Particle Scattering Function and the Radius of Gyration for a Broken Rodlike Chain Having a Length Distribution of Constituents

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In the previous paper,[1] the particle scattering factor of a broken rodlike chain was calculated. In the theory, the chain is assumed to be consisted of several rods alternatively joined by sequences of short rods or by flexible random coils. From comparison between the calculated results and the experimental data of the poly(sodium D-glutamate) in the helix-to-coil transition region,[2] the average helical sequence lengths of the polypeptide could be determined. It appears that the calculation procedure is useful for the conformational analysis of polypeptides and also for that of isotactic polystyrene in the gel state.[3]

In the model, however, all constituent rods as well as all short-rod sequences (random coils) were assumed to have equal lengths. In practice, the broken rodlike chains do not always have equal lengths of constituents. For example, polypeptides clearly have a distribution with respect to the lengths of the constituents. In the theory of Zimm–Bragg on the helix-to-coil transition of polypeptides, the distribution is automatically taken into account in their theory. The purpose of the present paper is to derive the particle scattering function and the radius of gyration of broken rodlike chains by the method proposed, taking into account the distributions in the length of the constituent rods and short rods (random coils).

As shown in Figure 1, the present broken rodlike chain is assumed to be composed of $N-1$ rods (R-region) alternatively joined by N sequences of short rods (random coils) (C-region). Free rotation is allowed between neighboring short rods and between a rod and a neighboring short rod. When all sequences of short rods as well as rods are numbered in succession, the ith sequence of short rods ($i = 1$ to N) includes m_i monomer units of effective length a and the jth rod ($j = 1$ to $N-1$) includes n_j monomer units of length a_1. If $m_i = m$ and $n_j = n$, the present model is reduced to the former model handled in the previous paper.[1]

The total scattering intensity, $\langle R_\theta \rangle$, is given as a sum of $\langle R_\theta \rangle_{RR}$, $\langle R_\theta \rangle_{CC}$, and $\langle R_\theta \rangle_{RC}$, where $\langle R_\theta \rangle_{RC}$, for example, means the scattering intensity when one scatterer is located in the R-region and another in the C-region:

$$\langle R_\theta \rangle = \langle R_\theta \rangle_{RR} + \langle R_\theta \rangle_{CC} + \langle R_\theta \rangle_{RC} \quad (1)$$

Following the same computational procedure as the previous one,[1] $\langle R_\theta \rangle_{RC}$, for example, is given by

$$\langle R_\theta \rangle_{RC} = 2\alpha W(\alpha) \sum_{k=1}^{N-1} \sum_{i=k}^{N-1} \left\{ \left(\frac{1-\mu^{m_k}}{1-\mu} \right) \times (A_i \Lambda(\beta_i))(\mu^{m_{k+1}} \mu^{m_{k+2}} \ldots \mu^{m_i})(\nu_k \nu_{k+1} \ldots \nu_{i-1}) + \left(\frac{1-\mu^{m_{i+1}}}{1-\mu} \right) \times (A_k \Lambda(\beta_k))(\mu^{m_{k+1}} \mu^{m_{k+2}} \ldots \mu^{m_i})(\nu_{k+1} \nu_{k+2} \ldots \nu_i) \right\} \quad (2)$$

where the definitions of h, α, μ, and $W(\alpha)$ and also A_i, β_i, ν_i, and $\Lambda(\beta_i)$ are given in the previous paper,[1] except a running index i.

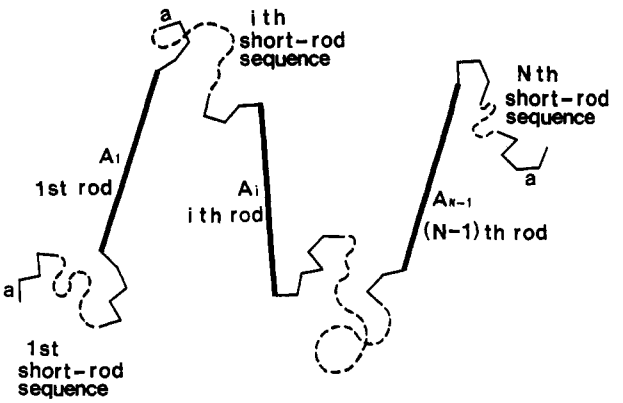

Figure 1. Broken rodlike chain represented by $N-1$ rods with each length $a_1 n_j$ ($j = 1$ to $N-1$) alternatively joined by N sequences of short rods with each length am_i ($i = 1$ to N).

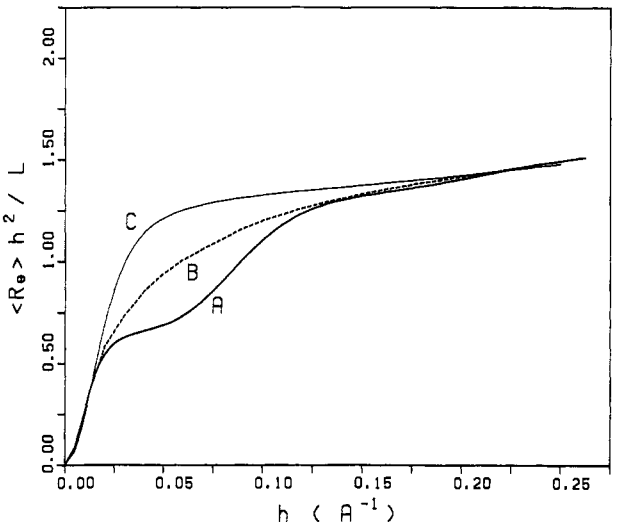

Figure 2. Comparison between broken rodlike chains (A) having constituents of equal lengths and (B) having a distribution with respect to the lengths of the constituents in the normalized Kratky plot. $T = 800$, $a_1 = 1.5$ Å, $a = 8$ Å, $N-1 = 10$ and $g = 0.5$. Symbol C represents the plot for a wormlike chain having a persistence length of 4.5 Å and a contour length of 800 × 3.5 = 2800 Å.

In the present computation, it is assumed that all constituent rods as well as all sequences of short rods can take all possible lengths allowed when N, a total number of monomer units (T), and a rod fraction (g) are given. The computation is carried out by the Monte Carlo method. In Figure 2 is shown the normalized Kratky plot for the present model, in comparison with that for the former model.[1] Employed molecular parameters are $T = 800$, $a_1 = 1.5$ Å, $a = 8$ Å, $N-1 = 10$ and a rod fraction (g) = 0.5. Any constituent rod was assumed to be consisted of more than three monomer units.

Although the former model (curve A) and the present model (curve B) can be discriminated at a moderate scattering vector region, they behave similarly at both sides of this region. Thus, it is suggested that the scattering behavior at a higher scattering vector region, in which the average helical sequence lengths were determined in the previous paper,[2] may be insensitive to the length distribution of constituents. That is, it may be concluded that the local conformation of poly(sodium D-glutamate) in aqueous solution estimated previously[2] is sufficiently reliable.

In the above calculation, the distribution in the constituent lengths is incorporated into the model by the Monte Carlo method. When this distribution is expressed

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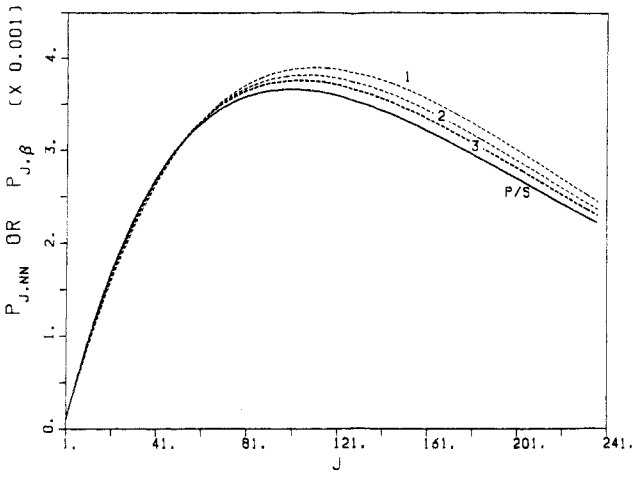

Figure 3. Comparison between $P_{j,NN}$ and $P_{j,\beta}$ at $g = 0.5$. See text for the meanings of $P_{j,NN}$ and $P_{j,\beta}$. A solid curve with symbol P/S denotes $P_{j,NN}$ for $\sigma = 0.0001$, and dotted curves with numbers 1–3 denote $P_{j,\beta}$ for T = 2000, 3000, and 5000, respectively.

in terms of the probability $P_{j,\beta}$ that the constituent rod to which a residue in a rod picked up at random belongs is j units long, the analytical expression for $P_{j,\beta}$ at $g = 0.5$ is given by[4]

$$x = j/(T/2) \tag{3}$$

$$f(j) = (N-1)(1-x)^{N-2} \tag{4}$$

$$P_{j,\beta} = \frac{jf(j)}{\sum_{j=1}^{T/2} jf(j)} = \frac{(N-1)N}{(T/2)} x(1-x)^{N-2} \tag{5}$$

where $f(j)$ is the probability that a constituent rod picked up at random will be j units long. A corresponding probability in the theory of Zimm–Bragg is given by $P_{j,NN}$. According to the theory of Poland and Scheraga,[5] $P_{j,NN}$ for a polypeptide having infinite T is

$$P_{j,NN} = \left(\frac{\sigma}{(1+\sigma^{1/2})}\right)\left(\frac{j}{(1+\sigma^{1/2})^j}\right) \tag{6}$$

where σ is a helix-initiation parameter. From the computational comparison between eqs 5 and 6 as shown in Figure 3, it can be seen that the dependence of $P_{j,\beta}$ on j is almost coincident with that of $P_{j,NN}$ on j, since N is related to σ through the relation, $N - 1 = (T/2)\sigma^{1/2}$.

Curve C in Figure 2 represents the calculated result for a wormlike chain[6] having a single persistence length of 4.5 Å. The wormlike chain model can also represent the particle scattering function of polypeptides, so far as we are concerned in the scattering behavior at a lower and a higher scattering vector regions.

Here, in addition, I note that the mean-squared radius of gyration, $\langle R_g^2 \rangle$, is also calculated for the present broken rodlike chain model. The calculated results are found to be in good agreement with one predicted by the Nagai theory[7,8] derived based on the Zimm–Bragg model. In the small scattering vector region such as $\langle R_g^2 \rangle h^2 \ll 1$, we have

$$\frac{\langle R_\theta \rangle}{L^2} = 1 - \frac{h^2 \langle R_g^2 \rangle}{3} + \dots \tag{7}$$

That is, from the initial slope of the plot of $\langle R_\theta \rangle / L^2$ against h^2, we can evaluate $\langle R_g^2 \rangle$. Analytical expression[9] of $\langle R_g^2 \rangle$ can also be obtained by the method of Zimm and Stockmayer.[10]

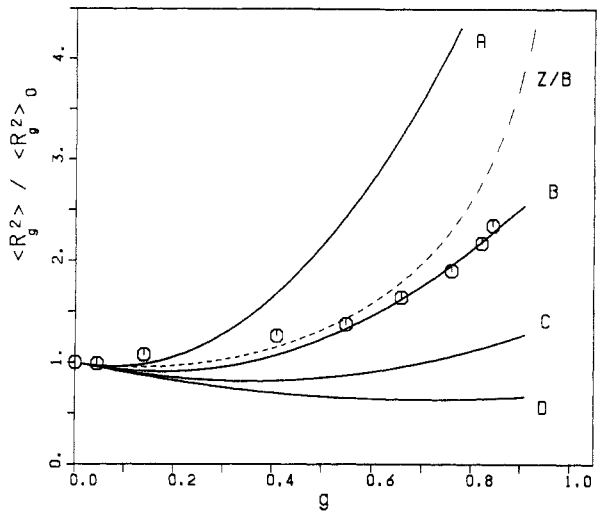

Figure 4. Dependence of the reduced radius of gyration on g for PBLG in a mixture of dichloroacetic acid and cyclohexanol.[11] Solid curves are theoretical ones for a broken rodlike chain with a = 16 Å,[11] a_1 = 1.5 Å,[11] T = 2180,[11] and N = 5 (A), 12 (B), 25 (C), and 50 (D). A dotted curve (Z/B) is a theoretical one for the Zimm–Bragg model with $\sigma = 0.0001$,[11] with the same a and a_1 as employed in the broken rodlike chain.

In Figure 4, the ratio of $\langle R_g^2 \rangle$ thus calculated to the radius of gyration of a pure random-coil chain, $\langle R_g^2 \rangle_0$, is plotted against g for poly(γ-benzyl L-glutamate) (PBLG; T = 2180) in a mixture of dichloroacetic acid and cyclohexanol.[11] Solid and dotted curves are theoretical ones for the present model and for the Zimm–Bragg model, respectively. It is seen that the present model can reproduce the observed behavior as astisfactorily as the Zimm–Bragg model if $N = 12$ is assumed.

According to the Nagai theory,[7,8] the average number of helical sequences, $N - 1$, is given by

$$N - 1 = \delta g^{1/2}(1-g)^{1/2} + g(2g-1) \tag{8}$$

$$\delta = (T)\sigma^{1/2} \tag{9}$$

under a condition that $T \gg 1$, $\sigma^{1/2} \ll 1$ and $T\sigma^{1/2} > 2$. Here, σ is 0.0001 for PBLG.[11] N (=12) evaluated for PBLG by the present model well agrees with the average N (=12) in the Zimm–Bragg model, estimated by eq 8 at a midpoint of the helix-to-coil transition ($g = 0.5$). Moreover, it is to be noted that such a good agreement between the present model and the Zimm–Bragg model is also found for poly(N^5-3-hydroxypropyl L-glutamine) (T = 1970) in a mixture of water and methanol.[12]

Finally, I stress that the polypeptides in the helix-to-coil transition region can be well explained by the theory of Zimm and Bragg, but there are some examples of broken rodlike chains which cannot be explained by their theory.

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Supplementary Material Available: Computational result of the scattering intensity for a broken rodlike chain having a length distribution of constituents (2 pages). Ordering information is given on any current masthead page.

References and Notes

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