Macromolecules **1984**, *17*, 1594–1598

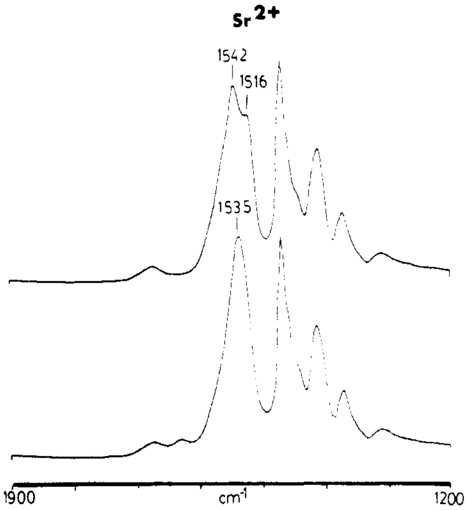

Figure 5. FT-IR spectra in the range 1900–1200 cm^{-1} of the strontium ionomer (A) quenched from the melt and immersed in water for 1 day and (B) after 1 week under vacuum over P_2O_5.

attributable to localized multiplet structures became better resolved and more distinct with increasing temperature. Although there was some theoretical justification that multiplets would be favored over clusters at elevated temperatures and, at that time, the infrared spectra in the hydroxyl stretching region suggested that water absorption was insignificant, it now appears that the elevated-temperature results may be explained in terms of a reduction of the concentration of water in the films upon raising the temperature.

Similarly, the long-term room-temperature, annealing results, which purported to show multiplet-to-cluster formation,[3] are now interpreted to be due to the slow adsorption of water into the films. Finally, we must reconsider the interpretation of the long-term annealing experiments performed at 80 °C.[4] A significant degree of crystallization of the ethylenic portion of the chains occurs at this temperature. In subsequently annealing this material at room temperature for extended periods of time, there is essentially no change in the spectra. (This is in marked contrast to the room-temperature annealing results of the quenched ionomer.) It was suggested that the development of crystallinity, formed by annealing at 80 °C, "freezes in" the "favored" multiplets structure and that the multiplet-to-cluster transformation at room temperature is prevented by the crystallites. Given the results presented in the current paper, we require an alternative explanation. It is feasible that the presence of the crystalline domains formed at 80 °C significantly reduces the rate of diffusion of water into the film at room temperature. Although plausible, we consider this to be somewhat speculative.

Eisenberg[2] has previously observed that studies on ethylene–methacrylic acid ionomers indicate that clusters are the only ionic species present and that single multiplet structures do not occur even at very low ion concentrations. If this observation applies to our essentially fully ionized samples then we must conclude that multiplets retain their structural integrity within clusters.

2. Water absorption obviously plays an important role in the overall structure on ionomers. However, different salts are affected to different degrees. Not only does hydration of the ionic domains occur, but water also is instrumental in the formation of acid–salts. Hydration and acid–salt formation leads to a broadening of the asymmetric carboxylate stretching vibration. The zinc ionomer appears to be the least affected by the water for reasons stated in the text.

Acknowledgment. We acknowledge the financial support of the National Science Foundation, Grant DMR-8206932, Polymers Program.

Registry No. (Ethylene)·(methacrylic acid) (copolymer) sodium salt, 25608-26-8; (ethylene)·(methacrylic acid) (copolymer) potassium salt, 26376-80-7; (ethylene)·(methacrylic acid) (copolymer) strontium salt, 88496-05-3; (ethylene)·(methacrylic acid) (copolymer) zinc salt, 28516-43-0; H_2O, 7732-18-5.

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Small-Angle Scattering of Polyelectrolyte Solutions

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ABSTRACT: The small-angle scattering intensity of polyelectrolyte solutions is calculated, assuming a wormlike chain polymer model. The calculation assumes that the probability of finding two monomers of different polymers within a distance R_0 is negligible because of strong electrostatic repulsion between the polyelectrolyte chains. The scattering intensity becomes a monotonically decreasing function of q for small R_0, but it has a broad maximum for large R_0 (q is the absolute value of the scattering vector). The maximum point q_m and the maximum intensity per monomer at q_m are approximately proportional to the square root of the monomer concentration and to its reciprocal value, respectively. The calculated values of q_m agree well with those of the small-angle neutron scattering of deuterated sodium poly(styrenesulfonate) solutions without added salts obtained by Nierlich and others. The result of the maximum intensity also agrees qualitatively with that experiment.

I. Introduction

The small-angle neutron and X-ray scattering curves of polyelectrolyte solutions have various characteristic forms according to the physical conditions,[1-4] and particularly with no added salts they have a broad peak in the region $q = 10^{-2}$–10^{-1} Å^{-1}, where q is the absolute value of the

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scattering vector $\mathbf{q}$

$$q = (4\pi/\lambda) \sin (\theta/2) \tag{1}$$

λ is the wavelength and θ is the scattering angle. These scattering curves have been discussed in the framework of several models, e.g., a lattice model of aligned rigid rods,[5] an isotropic model where the chain conformation is assumed to be a Gaussian succession of rodlike segments,[6] and that of a wormlike chain.[7,8]

Lifson and Katchalsky[5] solved the Poisson–Boltzmann equation for a cylindrically symmetric domain around the rodlike macroion, and from this result they showed that this polymer solution has a very small osmotic compressibility due to the counterions, and so its light scattering intensity is much damped. Recently, with the scaling theory and the correlation hole concept,[9] Hayter and others[10] showed that the scattering intensity of this polymer solution drops at small q and also decreases like q^{-1} at large q and that the maximum point q_m appears at a position nearly proportional to the square root of the solute concentration. These qualitative results coincide with recent small-angle neutron scattering experiments.[1]

In a previous paper[11] we calculated this scattering curve as a function of q, assuming a Gaussian radial distribution function of the rodlike segments in the random coil polymers, and derived the same qualitative results about q_m as did Hayter and others, together with the result that the maximum scattering intensity per monomer is inversely proportional to the square root of the concentration.[8] This calculation shows that the peak in the scattering curve appears when the repulsive interaction between the segments is strong and long range but does not appear when it is weak and short range.

Scattering curves with such a peak are obtained in some other cases. Two previous papers[12,13] calculated various scattering curves for solutions of homogeneous polymers and for mixed solutions of labeled and unlabeled polymers, assuming a Gaussian intermolecular potential among them, and showed that the peak appears at large interaction and high concentration. Benmouna and others[14] obtained scattering curves of this kind for solutions of charged spherical and rodlike macromolecules, introducing an effective potential to account for the Coulomb repulsion of macromolecules, and they interpreted the observed peak as a correlation hole effect. Although these calculations use different polymer models, their fundamental scattering equations based on the radial distribution function of polymers are the same,[15] and apart from the correlation hole concept, these theories show that the peak originates in the strong and long-range repulsions between the radiation scatterers and in their sufficiently high concentration. Mathematically the calculated maximum arises from the negative intermolecular term, which decays with q more rapidly than the positive intramolecular term. Also recently Benmouna and Benoit[16] calculated scattering curves for various copolymer solutions, using an approximation they called "Zimm's model" to consider the interchain interaction, and found that the curve has a peak for certain values of parameters such as the polymer concentration, the contrast factors, the relative compositions of the two components, and the second virial coefficient. They showed particularly that as the concentration increases, the repulsive interaction between chains due to the excluded volume effect may be important for producing the peak.

The previous paper[11] obtained the scattering curves for arbitrary values of the interaction parameters even in case of no maximum. The following calculation derives these by a more realistic chain polymer model.

II. Calculation of Small-Angle Scattering Intensity

In this calculation we neglect the internal structure of the monomer unit and regard it as a point scatterer of the radiation. The small-angle scattering intensity per unit volume of the polymer solution can be written as the Fourier transform of the two-body distribution function of the monomers $n(\mathbf{R}_1,\mathbf{R}_2)$ as

$$I(q) = C_I\left[n + \int_{-\infty}^{+\infty} (n(\mathbf{R}_1,\mathbf{R}_2) - n^2) \exp(-i\mathbf{q}\cdot\mathbf{R})\, d\mathbf{R}\right] \tag{2}$$

$$\mathbf{R} = \mathbf{R}_2 - \mathbf{R}_1 \tag{3}$$

where C_I is a constant and n is the average number of monomers in unit volume. Since $n(\mathbf{R}_1,\mathbf{R}_2)$ gives the simultaneous probability of finding two monomers at the points $\mathbf{R}_1$ and $\mathbf{R}_2$, it depends on only the relative coordinates $\mathbf{R}$ and can be written as the sum of the two-body distribution function for monomers in the same polymer $n_1(\mathbf{R}_1,\mathbf{R}_2)$ and that for monomers of different polymers $n_2(\mathbf{R}_1,\mathbf{R}_2)$

$$n(\mathbf{R}_1,\mathbf{R}_2) = n_1(\mathbf{R}_1,\mathbf{R}_2) + n_2(\mathbf{R}_1,\mathbf{R}_2) \tag{4}$$

They are normalized as

$$\int\int n_1(\mathbf{R}_1,\mathbf{R}_2)\, d\mathbf{R}_1\, d\mathbf{R}_2 = n_pN(N-1) = n(N-1) \tag{5}$$

$$\int\int n_2(\mathbf{R}_1,\mathbf{R}_2)\, d\mathbf{R}_1\, d\mathbf{R}_2 = n_p(n_p-1)N^2 = n(n-N) \tag{6}$$

where n_p is the average number of polymer molecules in unit volume, N is the total number of monomers in one polymer molecule, and the integrals are calculated over unit volume.

Now $n_1(\mathbf{R}_1,\mathbf{R}_2)$ can be written by the normalized intramolecular distribution function $f_{ij}(\mathbf{R})$ of the ith and jth monomers in the polymer

$$n_1(\mathbf{R}_1,\mathbf{R}_2) = n_p\sum_i\sum_j f_{ij}(\mathbf{R}) \qquad (i \neq j) \tag{7}$$

$$\int f_{ij}(\mathbf{R})\, d\mathbf{R} = 1 \qquad (i, j = 1, 2, ..., N) \tag{8}$$

Therefore the Fourier transform of $n_1(\mathbf{R}_1,\mathbf{R}_2)$ can be expressed by the molecular scattering factor of the polymer $P(q)$

$$n_1(q) = nNP(q) - n \tag{9}$$

$$P(q) = N^{-2}\sum_i^N\sum_j^N f_{ij}(q) \tag{10}$$

where $f_{ij}(q)$ is the Fourier transform of $f_{ij}(\mathbf{R})$. By the definition of $n_1(\mathbf{R}_1,\mathbf{R}_2)$, eq 7 and $n_1(q)$ do not contain the special terms with $i = j$

$$f_{ii}(\mathbf{R}) = \delta(\mathbf{R}) \qquad f_{ii}(q) = 1 \qquad (i = 1, 2, ..., N) \tag{11}$$

but eq 10 includes them. Here, $\delta(\mathbf{R})$ is the δ function.

Next, considering the strong electrostatic repulsion between the polyelectrolyte chains, we assume that the probability of finding two monomers from two different polymer molecules within a distance R_0 is negligible, but beyond this distance this probability is almost constant. Then if a monomer of a polymer A is somewhere nearer than R_0 to a point at coordinate $\mathbf{R}$, any monomer from polymers other than A is scarcely found at this point $\mathbf{R}$. Therefore, after introducing the origin of a coordinate system at the ith monomer of polymer A, one can write approximately the probability of not finding the monomer of the other polymers at $\mathbf{R}$ as (cf. Figure 1)

$$p_i(R) = C_0(l_0/R_0)\sum_j \int_{(S<R_0)} f_{ij}(\mathbf{R} + \mathbf{S})\, d\mathbf{S} \tag{12}$$

$$C_0 \leq 1 \tag{13}$$

where l_0 is the length of the chain per monomer, C_0 is a

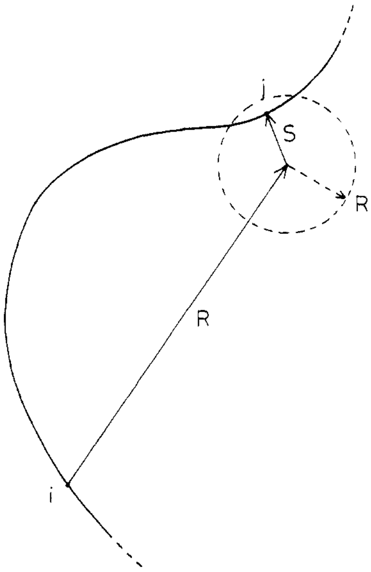

Figure 1.

constant, and the integral is carried out in a spherical region of radius R_0 ($S < R_0$). The factor $C_0(l_0/R_0)$ is added to eliminate an overestimation that comes from taking the sum over all the monomers of polymer A, because the spherical region can contain a chain segment of a mean length R_0 that consists of about R_0/l_0 monomers (cf. Appendix A). The same probability can be defined by introducing the origin at an arbitrary monomer of polymer A. So the average probability that no monomers of the other polymers are at a distance R from a monomer of polymer A is

$$p(R) = N^{-1}\sum_i p_i(R) \qquad (14)$$

The probability of the opposite event, that there is the possibility of finding a monomer of the other polymers at $\mathbf{R}$, is $1 - p(R)$, and the monomers are distributed with number density n in the solution. Therefore $n_2(\mathbf{R}_1,\mathbf{R}_2)$ can be given by (cf. eq 6)

$$n_2(\mathbf{R}_1,\mathbf{R}_2) = n^2(1 - p(R)) \qquad (15)$$

To calculate the Fourier transform of $p(R)$ we approximate the integral of eq 12 by another form physically more natural, introducing a function $\phi(S)$ as follows:

$$\int_{(S<R_0)} f_{ij}(\mathbf{R} + \mathbf{S})\, d\mathbf{S} = \int_{-\infty}^{+\infty} f_{ij}(\mathbf{R} + \mathbf{S})\phi(S)\, d\mathbf{S} \qquad (16)$$

$$\phi(S) = G_0 \exp(-S^2/R_0^2) \qquad (G_0 \approx 1) \qquad (17)$$

(cf. section IV). Using eq 10–17, one can calculate the Fourier transform of $n^2p(R)$ as

$$n^2p(q) = nNh\phi(q)P(q) \qquad (18)$$

$$h = \pi^{3/2}C_0G_0nl_0R_0^2 \qquad (19)$$

$$\phi(q) = \exp(-X^2/4) \qquad (20)$$

$$X = R_0q \qquad (21)$$

By eq 4 and 15, $I(q)$ of eq 2 can be given by the sum of $n + n_1(q)$ and $-n^2p(q)$. Therefore using eq 9 and 17, we obtain the equation for $I(q)$

$$I(q) = C_InNP(q)[1 - h\phi(q)] \qquad (22)$$

For the particular case $q = 0$ we have $P(0) = \phi(0) = 1$ (from eq 8, 10, 11, and 20), and eq 22 becomes

$$I(0) = C_InN[1 - h] \qquad (23)$$

This $I(0)$ should not be negative; hence

$$h \leq 1 \qquad (24)$$

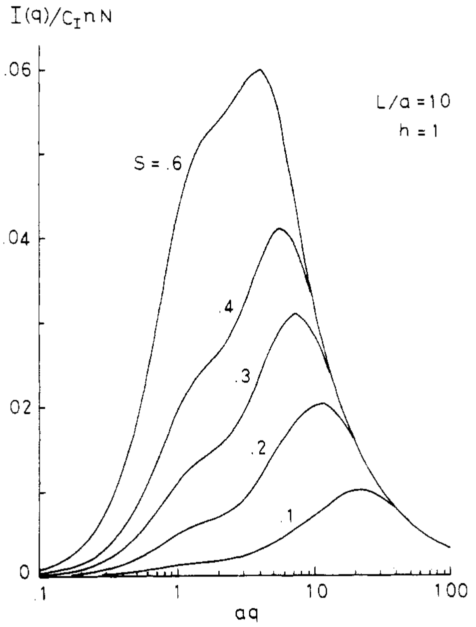

Figure 2. Scattering intensity curves of wormlike chain polymer solutions for $L/a = 10$, $h = 1$, and several values of $s = R_0/a$.

For various polymer models, $P(q)$ is generally a decreasing function of q, but $1 - \phi(q)$ is a monotonically increasing function converging to unity at large q. Therefore for very small h ($\ll 1$), $I(q)$ of eq 22 becomes a decreasing function similar to $P(q)$, but when h is large (~ 1), this $I(q)$ may have a maximum. In polyelectrolyte solutions without added salts the monomer interaction range can be supposed to be very large compared with nonelectrolyte polymer solutions, so that from eq 19 and 24 we can assume irrespectively of n

$$h = 1 \qquad (25)$$

(at sufficiently high concentration).

III. Calculation of Wormlike Chain Polymer Model

A. Scattering Curve. $P(q)$ and hence $I(q)$ of eq 22 can be calculated for particular chain models. We use here the result of the wormlike chain model in a previous paper,[17] assuming that the monomers are arranged on this mathematical model chain. According to this calculation, $P(q)$ is a function of two dimensionless variables aq and L/a, where a is the persistence length of this chain and L is the total length of the polymer. L can be written as

$$L = Nl_0 \qquad (26)$$

Using this $P(q)$ in eq 22, we calculated numerically $I(q)$ as functions of aq. Figures 2–4 illustrate these scattering curves for $L/a = 10$ and $h = 1$, 0.9, and 0.7, respectively. In the figures, s denotes the ratio

$$s = R_0/a \qquad (27)$$

B. Approximate Calculation. The previous calculation[17] shows for sufficiently large Lq

$$P(q) \approx \pi/Lq \qquad (Lq \gg 1) \qquad (28)$$

When this $P(q)$ is introduced into eq 22, we obtain an approximate equation valid for large Lq

$$I(q) = \pi C_Inl_0^{-1}R_0[1 - h\exp(-X^2/4)]/X \qquad (29)$$

The maximum point $X_m(h)$ as a function of h with this $I(q)$ can be determined numerically

$$X_m(h) = R_0q_m \qquad (30)$$

where R_0 is given by eq 19

$$R_0 = (\pi^{-3/2}h/C_0G_0l_0n)^{1/2} \qquad (31)$$

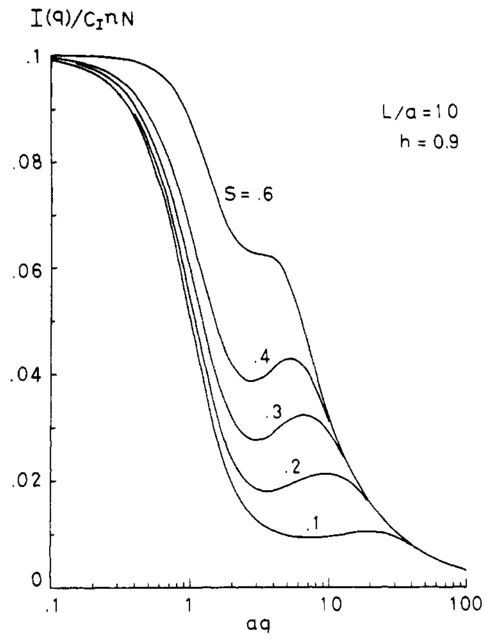

Figure 3. Scattering intensity curves of wormlike chain polymer solutions for $L/a = 10$, $h = 0.9$, and several values of $s = R_0/a$.

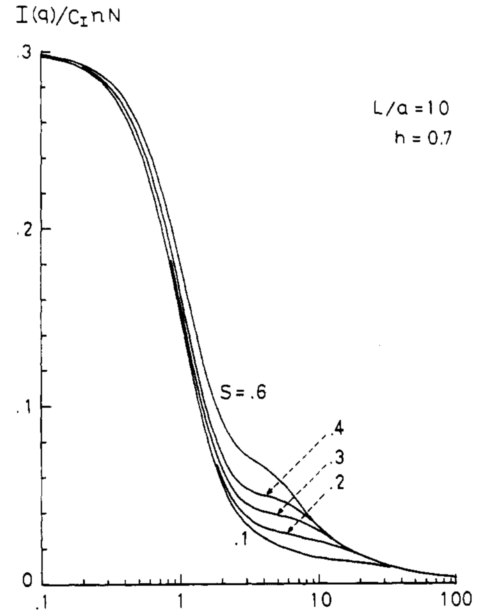

Figure 4. Scattering intensity curves of wormlike chain polymer solutions for $L/a = 10$, $h = 0.7$, and several values of $s = R_0/a$.

Therefore from eq 29–31 the maximum point q_m and the maximum intensity $I(q_m)$ can be written as

$$q_m = \pi^{3/4}(C_0 G_0 l_0)^{1/2} n^{1/2} h^{-1/2} X_m(h) \quad (32)$$

$$I(q_m)/n \propto R_0[1 - h \exp(-X_m(h)^2/4)]/X_m(h) \quad (33)$$

Particularly for $h = 1$, the numerical calculation gives

$$X_m(1) = 2.2418 \quad (34)$$

Since C_0, G_0, and l_0 are constants, in this case we have from eq 29–34 the qualitative results

$$R_0 \propto n^{-1/2} \quad (35)$$

$$q_m \propto n^{1/2} \quad (36)$$

$$I(q_m)/n \propto n^{-1/2} \quad (37)$$

In ordinary polymers with single carbon bonds in the main chain the monomer length is $l_0 = 2.5$ Å. Using this value and eq 34 in eq 32 and also assuming $C_0 = G_0 = 1$, q_m for $h = 1$ becomes

$$q_m = 8.36 n^{1/2} \text{ Å}^{-1} \quad (38)$$

These results are compared with the experimental results of small-angle neutron scattering of deuterated sodium poly(styrenesulfonate) solutions without added salts by Nierlich and others.[1] In Figures 5 and 6 the straight lines show the calculated values by eq 38 and 33, respectively, and the small dots show their experimental values. Figure 5 shows that eq 38 agrees well with the experimental values and Figure 6 shows that eq 33 qualitatively coincides with the experiments.

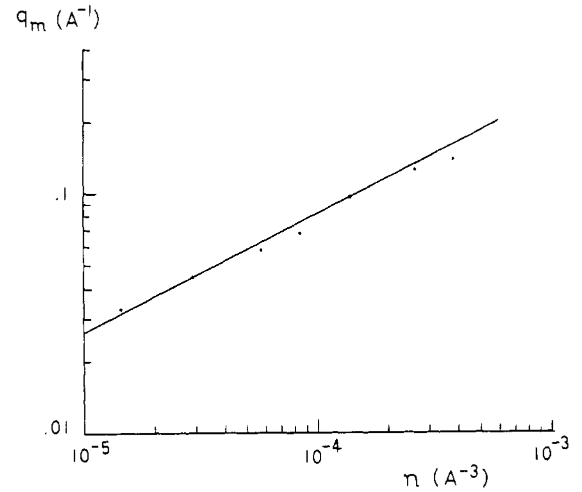

Figure 5. Comparison of the calculated values of q_m with the experimental values of ref 1.

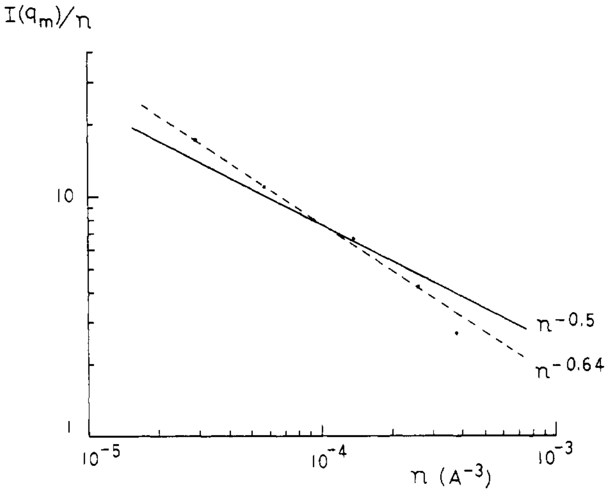

Figure 6. Comparison of the calculated values of $I(q_m)/n$ with the experimental values of ref 1.

IV. Results and Discussion

Figures 2–4 show that when $h = 1$, $I(q)$ has a maximum, but as h decreases, $I(q)$ increases at small aq. For sufficiently small h (<0.7), the maximum disappears and $I(q)$ becomes monotonically decreasing with q.

For $h = 1$ we derived the results of eq 35–38. The qualitative result of eq 36 has already been obtained by Hayter and others,[9] but eq 38 gives an absolute value. Furthermore, in this calculation these results are approximate ones, because they are derived by using two approximate equations: eq 28 for $P(q)$ and eq 17 for $\phi(S)$. Figure 7 shows that eq 28 is valid for only sufficiently large Lq; therefore a more correct calculation that uses the exact

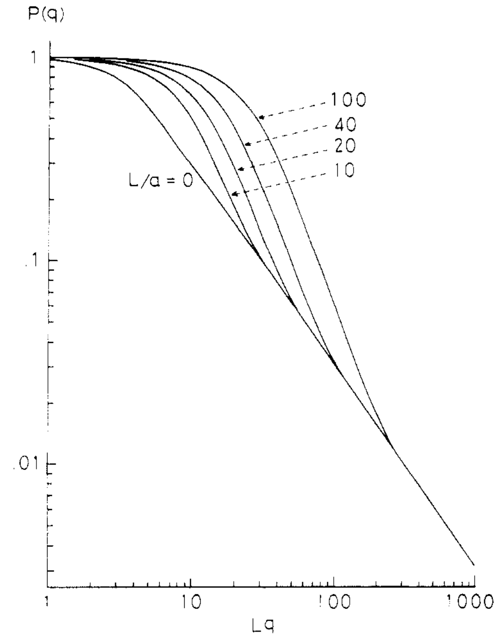

Figure 7. Molecular scattering factor of the wormlike chain polymer, $P(q)$, as a function of Lq (ref 17).

$P(q)$[17] may give a different concentration dependences of q_m and $I(q_m)$ when Lq_m is not large, and this result can be compared with the experimental values for very low molecular weight polymers.

The integral (12) or (16) can be calculated exactly by defining $\phi(S)$ as

$$\phi(S) = 1 \qquad \text{for } 0 \le S \le R_0 \tag{39a}$$

$$\phi(S) = 0 \qquad \text{for } S > R_0 \tag{39b}$$

and $\phi(q)$ becomes

$$\phi(q) = 3(\sin X - X \cos X)/X^3 \tag{40}$$

With this $\phi(q)$ in eq 18, h takes the same form as eq 19 and differs by only a numerical factor ($4\pi/3$ instead of $\pi^{3/2}$):

$$h = (4\pi/3)C_0G_0nl_0R_0^2 \tag{41}$$

However, the original assumption means only that $\phi(S)$ should be a decreasing function of S such that

$$\phi(S) = 1 \qquad \text{for } 0 \le S/R_0 \le 1 \tag{42a}$$

$$\phi(S) = 0 \qquad \text{for } S/R_0 > 1 \tag{42b}$$

Therefore this calculation used the convenient Gaussian form (17). It is mathematically clear that when $\phi(S)$ satisfies eq 42, it can be regarded as a function of S/R_0, so its Fourier transform $\phi(q)$

$$\phi(q) \propto \int_{-\infty}^{+\infty} \phi(S/R_0) \exp(-i\mathbf{q}\cdot\mathbf{S})\, d\mathbf{S} \tag{43}$$

depends on q only through $R_0q = X$, and h takes the same form as eq 19 or 41

$$h = C_hC_0G_0nl_0R_0^2 \qquad (C_h \approx 1) \tag{44}$$

where C_h is a numerical constant. Introducing this $\phi(q) = \phi(X)$ and eq 28 into eq 22, we obtain, in place of eq 29,

$$I(q) = \pi C_Inl_0^{-1}R_0[1 - h\phi(X)]/X \tag{45}$$

This equation is a function only of X like eq 29, and h is the same as in eq 19 except for the value of C_h. Consequently, if $\phi(X)$ is a monotonically decreasing function of X, we can derive from these the same qualitative results as eq 35–38. However, the absolute value of q_m will differ a little from eq 38. If $\phi(X)$ is not monotonically decreasing with X, as for example in eq 40, eq 45 may have more than two broad maxima. This case makes the discussion unnecessarily complex at present, so this is left to a future study.

Equation 19 shows that the interaction parameter h increases with the interaction distance R_0 and the concentration n. As mentioned in section II, for sufficiently strong interactions, h can always be assumed to be unity, irrespectively of n. From this assumption we derived the relations $R_0 \propto n^{-1/2}$, $q_m \propto n^{1/2}$, and $I(q_m)/n \propto n^{-1/2}$ (eq 35–39). But in the case of very weak interactions, where R_0 is very small and h is smaller than unity, both R_0 and h should be considered to depend on n, and their dependences on n cannot be determined by only the present assumptions. Therfore the n dependences of q_m and $I(q_m)$ also cannot be calculated from eq 32 and 33 only. A calculation of this case will be reported in another paper.

From eq 23 the assumption $h = 1$ for very strong interaction means that $I(q)$ has a very small value at $q \sim 0$. Thermodynamically $I(0)$ is related to the osmotic compressibility of the solution $\kappa = n^{-1}(\partial n/\partial \pi)_T$ (where π is the osmotic pressure of the solution)

$$I(0) \propto k_BTn^2\kappa \tag{46}$$

where k_B is the Boltzmann constant and T is the absolute temperature. Consequently this assumption agrees with the known fact that κ of polyelectrolyte solutions without added salts is very small compared with that for nonelectrolyte polymer solutions.

Appendix A

When a straight line intersects randomly a spherical surface of radius R_0, the mean length of the intercept is exactly R_0. Therefore when the polymer chain is rodlike and $|R|$ is sufficiently large, the mean number of monomers contained in the spherical domain is R_0/l_0, and we can assume $C_0 = 1$. But when the polymer chain is flexible, the mean number of monomers contained in the spherical domain is larger than R_0/l_0, and so we should assume $C_0 < 1$.

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