

How Does the Polymer Chain Expand by Intramolecular Electrostatic Repulsion

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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. 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 esterified PVA's were used as samples. The charge density was changed from 0.008 to 0.499 in degree of esterification α . 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. This supports that the isotropic model of de Gennes et al. is valid. The α dependence of q_m agrees with the theoretical prediction from the blob chain model for weakly charged polyelectrolytes proposed by Pfeuty and Khokhlov. This is the first and important experimental data which tells how the polymer chain expands by intramolecular electrostatic repulsion.

Keywords: Polyelectrolytes / Correlation length / Blob chain model / Isotropic model / SAXS

It is well-known that in salt-free solutions the polymer chains having flexible backbones will behave as half-rigid rods when they have high charge density. The driving force of the expansion is, of course, the intramolecular electrostatic repulsion between dissociation groups attached to the backbone. On the other hand, 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 half-rigid rod and a spherical coil. But, how? The mechanism of chain expansion by charges is one of the most interesting problems in the field of polyelectrolyte solutions.

As the charge density α 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.[1], Pfeuty[2], and Khokhlov[3-4]. 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 interchain correlation length in the semidilute region is related

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Scope of research

The structure and molecular motion of polymer substances are studied using mainly scattering methods such as neutron, X-ray and light with the intention of solving fundamentally important problems in polymer science. The main projects are: the mechanism of structural development in crystalline polymers from the glassy or molten state to spherulites; the dynamics in disordered polymer materials including low-energy excitation or excess heat capacity at low temperatures, glass transition and local segmental motions; formation process and structure of polymer gels; the structure and molecular motion of polyelectrolyte solutions; the structure of polymer liquid crystals.



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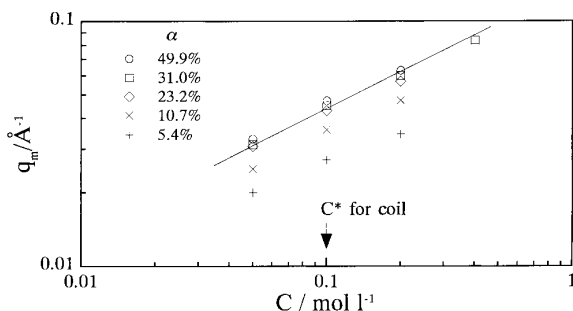


Figure 1. $q_{\max}$ vs. C plot in logarithmic scales for NaPVS solutions. $\alpha = 49.9\%$ (○), 31.0% (□), 23.2% (◇), 10.7% (×), and 5.4% (+). The straight line represents a slope of $1/2$.

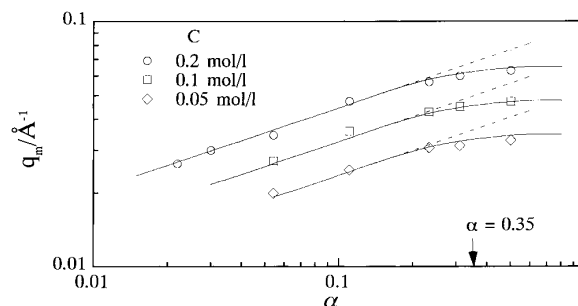


Figure 2. The $q_{\max}$ vs. α plot in logarithmic scales for NaPVS solutions. $C = 0.2$ mol/l (○), 0.1 mol/l (□), and 0.05 mol/l (◇). Dashed lines represent a slope of $1/3$. Solid lines are to guide the reader's eye.

to the density of the effective contour length, i.e., density of skeletal 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[1], the overlap concentration in rod limit was taken as N/L^3 where $L = a_0 N$ is contour length, a_0 and N being the length of a monomer and the degree of polymerization, respectively. For a chain consisting of blobs, replacing L by effective contour length L' , the interchain correlation length becomes

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

According to the blob model[2-4]

$$L' \sim \alpha^{2/3} N, \quad (2)$$

and so

$$\xi \sim \alpha^{1/3} C^{-1/2} \quad (3)$$

or

$$q_m \sim \alpha^{1/3} C^{1/2}, \quad (4)$$

where q is the length of scattering vector $q = 4\pi \sin \theta / \lambda$, 2θ and λ being scattering angle and X-ray wavelength, respectively. 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[5-7] where l_B is the Bjerrum length defined by $e^2/4\pi\epsilon kT$, e , ϵ , k and T being elementary charge unit, dielectric constant of solvent, Boltzmann constant and temperature, respectively. For $\alpha > a_0/l_B$, ξ and q_m become independent of α .

The SAXS measurements were carried out using a 6-m point focusing SAXS camera at the High-Intensity X-ray Laboratory of Kyoto University. In Figure 1, q_m is plotted against C for various α 's. For $\alpha \geq 0.107$, the relationship in equation 4 is satisfied in respect to the C -dependence. This behavior of q_m for $\alpha \geq 0.107$ in Figure 1 is essentially the same as in the previous experiments[8-9] for the salt-free semidilute solution of NaPSS with $\alpha = 1.0$. It is therefore expected that the present systems with $\alpha \geq 0.107$ also assume the 'isotropic structure'. For $\alpha \leq 0.054$, the exponent of C is rather small compared with $1/2$. Considering this phenomenon and the crossover concentration $C^* = 0.1$ 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 2 shows logarithmic plots of q_m against α for various concentrations. For $\alpha < 0.3$, the relationship in equation 4 is satisfied in respect to the α -dependence. The decrease of the correlation length with increasing α means that polyion blob chains expand with increasing α .

The leveling-off of q_m for $\alpha > 0.3$ is attributable to a phenomenon of counterion condensation. According to the condensation theory of Oosawa[5-6]-Manning[7], the counterion condensation occurs when the distance between the neighboring dissociation groups on the backbone chain is within the Bjerrum length l_B as above described. Since l_B is $7.16 \text{ \AA}$ in water at 25°C and $a_0 = 2.52 \text{ \AA}$ 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 $\alpha > 0.35$.

These results indicate that the structure of semidilute solutions of weakly charged polyelectrolytes can also be understood within a frame work of the 'isotropic model'[1], and the mechanism of chain expansion by charge obeys the 'blob chain model'[1-4].

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