Biophysical Chemistry 81 (1999) 45–57

Biophysical Chemistry

www.elsevier.nl/locate/bpc

Conformation of poly(methacrylic acid) in acidic aqueous solution studied by small angle X-ray scattering

Yoshio Muroga[a,*], Takahiro Yoshida[a], Seigou Kawaguchi[b]

[a] *Department of Applied Chemistry, School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan*
[b] *Department of Materials Science, Toyohashi University of Technology, Tempaku-cho, Toyohashi 441-8580, Japan*

Received 23 April 1999; received in revised form 9 June 1999; accepted 14 June 1999

Abstract

The nature of the contracted form of poly(methacrylic acid) PMA chain in salt-free acidic aqueous solution was studied by analyzing scattering curves registered by small-angle X-ray scattering, comparing it with those of PMA in methanol at 26°C and of partially neutralized PMA in aqueous solution containing added salt (the concentration of added salt, $Cs = 0.1$ M NaF). It is shown that the distribution of segments in the contracted form as well as that of PMA in methanol is that of a random-coil in a θ medium and that this distribution of segments is stable over a fair range of degrees of ionization α for Cs below 0.1 M. Moreover, the persistence length of PMA at $Cs = 0.1$ M (4 ± 0.5 Å) is substantially constant throughout the entire range of α, indicating that the contracted form of PMA changes to an expanded random-coil in a higher pH region without a significant change in the chain flexibility.

Keywords: Small angle X-ray scattering; Poly(methacrylic acid) (PMA); Debye function; Wormlike chain; Persistence length; Excluded volume effect

---

[*] Corresponding author. Tel.: +81-52-789-4605; fax: +81-52-789-3210.
E-mail address: ymuroga@apchem.nagoya-u.ac.jp (Y. Muroga)

PII: S0301-4622(99)00083-6

1. Introduction

From degree of ionization α dependence of the apparent ionization constant pK_a and the calorimetric data, Leyte and Mandel [1] and Crescenzi et al. [2], respectively, have suggested that poly(methacrylic acid) PMA chain in the low pH region takes on a contracted form, which changes to an expanded random-coil in a higher pH region. Such a contracted form has also been proposed from α dependence of intrinsic viscosity [η] [3,4]. However, the nature of the contracted form of PMA remains unclarified, as was recently pointed out by Morawetz [5]. Since [η] of PMA in 0.002 N aqueous HCl at 30°C [4] is proportional to the square root of the molecular weight, Katchalsky et al. suggested that the molecules are highly coiled and impermeable to the flow of the solvent and Davenport et al. [6] pointed out that the unionized PMA in aqueous solution has a very similar unperturbed dimension as poly(methyl methacrylate). Recently, Francois et al. [7] suggested that the uncharged PMA has an overall dimension intermediate between that of a compact sphere and a Gaussian coil, neglecting the effect of the cross-section of a polymer chain on the small-angle X-ray scattering (SAXS) curve.

To clarify the nature of the contracted form of PMA in acidic aqueous solution is important since it leads to an understanding of the role of hydrophobic interactions in determining structures of polyelectrolytes in aqueous solution. Needless to say, it is necessary for this purpose to analyze in detail not only the overall conformation but also the local conformation of the polymer chain and thus SAXS, which employs a wide range of a scattering vector, seems to be one of the most suitable methods. In the present work, we studied in detail the nature of the contracted form of PMA by analyzing scattering curves registered by SAXS, comparing it with those of conformation of PMA in methanol at 26°C and of partially neutralized PMA in aqueous solution containing added salt, where the former conformation has been shown to be substantially described by a random-coil in a θ medium [8] and the latter by a random-coil expanded predominantly by an excluded volume effect [9].

2. Materials and methods

Two samples of PMA with narrow molecular weight distribution, PMA-I and −II, were prepared by hydrolysis of poly(*tert*-butyl methacrylate), which was obtained by anionic polymerization of *t*-butyl methacrylate monomer at −78°C under high vacuum. The detail of the preparation is described elsewhere [10]. PMA-I has a weight-averaged molecular-weight $M_w = 2.68 \times 10^4$ and its ratio to number-averaged molecular-weight M_n, $M_w/M_n = 1.03$ and PMA-II has $M_w = 4.06 \times 10^4$ and $M_w/M_n = 1.04$. The stereoregularities of the samples are almost identical and characterized by Iso = 13%, Hetero = 52% and Syndio = 35% in triad representation.

The pH measurement was carried out for PMA-I in aqueous solution in the absence of added salt by a Corning M255 pH meter at 20 ± 1.0°C under administration of Ar gas over the solution in order to avoid contamination of the solution by atmospheric CO_2. The concentration of the sample solution Cp was 2.8 mM.

The SAXS experiments were carried out using synchrotron orbital radiation as an X-ray source set up in the Photon Factory of the High Energy Accelerator Organization at Tsukuba, Ibaragi, Japan. The wavelength of the X-ray was 1.488 Å and the distance between the sample and the detector was 950 mm. The scattered intensity was detected by a position-sensitive proportional counter (PSPC) with 512 channels over a scattering vector range from 0.02 to 0.25/Å. The details of the instrumentation and the procedure are described elsewhere [11]. Effects of slit-length and slit-width on the scattering curves could be neglected, because the size of the X-ray beam at the sample position was small enough compared with the camera length. Scattered intensities were registered on a relative scale, not on an absolute scale. Therefore, scattered intensities were allowed to be multiplied by a constant factor for comparison with theoretical curves.

In general, scattering from polymer chains in solution can be regarded to reflect interferences within an isolated polymer chain if Cp is lower than the critical concentration Cp^*, above which different solute molecules begin to overlap. Approximating Cp^* by $1/[\eta]$ and evaluating $[\eta]$ for PMA in 0.002 M HCl at 30°C by [4]

$$[\eta] = 6.6 \times 10^{-4} \times M^{0.5} \quad (\text{in dl}/\text{g}) \tag{1}$$

and $[\eta]$ for PMA in methanol at 26°C by [8]

$$[\eta] = 2.42 \times 10^{-3} \times M^{0.51} \quad (\text{in dl}/\text{g}) \tag{2}$$

Cp^* is estimated to be 9.3 and 7.5 g/dl for PMA-I and −II in the former solution and to be 2.3 and 1.8 g/dl in the latter solution, respectively. For the samples in acidic aqueous solution and in methanol, Cp was adjusted so that it can be lower than the corresponding Cp^*.

For partially neutralized PMA in aqueous solution containing added salt, however, Cp^* cannot be precisely estimated and thus Cp was varied in a range of 0.89–2.3 g/dl and the effect of concentrations was taken into account in the data analysis. NaF is employed as an added salt, considering that X-rays are far less absorbed by NaF than conventional NaCl.

3. Results and discussion

The potentiometric titration curve of PMA-I, A, in salt-free aqueous solution is shown in the form of pK_a ($= -\log K_a$) vs. α in Fig. 1, with B, extant data [1] for PMA in an aqueous solution containing 0.0033 M $NaNO_3$, where K_a is the apparent ionization constant of the polyacid. Clear humps in the low pH region are observed in both titration curves. From this observation, a contracted form is suggested for PMA in acidic aqueous solution with or without added salt.

To see whether the distributions of segments in PMA in acidic aqueous solution and in methanol solution are as expected for a random coil in a θ medium, their scattering curves are compared with the Debye function for a random coil in a θ medium. Since the Debye function is developed for a chain having no cross-section, it is necessary for the comparison to reduce the observed scattering intensity I_{obs} to that obtained if the polymer chain had no cross-section I_{thin}. For a rodlike chain [12], in general, I_{obs} is given by the product of I_{thin} and I_{cs}, where I_{cs} is a cross-sectional factor of the chain, which is proportional to $\exp\{-1/2\langle R_{cs}^2\rangle q^2\}$, wherein $\langle R_{cs}^2\rangle$ is the mean-square radius of the cross-section of the chain and q is the magnitude of the scattering vector, defined by $(4/\lambda)\sin(\theta/2)$ and λ is the wavelength of X-ray and θ is a scattering angle. As was done in our previous paper [13], it is assumed here that I_{obs} for a flexible polymer is also given by the product of I_{thin} and I_{cs} and the chain behaves as a rodlike chain in a high q range where

$$1/\langle R_g^2\rangle < q^2 < 1/\langle R_{cs}^2\rangle \tag{3}$$

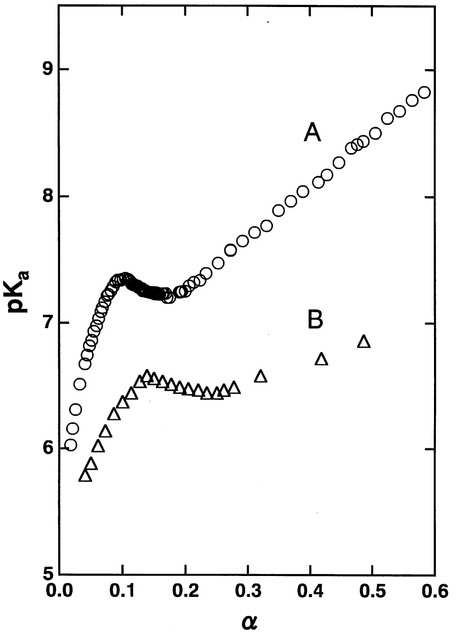

Fig. 1. Relation between apparent ionization constant pK_a and degree of ionization α for PMA-I in salt-free aqueous solution (○) and for PMA in aqueous solution containing 0.0033 M, $NaNO_3$ (△). The latter data are from Leyte [1].

Table 1

Summary of root mean-square radius of cross-section of polymer chain $\langle R_{cs}^2 \rangle^{1/2}$ (Å)

Sample	Solvent	α	Cp (g/dl)	$\langle \mathrm{R}_{cs}{}^2 \rangle^{1/2}$
PMA-I	H_2O	$\sim 0^a$	2.1	3.8 ± 0.2
PMA-I	H_2O	$\sim 0^a$	1.0	3.8 ± 0.2
PMA-II	H_2O	$\sim 0^a$	1.6	3.8 ± 0.2
PMA-II	H_2O	$\sim 0^a$	0.81	3.8 ± 0.2
PMA-I	CH_3OH	$\sim 0^a$	2.5	3.7 ± 0.3
PMA-II	CH_3OH	$\sim 0^a$	1.1	3.9 ± 0.3
PMA-I	0.1M NaF (aq.)	$\sim 0^a$	0.43	3.0 ± 0.3
PMA-II	0.1M NaF (aq.)	$\sim 0^a$	1.3	3.9 ± 0.3
PMA-II	0.1M NaF (aq.)	$\sim 0^a$	0.39	3.0 ± 0.3
PMA-II	0.1M NaF (aq.)	0.15	1.8	3.3 ± 0.3
PMA-II	0.1M NaF (aq.)	0.15	0.89	3.8 ± 0.3
PMA-II	0.1M NaF (aq.)	0.30	2.2	3.6 ± 0.3
PMA-II	0.1M NaF (aq.)	0.30	1.1	3.8 ± 0.3
PMA-II	0.1M NaF (aq.)	1.00	2.3	4.2 ± 0.3
PMA-II	0.1M NaF (aq.)	1.00	1.1	4.1 ± 0.3

[a] ~ 0, degree of neutralization = 0 and $\alpha \leq 0.02$.

Here $\langle R_g^2 \rangle$ is the mean-square radius of gyration of the chain. Thus, I_{thin} for PMA is given by $I_{\mathrm{obs}} \cdot \exp\{+1/2\langle \mathrm{R}_{cs}^2 \rangle q^2\}$.

$\langle R_{cs}^2 \rangle$ is experimentally evaluated from the slope of a straight line drawn in a q range given by Eq. (3) in the plot of $\ln(I_{\mathrm{obs}} q)$ vs. q^2. Fig. 2A,B show a plot of $\ln(I_{\mathrm{obs}} q)$ vs. q^2 for PMA-I and -II in acidic aqueous solution (pH = 2.3–2.8) and in methanol solution, respectively. The plots are linear in the high q range given by Eq. (3) and the slope gives $\langle R_{cs}^2 \rangle^{1/2}$ ranging from 3.7 to 3.9 Å (listed in Table 1), where an arrow on each curve designates a value of q^{*2} giving $q^{*2}\langle R_{cs}^2 \rangle = 1$ and $q^2 \langle R_g^2 \rangle > 1$ is well satisfied. The reduced scattering curves thus obtained are shown in the form of a Kratky plot, i.e. $I_{\mathrm{thin}} q^2$ vs. q for PMA in acidic aqueous solution (pH = 2.3–2.8) and in methanol solution in Fig. 3A,B, respectively. In Fig. 3A, two data for PMA-I with $C\mathrm{p} = 1.0$ g/dl (○) and 2.1 g/dl (+) and two data for PMA-II with $C\mathrm{p} = 0.81$ g/dl (△) and 1.6 g/dl (×) are normalized by a ratio of their concentrations. The data points thus normalized are almost coincident over the whole q range and, therefore, it is concluded that the scattering curves for PMA in the acidic aqueous solution are substantially free from interparticle interferences and reflect the scattering behavior of a single polymer chain.

As is clearly shown in Fig. 3A, the data for PMA-I and -II in acidic aqueous solution are well fitted, at least, in a q range lower than approximately $0.08/\mathrm{Å}$ by the Debye function (solid curves) computed with $\langle R_g^2 \rangle^{1/2} = 36 \pm 3$ and 40 ± 3 Å, respectively. Moreover, $\langle R_g^2 \rangle^{1/2}$ thus obtained are in a satisfactory agreement with 35 ± 4 and 36 ± 4 Å, respectively, obtained from the Guinier plot of the scattering data (not shown). In a q range higher than approximately $0.08/\mathrm{Å}$, however, the data points gradually deviate upward from the Debye function in which a polymer chain is assumed to behave as a flexible chain over the whole q range, showing that the local chain conformation of PMA cannot be represented by a flexible chain.

The scattering behavior for a semifexible chain in a θ medium is described by the scattering function $P(q)$ for a wormlike chain without the excluded volume effect, which is given by Sharp and Bloomfield [14] as

$$P(q) = 2u^{-2}\{\exp(-u) - 1 + u\} + 4/(15L_r) + 7/(15L_r u) - \{11/(15L_r) + 7/(15L_r u)\} \times \exp(-u) \tag{4}$$

where u and L_r are given in terms of the contour length of a polymer chain L and the persistence length y as

$$u = Lyq^2/3 \tag{5}$$

$$L_r = L/(2y) \tag{6}$$

and Eq. (4) is valid under the conditions,

$$L_r > 10 \text{ and } (2y\ q)^2 < 10 \tag{7}$$

Since Eq. (4) is also developed for a chain having no cross-section, the comparison between the scattering data and Eq. (4) is carried out in the Kratky plot of $I_{\mathrm{thin}}q^2$ vs. q. As is shown in Fig. 4A, by trial-and-error, the data for PMA-I and -II in acidic aqueous solution (pH = 2.3–2.8) are well fitted, over a whole q range, by Eq. (4) (solid

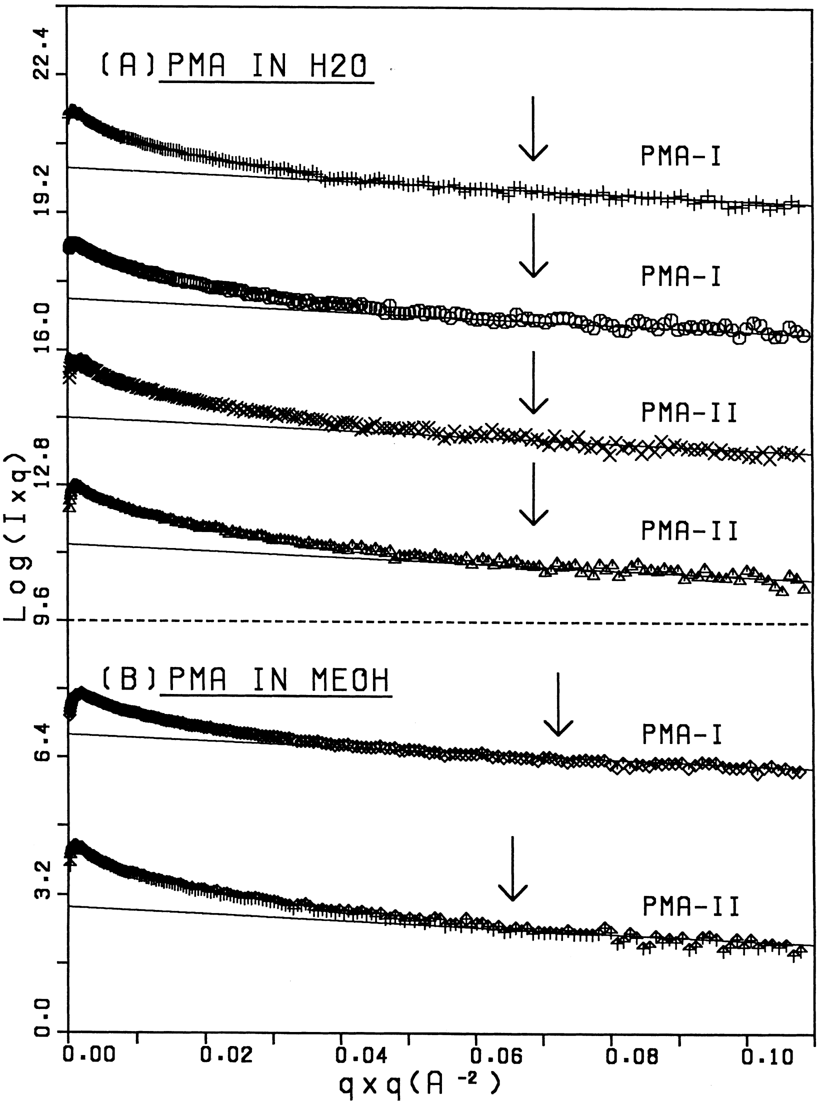

Fig. 2. Plot of $\ln(I_{\mathrm{obs}}q)$ vs. q^2 for (A) PMA-I at $C\mathrm{p} = 2.1$ g/dl (+) and 1.0 g/dl (○) and –II at $C\mathrm{p} = 1.6$ g/dl (×) and 0.81 g/dl (△) in salt-free acidic aqueous solution and (B) PMA-I at $C\mathrm{p} = 2.5$ g/dl (◇) and –II at $C\mathrm{p} = 1.1$ g/dl (↑) in methanol solution. An an arrow on each curve designates the value of q^{*2} giving $q^{*2}\ \langle R_{cs}^2\rangle = 1$, where $\langle R_{cs}^2\rangle$ is the mean-square radius of cross-section.

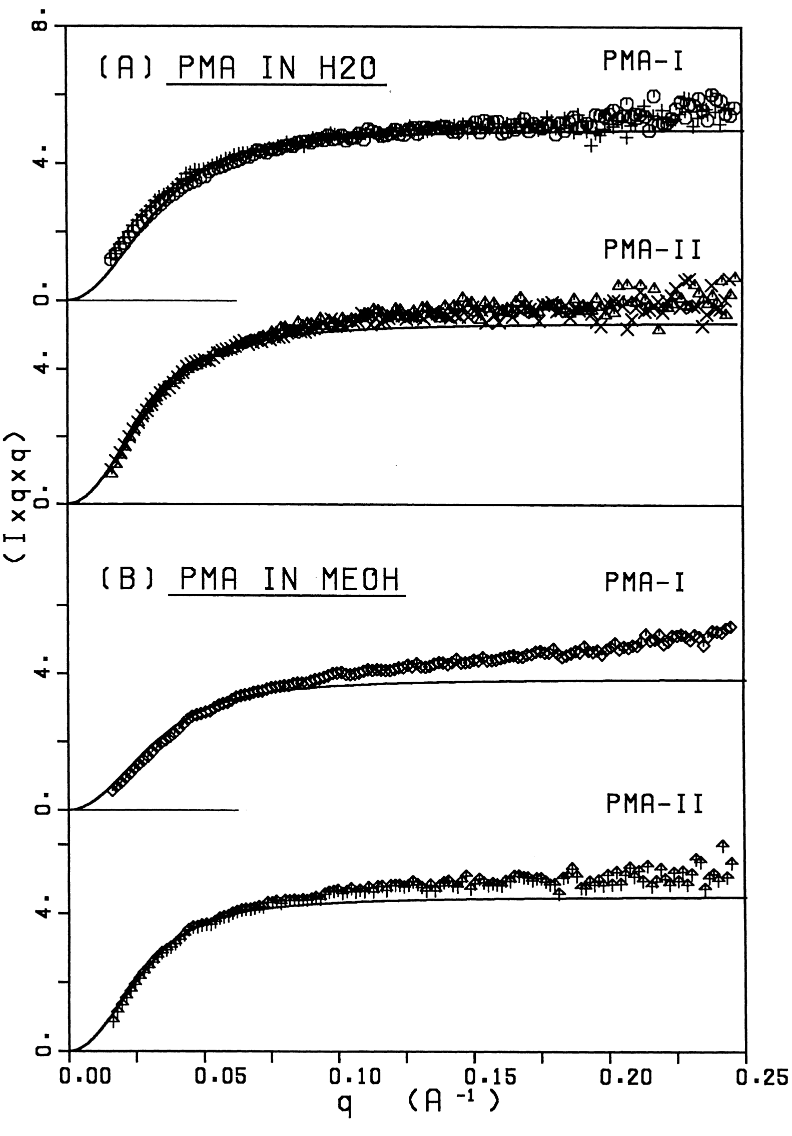

Fig. 3. Comparison between the Debye function and the data points for (A) PMA-I at $Cp = 2.1$ g/dl (+) and 1.0 g/dl (○) and −II at $Cp = 1.6$ g/dl (×) and 0.81 g/dl (△) in salt-free acidic aqueous solution and (B) PMA-I at $Cp = 2.5$ g/dl (◇) and −II at $Cp = 1.1$ g/dl (↑) in methanol solution. Solid curves for PMA-I and −II in salt-free acidic aqueous solution and PMA-I and −II in methanol solution are the Debye functions computed with $\langle R_g^2 \rangle^{1/2} = 36$, 40, 37, and 44 Å, respectively, where $\langle R_g^2 \rangle$ is the mean-square radius of gyration.

curves) computed with $y = 5 \pm 1$ Å and $L = 720$ Å and $y = 5 \pm 1$ Å and $L = 1090$ Å (listed in Table 2), respectively, where Eq. (7) is well satisfied. Since such a good fit between the data points and the theoretical curves is attained down to a sufficiently low $q \sim 0.02$/Å, the excluded volume effect is negligibe for these samples. The lengths of L thus evaluated are close to L corresponding to a trans-zigzag conformations, 780 and 1180 Å, respectively, but the lengths of y thus estimated are not sensitive to L employed, as long as L is in a range from 550 to 720 Å for PMA-I and from 830 to 1090 Å for PMA-II.

$\langle R_g^2 \rangle$ for a wormlike chain without an excluded

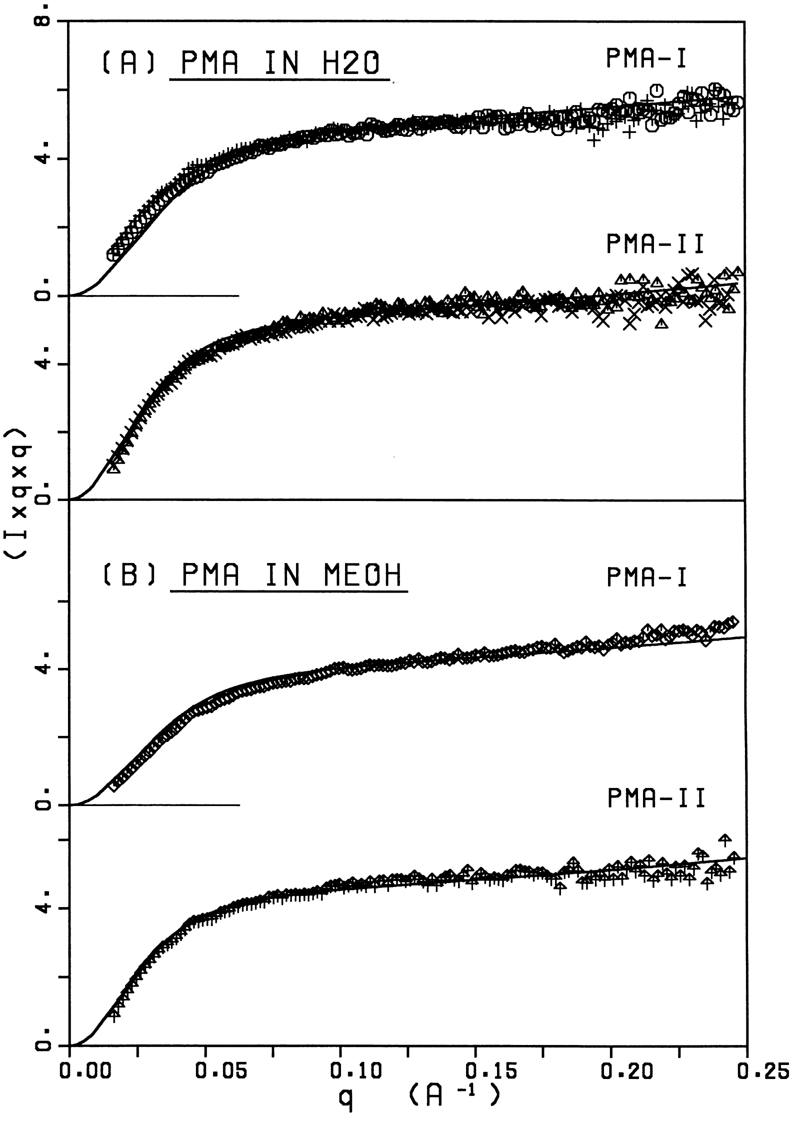

Fig. 4. Comparison between the the scattering function for a wormlike chain without an excluded volume effect and the data points for (A) PMA-I at $Cp = 2.1$ g/dl (+) and 1.0 g/dl (○) and −II at $Cp = 1.6$ g/dl (×) and 0.81 g/dl (△) in salt-free acidic aqueous solution and (B) PMA-I at $Cp = 2.5$ g/dl (◇) and −II at $Cp = 1.1$ g/dl (↑) in methanol solution. Solid curves for PMA-I and −II in salt-free acidic aqueous solution and PMA-I and -II in methanol solution are computed by Eq. (4) with the persistence length $y = 5.5$, 5.5, 6.0 and 6.0 Å, respectively, where $L = 720$ and 1090 Å are employed for PMA-I and −II, respectively.

volume effect is estimated by the relation [15]:

$$\langle R_g^2\rangle = (1/3)yL - y^2 + (2y^3/L) \times\{1-(y/L)(1-\exp(-L/y))\} \quad (8)$$

Substituting $y = 5 \pm 1$ Å and L ranging from 550 to 720 Å and $y = 5 \pm 1$ Å and L ranging from 830 to 1090 Å in Eq. (8), $\langle R_g^2\rangle^{1/2}$ is estimated to be 32 ± 3 and 39 ± 4 Å, respectively. These values of $\langle R_g^2\rangle^{1/2}$ also satisfactorily coincide with the observed ones for PMA-I and -II in acidic aqueous solution, 35 ± 4 and 36 ± 4 Å, respectively.

In Fig. 3B and Fig. 4B, the data for PMA in methanol solution are compared with the Debye function and also with Eq. (4). As a result, the scattering data for PMA-I and −II in a q range lower than approximately 0.075/Å are fitted by the Debye functions (solid curves) computed with $\langle R_g^2 \rangle^{1/2} = 37 \pm 3$ and 44 ± 3 Å, respectively, whereas the sacttering data over a whole q range are fitted with Eq. (4) (solid curves) computed with $y = 6 \pm 1$ Å and the same L as were employed above. Moreover, it is confirmed that $\langle R_g^2 \rangle^{1/2}$ employed in the Debye functions for PMA-I and −II, 37 ± 3 Å and 44 ± 3 Å, and those computed by Eq. (8), 35 ± 3 and 43 ± 3 Å, coincide well with the observed ones, 34 ± 4 and 42 ± 4 Å for PMA −I and -II, respectively.

From both analyses of the scattering curves and $\langle R_g^2 \rangle$, it is thus shown that the distribution of segments in the conformation of PMA in both acidic aqueous and in methanol solution is that of a random coil in a θ medium. This conclusion is predicted from Eqs. (1) and (2), respectively. The only difference between the two conformations is that y is slightly larger in methanol solution. This is consistent with evidence that the rms chain-end displacements are approximately 54% greater in the methanol solution [5].

In order to see how the addition of neutral-salt (NaF) and the presence of charges on the chain could affect the conformations of PMA in aqueous solution, the scattering behavior of unneutralized and partially neutralized PMA were studied with a 0.1 M added salt concentration (Cs). Taking into consideration that, in such a system, the charges may significantly interact not only intramolecularly but also intermolecularly, the scattering curves for these samples are compared with a scattering function $I(q)$ which includes contributions from both interactions. In general, $I(q)$ is given by the product of an interference factor between different particles $S(q)$ and a particle scattering factor for an isolated particle $P(q)$ as

$$I(q) \fallingdotseq S(q) \cdot P(q) \tag{9}$$

$S(q)$ is given by Kajiwara et al. [16] as

$$S(q) \fallingdotseq 1/(1 + K \cdot \exp(-\xi^2 q^2)) \tag{10}$$

wherein K is a constant approximately given by $2A_2 \mathrm{M_w} C\mathrm{p}$, A_2 is the second virial coefficient and ξ denotes the correlation length of the interaction, representing a range of interaction.

Utilizing $C\mathrm{p}^*$ of PMA in acidic aqueous solution, 9.3 and 7.5 g/dl for PMA-I and -II, respectively, and the extant data of [η] for PMA in 0.1 M NaBr aqueous solution [3], $C\mathrm{p}^*$ of charged PMA-II in added-salt aqueous solution ($Cs = 0.1$ M) is estimated to be 7.5, 3.2 and 1.2 g/dl at

Table 2
Molecular parameters obtained from analysis of scattering curves

Sample	Solvent	α	$M_w \times 10^{-4}$	Cp (g/dl)	y (Å)	ε
PMA-I	H_2O	~ 0[a]	2.68	2.1	5 ± 1	0
PMA-I	H_2O	~ 0[a]	2.68	1.0	5 ± 1	0
PMA-II	H_2O	~ 0[a]	4.06	1.6	5 ± 1	0
PMA-II	H_2O	~ 0[a]	4.06	0.81	5 ± 1	0
PMA-I	CH_3OH	~ 0[a]	2.68	2.5	6 ± 1	0
PMA-II	CH_3OH	~ 0[a]	4.06	1.1	6 ± 1	0
PMA-I	0.1M NaF(aq.)	~ 0[a]	2.68	0.43	4 ± 0.5	0
PMA-II	0.1M NaF(aq.)	~ 0[a]	4.06	1.3	4 ± 0.5	0
PMA-II	0.1M NaF(aq.)	~ 0[a]	4.06	0.39	4 ± 0.5	0
PMA-II	0.1M NaF(aq.)	0.15	4.06	1.8	4 ± 0.5	0
PMA-II	0.1M NaF(aq.)	0.15	4.06	0.89	4 ± 0.5	0
PMA-II	0.1M NaF(aq.)	0.30	4.06	2.2	4 ± 0.5	0.06
PMA-II	0.1M NaF(aq.)	0.30	4.06	1.1	4 ± 0.5	0.06
PMA-II	0.1M NaF(aq.)	1.00	4.06	2.3	4 ± 0.5	0.08
PMA-II	0.1M NaF(aq.)	1.00	4.06	1.1	4 ± 0.5	0.08

[a] ~ 0, degree of neutralization = 0 and α ≤ 0.02.

$\alpha = 0.15$, 0.30 and 1.0, respectively. Since Cp employed in the SAXS experiment in Fig. 6, 0.89, 1.1 and 1.1 g/dl at $\alpha = 0.15$, 0.30 and 1.0, respectively, are lower than the corresponding Cp*, 7.5, 3.2 and 1.2 g/dl, respectively, it is expected that PMA should behave as an isolated chain, at least, under the experimental conditions in Fig. 6. Thus, the use of the scattering function of an isolated particle as $P(q)$ could be justified.

Previous light scattering studies [17,18] show that the scattering behavior of a polyelectrolyte chain in the non-θ state is interpreted by the theory taking into accout the excluded volume effect rather than by the theory for the wormlike

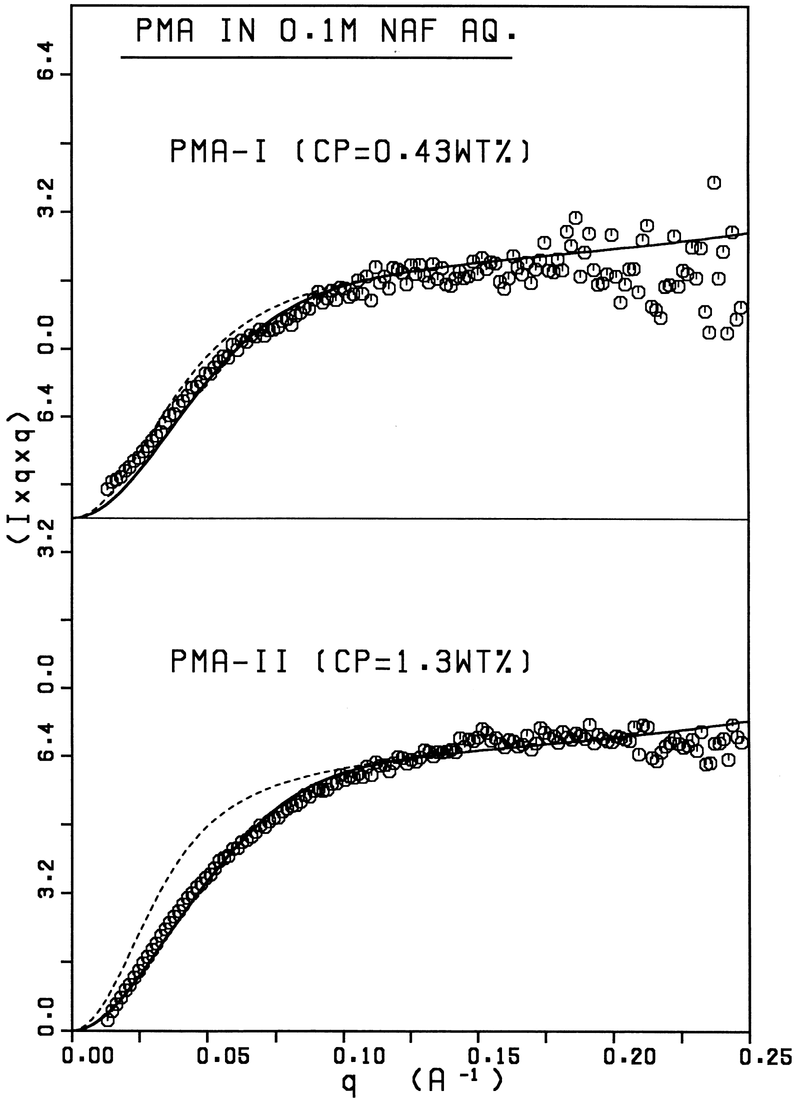

Fig. 5. Comparison between the the scattering function for a wormlike chain without an excluded volume effect and the data points for PMA-I at Cp = 0.43 g/dl and −II at Cp = 1.3 g/dl in 0.1 M NaF acidic aqueous solution. Solid and dotted curves are computed by Eq. (4) with and without interparticle interferences, respectively. The molecular parameters employed in the computation are listed in Table 2. The contour lengths $L = 720$ and 1090 Å are employed for PMA-I and -II, respectively.

chain. However, one cannot exclude the possibility that an excluded volume effect and the chain flexibility may simultaneously change with α or *Cs*. Taking into account this possibility, the scattering function for a wormlike chain with an excluded volume effect is adopted as $P(q)$ in the present study, which was given by Sharp and Bloomfield [14] in terms of L_r, y and the excluded volume parameter ε. It is assumed that, if there is any effect of Cp on $P(q)$, the effect would be reflected in L_r, y and ε.

The scattering data for PMA-I and -II having $\alpha = 0$, and for PMA-II having $\alpha = 0.15$, 0.30 and 1.0 at lower and higher Cp are compared with Eq. (4) or Eq. (9) in Figs. 5–7, respectively, where $\langle R_{cs}^2 \rangle^{1/2}$ employed are listed in Table 1. The best

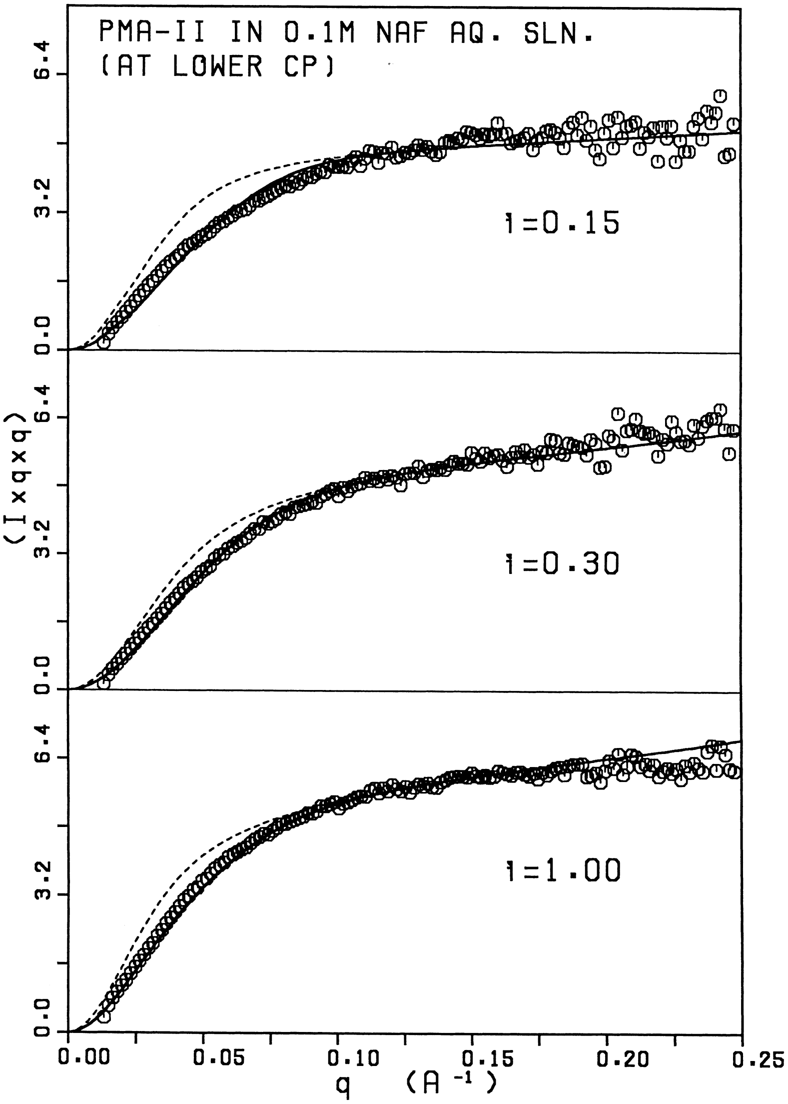

Fig. 6. Comparison between the data points for PMA-II having $\alpha = 0.15$ and $Cp = 0.89$ g/dl (top), $\alpha = 0.30$ and $Cp = 1.1$ g/dl (middle), and $\alpha = 1.0$ and $Cp = 1.1$ g/dl (bottom) in 0.1 M NaF aqueous solution and the scattering function for the wormlike chain with an excluded volume effect. Solid and dotted curves are computed by Eq. (9) with and without interparticle interferences, respectively. The molecular parameters employed in the computation are listed in Table 2. The contour lengths $L = 1090$ Å.

fit between them is attained with ε and y listed in Table 2 and A_2 in a reasonable range of 0.67×10^{-3}–2.2×10^{-3} (mol·ml/g^2) and ξ of 18 ± 2 Å. Solid and dotted curves in the figures are the theoretical ones computed by Eq. (4) or Eq. (9) with and without intermolecular interactions, i.e. with $S(q) \neq 1$ and $= 1$, respectively.

The scattering behavior in the figures and the results in Table 2 leads to the following important conclusions: scattering curves of PMA in an aqueous solution containing added salt ($Cs = 0.1$ M) having α ranging from 0 to 0.15 are also fitted by Eq. (4) without the excluded volume effect, although the persistence length for PMA in aque-

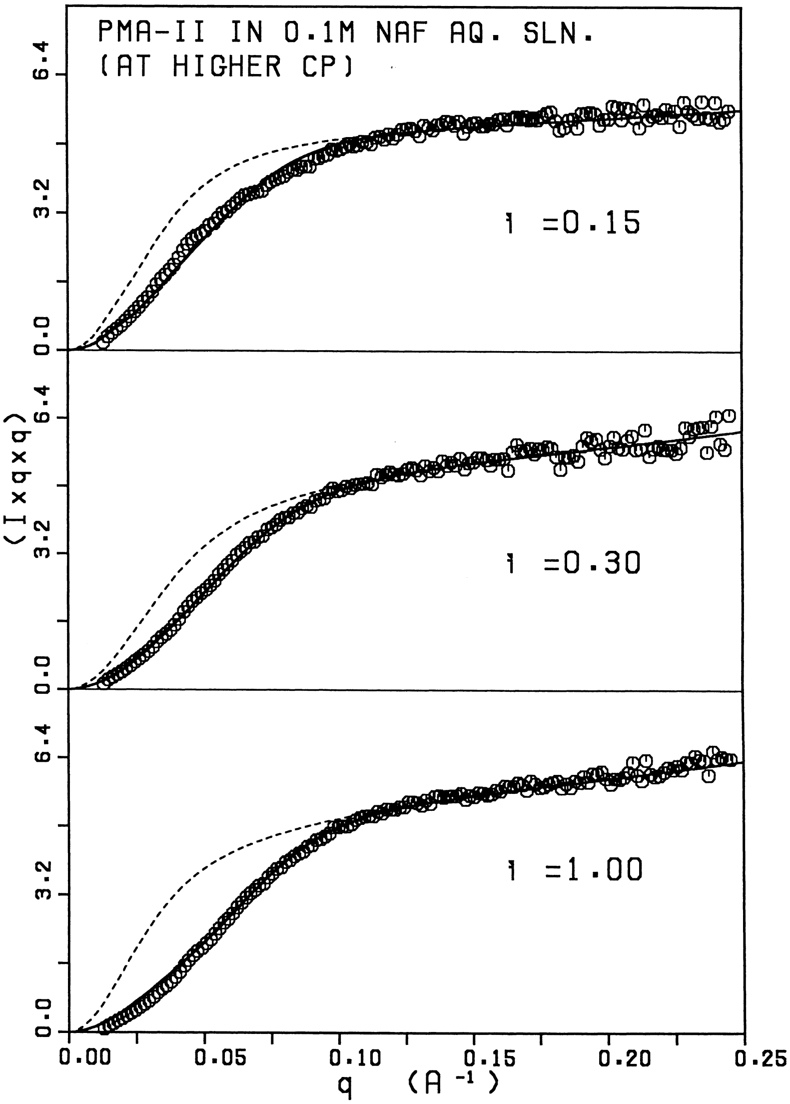

Fig. 7. Comparison between the data points for PMA-II having $\alpha = 0.15$ and $Cp = 1.8$ g/dl (top), $\alpha = 0.30$ and $Cp = 2.2$ g/dl (middle), and $\alpha = 1.0$ and $Cp = 2.3$ g/dl (bottom) in 0.1 M NaF aqueous solution and the scattering function of the wormlike chain with an excluded volume effect. Solid and dotted curves are computed by Eq. (9) with and without interparticle interferences, respectively. The molecular parameters employed in the computation are listed in Table 2. The contour lengths $L = 720$ Å.

ous solution containing added salt (4 ± 0.5 Å) is somewhat smaller than for PMA in salt-free acidic aqueous solution (5 ± 1 Å). Combining this result with the foregoing discussion, it has been shown that the distribution of segments in the conformation of PMA in acidic aqueous solution is that of a random coil in a θ medium, as long as *Cs* is lower than 0.1 M, and that the distribution of segments is constant over a fair range of α, until the electrostatic repulsive force between charged groups exceeds non-electrostatic force such as the hydrophobic attractive force between methyl groups or hydrogen-bonding between carboxylate groups. Taking into account that intramolecular hydrogen bonding or hydrophobic interaction must be responsible for the distribution of segments of PMA in acidic aqueous solution, however, it is clear that the conformational state would be far from a so called θ state, where neither intramolecular nor intermolecular interactions are allowed.

Scattering curves for PMA at $Cs = 0.1$ M (Figs. 5–7) are well described by Eq. (4) or Eq. (9) with a fixed persistence length of 4 ± 0.5 Å throughout the entire range of α, although it is necessary to take in a contribution from $S(q)$ which tends to be gradually accentuated with increasing α or Cp. Thus, it is shown that the contracted form of PMA changes to an expanded random coil in the higher pH region without a significant change in the chain flexibility, that is, predominantly by the excluded volume effect. The result that the expansion of random-coiled PMA chain in an aqueous solution occurs predominantly by the excluded volume effect is consistent with the results obtained for poly(acrylic acid) in our previous studies [19,20].

As was well reviewed by Nagasawa [9] and Dautzenberg et al. [21], the conformation of polyelectrolyte is, in general, decided by two factors of excluded volume effect and chain flexibility. These factors play quite different roles in molecular weight dependence of the chain conformation: as the molecular weight of polymer is raised, the chain conformation expanded by excluded volume effect deviates from Gaussian chain, whereas the chain conformation expanded with chain flexibility in wormlike chain approaches Gaussian chain. In our previous studies, it was shown that the conformations of poly(acrylic acid) having sufficiently large molecular weight (1.5×10^6) at various degrees of neutralization in added salt aqueous solution can be interpreted by the theory taking into account the excluded volume effect and no change in the chain flexibility was necessary [18]. Moreover, such a negligible effect of charge on the chain flexibility of poly(acrylic acid) has been directly confirmed from the experimental results obtained by proton NMR spectroscopy [19] and SAXS [20]. The present comparison between the theory of Sharp and Bloomfield and the experimental data also shows that the persistence length of polyelectrolyte chain, which reflects the chain flexibility, is found to be independent of the charge density and *Cs* and that the remarkable change of the expansion is caused by the excluded volume effect.

If the conformation of polyelectrolyte is described by a semiflexible chain, neglecting the excluded volume effect, the apparent persistence length may become a function of charge density and *Cs*, as was discussed by Odijk [22] and Skolnick and Fixman [23]. This model may be a good approximation for some purposes, particularly if the contribution of chain flexibility to the chain expansion is dominant. In fact, *Cs* dependences of the conformations for low molecular weight DNA [24] and for low molecular weight poly(styrene sulfonic-acid) [25] were well elucidated with the theory based on a wormlike chain and no excluded volume effects were necessary. (Other related experimental results, to which such explanations were given, are found in reference [21]) However, we would like to stress here that, in more general, the expansion of polyelectrolyte chain should be discussed in separate terms of excluded volume effect and chain flexibility (persistence length).

Acknowledgements

The authors are indebted to Prof. Morawetz of Polytechnic University for his interest and advice in this work. We are also indebted to Prof. Nagasawa especially for the discussion on the roles of

excluded volume effect and chain flexibility in the expansion of polyelectrolyte chain.

References

[1] J.C. Leyte, M. Mandel, J. Polym. Sci. Part A-1 2 (1964) 1879.
[2] V. Crescenzi, F. Quadrifoglio, F. Delben, J. Polym. Sci. Part A-2 10 (1972) 357.
[3] I. Noda, T. Tsuge, M. Nagasawa, J. Phys. Chem. 74 (1970) 710.
[4] A. Katchalsky, H. Eisenberg, J. Polym. Sci. 6 (1951) 145.
[5] H. Morawetz, Macromolecules 29 (1996) 2689.
[6] J.N. Davenport, P.V. Wright, Polymer 21 (1980) 293.
[7] C. Heitz, M. Rawiso, J. Francois, Polymer 40 (1999) 1637.
[8] N.M. Wiederhorn, A.R. Brown, J. Polym. Sci. 8 (1952) 651.
[9] M. Nagasawa, in: M. Nagasawa (Ed.), Molecular Conformation and Dynamics of Macromolecules in Condensed Systems, Elsevier, Amsterdam, 1988, p. 49.
[10] S. Kawaguchi, T. Takahashi, H. Tajima, Y. Hirose, K. Ito, Polym. J. 28 (1996) 735.
[11] T. Ueki, Y. Hiragi, Y. Izumi, et al., Photon Factory Activity Rep VI70–VI71 (1982/1983).
[12] G. Porod, in: O. Glatter, O. Kratky (Eds.), Small Angle X-ray Scattering, Academic Press, New York, 1982, p. 32.
[13] Y. Muroga, T. Muraki, I. Noda, H. Tagawa, A. Holtzer, M.E. Holtzer, J. Am. Chem. Soc. 117 (1995) 5622.
[14] P. Sharp, V.A. Bloomfield, Biopolymers 6 (1968) 1201, with a correction in C.W. Schmid, F.P. Rinehart, J.E. Hearst, Biopolymers 10 (1971) 833
[15] H. Benoit, P. Doty, J. Phys. Chem. 57 (1953) 958.
[16] T. Coviello, H. Maeda, Y. Yuguchi et al., Macromolecules 31 (1998) 1602.
[17] T. Kitano, A. Taguchi, I. Noda, M. Nagasawa, Macromolecules 13 (1980) 57.
[18] M. Nagasawa, I. Noda, T. Kitano, Biophys. Chem. 11 (1980) 435.
[19] Y. Muroga, I. Noda, M. Nagasawa, J. Phys. Chem. 73 (1969) 667.
[20] Y. Muroga, I. Noda, M. Nagasawa, Macromolecules 18 (1985) 1576.
[21] H. Dautzenberg, W. Jaeger, J. Kotz, B. Philipp, Ch. Seidel, D. Stscherbina, Polyelectrolytes; Formation, Characterization and Application, chapter 5, Hanser/Gardner Publications, Inc, Cincinnati, 1994.
[22] T. Odijk, J. Polym. Sci. 15 (1977) 477.
[23] J. Skolnick, M. Fixman, Macromolecules 10 (1977) 944.
[24] M. Mandel, J. Schouten, Macromolecules 13 (1980) 1247.
[25] M. Ragnetti, R. Oberthuer, Colloid Polym. Sci. 264 (1986) 32.