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Added Salt Effect on the Intermolecular Correlation in Flexible Polyelectrolyte Solutions: Small-Angle Scattering Study

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ABSTRACT: The intermolecular correlation due to electrostatic repulsion in flexible polyelectrolyte solutions as a function of ionic strength has been studied using small-angle neutron and X-ray scattering (SAXS and SANS) techniques. The ionic strength was changed by adding low molecular weight salts at a fixed polyion concentration ($C = 0.25$ mol/L). To solve the controversy about the added salt effect on the characteristic maximum in small-angle scattering of polyelectrolyte solutions, separation of the total scattering function into the intra- and intermolecular parts has been performed. With increasing the ionic strength of the solution the maximum position q_m in the total scattering function of SAXS and SANS slightly shifts toward the lower scattering vector and subsequently disappears, whereas the maximum position q_m^0 in the intermolecular scattering function slightly shifts to the higher scattering vector, but the peak itself does not disappear even for the highest ionic strength of the present study though it becomes weaker. The intramolecular scattering function is enhanced in the lower scattering vector ($q < q_m^0$) when the ionic strength increases. Thus, it turned out that the apparent shift of the maximum in the total scattering function is caused by the combination of the intra- and intermolecular scattering functions.

Introduction

In the past two decades, a lot of scattering studies on the structure of polyelectrolyte solutions of charged spheres, charged rodlike molecules, and charged flexible chains have been made using static light scattering (SLS),[1−10] small-angle X-ray scattering (SAXS),[11−17] and small-angle neutron scattering (SANS)[5,8,18−25] techniques. Most of the scattering curves for salt-free polyelectrolyte solutions show a characteristic maximum, and the maximum position q_m depends on the polyelectrolyte concentration C. Here q is the length of scattering vector: $q = (4\pi \sin \theta)/\lambda$, 2θ and λ being the scattering angle and the radiation wavelength, respectively. Especially, the relationships between q_m and C have extensively been studied.[1−8,11,13−17,19−21,23−24] All the above three types of polyelectrolyte solutions show very similar concentration dependence of q_m; in the dilute region[2,5,6,11,13] q_m is proportional to $C^{1/3}$ while in the semidilute region[1,3,5,7,8,13−17,19,20,23,24] q_m is proportional to $C^{1/2}$ though there is naturally no semidilute region in the case of the charged spheres.[21] The $q_m \sim C^{1/3}$ relationship in the dilute region can be easily understood as the correlation among centers of polyions, while the $q_m \sim C^{1/2}$ relationship in the semidilute region is assigned to the nearest-neighbor intersegmental correlation. The latter relationship is one of the evidences supporting the isotropic model proposed by de Gennes et al.,[26] which we believe the most reliable model.

On the other hand, the understanding in the added salt effect on the scattering maximum of polyelectrolyte solutions is still considerably insufficient. As was reviewed by Föster and Schmidt,[27] contradicting results have been reported, particularly for the q_m dependence on added salt concentration; some people reported that q_m was not affected[4,10,19] by the addition of salt while other people reported that q_m shifted toward smaller q.[11,14,16] Anyhow, the behavior of q_m in the total scattering function $I(q)$ seems to be somewhat apparent because q_m is easily affected by a small change of the intramolecular scattering function (form factor). Another unsolved problem in the added salt effect of polyelectrolytes is the observation of the so-called "isosbestic point"[4] or "still point",[9] at which all the $I(q)$ curves converge at one point independent of added salt concentration. This behavior is almost universally observed for charged spheres,[21] charged rodlike molecules,[5,10] charged flexible chains,[19] and even for dendric polyelectrolytes.[28,29]

These problems have been discussed usually using $I(q)$; however, analysis of $I(q)$ alone is insufficient and sometimes gives misunderstanding especially for the structure of salt-added polyelectrolyte solutions. Therefore, it is desirable to separate the total scattering function $I(q)$ into the intra- and intermolecular scattering functions because the separated functions are much easier to understand in physical meaning. A beautiful separation method of the intra- and intermolecular scattering functions has been developed by de Gennes and co-workers.[18] The essentials of the method as well as their physical meaning were explained by de Cloizeau and Jannink[30] to help the understanding of experimental results. This isotopic labeling method in SANS was successful[18,20,22] to some extent for the study of polyelectrolyte solutions. However, there remains a physically unreasonable point for the behavior of intermolecular scattering function; namely, it did not show positive values in any q region. Utilizing and improving this method, we will show how the intersegmental correlation peak actually behaves depending on added salt, and we will also present a qualitative explanation for the "still point".

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Correction for Incoherent Scattering

In the practical procedures to make the separation between the intra- and intermolecular scattering functions, the data analysis should be carried out as precisely as possible; otherwise, the separated structure functions would be physically unreasonable. Another purpose of this study is therefore to show that the exact estimation of incoherent background scattering is very important and to indicate how to subtract it. Conventionally, we assume that the fluctuation of the scattering length density within a monomer size is negligible in the SANS q region, and hydrogenated and deuterated polyions are not different in physical properties but only in scattering length density. When the average scattering length density of the solvent (mixture of hydrogenated and deuterated water in the present study) is equal to that of the hydrogenated polyion, the hydrogenated polyions do not produce effective coherent scattering; in other words, they are optically invisible. This, however, does not mean that incoherent scattering is simultaneously extinguished. Thus, the experimental scattering intensity from the solution, which includes the incoherent scattering of the mixture of deuterated and hydrogenated polyions, is given by

$$I_{\mathrm{exp}}(q,x) = xS_1(q) + x^2S_2(q) + xI_{\mathrm{inc,D}} + (1 - x)I_{\mathrm{inc,H}} + I_{\mathrm{solvent}} \quad (1)$$

where x is the fraction of the deuterated polyions in the whole polyions, $S_1(q)$ and $S_2(q)$ are the intra- and intermolecular scattering functions, and $I_{\mathrm{inc,D}}$ and $I_{\mathrm{inc,H}}$ are the incoherent scattering from the deuterated and hydrogenated polyions, respectively. I_{solvent} includes both the coherent and incoherent scattering of the solvent which was corrected for its volume fraction in the whole solution. $I_{\mathrm{inc,H}}$ can be experimentally estimated as the difference between $I_{\mathrm{exp}}(q,0)$ and I_{solvent}. $I_{\mathrm{inc,D}}$ is calculated to be 1/35 times $I_{\mathrm{inc,H}}$ from the incoherent scattering cross sections of the elements in deuterated and hydrogenated NaPSS. After removing the last three terms in eq 1, the net coherent scattering intensity for the mixture of the deuterated polyions and the hydrogenated polyions is obtained. Thus, the incoherent-free total scattering function $I(q,x)$ for the mixed solution of hydrogenated and deuterated polymers is obtained.

$$I(q,x) = xS_1(q) + x^2S_2(q) \quad (2)$$

Then, $I(q,x)/x$ is plotted against x at a given $q = q_1$; the intersection at $x = 0$ of this extrapolated line gives $S_1(q_1)$, and the slope gives $S_2(q_1)$. Such plots for various q's produce separated $S_1(q)$ and $S_2(q)$ functions. Substituting $x = 1$, eq 2 yields the total scattering function $I(q)$ for the unlabeled system.

Experimental Section

Materials. Both deuterated and hydrogenated sodium polystyrenesulfonates (NaPSS) were prepared from deuterated and hydrogenated polystyrenes (PS) by a previously reported method.[31] Weight-averaged molecular weight M_w and its distribution M_w/M_n of the parent PS were 72 000 and 1.03 for deuterated PS and 66 000 and 1.03 for hydrogenated PS, respectively. These PS's have nearly the same degree of polymerization $N \approx 640$ and hence almost the same chain contour length $L \approx 1600$ Å as the monomer length a_0 is 2.5 Å. The degree of sulfonation α was more than 0.99. The solvent mixture of deuterated and hydrogenated water was prepared so that the isotopic ratio would be D/H = 0.485/0.515, i.e., the scattering length density of the solvent would be equal to that of hydrogenated PSS. In this preparation the natural abundance of D atom in hydrogenated water and the isotopic purity in deuterated water were taken into account.

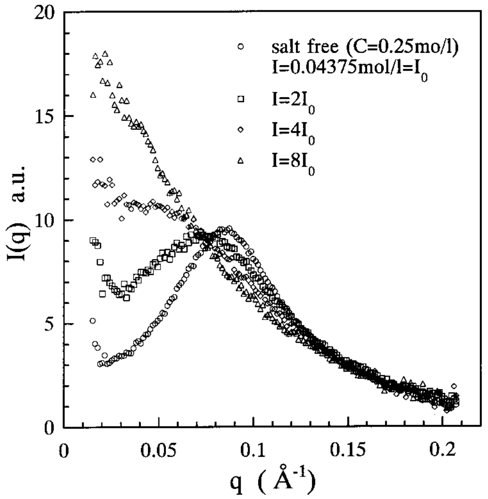

Figure 1. Ionic strength variation of the total SAXS function $I(q)$ vs q at fixed NaPSS concentration ($C = 0.25$ mol/L).

Analytical grade of sodium chloride (NaCl) was used as the added salt. The amount of added salt for a given ionic strength was calculated assuming the condensation theory of Oosawa[32,33]−Manning[34] as follows:

$$I = (0.35/2)C + C_s \quad (3)$$

where I, C, and C_s are ionic strength of the solution, monomer concentration of vinyl-type polyelectrolytes, and added salt concentration, respectively. When $C = 0.25$ mol/L and $C_s = 0$, then $I = (0.35/2) \times 0.25 = 0.043\,75$ mol/L, and here this value is designated as I_0.

SANS and SAXS Measurements. The SANS intensity measurements were carried out at 25 °C using the Small-Angle Neutron Scattering Instrument, University of Tokyo (SANS-U), installed at the exit of a cold neutron guide tube of JRR-3M, a 20 MW reactor with liquid hydrogen cold source. In this study, the sample-to-detector distance and the neutron wavelength were chosen to be 2 m and 7 Å, respectively. The scattering intensity from the solution sample was circularly averaged and corrected for the apparatus constants and then subjected to further analysis. The intensity data were obtained for a q range of ca. 0.015−0.17 Å^{-1}.

Supplementary measurements covering a wider ionic strength range were perform using a 6 m point-focusing SAXS camera[35] at the High-Intensity X-ray Laboratory of Kyoto University.

Results and Discussion

In advance of the detailed analysis of SANS results, a general survey of the added salt effect on the total SAXS function $I(q)$ vs q has been made. Figure 1 shows the results; the added salt concentrations are adjusted so as to yield 1, 2, 4, and 8 times as large as the ionic strength of salt-free NaPSS solution at $C = 0.25$ mol/L. In this figure q_m is observed to shift toward smaller q with increasing the ionic strength, agreeing with some literature[11,14,16] but contradicting other literature.[4,10,19] At around $q = 0.075$ Å^{-1}, all the $I(q)$ curves converge at one point independent of the ionic strength. This behavior is commonly observed for different polyelectrolyte systems; however, no theoretical explanation has been presented so far.[10] After the following analysis, these problems will be understood fairly well.

Figure 2 shows the SANS intensity curves from solutions of the mixture of the deuterated and hydro-

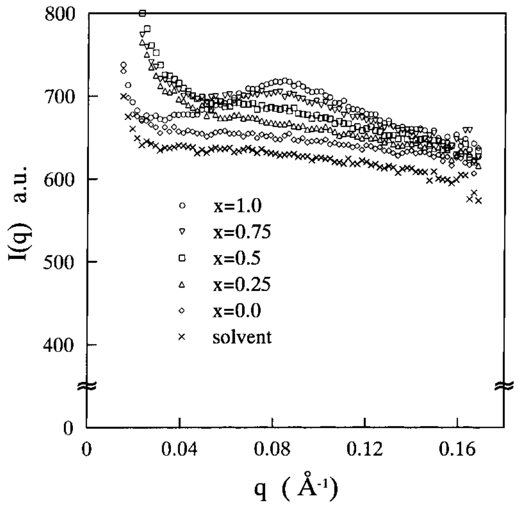

Figure 2. SANS intensity curves for the mixture of deuterated and hydrogenated NaPSS solution at fixed NaPSS concentration ($C = 0.25$ mol/L) and fixed ionic strength ($I = I_0 = 0.043\,75$ mol/L) and also for the pure solvent. x is the proportion of the deuterated polymer to the whole polymer. The solvent intensity is reduced by the specific volume of the pure solvent in the solution.

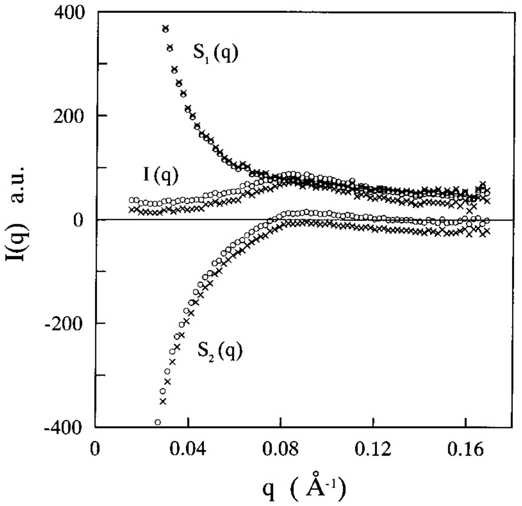

Figure 3. Incoherent-corrected and uncorrected scattering functions. Corrected and uncorrected are indicated by (○) and (×), respectively.

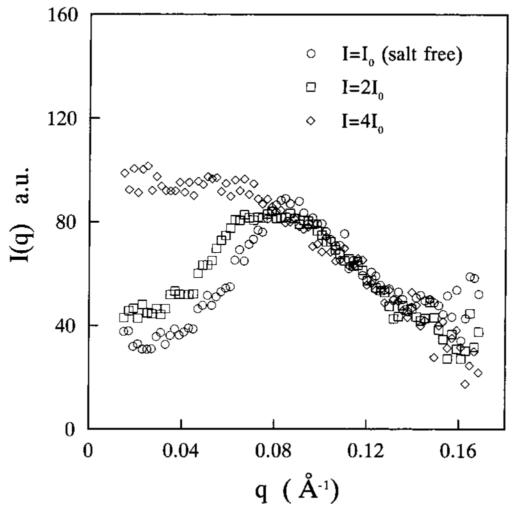

Figure 4. Ionic strength variation of the total SANS function $I(q)$ vs q at fixed NaPSS concentration ($C = 0.25$ mol/L).

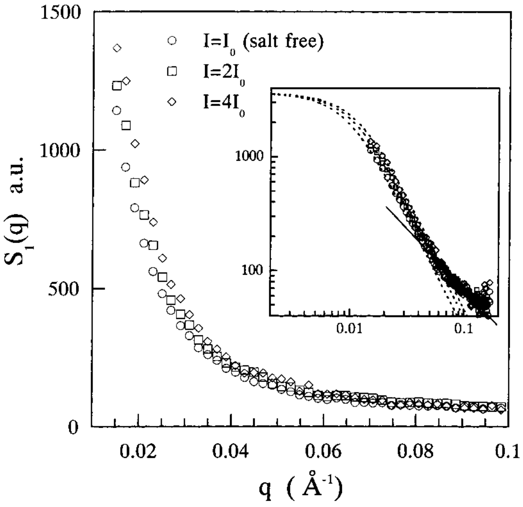

Figure 5. Ionic strength variation of $S_1(q)$. The insertion is shown in the logarithmic scales.

genated polyions as well as that of pure solvent as a function of the fraction x of the deuterated NaPSS. The scattering profile at $x = 0$ is very similar to that of the pure solvent, but it shows a certain amount of white excess intensity which is attributable to $I_{\text{inc,H}}$. Such excess intensity due to $I_{\text{inc,H}}$ as well as I_{solvent} was subtracted according to eq 1. Then, $S_1(q)$ and $S_2(q)$ were obtained following the prescribed method.[18] Figure 3 shows an example of the comparison of incoherent-corrected $S_1(q)$ and $S_2(q)$ as well as uncorrected $S_1(q)$ and $S_2(q)$. As this correction hardly affects the profile of $S_1(q)$, either $S_1(q)$ may be used when the intensity is not discussed. Similarly, the maximum positions in both corrected and uncorrected $S_2(q)$ do not differ, so that the average of intersegmental distance is not affected even if either $S_2(q)$ is used. However, the intensity is different between both cases; especially, the corrected $S_2(q)$ damp-oscillates around the axis $I(q) = 0$ as q increases, while the uncorrected $S_2(q)$ is always in the negative region. Considering that the zero intensity corresponds to the average density of the system, the former is physically more reasonable; $S_2(q)$ should oscillate with damping about the $I(q) = 0$ axis. Therefore, the incoherent-corrected scattering functions will be used in the following results and discussion.

Figure 4 shows the added salt effect on the total SANS function $I(q)$ vs q obtained by the method described above, which is very similar to the SAXS case as seen in Figure 1. The added salt concentrations are adjusted so as to yield 1, 2, and 4 times as high as the ionic strength of salt-free NaPSS solution at $C = 0.25$ mol/L. A broad but distinct maximum is observed for $I = I_0$ (salt free) and $I = 2I_0$. The q value corresponding to the intensity maximum q_m slightly shifts toward a lower q value for higher ionic strength. For the highest ionic strength $4I_0$, the maximum disappears and only a shoulder is observed. One estimates that the intersegmental distances from these data, which we designate as ξ, would become longer with increasing the ionic strength and finally unobservable. However, such an analysis would be incorrect since the apparent shift of q_m is caused by deformation of $S_1(q)$ rather than $S_2(q)$ as will be shown later. As seen from Figure 5, $S_1(q)$ increases in intensity with increasing ionic strength especially in the lower q region. This is a reasonable result because the total persistence length b_t and the radius of gyration R_g of the polyion decrease with

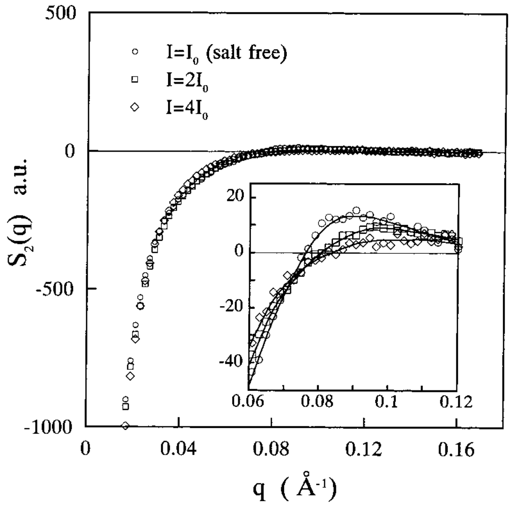

Figure 6. Ionic strength variation of $S_2(q)$. The insertion is an enlargement of the vicinity of the maximum.

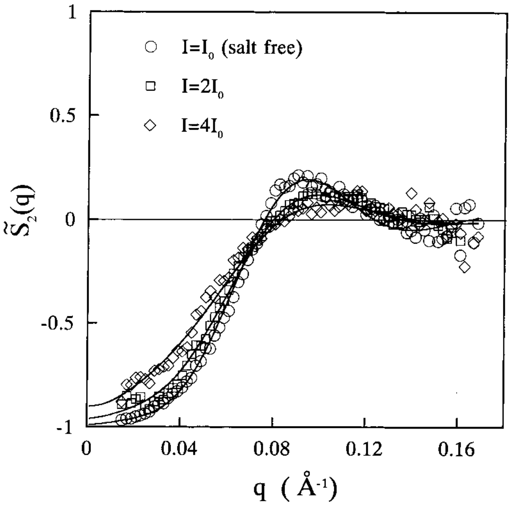

Figure 7. Ionic strength variation of $\tilde{S}_2(q)$. Indicated solid lines are used for the Fourier transform analysis.

increasing ionic strength, resulting in the increase of intensity in Debye's q region.[31] The increase of $S_1(q)$ at lower q's consequently gives rise to shifting the q_m of $I(q)$ toward smaller q and finally covers the characteristic peak. At around $q = 0.075$ Å^{-1}, where the "still point" is observed in $I(q)$, all the $S_1(q)$ behave identically independent of the ionic strength. Therefore, the origin of the "still point" is not due to the intramolecular reason.

The added salt effect on the real intermolecular structure must lie in the intermolecular scattering function $S_2(q)$. As is seen from Figure 6, the outline of the intermolecular scattering function appears to be little affected by the presence of added salt. However, if we go into detail, there is a maximum in $S_2(q)$ of every ionic strength as is seen in the enlargement shown in the insertion of Figure 6. This is of course due to the local structure of polyelectrolyte solutions which we want to know. The position of the maximum in $S_2(q)$ moves to higher q with increasing ionic strength contrary to that of $I(q)$. To obtain the local structure more clearly, the great effect of $S_1(q)$ should be removed, which may be roughly performed through dividing $S_2(q)$ by $S_1(q)$.[36] We designate this reduced function as

$$\tilde{S}_2(q) = S_2(q)/S_1(q) \tag{4}$$

Figure 7 shows such results; the peak positions of $\tilde{S}_2(q)$ are virtually identical to those of $S_2(q)$ in Figure 6, but the local correlation peaks become more conspicuous. The apparent peak position q_m of the total scattering function $I(q)$ shifts toward lower q with increasing ionic strength of the solution as seen from Figure 4, whereas the peak position q_m^0 of the reduced intermolecular scattering function $\tilde{S}_2(q)$ reversely moves to higher q with increasing ionic strength. It should be also noted that even for the highest ionic strength where the total scattering function $I(q)$ does not show a clear peak, a characteristic peak is still seen in $\tilde{S}_2(q)$ though it is weak and broad. With all the above reason, $S_2(q)$ or $\tilde{S}_2(q)$ should be used when the local structure of the salt-added polyelectrolyte solutions is discussed.

The "still point" is observed in both $\tilde{S}_2(q)$ and $S_2(q)$ at around $q = 0.075$ Å^{-1}. Therefore, the origin must be due to intermolecular reason. A possible explanation is as follows: addition of salt screens electrostatic repulsive force, consequently increasing the compressibility and the fluctuations of intersegmental distance. The increase of the compressibility raises the intensity in low-q region, and the fluctuation reduces the intensity at the intersegmental correlation peak. Thus, an intersection point must appear somewhere in between $q = 0$ and the intersegmental correlation peak for two solution systems with different values of ionic strength. Among more than three solution systems with different ionic strengths such an intersection may happen to appear at the almost same q values as the "still point". A recent theoretical calculation[37] of $I(q)$ for charged rodlike particles certainly shows such a point, mentioning nothing particular in regard to the reason.

Fourier Transform Analysis of $\tilde{S}_2(q)$ and $S_2(q)$. Intermolecular distances will be discussed by means of the Fourier transform of $\tilde{S}_2(q)$ and $S_2(q)$. The Fourier transforms of $\tilde{S}_2(q)$ and $S_2(q)$, denoted by $\tilde{g}(r)$ and $g(r)$, are given by

$$\tilde{g}(r) = 1 + (2\pi^2 r\rho_0)^{-1}\int_0^\infty q\, \tilde{S}_2(q) \sin(qr)\, \mathrm{d}q \tag{5}$$

$$g(r) = 1 + (2\pi^2 r\rho_0)^{-1}\int_0^\infty q\, S_2(q) \sin(qr)\, \mathrm{d}q \tag{6}$$

respectively, where ρ_0 is the average density. When the Fourier transform is made, a sufficiently wide q range of scattering intensity data is required, but the experimentally accessible q range is usually limited, resulting in truncation effect. To avoid this truncation effect, $\tilde{S}_2(q)$ and $S_2(q)$ were smoothly extrapolated toward zero in the high-q limit before the transformation.

Parts a and b of Figure 8 show $\tilde{g}(r)$ and $g(r)$, respectively. $\tilde{S}(r)$ shows a maximum at around $r = 65$ Å. This value is close to ξ_0 ($\approx$75 Å),[13] which is the expected value of intersegmental distance in the rod limit, but is quite different from the average distance between centers of mass r_0 ($\approx$165 Å).[13] As was described above, $\tilde{S}_2(q)$ and its Fourier transform $\tilde{g}(r)$ are sensitive to only local structure. The addition of salt shifts the maximum slightly toward smaller r. This behavior is similarly observed for charged spherical particles[21] and semiflexible polyelectrolytes.[9] Thus, the local structure of flexible polyelectrolytes in semidilute region has also a "liquidlike" one,[5,7] common to other kinds of polyelectrolytes.

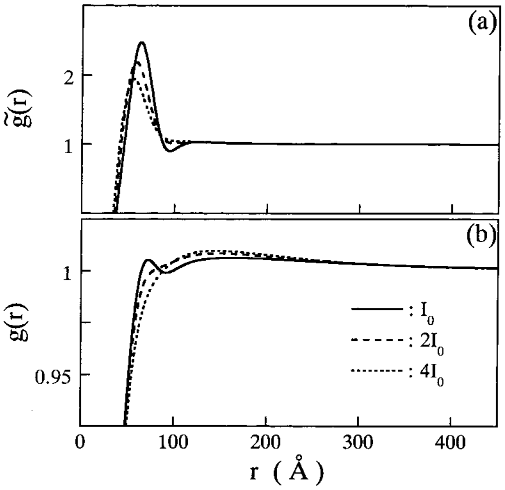

Figure 8. Ionic strength variation of Fourier transform of $\tilde{S}_2(q)$ and $S_2(q)$.

On the other hand, $g(r)$ shows two maxima at around r = 70 and 160 Å. The former maximum is virtually identical to that observed in $\tilde{g}(r)$, i.e., local structure. The latter broad maximum probably indicates a distribution of intermolecular distance, since the position of the maximum is very close to the average distance between centers of mass. Thus, $g(r)$ and its original function $S_2(q)$ imply not only the local structure but also the global distribution of distinct molecules. The addition of salt makes the former maximum in $g(r)$ obscure more rapidly than $\tilde{g}(r)$. This is probably because the former maximum (local structure) is located on a steep shoulder of the latter maximum (global structure), and hence it is apparently buried.

Dividing $S_2(q)$ by $S_1(q)$, which is equivalent to $I(q)/S_1(q) - 1$, is a well-established procedure to obtain the structure factor $S(q)$ for the system of noninterpenetrating particles.[5,21] This treatment has been formally applied also for flexible polyelectrolytes in the semidilute region,[20] i.e., the interpenetrating system, without sufficient explanation in its physical meaning. Our explanation and justification for such a procedure are as follows: $S_2(q)$ is an interference function between distinct polymer chains, in other words, a distribution function of other polymer chains from a certain polymer chain. Let us assume a homogeneous polymer chain system with each chain having a form factor $S_1(q)$, but without local structure, then the total scattering function $I(q)$ should be flat. In such an imaginary system, $S_2(q)$ should have a form of $-S_1(q)$, because $S_2(q)$ is caused from the hole,[38] which is caused by removing a single polymer chain. In this case, naturally $S_2(q)/S_1(q)$ gives unity independent of q_m, meaning no local structure. When the system has local structures, $S_2(q)$ deviates from the form of $-S_1(q)$, but the deviation is rather small compared to the whole amplitude (see Figure 9). Therefore, to extract the information about the inhomogeneity, i.e., local structure, $S_2(q)$ should be normalized by $S_1(q)$. We do not have further theoretical explanation at present; however, it may safely be said that the characteristic about difference between $\tilde{g}(r)$ and $g(r)$ helps us further understanding for the physical meaning of $\tilde{S}_2(q)$ and $S_2(q)$.

Analysis of $S_1(q)$. In the case of semiflexible polyelectrolytes, the most interesting parameter which is obtained by the analysis of $S_1(q)$ is the total persistence length b_t. Since the detailed analytical method has been presented in the previous paper,[31] only the point is reviewed here. The total persistence length b_t is obtained from $b_t = 1.91/q^*$, where q^* is a crossover point q^* between Debye function $S_1(q)_{\mathrm{Debye}}$ in the low q range[31,39] and the des Cloizeaux function $S_1(q)_{\mathrm{Cloizeaux}}$ in the high q range.[31,40] The insertion in Figure 5 shows an application of such analysis to the present data. Although the number of data is small, these are ionic strength dependence of b_t at a fixed polyelectrolyte concentration, while the concentration dependence of b_t has been frequently reported.[20,31,41] By subtraction of the intrinsic persistence length b_0 (= 9 Å[17] ~ 12 Å[20]) from the total persistence lengths b_t, the electrostatic persistence lengths b_e are obtained. These obtained b_e together with b_t are shown in Figure 10. As is seen from this figure, the relationship $b_e \propto I^{-1/2}$ held best when b_0 = 9 Å. This relation agree with the result obtained from the concentration dependence[20,31,41] $b_e \propto C^{-1/2}$. This is an evidence supporting the conversion rule between C and C_s as was given in eq 3.

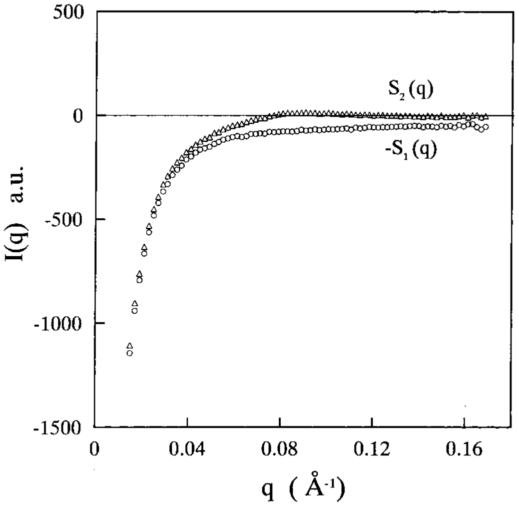

Figure 9. Comparison of $S_2(q)$ with $-S_1(q)$.

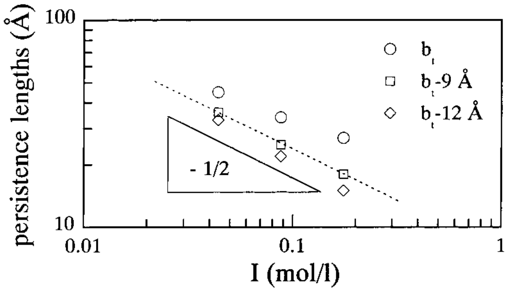

Figure 10. Ionic strength dependence of persistence length of NaPSS at fixed concentration (C = 0.25 mol/L).

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References and Notes

(1) Drifford, M.; Dalbiez, J. P. *J. Phys. Chem*. **1984**, *88*, 5368.
(2) Krause, R.; Maier, E. E.; Deggelmann, M.; Hagenbüchle, M.; Schulz, S. F.; Wever, R. *Physica A* **1989**, *160*, 135.
(3) Förster, S.; Schmidt, M. *Polymer* **1990**, *31*, 781.
(4) Li, X.; Reed, W. F. *J. Chem. Phys.* **1991**, *96*, 4568.
(5) Maier, E. E.; Krause, R.; Deggelmann, M.; Hagenbüchle, M.; Weber, R. *Macromolecules* **1992**, *25*, 1125.
(6) Johner, C.; Kramer, H.; Batzill, S.; Graf, C.; Hagenbüchle, M.; Martin, C.; Weber, R. *J. Phys. II* **1994**, *4*, 1571.
(7) Morfin, I.; Reed, W. F.; Rinaudo, M.; Borsali, R. *J. Phys. II* **1994**, *4*, 1001.
(8) Borsali, R.; Rinaudo, M.; Noirez, L. *Macromolecules* **1995**, *28*, 1085.
(9) Norwood, D. P.; Benmouna, M.; Reed, W. F. *Macromolecules* **1996**, *29*, 4293.
(10) Borsali, R.; Nguyen, H.; Pecora, R. *Macromolecules* **1998**, *31*, 1548.
(11) Patkowski, A.; Gulari, E.; Chu, B. *J. Chem. Phys.* **1980**, *73*, 4178.
(12) Kaji, K.; Urakawa, H.; Kanaya, T.; Kitamaru, R. *Macromolecules* **1984**, *17*, 1835.
(13) Kaji, K.; Urakawa, H.; Kanaya, T.; Kitamaru, R. *J. Phys. (Paris)* **1988**, *49*, 993.
(14) Wang, L.; Bloomfield, V. A. *Macromolecules* **1991**, *24*, 5791.
(15) Nishida, K.; Kaji, K.; Kanaya, T. *Macromolecules* **1995**, *28*, 2472.
(16) Essafi, W.; Lafuma, F.; Williams, C, E. *Eur. Phys. J. B* **1999**, *9*, 261.
(17) Nishida, K.; Kaji, K.; Kanaya, T. *J. Chem. Phys.* **2001**, *114*, 8670.
(18) Williams, C. E.; Nierlich, M.; Cotton, P. J.; Jannink, G.; Boué, F.; Daoud, M.; Farnoux, B.; Picot, C.; de Gennes, P. G.; Rinaudo, M.; Moan, M.; Wolff, C. *J. Polym. Sci., Polym. Lett. Ed.* **1979**, *17*, 379.
(19) Nierlich, M.; Williams, C. E.; Boué, F.; Cotton, J. P.; Daund, M.; Farnoux, B.; Jannink, G.; Picot, C.; Moan, M.; Wolff, C.; Rinaudo, M.; de Gennes, P. G. *J. Phys. (Paris)* **1979**, *40*, 701.
(20) Nierlich, M.; Boue, F.; Lapp, A.; Oberthür, R. *Colloid Polym. Sci.* **1985**, *263*, 955.
(21) Goodwin, J. W.; Ottewill, R. H.; Owens, S. M.; Richardson, R. A.; Hayter, J. B. *Makromol. Chem., Suppl.* **1985**, *10/11*, 499.
(22) Ono, M.; Okamoto, S.; Kanaya, T.; Nishida, K.; Urakawa, H.; Kaji, K.; Kitamaru, R. *Physica* **1986**, *138B*, 49.
(23) Milas, M.; Rinaudo, M.; Duplessix, R.; Borsali, R.; Lindner, P. *Macromolecules* **1995**, *28*, 3119.
(24) Ermi, B. D.; Amis, E. J. *Macromolecules* **1997**, *30*, 6937.
(25) Dubois, E.; Boué, F. *Macromolecules* **2001**, *34*, 3684.
(26) de Gennes, P. G.; Pincus, P.; Velasco, R. M.; Brochard, F. *J. Phys.* (*Paris*) **1976**, *37*, 1461.
(27) Föster, S.; Schmidt, M. *Adv. Polym. Sci.* **1995**, *120*, 51.
(28) Nisato, G.; Ivkov, R.; Amis, E. J. *Macromolecules* **1999**, *32*, 5895.
(29) Bodnár, I.; Silvia, A. S.; Deitcher, R. W.; Weisman, N. E.; Kim, Y. H.; Wagner, N. J. *J. Polym. Sci., Part B: Polym. Phys.* **2000**, *38*, 857.
(30) des Cloizeaux, J.; Jannink, G. In *Polymers in Solution*—*Their Modeling and Structure*; Clarendon Press: Oxford, 1990; p 244.
(31) Nishida, K.; Urakawa, H.; Kaji, K.; Gabrys, B.; Higgins, J. S. *Polymer* **1997**, *38*, 6083.
(32) Oosawa, F. *J. Polym. Sci.* **1957**, *23*, 421.
(33) Oosawa, F. In *Polyelectrolytes*; Marcel Dekker: New York, 1971.
(34) Manning, G. S. *J. Chem. Phys.* **1969**, *51*, 924.
(35) Hayashi, H.; Hamada, F.; Suehiro, S.; Masaki, N.; Ogawa, T.; Miyaji, H. *J. Appl. Crystallogr.* **1988**, *21*, 330.
(36) Jannink, G. *Makromol. Chem., Macromol. Symp.* **1986**, *1*, 67.
(37) Harnau, L.; Reineker, P. *J. Chem. Phys.* **2000**, *112*, 437.
(38) Daoud, M.; Coton, J. P.; Farnoux, B.; Jannink, G.; Sarma, G.; Benoit, H.; Duplessix, R.; Picot, C.; de Gennes, P. G. *Macromolecules* **1975**, *8*, 804.
(39) Glatter, O.; Kratky, O. In *Small-Angle X-ray Scattering*; Academic Press: London, 1982.
(40) des Cloizeaux, J. *Macromolecules* **1973**, *6*, 403.
(41) Nishida, K.; Kaji, K.; Kanaya, T.; Fanjat, N. *Polymer* **2002**, *43*, 1295.

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