as c^{-1}, as expected for three-body contacts.

These conclusions appear to be consistent with the following interpretation: in some highly solvating solvents formation of "microcrystals", including chain segments and solvent molecules, are responsible for the gelation phenomenon at low temperature and long-range heterogeneities in solutions at higher temperature.

This interpretation is in complete contradiction with the hypothesis of Boyer et al.,[13] who propose a segment–segment interaction mechanism. They claim that such a point of view is consistent with the solubility parameters of the solvents. This type of analysis entails that poor solvents must promote gelation. It is then difficult to understand the fact that CS_2, which is well-known to be at room temperature a very good solvent for aPS (parameter $\chi = 0.4$) is precisely the better gelation solvent. In addition, results reported in this paper are hardly accountable by such a mechanism. Our results suggest that the local organization of the solvent molecules around the polymer plays the prominent role. This is not surprising if we consider that the partial specific volume of polymers in solution is strongly dependent on the form and the size of solvent molecules,[21,22] an effect that is never taken into consideration in the thermodynamic theories.

If our hypothesis is correct the existence of these "complex crystals" remains to be confirmed. Yet the possibility of polymer crystallization including solvent molecules has been recently shown by Tadokoro et al.[23] in the case of syndiotactic (methyl methacrylate). This polymer, which is otherwise uncrystallizable from the bulk, can form crystalline structures in the presence of solvent. There is strong evidence that the solvent participates in the crystalline lattice, hence forming a complex. Such a crystallization process might exist for atactic polystyrene as well. Guenet et al.[9] have suggested that the stereoregular sequences (isotactic or syndiotactic) could form "crystals". If one considers the stereoregularity data on aPS it appears that the mean length of such sequences is very low but it is not known so far what is the critical size of such "crystals" to be stable and accordingly to act as junction points.

Acknowledgment. We are indebted to Dr. D. Sarazin for his help in light scattering experiments.

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Small-Angle Scattering of Polyelectrolyte Solutions

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Received June 5, 1985

ABSTRACT: The calculation of the small-angle scattering of polyelectrolyte solutions in previous papers is extended to the case of dilute and low molecular weight polyelectrolyte solutions, using the same assumption that the probability of finding two monomers from different polymers within a distance R_0 is negligible. When the monomer concentration n is sufficiently high, R_0 is very small compared with the polymer length, and the maximum point of the scattering intensity, q_m, is given by the relation $q_m = 7.24n^{1/2}$ (Å^{-1}), where q is the absolute value of the scattering vector. As n decreases, the relation between q_m and n deviates from this relation, and for sufficiently small n it becomes $q_m = 3.97(n/N)^{1/3}$ (Å^{-1}), where N is the degree of polymerization of the polyelectrolyte. The result agrees well with experimental results of small-angle neutron and X-ray scattering and of light scattering of sodium poly(styrenesulfonate) solutions without added salts.

I. Introduction

In previous papers[1] the small-angle scattering of polyelectrolyte solutions was calculated, using a wormlike chain polymer model.[2] With the assumption of a strong electrostatic repulsion between the polymer chains, this theory can explain the results from small-angle neutron and X-ray scattering experiments that the scattering intensity of the polyelectrolyte solutions has a broad maximum in no added salts,[3-9] and that this maximum point q_m is proportional to the square root of the monomer concentration n.[3,6] Although these qualitative results have already been obtained theoretically by Hayter and others,[8] and by the recent paper,[10] this calculation further determined the absolute value of q_m

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

which agrees well with the experimental values,[3] where q is the absolute value of the scattering vector $\mathbf{q}$

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$$q = (4\pi/\lambda)\sin(\theta/2) \qquad (2)$$

λ and θ are the wavelength and the scattering angle, respectively.

To derive these results, the calculation assumed tacitly that the monomer concentration is sufficiently high, and the average distance between neighboring polymer chains or the assumed characteristic interaction distance R_0 is very small compared with the length of the polymer. Consequently for very dilute polyelectrolyte solutions or for solutions of very low molecular weight polymers, this result may not agree with experimental values. In fact a recent small-angle X-ray scattering experiment[11] of sodium poly(styrenesulfonate) solutions shows that q_m has a weaker concentration dependence than the relation of $q_m \propto n^{1/2}$ in a very dilute concentration range and in very low molecular weight polymers.

The following calculcation extends the previous method to these cases, eliminating the above assumption ($R_0 \ll$ polymer length).

II. Calculation of Small-Angle Scattering Intensity

In the previous papers[1] the small-angle scattering intensity per unit volume of the polyelectrolyte solutions is calculted from the equation

$$I(q) = C_I\left[n + \int_{-\infty}^{+\infty} (n(\mathbf{R}_1,\mathbf{R}_2) - n^2)\exp(-i\mathbf{q}\cdot\mathbf{R})\,d\mathbf{R}\right] \qquad (3)$$

$$\mathbf{R} = \mathbf{R}_2 - \mathbf{R}_1 \qquad (4)$$

$$n(\mathbf{R}_1,\mathbf{R}_2) = n_1(\mathbf{R}_1,\mathbf{R}_2) + n_2(\mathbf{R}_1,\mathbf{R}_2) \qquad (5)$$

where C_I is a constant, n is the average number of monomers in unit volume, and $n_1(\mathbf{R}_1,\mathbf{R}_2)$ and $n_2(\mathbf{R}_1,\mathbf{R}_2)$ are the two-body distribution functions of the monomers of the same polymer and those of different polymers, respectively. In eq 3 the Fourier transform of $n_1(\mathbf{R}_1,\mathbf{R}_2)$ can be written by the molecular scattering factor $P(q)$ of the polymer

$$n + \int_{-\infty}^{+\infty} n_1(\mathbf{R}_1,\mathbf{R}_2)\exp(-i\mathbf{q}\cdot\mathbf{R})\,d\mathbf{R} = nNP(q) \qquad (6)$$

$$P(q) = N^{-2}\sum_i^N\sum_j^N f_{ij}(q) \qquad (7)$$

where N is the total number of monomers in one polymer molecule and $f_{ij}(q)$ is the Fourier transform of the normalized intramolecular distribution function of the distance between the ith and jth monomers, $f_{ij}(R)$.

Next, in order to determine $n_2(\mathbf{R}_1,\mathbf{R}_2)$, the theory assumed that the probability of finding two monomers from two different polymer molecules within a distance R_0 is negligible, owing to the strong electrostatic repulsion between the polymer chains. This assumption implies that if a polymer chain intersects a spherical surface of radius R_0 any monomer of the other polymer chains cannot be found at the center of this spherical domain. Therefore by the introduction of the origin of a coordinate system at the ith monomer of a polymer, the probability of not finding the monomer of the other polymers at point $\mathbf{R}$ was written as

$$p_i(\mathbf{R}) = C_0\nu^{-1}\sum_j^N \int f_{ij}(\mathbf{R} + \mathbf{S})\,d\mathbf{S} \qquad (S < R_0) \qquad (8)$$

$$C_0 < 1 \qquad \nu = R_0/l_0 \qquad (9)$$

where C_0 is a constant, l_0 is the length of the polymer chain per monomer, and the integral is carried out over a spherical domain of radius R_0. Equation 8 calculates all the chain configurations that intersect the spherical domain of radius R_0 with the center at distance $\mathbf{R}$ from its monomer i. But as mentioned previously,[1] when the polymer chain intersects this domain, the chain segment intercepted by the spherical surface consists of about $\nu = R_0/l_0$ monomers; therefore the sum $\sum^N{}_j$ of the integrals, which is taken over all N monomers in the molecule, includes ν times the same chain configuration, and the factor ν^{-1} eliminates this multiple estimation.

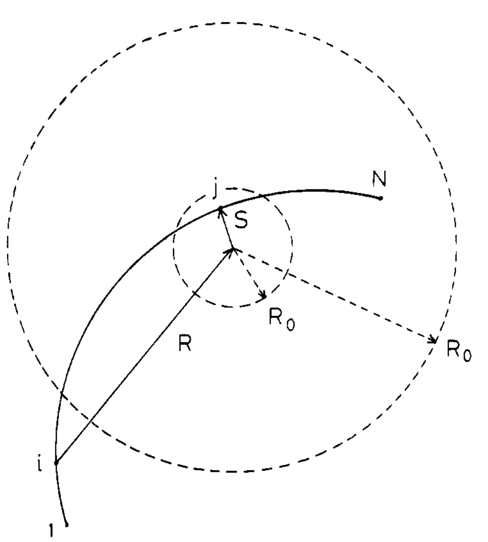

Figure 1. Spherical domain of integration in eq 8. The dashed curves show two cases for small R_0 ($\ll L$) and for large R_0 ($\sim$L).

This estimated value of ν is however correct only when the radius R_0 is sufficiently small compared with the length of the polymer L, because this is obtained by neglecting the chain ends, namely by assuming L to be infinite.[1] The previous calculation shows that R_0 increases with decreasing monomer concentration n as $R_0 \propto n^{-1/2}$. So for very low concentration or for very low molecular weight polymers, R_0 is not small compared with L. In such cases the chain segment intercepted in the spherical surface can contain the chain ends; hence its average length or the average number of monomers it contains depends not only on L but also on the curvature of the chain (cf. Figure 1).

Although the calculation of this average segment length is generally complex, it becomes especially simple for straight rodlike polymers, and we can calculate it for this polymer as

$$L_s = L/(1 + (3/4)L/R_0) \qquad (10)$$

For very long L or for very small R_0 this becomes

$$L_s = (4/3)R_0 \qquad (L/R_0 \gg 1) \qquad (11)$$

(This value is larger by the factor $^4/_3$ than the previous R_0 value.[1]) And for very small L or for very large R_0, it tends to a reasonable value

$$L_s \sim L \qquad (L/R_0 \ll 1) \qquad (12)$$

Thus using this L_s, we can assume a new value of ν which is more correct than eq 9

$$\nu = L_s/l_0 \qquad (13)$$

With this assumption, the equation of the scattering intensity can be derived by the same procedure as the previous case.[1] That is, inserting eq 13 into eq 8 and averaging this $p_i(\mathbf{R})$ over all N monomers in the molecule, we obtain the average probability that no monomer of the other polymers are at distance $\mathbf{R}$ from a monomer of the polymer

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

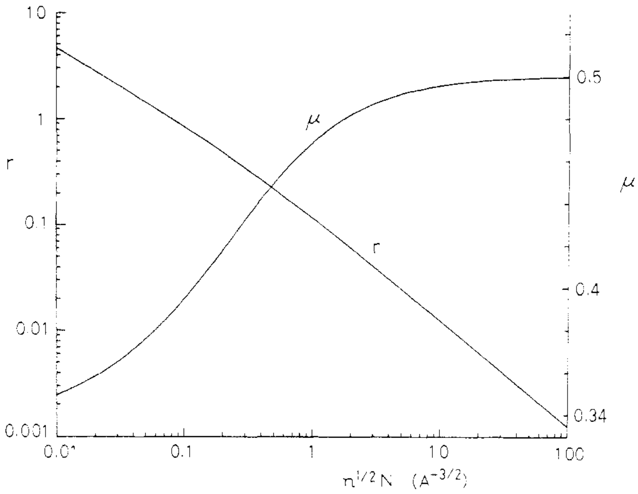

Figure 2. μ and r as functions of $n^{1/2}N$ by eq 36–40 and 44.

The opposite event that the polymer chain which passes through the origin does not intersect the spherical surface occurs with probability $1 - p(\mathbf{R})$. Therefore assuming that the monomers are found at $\mathbf{R}$ with probability n under this condition, we can write $n_2(\mathbf{R}_1,\mathbf{R}_2)$ as

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

The Fourier transform of $n_2(\mathbf{R}_1,\mathbf{R}_2) - n^2 = -n^2p(\mathbf{R})$ can be calculated in the same way as the previous case[1]

$$-n^2\int_{-\infty}^{+\infty} p(\mathbf{R}) \exp(-i\mathbf{q}\cdot\mathbf{R})\, d\mathbf{R} = nNh\phi(q)P(q) \tag{16}$$

$$h = \pi^{3/2}C_0G_0nl_0R_0^3/L_s \qquad G_0 \approx 1 \tag{17}$$

$$\phi(q) = \exp(-X^2/4) \tag{18}$$

$$X = R_0q \tag{19}$$

Therefore using eq 6 and 16 in eq 3, we can write the scattering intensity (per unit volume of the solution) also in the same form as the previous one[1]

$$I(q) = C_InNP(q)[1 - h\phi(q)] \tag{20}$$

The result differs from the previous case by only a constant factor R_0/L_s in eq 17 for an interaction parameter h. With eq 10 in eq 17, h becomes

$$h = (3/4)\pi^{3/2}C_0G_0l_0nR_0^2(1 + (4/3)(R_0/L)) \tag{21}$$

In the previous case h is given by[1]

$$h = \pi^{3/2}C_0G_0l_0nR_0^2 \tag{22}$$

III. Maximum Point q_m of Scattering Intensity

We consider the same stiff-chain polymer model as in the previous papers.[1] For sufficiently large q, $P(q)$ of this chain polymer becomes[3]

$$P(q) = \pi/Lq \qquad Lq \gg 1 \tag{23}$$

where L can be given by

$$L = Nl_0 \tag{24}$$

By the introduction of this $P(q)$ into eq 20, $I(q)$ becomes

$$I(q) = \pi C_Il_0^{-1}nR_0[1 - h \exp(-X^2/4)]/X \tag{25}$$

As mentioned in the previous papers,[1] for polyelectrolyte solutions without added salts, h can be assumed to be very close to unity

$$h \lesssim 1 \tag{26}$$

and $I(q)$ has a maximum point q_m. Denoting by $X_m(h)$ the maximum point of eq 25, we can write q_m by eq 19 as

$$q_m = X_m(h)/R_0 \tag{27}$$

$$X_m(1) = 2.2418 \tag{28}$$

Therefore to calculate q_m, we determine R_0 from eq 21 and 26. Equation 21 can be written as

$$r^2(r + 3/4) - 3a^2/4 = 0 \tag{29}$$

$$r = R_0/L \tag{30}$$

where a is given by (from eq 21 and 24)

$$a^2 = a_0^2l_0^{-3}n^{-1}N^{-2} \propto n^{-1}N^{-2} \tag{31}$$

$$a_0^2 = 4h/3\pi^{3/2}C_0G_0 \tag{32}$$

A. Concentration and Molecular Weight Dependences of q_m. By assuming the relation

$$r \propto a^{2\mu} \tag{33}$$

we can write R_0 and q_m from eq 30–33 and 27 as

$$R_0 = Lr \propto n^{-\mu}N^{-2\mu+1} \tag{34}$$

$$q_m \propto n^{\mu}N^{2\mu-1} \tag{35}$$

and μ can be calculated from eq 29 as

$$\mu = d(\log r)/d(\log a^2) = 2^{-1}(1 + 4r/3)/(1 + 2r) \tag{36}$$

The cubic equation (29) can be solved as

$$r = a/[\cos(\phi/3) + 3^{-1/2} \sin(\phi/3)] \tag{37}$$

$$\phi = \sin^{-1}(2(3^{1/2})a) \tag{38}$$

for $a^2 \leq 12^{-1}$ and

$$r = (3^{1/2}/2)a/\cosh(\psi/3) \tag{39}$$

$$\psi = \cosh^{-1}(2(3^{1/2})a) \tag{40}$$

for $a^2 \geq 12^{-1}$. Therefore n and N dependences of R_0 and q_m can be calculated from eq 31 and 34–40.

Particularly when $n^{1/2}N$ is very large, we obtain from these $a \ll 1$, $r \ll 1$, and

$$\mu = 1/2 \qquad R_0 \propto n^{-1/2} \qquad q_m \propto n^{1/2} \tag{41}$$

and when $n^{1/2}N$ is very small, we obtain $a \gg 1$, $r \gg 1$, and

$$\mu = 1/3 \qquad R_0 \propto (n/N)^{-1/3} \qquad q_m \propto (n/N)^{1/3} \tag{42}$$

In the general case, μ can be calculated from eq 36–40 for a given value of a.

In ordinary polymers with single carbon bonds in the main chains, the monomer length can be chosen as l_0 = 2.5 Å. Using this value and assuming $C_0 = G_0 = 1$, we obtain a_0 and a for $h = 1$ from eq 31 and 32 as

$$a_0 = 0.4893 \tag{43}$$

$$a = 0.1238/n^{1/2}N \tag{44}$$

Using this a in eq 36–40, we can obtain r and μ as a function of $n^{1/2}N$. Figure 2 shows these results.

B. Absolute Value of q_m. Using eq 37–40, 30, 31, and 24 in eq 27, we can write q_m as

$$q_m = X_m(h)a_0^{-1}l_0^{1/2}n^{1/2}y \tag{45}$$

where y is defined by

$$y = \cos(\phi/3) + 3^{-1/2} \sin(\phi/3) \qquad (\text{for } a^2 < 12^{-1}) \tag{46}$$

$$y = 2(3^{-1/2}) \cosh(\psi/3) \qquad (\text{for } a^2 > 12^{-1}) \tag{47}$$

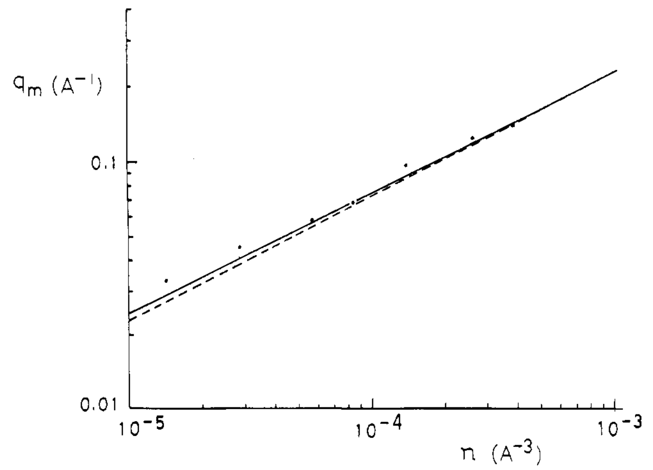

Figure 3. Comparison of calculated values of q_m with its experimental values by small-angle neutron scattering of deuterated sodium poly(styrenesulfonate) solutions without added salts (obtained by Nierlich and others[3]) M = 72 000, N = 343. The solid and dashed curves show respectively the theoretical values of q_m by eq 48 and 49 and by eq 50 for infinite $n^{1/2}N$.

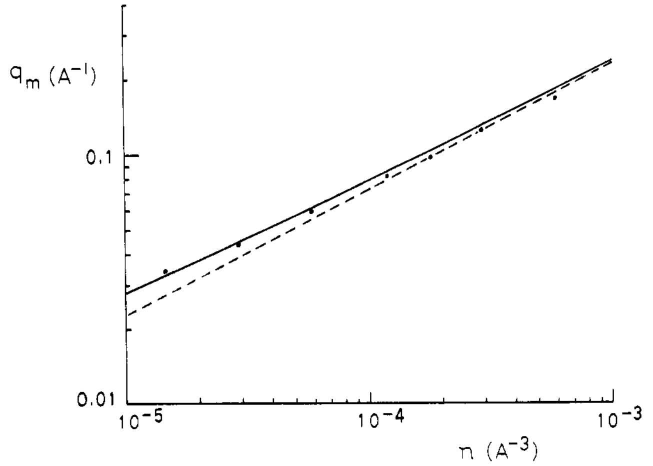

Figure 4. Comparison of calculated values of q_m with its experimental values by small-angle X-ray scattering of sodium poly(styrenesulfonate) solutions without added salts (obtained by Kaji and others[11]) M = 18 000, N = 87.4. The solid and dashed curves show respectively the theoretical values of q_m by eq 48 and 49 and by eq 50 for infinite $n^{1/2}N$.

Then under the assumption of the same values of a_0 and l_0 for ordinary polymers as in section A and also $X_m(1)$ of eq 28, eq 45 gives the absolute value of q_m as

$$q_m = 7.24n^{1/2}[\cos(\phi/3) + 3^{-1/2}\sin(\phi/3)] \quad (\text{Å}^{-1}) \tag{48}$$

for high concentration ($a^2 \leq 12^{-1}$) and

$$q_m = 8.36n^{1/2}\cosh(\psi/3) \quad (\text{Å}^{-1}) \tag{49}$$

for low concentration ($a^2 \geq 12^{-1}$).

When $n^{1/2}N$ becomes infinity, a and ϕ tend to zero, and eq 48 gives

$$q_m = 7.24n^{1/2} \quad (\text{Å}^{-1}) \tag{50}$$

For a particular concentration of $a^2 = 12^{-1}$, we can obtain $\phi = \pi/2$ and $\psi = 0$, and eq 48 and 49 become

$$q_m = 8.36n^{1/2} \quad (\text{Å}^{-1}) \tag{51}$$

Also when $n^{1/2}N$ becomes zero, a tends to infinity, and using eq 40 and 44 in eq 49, we can obtain

$$q_m = 3.97(n/N)^{1/3} \quad (\text{Å}^{-1}) \tag{52}$$

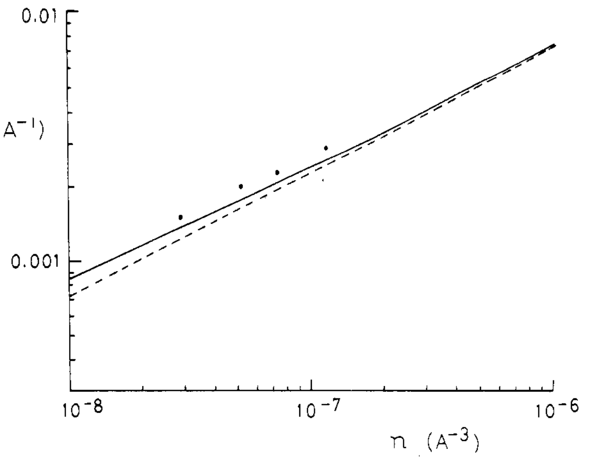

Figure 5. Comparison of calculated values of q_m with its experimental values by light scattering of sodium poly(styrenesulfonate) solutions without added salts (obtained by Drifford and Dalbiez[12]) M = 780 000, N = 3786. The solid and dashed curves show respectively the theoretical values of q_m by eq 48 and 49 and by eq 50 for infinite $n^{1/2}N$.

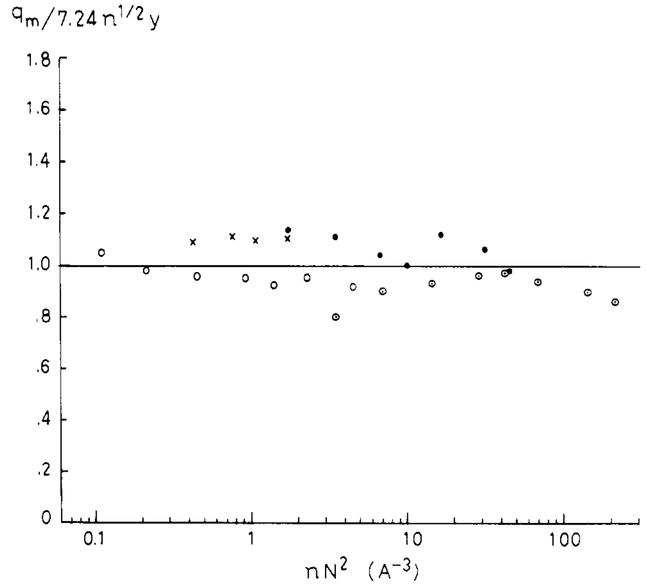

Figure 6. Comparison of the theoretical value of $q_m/7.24n^{1/2}y$ (=1) with its experimental values: (●) small-angle neutron scattering of deuterated sodium poly(styrenesulfonate) solutions (M = 72 000, N = 343),[3] (○) and (⊙) small-angle X-ray scattering of sodium poly(styrenesulfonate) solutions (M = 18 000, N = 78.4 and M = 100 000, N = 485),[11] and (×) light scattering of the same solutions (M = 78 000, N = 3786).[12] The solid line shows the theoretical value.

IV. Comparison with Experimental Results

The results in secretion III are derived by assuming eq 23 and hence $Lq_m \gg 1$. For smaller values of Lq, $P(q)$ has a more complex form than eq 23. As the concentration decreases, the experimental value of Lq_m becomes small. Consequently for very short chain polymers or for very low concentrations, $Lq_m \lesssim 1$, and the n and N dependences of q_m may have more complex forms than the present results.

Figures 3–6 show comparisons of the calculated results with experimental values which satisfy the condition $Lq_m \gg 1$. In Figures 3–5 the full curves and the broken lines show respectively the theoretical values of q_m by eq 48 and 49 and by eq 50. The small dots show the experimental values of the small-angle neutron scattering of deuterated sodium poly(styrenesulfonate) solutions (M = 72 000 Figure 3),[3] the small-angle X-ray scattering of sodium poly(styrenesulfonate) solutions (M = 18 000 Figure 4),[11] and the light scattering of sodium poly(styrenesulfonate) solutions (M = 780 000 Figure 5).[12]

The calculation of section III predicts that the experimental values of

$$A = q_m/7.24n^{1/2}y \tag{53}$$

becomes unity irrespectively of n and N, where y is the value given by eq 46 and 47. The experimental value of y can be obtained from n and N, using eq 38 or 40 and 44. Figure 6 shows comparison of this theoretical value (=1) with the experimental values.[3,11,12] Both values are in coincidence within an error of about 10%.

V. Concluding Remarks and Discussion

As we have seen in section III, with decreasing monomer concentration n, the n and N dependences of the calculated q_m change from $q_m \propto n^{1/2}$ to $q_m \propto (n/N)^{1/3}$, and this tendency coincides with the experimental results.[3,11,12] This proves the validity of the theoretical model and assumption.

This calculation shows that this change of the n dependence of q_m is continuous with n, and there is no distinct boundary concentration. However, as $a^2 \gg 1$ or $a^2 \ll 1$, r is proportional to $a^{2/3}$ or to a from eq 29. Therefore we can define a rough boundary concentration n_c by

$$a^2 = 1 \tag{54}$$

Using eq 31 and 32 in this equation, this n_c becomes

$$n_c = a_0^2 l_0^{-3} N^{-2} \tag{55}$$

Assuming the values $a_0 = 0.4893$ and $l_0 = 2.5$ Å for ordinary polymers, we have

$$n_c N^2 = 0.01532 \qquad (\text{Å}^{-3}) \tag{56}$$

or

$$n_c L^2 l_0 = 0.2394 \tag{57}$$

For instance, for sodium poly(styrenesulfonate) molecule of molecular weight $M = 4600$ ($N = 22.3$) and that of $M = 8000$ ($N = 38.8$), this n_c becomes 3.08×10^{-5} Å^{-3} = 10.5 g/L and 1.02×10^{-5} Å^{-3} = 0.350 g/L, respectively. By eq 55 this n_c is proportional to M^{-2}, so for the polymers of larger molecular weight it has much smaller values than these.

Since L_s of eq 10 is calculated for the straight rodlike polymer, the present result is applicable only to this polymer. It is however considered that even in case of a flexible wormlike chain this intercepted segment length should coincide with that of a straight rodlike polymer so long as R_0 is sufficiently small compared with the mean radius of curvature of the chain, but that it approaches to L when R_0 becomes sufficiently large compared with the mean polymer radius $\langle R \rangle$. Therefore, for large R_0, L_s of this polymer can be approximately assumed as

$$L_s = L/(1 + (3/4)\langle R \rangle / R_0) \tag{58}$$

in place of eq 10. In the wormlike chain $\langle R \rangle$ is generally smaller than L, so this L_s is larger than that of eq 10. On the other hand eq 17 gives

$$R_0 \propto L_s^{1/3} \tag{59}$$

because h is assumed to be constant (=1), and using this in eq 27, we obtain

$$q_m \propto R_0^{-1} \propto L_s^{-1/3} \tag{60}$$

This result concludes that q_m for a wormlike chain polymer is smaller than that of a rodlike polymer with the same length.

Acknowledgment. The author thanks Dr. K. Kaji of Institute for Chemical Research of Kyoto Univeristy for providing experimental data of the small-angle X-ray scattering before publication.

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