Charge Density Dependence of Correlation Length Due to Electrostatic Repulsion in Polyelectrolyte Solutions

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ABSTRACT: The electrostatic correlation lengths ξ in salt-free polyelectrolyte solutions have been measured as functions of charge density and polymer concentration using a small-angle X-ray scattering (SAXS) technique. In this case a water-soluble poly(vinyl alcohol) (PVA) was employed as a parent polymer to avoid increasing hydrophobic interactions with decreasing the charge density; partially sulfuric acid esterificated PVA's were used as samples. The charge density defined by degree of esterification α was changed from 0.008 to 0.499. It was found that the maximum position q_m of a characteristic SAXS peak, which is attributable to the electrostatic interchain correlation, is proportional to the square root of polymer concentration C at any charge density as long as the solution is in the semidilute region. This supports that the isotropic model by de Gennes et al. is valid. The α dependence of q_m agreed with the theoretical prediction from a blob chain model for weakly charged polyelectrolytes proposed by Pfeuty and Khokhlov. Thus, it was experimentally shown that, when the counterion condensation does not take place ($\alpha < 0.3$), the relation $q_m \sim \xi^{-1} \sim \alpha^{1/3}C^{1/2}$ is valid for semidilute solutions. This also indicates that the charge density dependence of the correlation length can be understood within a framework of the isotropic model.

Introduction

The intra- and intermolecular static structures of polyelectrolyte solutions with high charge densities have been extensively studied using various methods such as small-angle X-ray scattering (SAXS),[1,2] small-angle neutron scattering (SANS),[3–6] light scattering (LS),[7–9] and transient electric birefringence (TEB).[10] From these studies, it has turned out that polyions have a considerable degree of stiffness or persistance length, which increases with decreasing polymer concentration C. Even in the semidilute regions their persistence lengths are 1 or 2 orders of magnitude larger than those of the usual neutral flexible polymers. Theoretical approaches to the structure of polyelectrolyte solutions have been made by de Gennes et al.[11] and Odijk[12] and several scattering experiments to confirm their models have been conducted.[1–3,13]

Small-angle scattering studies revealed that salt-free polyelectrolyte solutions usually show a characteristic maximum in the scattering curves $I(q)$ as a function of the length of scattering vector $q = (4\pi/\lambda) \sin \theta$, with 2θ and λ being the scattering angle and X-ray wavelength, respectively. In the semidilute region the maximum position q_m is proportional to $C^{1/2}$, while in the dilute region q_m is proportional to $C^{1/3}$. The $q_m \sim C^{1/2}$ relationship for the semidilute region is consistent with the concept of correlation holes in the isotropic model proposed by de Gennes et al.[11] (Figure 3 of ref 11), and the $q_m \sim C^{1/3}$ relationship for the dilute region can be easily understood as the interference between centers of polyions. Such behavior reflects the existence of the electrostatic repulsive forces among segments of overlapped polyions or among centers of polyions, resulting in some order structure. These simple scaling relationships between q_m and C have been successfully applied to the determination of the dilute–semidilute crossover concentrations in polyelectrolyte solutions as an experimental guide.[2] In this sense it may be said that the elucidation of the static structure of polyelectrolyte solutions has been rather well established for polyions having high charge densities. Recently Candau et al. have intensively studied weakly acidic polyelectrolytes[14] such as poly(acrylic acid) and poly(methacrylic acid) as a function of the degree of ionization. They considered that in such systems hydrophobic interactions are balanced by electrostatic repulsive forces, which results in microphase separation, and applied the random-phase approximation theory[15,16] to explain their scattering experiments. On the other hand, strongly acidic polyelectrolytes with a low fraction of ionic groups are insufficiently understood. Though there are some theoretical works,[11,17–20] experimental works have hardly been done except for ionomers, i.e., water-insoluble polymers containing a low fraction of ionic groups.[21]

In this study we therefore study the structure of aqueous solutions of strongly acidic polyelectrolytes containing a low fraction of ionic groups, especially the charge density dependence of the correlation length in the solutions using a SAXS technique, and the results will be compared with the blob chain model. This model was developed by de Gennes et al.[11] and Pfeuty[17] and later modified by Khokhlov et al.[18,19] It should be here noted that, if polyions are weakly charged and their backbones are hydrophobic as in poly(sodium styrenesulfonate) (NaPSS), the structure depends on both the electrostatic and hydrophobic interactions. The latter effect sometimes causes inter- and intramolecular aggregation,[21] so that in the present study we use a water-soluble poly(vinyl alcohol) (PVA) as a backbone polymer.

Theoretical Section

In what follows we will discuss the charge density dependence of the correlation length ξ or that of the peak position q_m for flexible polyelectrolyte solutions. As will be shown later, the peak position q_m decreases with decreasing the charge density α at constant C. Here α is defined as the degree of esterification, i.e., the number fraction of charged monomers per polymer molecules. This means that the correlation length ξ increases with decreasing α as if the system were diluted. Such behavior causes us anxiety that the isotropic model may possibly be invalid because at first sight ξ seems to be constant independent of α in this model. However, the C dependence of ξ indeed sup-

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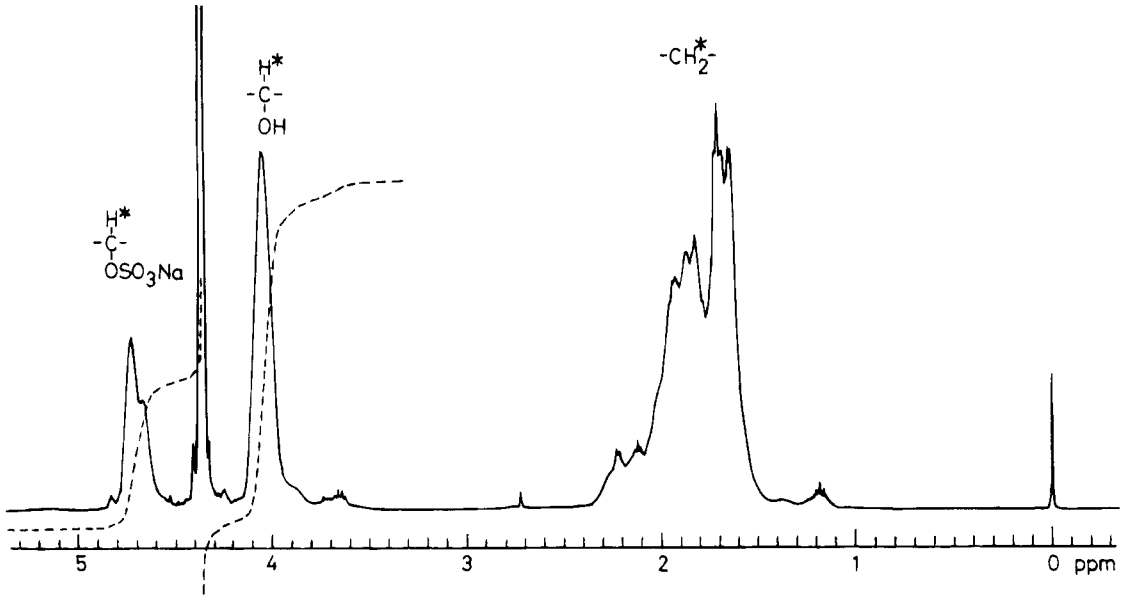

Figure 1. NMR spectra (solid line) and integrated spectra (dashed line) of the sodium salt of a partially sulfuric acid esterificated poly(vinyl alcohol) at 400 MHz relative to TMS as standard, in D_2O as solvent at 65 °C.

ported the isotropic model as was shown in previous papers.[1,2] How can we solve such a contradiction? In salt-free semidilute solutions flexible polyelectrolytes will behave as semiflexible chains when they have high charge densities, while without charges, they will behave as coils. So it is natural to consider that the low charge density polyions in salt-free solutions should have an intermediate conformation, something between a semiflexible rod and a spherical coil. As the charge density decreases, however, the flexibility of polyion chains does not continuously increase, but they collapse into blobs below a critical value of the charge density. This type of conformation has been modeled as a chain of blobs by de Gennes et al.,[11] Pfeuty,[17] and Khokhlov.[18,19] A single blob chain consists of a sequence of blobs inside which the chain conformation is approximated as Gaussian. The effective contour length of this blob chain is defined by the sum of blob diameters. As α decreases, the blob diameter increases proportionally to the square root of the molecular weight M_b of a blob while the number of blobs in a chain decreases proportionally to M_b. The contour length therefore decreases with decreasing α. Further, since the correlation length in the semidilute region is related to the density of the effective contour length, i.e., density of lines, the interchain correlation length ξ also increases with decreasing α under the constant C condition. Thus, based on this model, the α dependence of the correlation length can be derived. When the correlation length $\xi \sim C^{-1/2}$ was derived in the isotropic model,[11] the overlap concentration in rod limit was taken as N/L^3 where $L = a_0N$ is the contour length, with a_0 and N being the monomer length and the degree of polymerization, respectively. For a chain consisting of blobs, replacing L by effective contour length L', the interchain correlation length becomes

$$\xi \sim (CL'/N)^{-1/2} \tag{1}$$

According to the blob model[17,19]

$$L' \sim \alpha^{2/3}N \tag{2}$$

and so

$$\xi \sim \alpha^{-1/3}C^{-1/2} \tag{3}$$

or

$$q_m \sim \alpha^{1/3}C^{1/2} \tag{4}$$

Equations 3 and 4 are basic relations in the semidilute region for understanding the α dependence of the correlation length ξ and the peak position q_m, respectively. Here, it should be noted that these equations are valid only for $\alpha \leq a_0/l_B$ because of the Oosawa–Manning counterion condensation theory[25-27] where l_B is the Bjerrum length defined by $e^2/4\pi\epsilon kT$, with e, ϵ, k, and T being the elementary charge unit, the solvent dielectric constant, Boltzmann's constant, and temperature, respectively. For $\alpha > a_0/l_B$, ξ and q_m become independent of α.

Experimental Section

Materials. The sodium salt of partially sulfuric acid esterificated poly(vinyl alcohol) (NaPVS) was prepared by a conventional method.[22] PVA, which was kindly presented from Unitika Chemical Co. Ltd. was treated with 40–80% H_2SO_4 solution, and the reaction was stopped by neutralizing with Na_2CO_3. The crude product was purified by deionization using ion-exchange resins (Amberlite IRA-400 and IR-120B) and then completely reneutralized with NaOH. The purified sample was lyophilized and kept in a desiccator until use. NaPVS with degrees of esterification $\alpha = 0.008-0.499$ were obtained by changing the concentration of sulfuric acid; α was measured with a 400-MHz ^{1}H-NMR (JEOL) spectrometer. In Figure 1, peaks from α-protons of the esterificated and nonesterificated monomer unit (chemical shift $\delta = 4.7$ and 4.05 ppm, respectively) and a sharp peak from residual protons in heavy water (D_2O) ($\delta = 4.35$ ppm) could be successfully separated only at 65 °C, but peaks due to methylene protons ($\delta = 1.5-2.3$ ppm) could not be separated at any temperature. The degree of esterification was determined from the integrated spectra of such α-protons. Weight-averaged molecular weight M_w and its distribution M_w/M_n of the parent PVA were determined by gel permeation chromatography (GPC). In the GPC measurements a 0.25 wt % tetrahydrofuran solution of poly(vinyl acetate) converted from the parent PVA by acetylation was developed, and $M_w = 142\,300$ and $M_w/M_n = 1.97$ were obtained using the Mori's equation.[23]

SAXS Measurements. The SAXS intensity measurements were carried out at 25 °C using a 6-m point-focusing SAXS

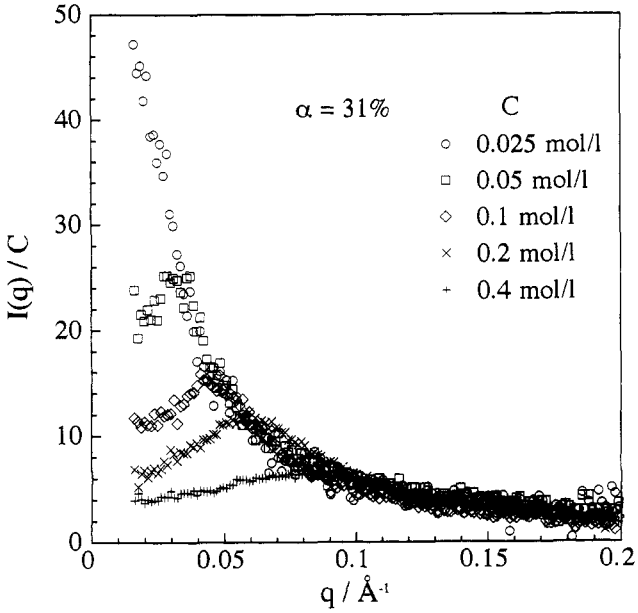

Figure 2. Concentration dependence of SAXS curves for NaPVS solutions with α = 31%. The scattering intensity from a water solvent was subtracted from each curve. C = 0.025 (○), 0.05 (□), 0.1 (◇), 0.2 (×), and 0.4 mol/L (+).

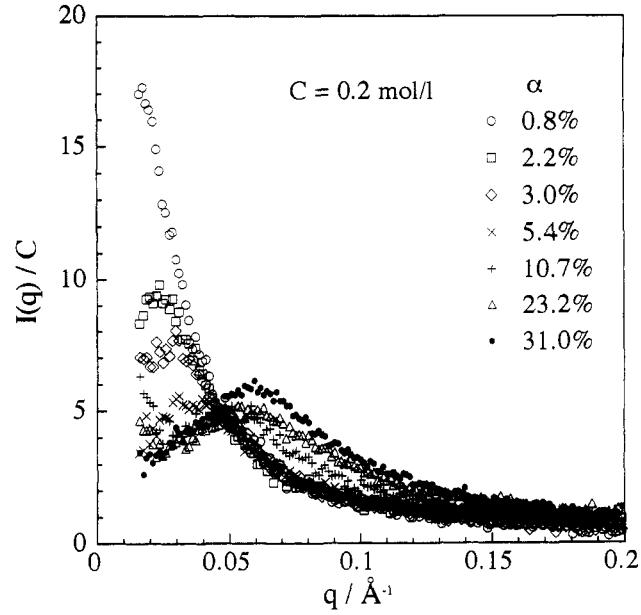

Figure 3. Charge density dependence of SAXS curves for NaPVS solutions when C = 0.2 mol/L. The scattering intensity from a water solvent was subtracted from each curve. α = 0.8% (○), 2.2% (□), 3.0% (◇), 5.4% (×), 10.7% (+), 23.2% (△), and 31.0% (●).

camera at the High-Intensity X-ray Laboratory of Kyoto University.[24] This camera utilizes Ni-filtered Cu Kα radiation from a 3.5-kW rotating-anode X-ray generator (RU-1000C3, Rigaku Denki Co. Ltd., Japan), a Franks-type double-focusing point collimator, and a two-dimensional position-sensitive proportional counter. The scattering intensity from the sample solution was circularly averaged, and then that from water as solvent was subtracted. The intensity data were obtained for a q range of ca. 0.015–0.2 Å^{-1}.

Results and Discussion

Before going to the experimental results we will discuss the concentration region where the experiments were carried out. The experiments were carried out for a concentration range of 0.025–0.4 mol/L. The chain overlap concentrations C^* are around 0.1 and 10^{-3} mol/L when polyions are assumed to be coil and rod conformations, respectively. For the rod limit, all the concentrations studied can be considered semidilute, whereas for the coil limit the concentrations lower than 0.1 mol/L become dilute. Thus, the determination of the dilute–semidilute crossovers for low charge density polyelectrolyte solutions is a complicated problem because it depends on charge density. It is, however, safe to say at least that the solutions with C > 0.1 mol/L meet the condition of semidilute for any charge density.

According to our preliminary study,[28] the intrinsic viscosity [η] of a PVA-based polyelectrolyte with α = 0.022 at a concentration of added salt $C_s = 10^{-3}$ mol/L was more than 2 times that of the original PVA solution. This means that, even if they have such a low charge density, polyelectrolyte chains are expanded considerably at low ionic strength. It is therefore expected that even the solutions with C < 0.1 mol/L have the possibility of being in the semidilute region depending on α.

The observed SAXS curves after correction are shown in Figures 2 and 3 as functions of C and α, respectively. All measurements were conducted in the salt-free condition. The intensity was normalized by the concentration in a number of monomer units per unit volume. Each curve in these figures has a characteristic maximum, which is well-known as a correlation peak

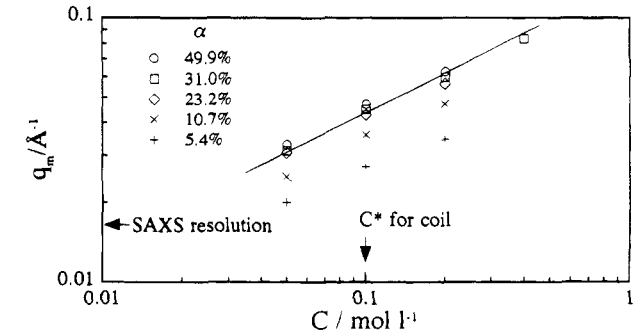

Figure 4. q_{max} vs C plot in logarithmic scales for NaPVS solutions. α = 49.9% (○), 31.0% (□), 23.2% (◇), 10.7% (×), and 5.4% (+). The straight line represents a slope of 1/2.

due to strong electrostatic repulsion in the case of salt-free polyelectrolyte solutions with high charge density. It is clear from Figure 2 that with increasing C, the peak position q_m increases and the maximum intensity decreases. In Figure 4, q_m is plotted against C for various α's. For α ≥ 0.107, the following relationship is observed in the whole concentration range of this study,

$$q_m \sim C^{1/2} \tag{5}$$

According to the isotropic model for semidilute solutions,[11] the correlation length ξ is given as a function of C independent of N:

$$\xi \sim C^{-1/2} \tag{6}$$

This relation agrees with eq 5 because of $\xi = 2\pi/q_m$. Thus, the characteristic maximum in $I(q)$ for salt-free high charge density polyelectrolyte solutions is usually interpreted as evidence of the correlation holes which are caused by electrostatic repulsive forces among polyion segments. The behavior of q_m for α ≥ 0.107 in Figure 4 is essentially the same as that in the previous experiments[1,2] for the salt-free semidilute solution of NaPSS with α = 1.0. It is therefore expected that the

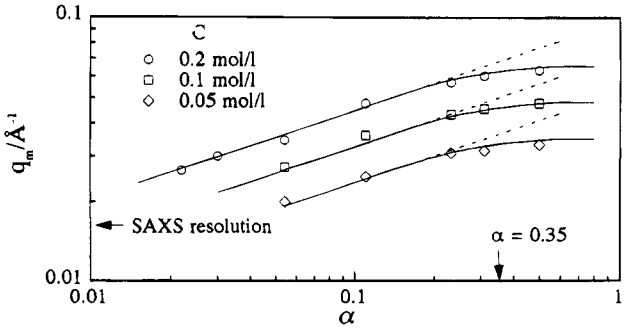

Figure 5. q_m vs α plot in logarithmic scales for NaPVS solutions. C = 0.2 (○), 0.1 (□), and 0.05 mol/L (◇). Dashed lines represent slopes of 1/3. Solid lines are to guide the reader's eye.

present systems with α ≥ 0.107 also assume the "isotropic structure". For α ≤ 0.054, the exponent of C is rather small compared with 1/2. Considering this phenomenon and the crossover concentration $C^* \approx 0.1$ mol/L for the coil limit, these systems may no longer be regarded as semidilute in the whole range observed, especially at $C < 0.1$ mol/L, but they may be somewhere in the crossover region.

Figure 5 shows logarithmic plots of q_m against α for various concentrations. In the case of $C = 0.2$ mol/L, q_m increases with α for α < 0.3 and the following relationship is obtained:

$$q_m \sim \alpha^n \tag{7}$$

n is 0.3−0.35, while it levels off for α > 0.3. The decrease of the correlation length with increasing α means that polyion blob chains expand with increasing α. The mechanism of chain expansion by charge is one of the most interesting problems in the field of polyelectrolyte solutions. In order to apply eq 4 to the experimental data, the condition of $C > C^*$ should be required. This condition is completely satisfied only when $C = 0.2$ mol/L. When $C = 0.2$ mol/L, the exponent n agrees with the theoretical value of 1/3 in eq 4 within experimental error as seen in Figure 5. In other words, the blob chain model can describe the experimental data. For the comprehensive understanding of the mechanism of chain expansion by charge, more experimental information would, however, be necessary especially on the conformation of an isolated chain. At the present stage, we may conclude that the "isotropic-like structure" does not contradict the experiments. The solutions investigated in this study are intrinsically water-soluble, and neither gelation nor precipitatation takes place even for the lowest α (=0.008) so that the theory of weakly charged polyelectrolytes in a poor solvent[16] is inapplicable to the present case.

The leveling off of q_m for α > 0.3 is attributable to a phenomenon of counterion condensation. According to the condensation theory of Oosawa[25,26]–Manning,[27] the counterion condensation occurs when the distance between the neighboring dissociation groups on the backbone chain is within the Bjerrum length l_B as described in the Theoretical Section. Since l_B is 7.16 Å in water at 25 °C and $a_0 = 2.52$ Å for a vinyl type of polymers, the critical charge density $\alpha = a_0/l_B$, at which the counterion condensation begins to occur, is 0.35. This almost corresponds to the observed value of 0.3. The structural change by electrostatic interaction is therefore no longer expected for α > 0.35, but the steric effect of dissociation groups on the chain conformation and hydrophilicity may somewhat change. The latter effect would be remarkable in the case of polymers having intrinsically hydrophobic backbones.

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