in the r range investigated. Already at $\alpha = 0.01$, however, the values of $g(r)$ are significantly smaller than unity near the origin. With increasing r, $g(r)$ monotonically increases and reaches unity at $r = 120$–150 Å. No oscillations indicating an ordered structure are observed. The shape of $g(r)$ curves is in agreement with the correlation hole concept. The non-monotonic dependence of the radius of the correlation hole on α is explained by the overlap of macroions at higher degrees of neutralization.

(Keywords: small-angle scattering; polyelectrolytes; poly(methacrylic acid); intermolecular correlation function; correlation hole)

INTRODUCTION

In recent papers[1,2] we have reported structure parameters of poly(methacrylic acid) (PMA) chains in salt-free solutions based on small-angle X-ray (SAXS) and neutron (SANS) scattering data. The combination of these methods provided information on the cross-section of hydrated polyion and on counterion binding[1].

This information could be obtained despite the interference effects which affect the shape of the inner part of scattering curves. An elucidation of the polyelectrolyte structure at the molecular and supermolecular level is, however, a more complicated problem. For this purpose, Kaji *et al.*[3] used the distance distribution analysis of SAXS data. They found two maxima on the distance distribution functions of semidilute solutions of poly(vinyl hydrogen sulphate) and ascribed them to intra- and intermolecular correlations, respectively. Their procedure, however, did not allow these two contributions to be separated uniquely.

As has been shown by Williams *et al.*[4], the contributions of both intra- and intermolecular interferences to scattering can be extracted by performing SANS measurements on mixtures of a normal and labelled (deuterated) polymer. The method was later generalized by Akcasu *et al.*[5] and Benoît *et al.*[6]

In a previous work[2] we used this method to extract the single-particle scattering function (coming from the intraparticle interferences) of PMA, and determined the radius of gyration and expansion coefficients of polyions as a function of the degree of neutralization.

In the present paper we report the results of the distance distribution analysis based on the intermolecular scattering function. Such an analysis is expected to provide valuable information on the supermolecular structure of polyelectrolyte solutions.

EXPERIMENTAL

Samples

Poly(methacrylic acid) ($M_w^H = 23\,000$, polydispersity index $u = M_w/M_n - 1 = 0.2$) 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 was Na^+ and the polymer concentration was 0.46 base mol l^{-1} (0.04 g cm^{-3}).

Small-angle neutron scattering measurements

The measurements were made with a time-of-flight small-angle spectrometer[7] at the IBR-2 pulse reactor[8] at the Joint Institute for Nuclear Research in 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 a vanadium standard placed in the primary beam between the sample and detector (I_{SV}). The scattering cross-section per unit volume of sample with thickness d can be expressed as

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* Present address: Joint Institute for Nuclear Research, Dubna, USSR.
† To whom correspondence should be addressed

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

where Ω_S and Ω_V are solid angles at which the detector is seen from the position of the sample and the standard, respectively; T_V, d_V and $(d\Sigma/d\Omega)_V$ are the transmission, thickness and differential scattering cross-sections of the vanadium standard, respectively. The contribution of incoherent scattering was assessed by means of scattering measurements on D_2O/H_2O mixtures containing the same number of protons as the samples investigated.

THEORETICAL

The intensity of coherent scattering from an incompressible solution of normal (H) and labelled (D) macromolecules can be written as[5,6]

$$I(h)=(a_D-a_H)^2c_D(1-c_D)P(h)+(a_P-a_0)^2[P(h)+Q(h)] \tag{1}$$

where the scattering functions $P(h)$ and $Q(h)$ come from intramolecular and intermolecular interferences, respectively; $h=(4\pi/\lambda)\sin\theta$ is the modulus of the scattering vector (with λ the wavelength and 2θ the scattering angle); a_D, a_H and a_0 are the scattering lengths of the labelled monomer, normal monomer and solvent, respectively. The last quantity refers to the volume equal to the partial volume of the monomeric unit. The mean scattering length of the monomer is

$$a_P=c_Da_D+(1-c_D)a_H \tag{2}$$

where c_D is the fraction of monomers that are deuterated.

In principle, one needs two measurements to extract both scattering functions using equation (1). For linear polyelectrolytes, however, the intramolecular function of the deuterated polyion may differ from that of the normal polyion even if the polymerization degrees of both species coincide. This is due to the polyion hydration, which affects cross-section scattering factors of the labelled and normal polymer in a different manner[1]. Under such circumstances, it is advisable to perform measurements at three different values of c_D.

One possible way is to perform measurements at $c_D=0$ (normal polymer), $c_D=1$ (deuterated polymer) and $c_D=\bar{c}_D\equiv(a_0-a_H)/(a_D-a_H)$ (the mixture of the normal and deuterated polymer with $a_P=a_0$). Denoting corresponding scattering intensities by I_H, I_D and I_{HD}, respectively, and using equation (1), we obtain

$$I_{HD}(h)=(a_D-a_H)^2\bar{c}_D(1-\bar{c}_D)P(h) \tag{3a}$$

and

$$\bar{c}_DI_D(h)+(1-\bar{c}_D)I_H(h)-I_{HD}(h)=\overline{(\Delta a)^2}Q(h) \tag{3b}$$

where the contrast factor $\overline{(\Delta a)^2}$ is defined as

$$\overline{(\Delta a)^2}=\bar{c}_D(a_D-a_0)^2+(1-\bar{c}_D)(a_H-a_0)^2 \tag{4}$$

It is assumed in equations (1) and (3) that normal and deuterated polymers are identical except for their scattering lengths. Therefore, it is desirable to match the polymerization degrees of the labelled and unlabelled polymers as closely as possible.

The correlation function is defined as[9]

$$\gamma(r)=\langle\eta(\mathbf{x})\eta(\mathbf{x}+\mathbf{r})\rangle \tag{5}$$

where $\eta(\mathbf{x})=\rho(\mathbf{x})-\bar{\rho}$ is the excess scattering density and the brackets $\langle\ \rangle$ stand for the average over sample volume ($\mathbf{x}$) and over all orientations of the vector $\mathbf{r}$. The correlation function is closely related to the distance distribution function[10,11]:

$$p(r)=4\pi r^2\gamma(r) \tag{6}$$

The scattering cross-section then can be written as

$$\frac{d\Sigma(h)}{d\Omega}=\int_0^\infty p(r)\frac{\sin(hr)}{hr}dr \tag{7}$$

The function $p(r)$ and consequently $\gamma(r)$ can be calculated from experimental scattering data by means of a conventional Fourier inversion or using the indirect transformation method[10,11]. Combination of scattering data according to equation (3b) gives the intermolecular scattering function, $Q(h)$; correspondingly $\gamma(r)$ reflects only correlations between segments belonging to different macromolecules.

RESULTS AND DISCUSSION

Figure 1 shows the intermolecular interference curves $Q(h)$ for PMA at several degrees of neutralization. The curves were obtained by combining the scattering data

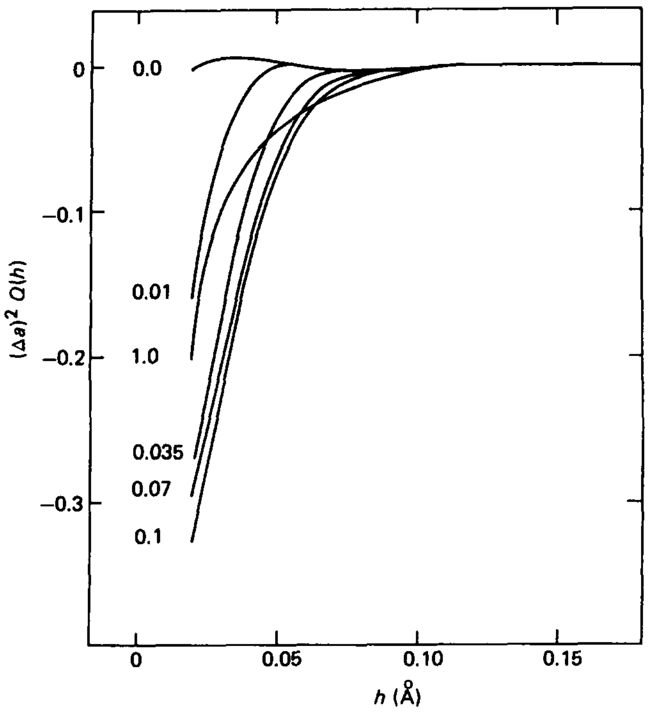

Figure 1 Intermolecular scattering cross-section per unit volume of PMA solutions neutralized by NaOD at several degrees of neutralization. Polymer concentration is 0.46 base mol l^{-1} ($\simeq$0.039 g cm^{-3}). The numbers on the curves denote the degree of neutralization

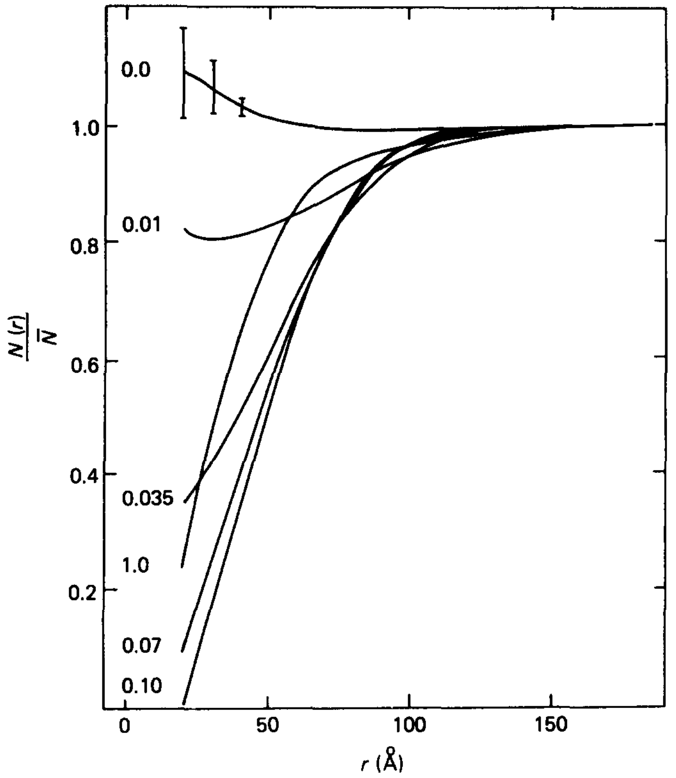

Figure 2 Relative concentration of monomer units belonging to foreign macromolecules in the vicinity of a reference unit, averaged over all choices of the reference unit (intermolecular correlation function). The mean concentration is $\bar{N} = 2.8 \times 10^{20}$ monomer units/cm^3. The numbers on the curves denote the degree of neutralization

obtained with solutions of a proper mixture of normal and deuterated PMA ($a_P = a_0$) with those of the solutions of pure components (normal, deuterated) according to equation (3b).

For un-ionized chains ($\alpha = 0$), the intermolecular interference gives only a small contribution to the total scattering. At $\alpha = 0.01$, however, the interparticle interference is already very important. The presence of a relatively small number of charges causes substantial structural changes.

The shapes of the $Q(h)$ curves for $\alpha > 0$ are very similar. At high scattering vectors ($h > 0.12$ Å^{-1}) the $Q(h)$ values are equal to zero within experimental error. Therefore, the scattering curve is proportional to the single-particle scattering factor in this region. Under such circumstances, the parameters of polyion cross-section can be determined without employing labelled samples[1]. At low h, the interchain interference function is negative. With increasing h the absolute values of $Q(h)$ decrease and reach zero at $h = 0.05$–0.12 Å^{-1} depending on the degree of neutralization. Similar results have been obtained by Williams[4] for semidilute aqueous solutions of sodium poly(styrene sulphonate).

For a discussion of the structure changes it is convenient to transform $Q(h)$ into real space. We used Glatter's program ITP[10,11] to calculate the distance distribution, $p(r)$ and the correlation function, $\gamma(r)$. The latter can be expressed in terms of local concentration of monomer units, $N(\mathbf{x})$:

$$\gamma(r) = \overline{(\Delta a)^2}[\langle N(\mathbf{x})N(\mathbf{x}+\mathbf{r})\rangle - \bar{N}^2] \qquad (8)$$

where $\bar{N}$ is the mean concentration (monomer units/cm^3) and $\overline{(\Delta)^2}$ is the mean-square excess scattering amplitude per monomer unit as given by equation (4). Averaging in equation (8) gives

$$\gamma(r) = \overline{(\Delta a)^2}[\bar{N}N(r) - \bar{N}^2] \qquad (9)$$

where $N(r)$ is the concentration of monomer units at a distance r from a reference unit, averaged over all choices of reference unit. Of interest in this work is the correlation function based on the intermolecular interference function. In such a case, the function $N(r)$ describes the concentration of monomer units not belonging to the same macromolecule as the reference unit.

The mean concentration was calculated according to $\bar{N} = cN_A/M_0$ (c is the polymer concentration (g cm^{-3}), N_A is Avogadro's number and M_0 is the formula weight of the monomer unit). For our solutions with $c = 0.039$ g cm^{-3}, the value $\bar{N} = 2.8 \times 10^{20}$ monomeric units/cm^3 was obtained.

The relative concentration of monomer units belonging to foreign macromolecules in the vicinity of a monomer unit (intermolecular correlation function) has been calculated from the distance distribution function as

$$g(r) \equiv N(r)/\bar{N} = 1 + p(r)/4\pi r^2 \overline{(\Delta a)^2} \bar{N}^2 \qquad (10)$$

The results are shown in *Figure 2*.

At $\alpha = 0$, the relative concentration $N(r)/\bar{N}$ is nearly equal to unity over almost the whole r range investigated. This means that virtually no correlation exists between the positions of segments of different macromolecules. Small positive deviations from unity at $r < 40$ Å could indicate formation of some contacts between neutral macromolecules. Possible contact sites are hydrophobic methyl groups which are believed to be responsible for the 'compact' conformation of PMA at low charge densities[12]. However, one must be careful with this conclusion, because the observed deviations are approximately equal to the estimated standard deviations.

As has already been pointed out, a small number of charges suffice to change the supermolecular structure significantly. These changes are due to electrostatic repulsive interactions. Charged segments repel each other; as a result, the correlation function becomes smaller than unity near the origin. For example, at $r = 20$ Å (radius of cross-section of hydrated polyion varies from 12 to 9 Å for $\alpha = 0$–1[1]), the values of $N(r)/\bar{N}$ are 0.83, 0.35 and 0.09 at $\alpha = 0.01$, 0.035 and 0.07, respectively.

The following common features of the correlation curves for $\alpha \geqslant 0.035$ are apparent from *Figure* 2. At small distances the $N(r)/\bar{N}$ values are much smaller than unity. With increasing r, $N(r)/\bar{N}$ increases monotonically and reaches unity at $r = 120$–150 Å. No oscillations which would indicate an ordered structure are observed. These features of the experimentally derived correlation curves are in agreement with those suggested by de Gennes on the basis of the correlation hole concept[13].

As a parameter characterizing the size of the correlation hole we chose the distance R_0 at which the correlation function equals $1 - e^{-1}$. The characteristic radius R_0 is shown in *Figure 3* as a function of the degree of neutralization. At low degrees of neutralization ($\alpha < 0.1$), R_0 increases with increasing α. At higher values,

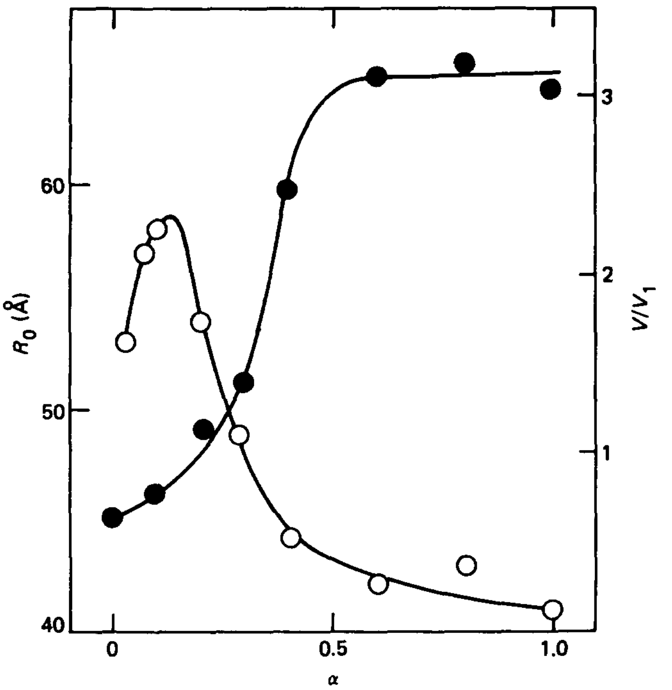

Figure 3 Radius of the correlation hole, R_0 (○), defined as $N(R_0)/\bar{N} = 1 - e^{-1}$, and the overlap parameter, V/V_1 (●) (see text), for the solution of PMA in D_2O neutralized by NaOD as a function of the degree of neutralization α. Notice that R_0 begins to decrease with increasing α when polyions begin to overlap ($V/V_1 \simeq 1$)

however, the characteristic radius decreases sharply up to $\alpha \simeq 0.5$ and for $\alpha > 0.5$ it remains nearly constant.

The increase of R_0 at low α can be explained by the increase in the charge density of polyions resulting in the enhancement of repulsive interactions.

We believe that the observed decrease of R_0 at higher α is due to the overlap of polyions. The extent of the overlap can be characterized by V/V_1, where V is the volume occupied by one swollen macromolecule and $V_1 = M/N_A c$ is the solution volume per macromolecule. The volume V was estimated as $V = (4\pi/3)(5/3)^{3/2} R_g^3$, where R_g is the radius of gyration of polyion. The R_g values vary from 39.8 to 66.8 Å for $\alpha = 0$–1.0 as shown in the previous publication[2]. The ratio V/V_1 as a function of the degree of neutralization is presented in *Figure 3* together with the radius of the correlation hole. We can see that V/V_1 is smaller than unity at low α and, therefore, configurations not requiring overlap of the macromolecules are possible. At α between 0.1 and 0.2, V/V_1 reaches unity and, consequently, the macromolecules must necessarily overlap. At high α (> 0.5), the overlapping is expected to be very strong because V/V_1 is about 3 in this range. Penetration of macromolecules into the volume occupied by another macromolecule leads to an increase in the probability of finding segments belonging to foreign macromolecules within small distances from a reference segment. In other words, as a result of increasing overlap of chains, the radius of the correlation hole decreases.

It is easily understood that the integral

$$P = \int_0^\infty 4\pi r^2 [\bar{N} - N(r)]\,\mathrm{d}r$$

should be equal to the degree of polymerization. We calculated this integral from our data for all ionized samples ($\alpha > 0$) and obtained the result $P = 260 \pm 50$, which is in a satisfactory agreement with the polymerization degrees of the macromolecules investigated ($P_w^H = 267$, $P_w^D = 206$).

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