effects may occur in other types of polymer single crystals.

Finally, it is worth noting that these observations may be of some importance in crystal structure analysis of polymers. The exact symmetry of a crystal is crucial for the determination of its structure. If the crystals contain microdomains, the X-ray or electron diffraction pattern may contain "mixed" symmetry elements leading to an incorrect crystal structure analysis.

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Conformational Analysis of Broken Rodlike Chains. 1. Scattering Function of Rods Joined Together by Flexible Coils

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ABSTRACT: The particle-scattering function for rods joined together by flexible coils is derived by using Hermans' technique, which was originally used for freely hinged rods. It is shown that the scattering function derived can be reduced to that for freely hinged rods and also for randomly coiled chain by changing the content of flexible coils in the particle. Moreover, it is pointed out that the reduced particle scattering function is independent of molecular weight distribution in the high wave vector region, available in small-angle X-ray scattering experiments, so that the reduced particle scattering function may be used for studying the conformation of polypeptides with a broad molecular weight distribution.

Introduction

It is well-known that most polypeptides such as poly(L- or D-glutamate), poly(L-lysine) or DNA show the helix-to-coil transition. A polymer in its helix region is not a rigid rod but may have a structure of freely hinged rods, while that in its helix-to-coil transition region may be represented by several rods joined together by flexible coils. Those structures are sometimes called "broken rods". However, detail in its structures has not yet been clarified. To study the detail in their molecular conformations, the particle-scattering function in light scattering (LS) or small-angle X-ray scattering (SAXS) may be useful. The particle-scattering function for freely hinged rods has been presented by Hermans and Hermans,[1] and the particle-scattering functions of polymers having the conformations of random coil, rigid rod, and wormlike chains[2-5] have already been calculated. However, the particle-scattering function for the broken rod in the helix-to-coil transition region has not been derived.

In the present paper, it is shown that Hermans' technique can be extended to the calculation of the scattering function of a molecule consisting of several rods joined together by flexible coils. Application of the results to analysis of the conformation of poly(sodium D-glutamate) in the helix-to-coil transition region is given in the following paper[6] in this issue.

In general, the particle-scattering function in LS or SAXS is sensitive to molecular weight distribution. However, it is shown that the functional form in the large wave vector region, which can be attained in SAXS, is insensitive to molecular weight distribution since the scattering from only a part of the chain can be observed.

Computation Result

Let $\vec{s}_0$ be the unit vector in the direction of the primary beam, $\vec{s}$ the vector in the direction of the scattered beam, $\vec{r}_{jk}$ the distance vector between the j and k scatterers, and $\tilde{\lambda}$ the wave length of the light in the solution. The wave vector $\vec{h}$ is defined by

$$\vec{h} = 2\pi(\vec{s} - \vec{s}_0)/\tilde{\lambda} \qquad (1)$$

The absolute value of $\vec{h}$ is

$$h = (4\pi/\tilde{\lambda}) \sin(\theta/2) \qquad (2)$$

where θ is the scattering angle. The scattering intensity is proportional to

$$R_\theta = \sum_j \sum_k \exp[i\vec{h}\cdot\vec{r}_{jk}] \qquad (3)$$

As is shown in Figure 1, a rod of length A and a rod of length a are named R rod and C rod, respectively, and all rods are numbered in succession: the first C rod is numbered 1 and the last R rod is numbered $N(n+1)$. Here, let the position of a scatterer in the R rod be denoted by P and that in the C rod by Q. If the position of P in the $k(n+1)$th R rod is measured as a distance between P and the end of the $(k(n+1)-1)$th rod, it is given by the distance $Ax_{k(n+1)}$, where x varies from 0 to 1. When the scatterers are distributed continuously in the rod, the scattering from a scatterer at P should be regarded as that from an element

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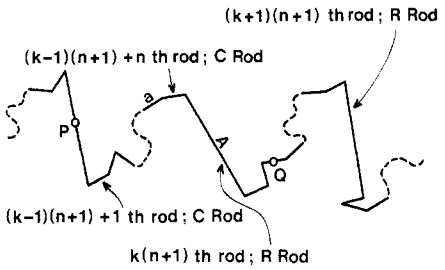

Figure 1. Broken rod consisting of rods named R with length A and rods named C with length a.

of length $A\ \mathrm{d}x_{k(n+1)}$ at point P. In a similar way, the scattering from point Q in the $(l(n+1)+m)$th C rod can be regarded as that from an element of length $a\ \mathrm{d}y_{l(n+1)+m}$ at point Q, whose position is given by the distance $ay_{l(n+1)+m}$ between Q and the end of the $(l(n+1)+m-1)$th rod, where y varies from 0 to 1. In the following calculation, three cases are separately treated: case I is where two scatterers are in R rods, case II is where they are in C rods, and case III is where one is in a R rod and the other is in a C rod.

Case I. If the beginning of the first C rod is at the origin **O**, vector $\vec{\mathbf{OP}}$ will be given by

$$\vec{\mathbf{R}}_{k(n+1)} = A\sum_{i=1}^{k-1}\vec{\mathbf{U}}_{i(n+1)} + a\sum_{h=1}^{n}\ \sum_{j=0}^{k-1}\vec{\mathbf{U}}_{j(n+1)+h} + Ax_{k(n+1)}\vec{\mathbf{U}}_{k(n+1)} \tag{4}$$

where $\vec{\mathbf{U}}_{i(n+1)}$ is a unit vector parallel to the direction of the $(i(n+1))$th rod. Thus, eq 3 becomes

$$R_\theta = A^2\sum_k \sum_l \int_0^1 \mathrm{d}x_{k(n+1)} \int_0^1 \mathrm{d}x_{l(n+1)}\ \exp[i\vec{\mathbf{h}}\cdot(\vec{\mathbf{R}}_{k(n+1)} - \vec{\mathbf{R}}_{l(n+1)})] \tag{5}$$

Here, terms with $k = l$, S_k, are separated from those with $k \neq l$, $S_{k,l}$:

$$R_\theta/A^2 = \sum_{k=1}^{n} S_k + \sum_k\ \sum_{l\neq k} S_{k,l} \tag{6}$$

where S_k is given by

$$S_k = \int_0^1 \mathrm{d}x_{k(n+1)} \int_0^1 \mathrm{d}\xi_{k(n+1)}\ \exp[i\vec{\mathbf{h}}\cdot A(x_{k(n+1)} - \xi_{k(n+1)})\vec{\mathbf{U}}_{k(n+1)}] \tag{7}$$

and $S_{k,l}$ is given by

$$S_{k,l} = \int_0^1 \mathrm{d}x_{k(n+1)} \int_0^1 \mathrm{d}x_{l(n+1)}\ \exp[i\vec{\mathbf{h}}\cdot\vec{\mathbf{v}}_{k,l}] \tag{8}$$

where, if $l < k$,

$$\vec{\mathbf{v}}_{k,l} = Ax_{k(n+1)}\vec{\mathbf{U}}_{k(n+1)} + A(1 - x_{l(n+1)})\vec{\mathbf{U}}_{l(n+1)} + a\sum_{h=1}^{n}\ \sum_{j=1}^{k-1}\vec{\mathbf{U}}_{j(n+1)+h} + A\sum_{i=l+1}^{k-1}\vec{\mathbf{U}}_{i(n+1)} \tag{9}$$

and, if $l > k$,

$$\vec{\mathbf{v}}_{k,l} = Ax_{l(n+1)}\vec{\mathbf{U}}_{l(n+1)} + A(1 - x_{k(n+1)})\vec{\mathbf{U}}_{k(n+1)} + a\sum_{h=1}^{n}\ \sum_{j=\mathrm{k}}^{l-1}\vec{\mathbf{U}}_{j(n+1)+h} + A\sum_{i=k+1}^{l-1}\vec{\mathbf{U}}_{i(n+1)} \tag{10}$$

As the direction of any rod in space is assumed to be entirely independent of the position of the others, the averaging over all conformations of the molecule is replaced by independently averaging over all possible directions of the rods. Denoting the averaging by $\langle\ \rangle$ and making use of the fact that

$$\langle\exp(i\vec{\beta}\cdot\vec{\mathbf{z}})\rangle = (\sin \beta z)/\beta z \tag{11}$$

holds in this case, we obtain $\langle S_k\rangle$ as follows:

$$\langle S_k\rangle = 2\Lambda(\beta) - (4/\beta^2)\sin^2(\beta/2) \tag{12}$$

with

$$\vec{\beta} = A\vec{\mathbf{h}} \tag{13}$$

and

$$\Lambda(\beta) = (1/\beta)\int_0^\beta (\sin t/t)\ \mathrm{d}t \tag{14}$$

In a similar way, we find $\langle S_{k,l}\rangle$ for $l < k$

$$\langle S_{k,l}\rangle = \left(\frac{\sin \alpha}{\alpha}\right)^{n(k-l)}\left(\frac{\sin \beta}{\beta}\right)^{k-l-1} \times \int_0^1 \frac{\sin \beta x_{k(n+1)}}{\beta x_{k(n+1)}}\ \mathrm{d}x_{k(n+1)} \int_0^1 \frac{\sin \beta(1 - x_{l(n+1)})}{\beta(1 - x_{l(n+1)})}\ \mathrm{d}x_{l(n+1)} \tag{15}$$

where

$$\vec{\alpha} = a\vec{\mathbf{h}} \tag{16}$$

The same formula is obtained for $l > k$, except that the exponents $k-l$ and $k-l-1$ must be replaced by $l-k$ and $l-k-1$, respectively. Both integrals in eq 15 are equal to $\Lambda(\beta)$. If summations in eq 6 are carried out, the averaged scattering intensity for case I, $\langle R_\theta\rangle_{\mathrm{RR}}$, is obtained as follows:

$$\langle R_\theta\rangle_{\mathrm{RR}}/A^2 = 2N\left\{\Lambda(\beta) - \left(\frac{2}{\beta^2}\right)\sin^2\left(\frac{\beta}{2}\right)\right\} + 2\Lambda^2(\beta)\left(\frac{\mu^n}{1 - \mu^n\nu}\right)\left\{N - \frac{1 - (\mu^n\nu)^N}{1 - \mu^n\nu}\right\} \tag{17}$$

where

$$\mu = \frac{\sin \alpha}{\alpha} \tag{18}$$

$$\nu = \frac{\sin \beta}{\beta} \tag{19}$$

Equation 17 has the property that $\langle R_\theta\rangle_{\mathrm{RR}}/A^2$ tends to the value N^2 when the scattering angle θ becomes zero, as it should be.

Case II. When two scatterers are in the same or different C rods, the averaged scattering intensity, $\langle R_\theta\rangle_{\mathrm{CC}}$, is derived exactly the same way as in case I:

$$\langle R_\theta\rangle_{\mathrm{CC}}/a^2 = nN\left\{2W(\alpha) - \frac{4}{\alpha^2}\sin^2\left(\frac{\alpha}{2}\right)\right\} + 2NW^2(\alpha)\left\{\frac{n}{1 - \mu} - \frac{1 - \mu^n}{(1 - \mu)^2}\right\} + 2W^2(\alpha)\left(\frac{1 - \mu^n}{1 - \mu}\right)^2\left(\frac{\nu}{1 - \mu^n\nu}\right)\left\{N - \frac{1 - (\mu^n\nu)^N}{1 - \mu^n\nu}\right\} \tag{20}$$

where

$$W(\alpha) = (1/\alpha)\int_0^\alpha (\sin t/t)\ \mathrm{d}t \tag{21}$$

When the scattering angle θ becomes zero, $\langle R_\theta\rangle_{\mathrm{CC}}/a^2$ tends to the value n^2N^2.

Case III. When one scatterer is in a C rod and the other one is in a R rod, the averaged scattering intensity, $\langle R_\theta\rangle_{\mathrm{RC}}$, is obtained as follows:

$$\langle R_\theta \rangle_{\mathrm{RC}}/aA = 2\Lambda(\beta)W(\alpha)\left(\frac{1-\mu^n}{1-\mu}\right)\left(\frac{1}{1-\mu^n\nu}\right)\times \left\{2N - \frac{(1+\mu^n\nu)(1-(\mu^n\nu)^N}{1-\mu^n\nu}\right\} \quad (22)$$

As it should be, when the scattering angle θ becomes zero, $\langle R_\theta \rangle_{\mathrm{RC}}/aA$ tends to $2nN^2$.

The total averaged scattering intensity from a polymer chain, $\langle R_\theta \rangle_0$, is given as a sum of each contribution:

$$\langle R_\theta \rangle_0 = \langle R_\theta \rangle_{\mathrm{RR}} + \langle R_\theta \rangle_{\mathrm{CC}} + \langle R_\theta \rangle_{\mathrm{RC}} \quad (23)$$

where $\langle R_\theta \rangle_{\mathrm{RR}}$, $\langle R_\theta \rangle_{\mathrm{CC}}$, and $\langle R_\theta \rangle_{\mathrm{RC}}$ are given by eq 17, 20, and 22, respectively. It is easily ascertained that, when $n = 1$ and $a = \mathrm{A}$ in eq 23, the total scattering intensity is reduced to that from a random zigzag chain with $2N$ segments.

In order to get the averaged scattering intensity from N rods joined by random coils, $\langle R_\theta \rangle$, n in $\langle R_\theta \rangle_0$ is allowed to become infinite while a tends to zero in such a manner that $na^2 = \langle r^2 \rangle$ remains finite. In this limit, making use of the approximation

$$\mu^n \fallingdotseq \exp\left(-\frac{na^2}{6}\right) \quad (24)$$

the following final result can be obtained:

$$\langle R_\theta \rangle = NA^2\left\{2\Lambda(\beta) - \frac{4}{\beta^2}\sin^2\frac{\beta}{2}\right\} + 2NA^2\Lambda^2(\beta)\left(\frac{e^{-w}}{1-\nu e^{-w}}\right) - 2A^2\Lambda^2(\beta)\left(\frac{e^{-w}}{1-\nu e^{-w}}\right)\left(\frac{1-(\nu e^{-w})^N}{1-\nu e^{-w}}\right) + n^2N^2a^2\left\{\frac{2}{Nw} - 2\left(\frac{1-e^{-w}}{Nw}\right)^2\left(\frac{\nu}{1-\nu e^{-w}}\right)\times \left(\frac{1-(\nu e^{-w})^N}{1-\nu e^{-w}}\right) - 2\frac{(1-e^{-w})(1-\nu)}{Nw^2(1-\nu e^{-w})}\right\} + \frac{2naA\Lambda(\beta)(1-e^{-w})}{w(1-\nu e^{-w})}\left\{2N - \frac{(1+\nu e^{-w})(1-(\nu e^{-w})^N)}{1-\nu e^{-w}}\right\} \quad (25)$$

where w is defined by

$$w = \frac{n\alpha^2}{6} = \frac{na^2}{6}\left(\frac{4\pi}{\tilde{\lambda}}\right)^2 \sin^2\left(\frac{\theta}{2}\right) \quad (26)$$

When the scattering angle θ tends to zero, $\langle R_\theta \rangle$ tends to $(NA + nNa)^2$. This procedure of tending n to infinity and a to zero is equivalent to the assumption that the conformation of a random coil portion follows the Gaussian distribution function.

As it should be, when A becomes zero, $\langle R_\theta \rangle$ becomes one for a Gaussian chain composed of nN segments:

$$\frac{\langle R_\theta \rangle}{(nNa)^2} = \left(\frac{2}{Z^2}\right)(Z - 1 + e^{-Z}) \quad (27)$$

where Z is defined as

$$Z = wN \quad (28)$$

Equation 27 is a well-known Debye function.

Moreover, as the rod length a tends to zero, i.e., the polymer chain becomes N freely hinged rods of length A, eq 25 is reduced to

$$\langle R_\theta \rangle_{\mathrm{RR}}/A^2 = 2N\left\{\Lambda(\beta) - \left(\frac{2}{\beta^2}\right)\sin^2\left(\frac{\beta}{2}\right)\right\} + 2N\Lambda^2(\beta)\left(\frac{1}{1-\nu}\right) - 2\Lambda^2(\beta)\cdot(1-\nu^N)\left(\frac{1}{1-\nu}\right)^2 \quad (29)$$

This formula is the same one as that derived by Hermans and Hermans[1] for N freely hinged rods of length A.

As is well-known, at a sufficiently small scattering angle, the reduced scattering function, $P(\theta)$ should follow the standard expression,

$$\langle R_\theta \rangle/(NA + nNa)^2\ (\equiv P(\theta)) = 1 - h^2\langle R_{\mathrm{G}}{}^2 \rangle/3 + \ldots \quad (30)$$

$$\langle R_\theta \rangle/(NA + nNa)^2 = \exp\left(-h^2\frac{\langle R_{\mathrm{G}}{}^2 \rangle}{3}\right) \quad (31)$$

where $\langle R_{\mathrm{G}}{}^2 \rangle$ is a mean-squared radius of gyration. We get a corresponding expression for a broken rodlike chain by series expansion of eq 25 as follows:

$$\frac{\langle R_\theta \rangle}{(NA + nNa)^2}(\equiv P(\theta)) = 1 - \frac{h^2}{18}\frac{1}{(NA+nNa)^2}\left[N^2A^2\left\{\frac{A^2}{2N} + (N-1)A^2 + \left(\frac{N^2-1}{N}\right)na^2\right\} + n^2N^2a^2\left(nNa^2 - \frac{A^2}{N} + NA^2\right) + 2nN^2aA\left\{\frac{3(2N-1)na^2}{2N} + \frac{(5N-3)A^2}{2N}\right\}\right] + \ldots \quad (32)$$

That is, we have $\langle R_{\mathrm{G}}{}^2 \rangle$ as a prefactor of $h^2/3$ in the right side of eq 32. If $a = 0$ and $N = 1$, i.e., in the case of a single rod of length A, we have $\langle R_{\mathrm{G}}{}^2 \rangle = A^2/12$, while, if $A = 0$, i.e., in the case of a Gaussian coil of nN segments of length a, we have $\langle R_{\mathrm{G}}{}^2 \rangle = nNa^2/6$, as expected. We can see that the limiting form such as eq 31 holds only when h is lower than, say, 0.014 Å^{-1} if the contour length L = 2000 Å, A = 50 Å, a = 5 Å, N = 20, and n = 10 at the helical content, f = 0.5, whereas a corresponding h is 0.008 Å^{-1} for a freely hinged rod of L = 2000 Å, A = 50 Å, and N = 40 and 0.024 Å^{-1} for a random coil of L = 2000 Å, a = 5 Å, N = 20, and n = 20.

At the limit of high angles, moreover, the reduced scattering intensity $\langle R_\theta \rangle/(NA + nNa)^2$ ($\equiv P(\theta)$) should be inversely proportional to molecular weight, or N, in general. It can be easily shown that $\langle R_\theta \rangle/(NA + nNa)^2$ ($\equiv P(\theta)$), given by eq 25, is inversely proportional to N at high angles if N is sufficiently large.

Discussion

Equation 25 can represent scattering behaviors of all types of polymer chains from a broken rod to a randomly coiled chain. It is important to observe the behavior of $\langle R_\theta \rangle$ as a function of a fraction of rod portions to a whole polymer chain, f, defined by

$$f = \frac{NA}{nNa + NA} \quad (33)$$

while the contour length of a polymer chain, L, given by $NA + nNa$, is kept constant. In Figure 2 is shown the variation of reduced scattering intensities $\langle R_\theta \rangle/(NA + nNa)^2$ with f, in the form of the Kratky plot, i.e., $I(\theta)h^2$ vs h. In the simulation, A and n are changed with f through the relations $A = (L/N)f$ and $n = (L/Na)(1 - f)$, while L, N, and a are kept constant throughout variation of f, L = 500 Å, N = 10, and a = 3 Å. The curves are significantly affected by f, and as f is changed from zero to unity, the

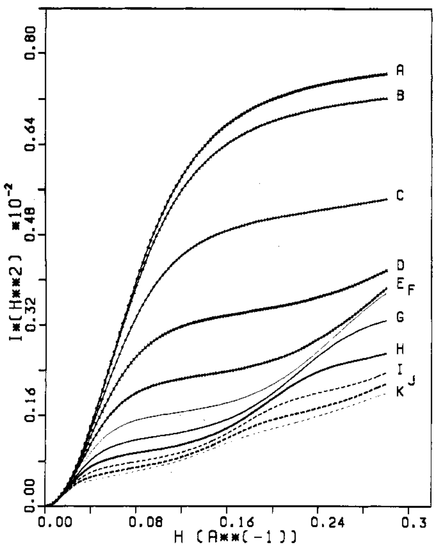

Figure 2. Change of Kratky plot of a broken rodlike chain with a fraction of rod portions to a whole polymer chain, f; A, 0.0 (random coil); B, 0.1; C, 0.2; D, 0.3; E, 0.4; F, 0.5; G, 0.6; H, 0.7; I, 0.8; J, 0.9; K, 1.0 (freely hinged rod). L = 500 Å, N = 10, and a = 3 Å. See text for the notation.

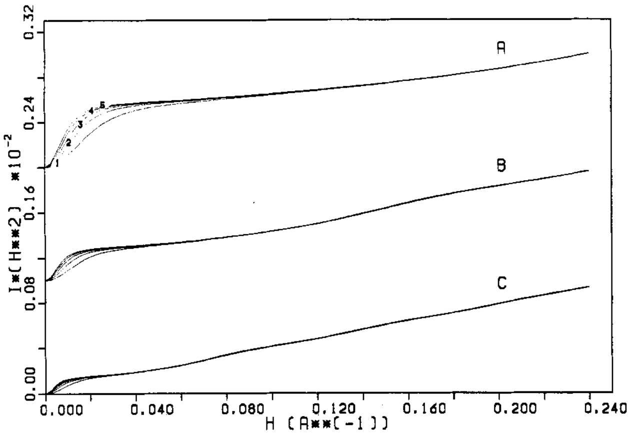

Figure 3. Change of the normalized Kratky plot of freely hinged rods with contour length, L: 1, 1000; 2, 2000; 3, 3000; 4, 4000; 5, 5000 Å. Rod length, A, is fixed at 25, 50, and 100 Å for A, B, and C, respectively. Curves A and B were shifted a distance of 0.2 × 10^{-2} and 0.1 × 10^{-2} upward along the ordinate, respectively.

scattering curve is smoothly converted from one extreme case of a randomly coiled chain to the other extreme case of a random zigzag chain. Moreover, it is observed that the oscillation in the Kratky plots becomes marked as A becomes larger, reflecting the fact that the terms $\Lambda(\beta)$, sin $(\beta/2)$, and ν in eq 25 involve the quantity Ah.

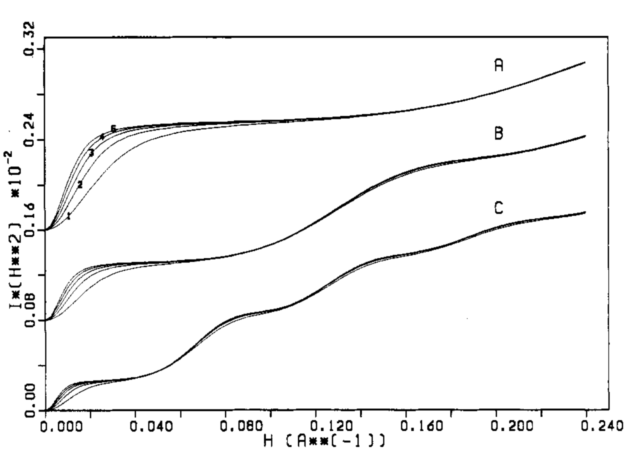

Figure 4. Change of the normalized Kratky plot of broken rods with contour length, L: 1, 1000; 2, 2000; 3, 3000; 4, 4000; 5, 5000 Å. Rod length, A, is fixed at 25, 50, and 100 Å for A, B, and C, respectively. Coil length, a = 5 Å. Rod content, f = 0.5. Curves A and B were shifted a distance of 0.16 × 10^{-2} and 0.08 × 10^{-2} upward along the ordinate, respectively.

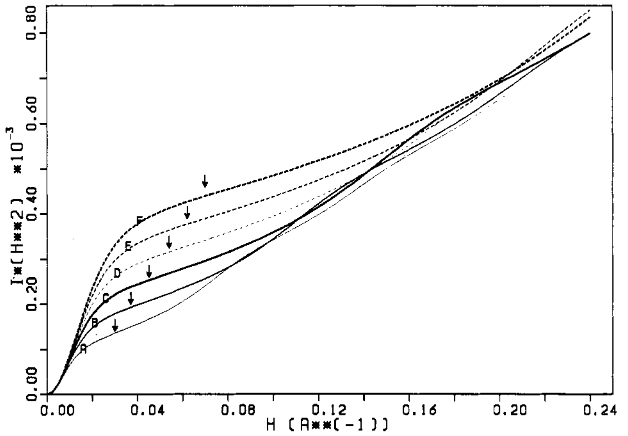

Figure 5. Change of the Kratky plot of freely hinged rods with the rod number, N: A, 10, B, 15; C, 20; D, 25; E, 30; F, 35. Contour length, L, is fixed at 1000 Å. Arrows in the figure indicate the values of h, above which the normalized particle-scattering function becomes insensitive to molecular weight.

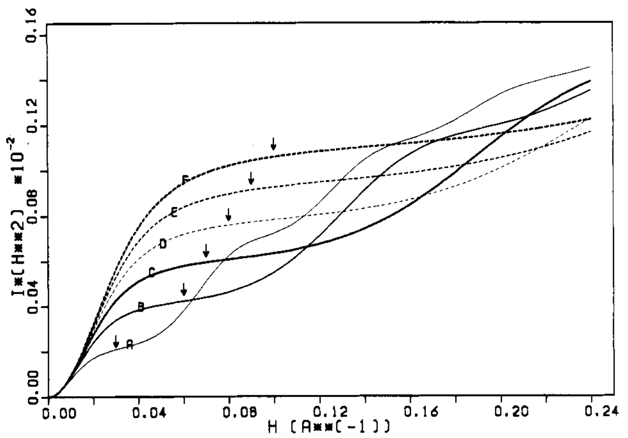

Figure 6. Change of the Kratky plot of broken rods with the rod number, N: A, 5, B, 10; C, 15; D, 20; E, 25; F, 30. Contour length, L, is fixed at 1000 Å. Coil length, a = 5 Å. Rod content, f = 0.5. Arrows in the figure indicate the values of h, above which the normalized particle-scattering function becomes insensitive to molecular weight.

As is well-known, in general, the particle-scattering function in light scattering (LS) is sensitive to molecular weight distribution, so the particle scattering function could be unambiguously analyzed only if the sample has a narrow molecular weight distribution. But it is not easy to obtain such an ideally prepared polypeptide. In the high h region in SAXS, however, it can be expected that the functional form of $I(h)$ vs h becomes independent of molecular weight distribution, since the scattering from only a part of the chain can be observed. In order to ascertain this expectation, the theoretical curves were calculated with fixed rod lengths A and various contour lengths L. In Figures 3 and 4 are shown such theoretical scattering curves in the form of Ih^2 vs h for freely hinged rods and broken rods, respectively. In both figures, the reduced scattering intensities, $\langle R_\theta \rangle/(NA + nNa)^2$, were normalized by multiplying them by the contour length, L. The contour length, L, is changed from 1000 to 5000 Å for three cases of A = 25, 50, and 100 Å. In Figure 4, coil length, a, and rod content, f, are fixed at 5 Å and 0.5, respectively. It is seen that, for each length of A, all such normalized theo-

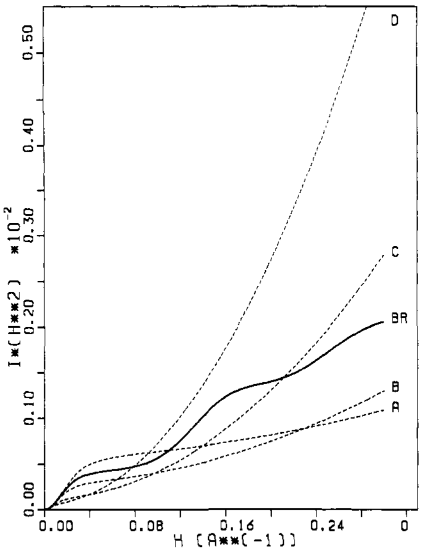

Figure 7. Comparison between the Kratky plot of broken rods (BR), characterized by $f = 0.5$, $L = 1000$ Å, $N = 10$, $n = 50/3$, $A = 50$ Å, and $a = 3$ Å, and those of wormlike chains with persistence lengths: A, 10; B, 20; C, 50; D, 100 Å. See text for the notation.

retical curves behave in exactly the same way above ca. 0.03–0.10 Å^{-1} in h, except in the case of very low molecular weight.

While such a normalized theoretical curve is insensitive to the contour length of a molecule, a theoretical curve can be proved to be sensitive to rod length, A. This is shown in Figures 5 and 6 for freely hinged rods and broken rods, respectively, where L is fixed at 1000 Å and the rod number, N, is changed from 10 to 35 in Figure 5 and from 5 to 30 in Figure 6. The rod length, A, is simultaneously changed through the relations $NA = L$ and $2NA = \mathrm{L}$. In Figure 6, the coil length, a, and rod cotent, f, are fixed at 5 Å and 0.5, respectively. The values of h, above which the normalized particle-scattering function becomes insensitive to molecular weight, are indicated by arrows in the figures. From the above observations, it can be safely concluded that we can analyze the conformation of a polypeptide by comparing the experimental normalized particle-scattering function with the calculated one in Figures 5 and 6 in the high h region, even if the sample has a broad molecular weight distribution.

It is interesting to see whether the scattering behavior of such a broken rod could be replaced by that of a wormlike chain with a mean persistence length (P_1) averaged along a polymer chain or not. The reduced scattering intensity of wormlike chains is given by Sharp and Bloomfield[7] as follows:

$$P(\theta) = 2u^{-2}\{\exp(-u) - 1 + u\} + \frac{4}{15L_{\mathrm{r}}} + \frac{7}{15L_{\mathrm{r}}u} - \left\{\frac{11}{15L_{\mathrm{r}}} + \frac{7}{15L_{\mathrm{r}}u}\right\}\exp(-u) \quad (34)$$

where u and L_{r} are given by

$$u = \frac{LP_1}{3}h^2 \quad (35)$$

$$L_{\mathrm{r}} = \frac{L}{2P_1} \quad (36)$$

Equation 34 is valid for $L_{\mathrm{r}} > 10$. In the case of a polymer chain composed of rods joined by flexible coils, which is characterized by $L = 1000$ Å, $f = 0.5$, $A = 50$ Å, $a = 3$ Å, $N = 10$, and $n = 50/3$, eq 25 is compared with eq 34 in Figure 7. It is clear that broken rod polymers cannot be represented by the wormlike chain model.

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