
STRUCTURE OF POLYELECTROLYTE SOLUTIONS, SAXS STUDY OF POLY(ASPARTIC ACID)

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Dedicated to Dr M. Bohdanecký on the occasion of his 60th birthday.

The position of the maximum on small-angle scattering curves of solutions of poly(aspartic acid) neutralized with NaOH is proportional to the third root of concentration. The course of the interference function and the characteristic interchain distance were determined. The data may be interpreted using a model of ordered chains and assuming that the chain length per one monomer unit is smaller than would correspond to the all *trans*-conformation.

An important feature of small-angle scattering curves of polyelectrolyte solutions consists in a broad maximum in the range $h \sim 1 \text{ nm}^{-1}$, arising as a consequence of a strong electrostatic interaction between polyions. For the majority of linear polyelectrolytes investigated up to now, the position of the maximum varies with the square root of concentration¹⁻³. A more detailed bibliography regarding this phenomenon can be found in ref.⁴. In the interpretation of scattering curves, various structural models are used for which both a different shape of the individual chains and their mutual ordering is assumed. A cylindrical model¹⁻³ is the most frequent one: according to it, polyions are straightened and arranged in parallel. Using the position of the maximum on the scattering curve (h_1) and Bragg's equation, the chain distance is determined by

$$d_B = 2\pi/h_1. \quad (1)$$

On the basis of energetic stability of various arrangement of the polyions de Gennes and coworkers⁵ suggest an isotropic model assuming partially flexible chains oriented randomly. Both models predict that the position of the maximum on the scattering curve should be proportional to the square root of concentration, and are thus in agreement with the reported experimental data.

A basically different model has been suggested by Ise and coworkers⁶. According to them, two types of regions, *i.e.*, ordered and disordered, coexist in solution. At the same time, they assume that the maximum on the scattering curve arises due to the tridimensional ordering of polymer coils.

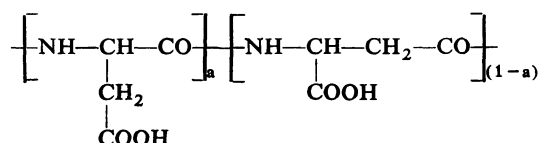
It has been shown recently^{7,8} that the existence of a maximum on the scattering curves of polyelectrolytes need not necessarily imply the existence of a regular arrangement of the polyions. A maximum may also appear on the scattering curve of chains composed of randomly oriented segments, if we assume that owing to the repulsive interaction the probability of the occurrence of another segment in the vicinity of the chosen one is small, compared with the average probability (correlation hole effect).

This study reports scattering data of solutions of poly(aspartic acid), differing in some respect from the scattering data of linear polyelectrolytes published so far. The data are interpreted using a slightly modified cylindrical model.

EXPERIMENTAL

Sample Preparation

Poly(α, β , -D,L-aspartic acid) was prepared from D,L-aspartic acid by thermal polycondensation followed by hydrolysis⁹. Aspartic acid in the polymer is racemic and bound in the α or β peptidic bond. The distribution of D and L units and α and β bonds in the chain is random:



Poly (D,L-aspartic acid) with the participation of the α bond ($a = 0.25$) was used in the measurement (sample I from ref.⁹). Solutions in the concentration range $1.03 - 14.60 \text{ g dm}^{-3}$ were prepared by dissolving a dry polymer in boiled distilled water; the exact concentration was determined potentiometrically. The solutions were neutralized with a carbonate-free NaOH (degree of neutralization $\alpha = 1$).

Small-angle X-ray scattering (SAXS).

The scattering curves were measured on a Kratky camera (CuK α radiation, recorded with a proportional detector, monochromatization with a β -filter and pulse analyzer). The collimation corrections were performed by employing O'Glatter's program¹⁰. The scattering curves are presented as functions of the magnitude of the scattering vector $h = (4\pi/\lambda) \sin(\theta/2)$, where θ is the scattering angle. For their interpretation we use the relation for the intensity of scattering on a set of N particles¹¹.

$$I(\mathbf{h}) = N \langle F^2(\mathbf{h}) \rangle B(\mathbf{h}) . \quad (2)$$

where $\langle F^2(\mathbf{h}) \rangle$ is the mean squared value of the scattering amplitude of a particle. In a general case, the interference function $B(\mathbf{h})$ may be written as

$$B(\mathbf{h}) = 1 + \langle \sum_k \sum_{1 \neq k} F_k(\mathbf{h}) F_1(\mathbf{h}) \cos \mathbf{hR}_{k1} \rangle / N \langle F^2(\mathbf{h}) \rangle, \quad (3)$$

where $F_k(\mathbf{h})$ is the scattering amplitude of the k -th particle and \mathbf{R}_{k1} denotes the interparticle vector. If the position of the particle does not affect the probability of its various orientations, relation (3) may be simplified to

$$B(\mathbf{h}) = 1 + \langle \sum_k \sum_{1 \neq k} \cos \mathbf{hR}_{k1} \rangle \langle F(\mathbf{h}) \rangle^2 / N \langle F^2(\mathbf{h}) \rangle. \quad (4)$$

The interference function involves information about arrangement of particles in the sample. For systems without long-range ordering and at sufficiently large values of the argument, $B(\mathbf{h}) = 1$, and the scattering intensity for these \mathbf{h} values is given by scattering on the individual particles only.

RESULTS AND DISCUSSION

The shape of small-angle scattering curves of solutions of sodium poly(aspartate) (Fig. 1) does not differ to any important degree from that of curves of similar solutions published earlier. With increasing concentration of the polymer, the maximum is shifted towards higher values of the scattering vector \mathbf{h} . However, as can be seen from Fig. 2 and Table I, h_m does not increase with the expected square root of concentration, but approximately with the third. In this respect, the behaviour of this polymer differs from that of sodium salts of poly(methacrylic acid)^{1,3}, poly(α -L-glutamic acid)² or poly(styrenesulphonic acid)¹². We do not believe, however, that a deviation in the concentration dependence of h_m should necessarily prove a qualitative difference between the structure of poly(aspartic acid) and that of solutions of these polyelectrolytes. It should be pointed out, that the position of the maximum on the experimental scattering curve is not only determined by the interchain distances, but depends also on the course of the scattering curve of an individual chain.

More direct information about the chain ordering may be obtained from the interference function $B(\mathbf{h})$. The evaluation of $B(\mathbf{h})$ from the experimental scattering curve is possible only if the scattering curve of an individual chain $F^2(\mathbf{h})$ is known, but it is virtually impossible to measure such curve for strongly interacting linear polyions using X radiation. We therefore employed an approximative relation

$$\langle F^2(\mathbf{h}) \rangle_{\mathbf{h}}^* = \exp\left(\frac{-h^2 R_q}{2}\right) \cdot \pi / hL. \quad (5)$$

This relation describes scattering from a system of rodlike particles having the length L and the radius of gyration of the cross-section R_q ; it holds if conditions

$$hR_q \leq 1, \quad hL \gg 1 \quad (6a,b)$$

TABLE I

Structural parameters of poly(Na-Asp) solution. Symbols: c is concentration of polymer solution, h_1 is position of the maximum on the scattering curve, h_B is position of the maximum on the interference function, D is chain distance according to relation (7), D_{\min} is the theoretical distance between fully extended chains for a hexagonal lattice (relation (8)), and $l/l_{\max} = (D_{\min}/D)^2$ is a parameter describing chain contraction (*cf.* text)

c $\text{g} \cdot \text{dm}^{-3}$	h_1 nm^{-1}	h_B nm^{-1}	D nm	D_{\min} nm	l/l_{\max}
1.03	0.74	0.82	8.8	6.82	0.60
2.04	0.89	1.18	6.1	4.85	0.63
4.13	1.27	1.44	5.0	3.41	0.47
6.95	1.37	1.85	3.9	2.63	0.45
10.41	1.58	2.2	3.3	2.15	0.42
14.60	1.69	—	—	1.81	—

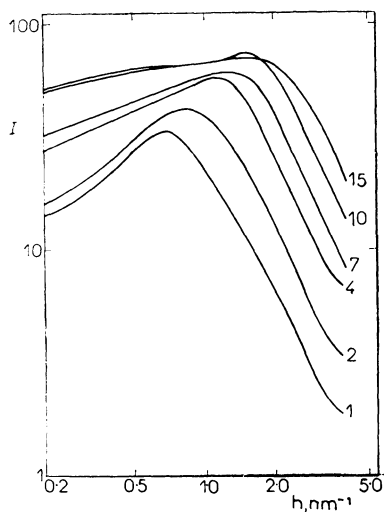


FIG. 1

Small-angle scattering curves of poly(Na-Asp). Numbers at curves denote approximate concentrations of polymer solution in $\text{g} \cdot \text{dm}^{-3}$; for exact concentrations *cf.* Table I

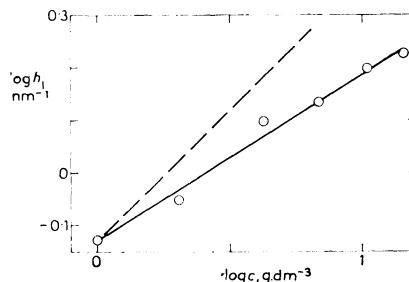


FIG. 2

Concentration dependence of the position of the maximum on the scattering curve of poly(Na-Asp); ----- theoretical line

are fulfilled. For a flexible chain, relation (5) can be used if the condition (6b) is valid for its persistent length. The radius of gyration of the chain cross-section of poly-(aspartic acid) neutralized with NaOH, poly(Na-Asp), was estimated as 0.34 nm, using the slope of the dependence $\log I(\mathbf{h}) \mathbf{h}$ on \mathbf{h}^2 in the range where the scattering curve is not greatly influenced by the interparticle interference. This value is higher than 0.22 nm obtained assuming a circular chain cross-section *in vacuo*. The higher value of the radius of gyration is probably a result of hydration of the chain¹³ and departures from the circular cross-section.

The interference functions for the individual polymer concentrations (Fig. 3) were obtained by dividing the experimental scattering curves by function (5). At low concentrations, a maximum (\mathbf{h}_B) can be seen on the $B(\mathbf{h})$ curves. With increasing concentration the maximum becomes less pronounced and is shifted towards higher \mathbf{h} values. The maximum on $B(\mathbf{h})$ may be suppressed with increasing concentration due to two reasons: a) The relative fluctuation of chain distances $\delta/D \sim 1/\sqrt{D}$ increases with increasing concentration⁵. b) Deviations from the parallel chain ordering lead to a decrease of factor $\langle F(\mathbf{h}) \rangle^2 / \langle F^2(\mathbf{h}) \rangle$ in relation (4). This effect is more pronounced at higher \mathbf{h} values.

The interchain distance D may be calculated as

$$D = K_\sigma \cdot 2\pi/\mathbf{h}_B, \quad (7)$$

where $K_\sigma = 1.15$ for an ideal hexagonal two-dimensional lattice of parallel macromolecules. Certainly, the arrangement of polyelectrolyte chains in solution is far

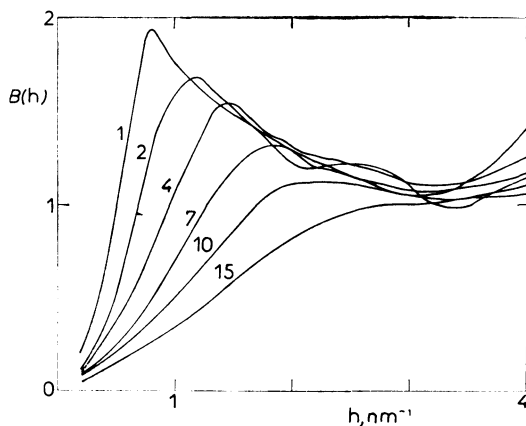


FIG. 3

Interference function of poly(Na-Asp). Numbers at curves denote approximate concentrations of polymer solution in g dm^{-3} ; for exact concentrations *cf.* Table I

from such ideal structure. In this case a few per cent lower value of K_e should be expected.

The theoretical chain distance in a hexagonal twodimensional lattice is

$$D_{th} = [m/N_A l c \cos(\pi/6)]^{1/2}, \quad (8)$$

where m , l respectively are mass and length per a repeating polyion unit, N_A is the Avogadro number, and c is the concentration of polymer solution (g/cm^3). In Table I, experimental D values are given, together with the minimal estimated distances between polyions D_{min} , calculated according to Eq. (8) with $m = 115$ and $l = 0.46$ nm. The latter value was calculated on the basis of the structure of the monomer unit and at a given content on the α and β peptide bonds, assuming the *trans*-conformation; it may therefore be regarded as maximal for the given sample (l_{max}).

The experimental distances (D) exceed the theoretical values of D_{min} by 30–50%. Several factors may contribute to these departures. On the one hand, there are irregularities in the chain ordering (distribution of distances and orientations), on the other, deviations of chain conformations from the fully extended chain should be considered. The former factors lead to an overestimate of experimental distances compared with the real ones, while transition from the fully extended conformation to less extended ones correspond to an increase in the actual chain distances. Hence, both factors may lead to an increase in the observed D value compared with D_{min} . We believe that the latter plays a more important role.

In order to evaluate a change conformation which would correspond to the observed deviations of D and D_{min} , we calculated the length per one repeating unit for $D = D_{min}$. Table I gives l/l_{max} . At all concentrations under investigation, this ratio is markedly lower than unity which suggests that the chains are not fully extended. In the concentration range studied, l/l_{max} decreases from 0.6 to 0.4. The corresponding decrease in the radius of gyration of the chain would be 20%. Similar results were also obtained for poly(Asp) samples with a different content of α and β peptide bonds¹⁴.

Determination of the course of the chain scattering factor would greatly contribute to the determination of the structure of polyelectrolytes. The use of the approximative scattering factor Eq. (5) without the possibility of verifying to what extent the conditions of applicability have been fulfilled may lead to uncertainties in the determination of the course of the interference curve. Moreover, knowledge of the scattering factor will bring information about the shape of the chain, allowing us to choose between the various structure models. The scattering factor of interacting polyions can be measured using the small-angle neutron scattering, if a mixture of protonated and deuterated polyions is used¹⁵. Measurement of this scattering factor of the polyelectrolyte chain will be dealt with in our forthcoming papers.

REFERENCES

1. Moan M.: *J. Appl. Cryst.* **11**, 519 (1978).
2. Rinaudo M., Domard A.: *J. Polym. Sci., Polym. Lett. Ed.* **15**, 411 (1977).
3. Pleštil J., Mikeš J., Dušek K.: *Acta Polym.* **30**, 29 (1979).
4. Ise N., Okubo T.: *Accounts Chem. Res.* **13**, 303 (1980).
5. De Gennes P. G., Pincus P., Velasco R. M.: *J. Phys. (Paris)* **37**, 1461 (1976).
6. Ise N., Okubo T., Yamamoto K., Kawai H., Hashimoto T., Fujimura M., Hiragi Y.: *J. Amer. Chem. Soc.* **102**, 7901 (1980).
7. Benmouna M., Weill G., Benoit H., Akcosu Z.: *J. Phys. (Paris)* **43**, 1679 (1982).
8. Koyama R.: *Physica (Utrecht)* **120B**, 418 (1983).
9. Pivcová H., Saudek V., Drobník J.: *Polymer* **23**, 1237 (1982).
10. Glatter O.: *J. Appl. Cryst.* **7**, 147 (1974).
11. Guinier A., Fournet G.: *Small-Angle Scattering of X-Rays*, p. 30. Wiley, New York 1955.
12. Nierlich M., Williams C. E., Boné F., Cotton J. P., Daoud M., Farnoux B., Jannink G., Picot C., Moan M., Wolff C., Rinaudo M., de Gennes P. G.: *J. Phys. (Paris)* **40**, 701 (1979).
13. Pleštil J., Mikeš J., Dušek K., Ostanevich Yu. M., Kunchenko A. B.: *Polymer Bull.* **4**, 225 (1981).
14. Pleštil J., Hlavatá D.: Unpublished results.
15. Akcasu A. Z., Summerfield G. C., Jahnshan S. N., Han C. C., Kim C. Y., Yu H.: *J. Polym. Sci., Polym. Phys. Ed.* **18**, 863 (1980).

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