Radius of Gyration and Scattering Function of a Broken Rodlike Chain and Their Applications to Conformational Analysis of a Polymer Chain in the Gel State

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ABSTRACT: An analytical expression is given for the mean-squared radius of gyration, $\langle R_g^2 \rangle$, of a broken rodlike chain model having random distributions with respect to both the lengths of constituent rods and random coils. The expressions of $\langle R_g^2 \rangle$ and also of the scattering function are employed in the analysis of the observed $\langle R_g^2 \rangle$ and the scattering curve for isotactic polystyrene gel to obtain the conformation of a single chain in the gel state. It is shown that both observed data are in more satisfactory agreement with the present equations than with the previous equations in which the length distribution of the constituents are not taken into account.

Introduction

The conformation of a polymer chain can be well studied through comparison between the observed radius of gyration, $\langle R_g^2 \rangle$, and the observed particle-scattering function and theoretical ones computed for suitable models. A random-coil chain, wormlike chain, rigid rod, and freely-hinged rod have been usefully employed as such models. However, there surely exist different categories of polymers, the conformations of which cannot be represented by these models.

A typical example for the polymers belonging to this category may be block copolymers consisting of soft segments and hard segments alternatively joined along the main chains, among which liquid crystalline polymers are especially drawing much attention recently.[1-4] In these polymers, part of the hard segments and of the soft segments may be represented by rigid rods and random coils, respectively. On the basis of the small-angle neutron scattering data, moreover, Guenet *et al.*[5] have clarified that a single polymer chain in isotactic polystyrene gel can be classified in such a category of polymers. That is, the crystallized parts and the amorphous parts along the polymer chain may be represented by rigid rods and random coils, respectively. From the necessity to analyze such a new type of polymer conformations or configurations, the analytical expressions of the particle scattering function and $\langle R_g^2 \rangle$ for the polymers in this category have been wanted in various fields of polymer science. Guenet *et al.*,[5] moreover, have pointed out that rods as well as random coils should have a length distribution for the model of the chain conformation in polystyrene gel.

We recently obtained[6] the analytical expression of the particle scattering function for a broken rodlike chain model consisting of several rods alternatively joined by random coils, taking into account random distributions with respect to the lengths of constituent rods and random coils. The purpose of the present study is to derive the analytical expression of $\langle R_g^2 \rangle$ for this model. $\langle R_g^2 \rangle$ thus obtained as well as the scattering function for the model are employed to analyze the neutron scattering curve and $\langle R_g^2 \rangle$ for the isotactic polystyrene in the gel state, obtained by Guenet *et al.*[5]

Garcia Molina and Garcia de la Torre[7] calculated $\langle R_g^2 \rangle$ for a randomly-broken chain, the units of which have identical length and can take either the random-coil state or the rod state. This model is, however, not suitable for polymers which have different pitches in the random-coil state and the rod state.

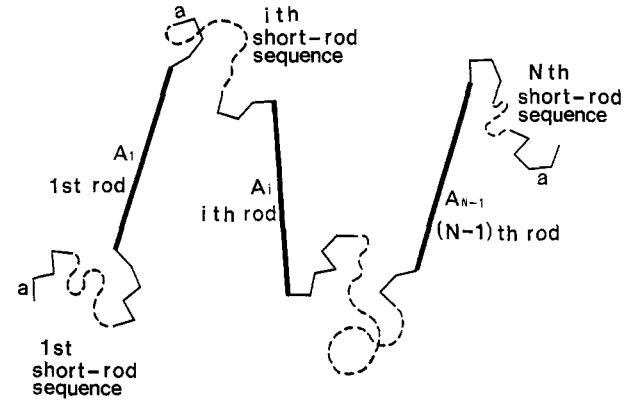

Figure 1. Broken rodlike chain represented by $N-1$ rods with each length $a_1 n_j$ ($j = 1$ to $N-1$) alternatively joined by N sequences of short rods with each length am_i ($i = 1$ to N).

Analytical Expression of $\langle R_g^2 \rangle$

As was explained in the previous paper,[6] a broken rodlike chain is made of $N-1$ rods (R region) alternatively joined by N random-coil portions (C region) (Figure 1). Free rotation is allowed between a rod and a neighboring random-coil portion. A random-coil portion is assumed to be made of monomers of effective bond length a, in which rotation around the joint connecting adjacent monomers is also assumed to be free. All random-coil portions and rod portions are numbered in succession. The first random-coil and rod portions are numbered 1, while the last ones are numbered N and $N-1$, respectively. That is, the ith random-coil portion is made of m_i monomers of effective length a, while the jth rod is made of n_j monomers of length a_1, where the suffix i can be changed from 1 to N and the suffix j from 1 to $N-1$. The length of a rod portion made of n_j monomers is $n_j a_1$ and the mean-squared end-to-end distance of a random-coil portion made of m_i monomers is $m_i a^2$. In the present treatment, it is assumed that m_i and n_j can evenly take all possible magnitudes.

When the broken rodlike chain is consisted of T monomers and the total number of monomers constituting rod portions is S, the following relations hold between T

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and S and the above parameters:

$$\sum_{i=1}^{N} m_i + \sum_{j=1}^{N-1} n_j = T \tag{1}$$

$$\sum_{j=1}^{N-1} n_j = S \tag{2}$$

A fraction (f_T) of monomers in the rod portions to the total monomers is thus given as

$$f_T = \frac{\sum_{j=1}^{N-1} n_j}{\sum_{i=1}^{N} m_i + \sum_{j=1}^{N-1} n_j} \tag{3}$$

The extended length of the broken rodlike chain, L, is given by

$$L = a\sum_{i=1}^{N} m_i + a_1\sum_{j=1}^{N-1} n_j \tag{4}$$

and the ratio (f) of the total length of the rod portions to L is

$$f = \frac{a_1\sum_{j=1}^{N-1} n_j}{L} = \left\{1 + \frac{a}{a_1}\left(\frac{1}{f_T} - 1\right)\right\}^{-1} \tag{5}$$

The scattering intensity $\langle I_\theta \rangle$ for the broken rodlike chain was given in the previous paper[6] as a sum of the contributions from two scatterers which are both located either in the R or C region and from two scatterers located in different regions, R and C regions, $\langle I_\theta \rangle_{rr}$, $\langle I_\theta \rangle_{cc}$, and $\langle I_\theta \rangle_{rc}$, respectively. That is,

$$\langle I_\theta \rangle = \langle I_\theta \rangle_{rr} + \langle I_\theta \rangle_{cc} + \langle I_\theta \rangle_{rc} \tag{6}$$

The mean-squared radius of gyration $\langle R_g^2 \rangle$ can be derived from the expansion form of $\langle I_\theta \rangle$ in the region of $\langle R_g^2 \rangle h^2 \ll 1$:

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

Here, the absolute magnitude of the scattering vector h is defined by

$$h = (4\pi/\tilde{\lambda}) \sin(\theta/2) \tag{8}$$

where θ is the scattering angle and $\tilde{\lambda}$ the wavelength of the light in the solution. If $a^2h^2 \ll 1$ and also $a_1^2 n_j^2 h^2 \ll 1$, $\langle I_\theta \rangle$ can be expanded with respect to h^2 as follows:

$$\langle I_\theta \rangle_{rr} = (a_1\sum_{i=1}^{N-1} n_i)^2 - \frac{h^2}{18}\Bigg[(N-1)^2 a_1^2 \langle n \rangle^2 \Bigg\{ \frac{a_1^2\langle n \rangle^2}{2(N-1)} \frac{\langle n_i^4 \rangle}{\langle n \rangle^4} + 2\frac{(N-2)}{(N-1)} a_1^2 \langle n \rangle^2 \frac{\langle n_i^3 n_j \rangle}{\langle n \rangle^4} + \frac{(N-2)(N-3)}{(N-1)} a_1^2 \langle n \rangle^2 \frac{\langle n_i n_k^2 n_j \rangle}{\langle n \rangle^4} + \frac{N(N-2)}{(N-1)} a^2 \langle m \rangle \frac{\langle n_i m_k n_j \rangle}{\langle n \rangle^2 \langle m \rangle} \Bigg\} \Bigg] + O(h^4) \tag{9}$$

$$\langle I_\theta \rangle_{cc} = (a\sum_{i=1}^{N} m_i)^2 - \frac{h^2}{18}\Bigg[N^2 a^2 \langle m \rangle^2 \Bigg\{ \langle m \rangle N a^2 + \frac{(N+1)(N-1)}{N} a_1^2 \langle n \rangle^2 \frac{\langle m_i n_j^2 m_k \rangle}{\langle m \rangle^2 \langle n \rangle^2} \Bigg\} \Bigg] + O(h^4) \tag{10}$$

$$\langle I_\theta \rangle_{rc} = \{2aa_1(\sum_{i=1}^{N-1} n_i)(\sum_{j=1}^{N} m_j)\} - \frac{h^2}{18} 2\langle m \rangle \langle n \rangle N(N-1) aa_1 \Bigg\{ \frac{3}{2} a^2 \langle m \rangle \frac{\langle m_k^2 n_{i-1} \rangle}{\langle n \rangle \langle m \rangle^2} + a^2(N-2)\langle m \rangle \frac{\langle m_k m_j n_{i-1} \rangle}{\langle n \rangle \langle m \rangle^2} + a_1^2 \langle n \rangle^2 \frac{\langle m_k n_{i-1}^3 \rangle}{\langle m \rangle \langle n \rangle^3} + (N-2)\langle n \rangle^2 a_1^2 \frac{\langle m_k n_j^2 n_{i-1} \rangle}{\langle m \rangle \langle n \rangle^3} \Bigg\} + O(h^4) \tag{11}$$

where $\langle\ \rangle$ denotes the average of an indicated sequence over a whole chain and is defined as follows:

$$\langle m \rangle = \frac{1}{N}\sum_{i=1}^{N} m_i \tag{12}$$

$$\langle n \rangle = \frac{1}{(N-1)}\sum_{j=1}^{N-1} n_j \tag{13}$$

$$\langle n_i^4 \rangle = \frac{1}{(N-1)}\sum_{i=1}^{N-1} n_i^4 \tag{14}$$

$$\langle n_i^3 n_j \rangle = \left(\frac{(N-1)(N-2)}{2}\right)^{-1} \sum_{i=1}^{N-2} \sum_{j=i+1}^{N-1} (n_i^3 n_j) \tag{15}$$

$$\langle n_i n_k^2 n_j \rangle = \left(\frac{(N-1)(N-2)(N-3)}{6}\right)^{-1} \sum_{i=1}^{N-2} \sum_{k=i+1}^{j-1} \sum_{j=i+1}^{N-1} (n_i n_k^2 n_j) \tag{16}$$

$$\langle n_i m_k n_j \rangle = \left(\frac{N(N-1)(N-2)}{6}\right)^{-1} \sum_{i=1}^{N-2} \sum_{k=i+1}^{j} \sum_{j=i+1}^{N-1} (n_i m_k n_j) \tag{17}$$

$$\langle m_i n_j^2 m_k \rangle = \left(\frac{(N+1)N(N-1)}{6}\right)^{-1} \sum_{i=1}^{N-1} \sum_{j=i}^{k-1} \sum_{k=i+1}^{N} (m_i n_j^2 m_k) \tag{18}$$

The ratios of $\langle n_i^3 n_j \rangle / \langle n \rangle^4$ and $\langle m_i n_j^2 m_k \rangle / \langle m \rangle^2 \langle n \rangle^2$, *etc.*, are polydispersity indexes reflecting a distribution of the constituent rod and coil lengths in the broken rodlike chain. $O(h^4)$ denotes remaining terms higher than h^4.

The value of $\langle m_i n_j^2 m_k \rangle$, for instance, is evaluated as follows:

$$\langle m_i n_j^2 m_k \rangle = \frac{\sum_{m_1}\sum_{m_2}\cdots\sum_{m_N} \times \sum_{n_1}\sum_{n_2}\cdots\sum_{n_{N-1}} (m_i n_j^2 m_k)}{\sum_{m_1}\sum_{m_2}\cdots\sum_{m_N} \times \sum_{n_1}\sum_{n_2}\cdots\sum_{n_{N-1}}} \tag{19}$$

The summations are carried out keeping the total number of monomers in the rod portions (S) as well as in the whole molecule (T) constant. Here, it is assumed that a rod portion is made up of more than t monomers, while a coil

portion is made up of more than one monomer:

$$m_i \geq 1 \tag{20}$$

$$n_j \geq t \tag{21}$$

t is taken as 3, as is usual. Thus, f_T takes a value between the following minimum, $f_{T,\min}$ and maximum, $f_{T,\max}$.

$$f_{T,\min} = t(N-1)/T \tag{22}$$

$$f_{T,\max} = (T-N)/T \tag{23}$$

When the limitations of eqs 20–23 are taken into consideration, the average value of eq 19 is written as:

$$\langle m_i n_j^2 m_k \rangle = \frac{\displaystyle\sum_{m_{N-1}=1}^{T-S} \sum_{m_{N-2}=1}^{T-S-m_{N-1}} \cdots \sum_{m_1=1}^{T-S-\mathrm{Sum}(m_i)} \times \sum_{n_{N-2}=t}^{S} \sum_{n_{N-3}=t}^{S-n_{N-2}} \cdots \sum_{n_1=t}^{S-\mathrm{Sum}(n_j)} (m_i n_j^2 m_k)}{\displaystyle\sum_{m_{N-1}=1}^{T-S} \sum_{m_{N-2}=1}^{T-S-m_{N-1}} \cdots \sum_{m_1=1}^{T-S-\mathrm{Sum}(m_i)} \times \sum_{n_{N-2}=t}^{S} \sum_{n_{N-3}=t}^{S-n_{N-2}} \cdots \sum_{n_1=t}^{S-\mathrm{Sum}(n_j)}} \tag{24}$$

where

$$\mathrm{Sum}(m_i) = \sum_{i=2}^{N-1} m_i \tag{25}$$

$$\mathrm{Sum}(n_j) = \sum_{j=2}^{N-2} n_j \tag{26}$$

Here, the summations in eq 24 are replaced by integrations and the method of Zimm and Stockmayer[8] is applied:

$$\sum_{m_{N-1}=1}^{T-S} \sum_{m_{N-2}=1}^{T-S-m_{N-1}} \cdots \sum_{m_1=1}^{T-S-\mathrm{Sum}(m_i)} \times \sum_{n_{N-2}=t}^{S} \sum_{n_{N-3}=t}^{S-n_{N-2}} \cdots \sum_{n_1=t}^{S-\mathrm{Sum}(n_j)} (m_i n_j^2 m_k) = \int_0^{T-S-N} \mathrm{d}m'_{N-1} \int_0^{T-S-N-m'_{N-1}} \mathrm{d}m'_{N-2} \cdots \int_0^{T-S-N-\mathrm{Sum}(m'_i)} \mathrm{d}m'_1 \int_0^{S-t(N-1)} \mathrm{d}n'_{N-2} \int_0^{S-t(N-1)-n'_{N-2}} \mathrm{d}n'_{N-3} \cdots \int_0^{S-t(N-1)-\mathrm{Sum}(n'_j)} \mathrm{d}n'_1 (m_i n_j^2 m_k) \tag{27}$$

where

$$\mathrm{Sum}(m'_i) = \sum_{i=2}^{N-1} m'_i \tag{28}$$

$$\mathrm{Sum}(n'_j) = \sum_{j=2}^{N-2} n'_j \tag{29}$$

The final results for all of the averages are obtained as follows:

$$\langle n \rangle = \frac{V}{N-1} + t \tag{30}$$

$$\langle n_j^4 \rangle = \frac{24V^4}{(N-1)N(N+1)(N+2)} + \frac{24tV^3}{(N-1)N(N+1)} + \frac{12t^2V^2}{(N-1)N} + \frac{4t^3V}{N-1} + t^4 \tag{31}$$

$$\langle n_i^3 n_j \rangle = \frac{6V^4}{(N-1)N(N+1)(N+2)} + \frac{12tV^3}{(N-1)N(N+1)} + \frac{9t^2V^2}{(N-1)N} + \frac{4t^3V}{N-1} + t^4 \tag{32}$$

$$\langle n_i n_k^2 n_j \rangle = \frac{2V^4}{(N-1)N(N+1)(N+2)} + \frac{6tV^3}{(N-1)N(N+1)} + \frac{7t^2V^2}{(N-1)N} + \frac{4t^3V}{N-1} + t^4 \tag{33}$$

$$\langle m \rangle = W/N + 1 \tag{34}$$

$$\langle n_i m_k n_j \rangle = \frac{V^2W}{N^2(N-1)} + \frac{V^2}{N(N-1)} + \frac{2tVW}{N(N-1)} + \frac{2tV}{N-1} + \frac{t^2W}{N} + t^2 \tag{35}$$

$$\langle m_i n_j^2 m_k \rangle = \frac{2V^2W^2}{N^2(N+1)(N-1)} + \frac{4V^2W}{N^2(N-1)} + \frac{2tVW^2}{N(N+1)(N-1)} + \frac{2V^2}{N(N-1)} + \frac{t^2W^2}{N(N+1)} + \frac{4tVW}{N(N-1)} + \frac{2tV}{N-1} + \frac{2Wt^2}{N} + t^2 \tag{36}$$

$$\langle m_k^2 n_i \rangle = \frac{2VW^2}{N(N+1)(N-1)} + \frac{2W^2t}{N(N+1)} + \frac{2VW}{N(N-1)} + \frac{2tW}{N} + \frac{V}{N-1} + t \tag{37}$$

$$\langle m_k m_j n_{i-1} \rangle = \frac{VW^2}{N(N+1)(N-1)} + \frac{tW^2}{N(N+1)} + \frac{2VW}{N(N-1)} + \frac{2tW}{N} + \frac{V}{N-1} + t \tag{38}$$

$$\langle m_k n_{i-1}^3 \rangle = \frac{6V^3W}{N^2(N-1)(N+1)} + \frac{6tV^2W}{N^2(N-1)} + \frac{3t^2VW}{N(N-1)} + \frac{Wt^3}{N} + \frac{6V^3}{N(N+1)(N-1)} + \frac{6tV^2}{N(N-1)} + \frac{3t^2V}{N-1} + t^3 \tag{39}$$

$$\langle m_k n_j^2 n_{i-1} \rangle = \frac{2V^3W}{N^2(N-1)(N+1)} + \frac{2V^2W}{N^2(N-1)} + \frac{2tV^2W}{N^2(N-1)} + \frac{2t^2VW}{N(N-1)} + \frac{2V^3}{N(N+1)(N-1)} + \frac{2tV^2}{N(N-1)} + \frac{2tV^2}{N(N-1)} + \frac{2t^2V}{N-1} + \frac{t^2V}{N-1} + \frac{t^2VW}{N(N-1)} + \frac{t^3W}{N} + t^3 \tag{40}$$

where

$$V = S - t(N-1) \tag{41}$$

$$W = T - S - N \tag{42}$$

In summary, $\langle R_g^2 \rangle$ of the broken rodlike chain type II can be obtained by substituting eqs 30–40 with eqs 41 and 42 into eqs 9–11 and then substituting the expansion forms of $\langle I_\theta \rangle_{rr}$, $\langle I_\theta \rangle_{cc}$, and $\langle I_\theta \rangle_{rc}$ thus obtained into eq 6 and comparing the result with eq 7. If all values of polydispersity indexes are equal to unity, the present broken

rodlike chain model is reduced to the previous model[9] and its $\langle R_g^2 \rangle$ is given as follows:[10]

$$\langle R_g^2 \rangle = \frac{f^2}{6}\left\{\frac{A^2}{2(N-1)} + (N-2)A^2 + \frac{N(N-2)}{N-1}ma^2\right\} + \frac{(1-f)^2}{6}\left\{mNa^2 - \frac{A^2}{N} + NA^2\right\} + \frac{2f(1-f)}{6}\left\{\left(N-\frac{1}{2}\right)ma^2 + (N-1)A^2\right\} \quad (43)$$

where

$$A = a_1 n \quad (44)$$

As is easily understood from the procedures given here and in our previous paper,[9] the present computation method of $\langle R_g^2 \rangle$ for the broken rodlike chain with N coils and $N-1$ rods can also be applied to obtain $\langle R_g^2 \rangle$ of the broken rodlike chain with one end of coils or rods (N coils and N rods) and the chain with both ends rods ($N-1$ coils and N rods). To be noted, in any type of those chains, the final expression for $\langle R_g^2 \rangle$ is valid for sufficiently small N compared with T, because the summations such as given in eq 24 are replaced by integrations (eq 27).

Application of the Broken Rodlike Chain

Guenet *et al.* recently obtained[5] the scattering curve and $\langle R_g^2 \rangle$ for the isotactic polystyrene in the gel state by small-angle neutron scattering. In order to obtain the detail of the chain conformation of a single polymer chain in the state, they compared the observed scattering curve with the theoretical one[9] for the broken rodlike chain type I, derived assuming that all constituent rods as well as all random coils have equal lengths. As a result, they concluded that the degree of disorder in the chain conformation may increase with the molecular weight. As was pointed out by Guenet *et al.*,[5] however, when we take into account that the gelation process should proceed without any regulation so that the trajectory of a single chain would randomly penetrate through the crystalline and amorphous regions, the broken rodlike chain type II handled in the present study, *i.e.*, the broken rodlike chain having random distributions with respect to the lengths of the constituent rods and random coils, seems to be more suitable for that conformational analysis.

Now, we analyze the scattering curves and $\langle R_g^2 \rangle$ for two kinds of isotactic polystyrenes (sample code: D0.74 and D2.5 in the paper[5] of Guenet *et al.*) by the broken rodlike chain type II. As is shown in the preceding section, we can specify the chain if we give the values to five parameters: total number of monomers (T), a fraction (f_T) of monomers in the rod portions against T, the number of rods ($N-1$) or the number of random-coil portions (N), the effective bond length in the random-coil state (a), and the pitch of the monomer in the rod portion (a_1). Now, it is reasonably assumed that the conformation of the chain in the crystalline region takes a 3_1 helical form, as was suggested in the study of Guenet *et al.*,[5] and takes a random-coil form in the amorphous region. Accordingly, the magnitude of a and a_1 could be assigned 20 and 2.2 Å, respectively. Moreover, since the molecular weights of the deuterated isotactic polystyrene are known in their paper,[5] *i.e.*, $T = 660$ and 2230 for samples D0.74 and D2.5, respectively, N and f_T are left as unknown parameters.

The method of trial and error is here employed to find a combination of N and f_T which gives $\langle R_g^2 \rangle^{1/2}$ as close as possible to the observed one and gives the theoretical scattering curve fitting of the observed one. The theoretical scattering curve for the chain having specified N rods and $N-1$ coil portions was obtained by generating a sufficiently large number of chains having various lengths of constituting rods as well as of coil portions with the Monte Carlo method and by computing the scattering intensity for each chain as a function of h with the equations given in our previous paper[6] and then averaging their results over the number of chains.

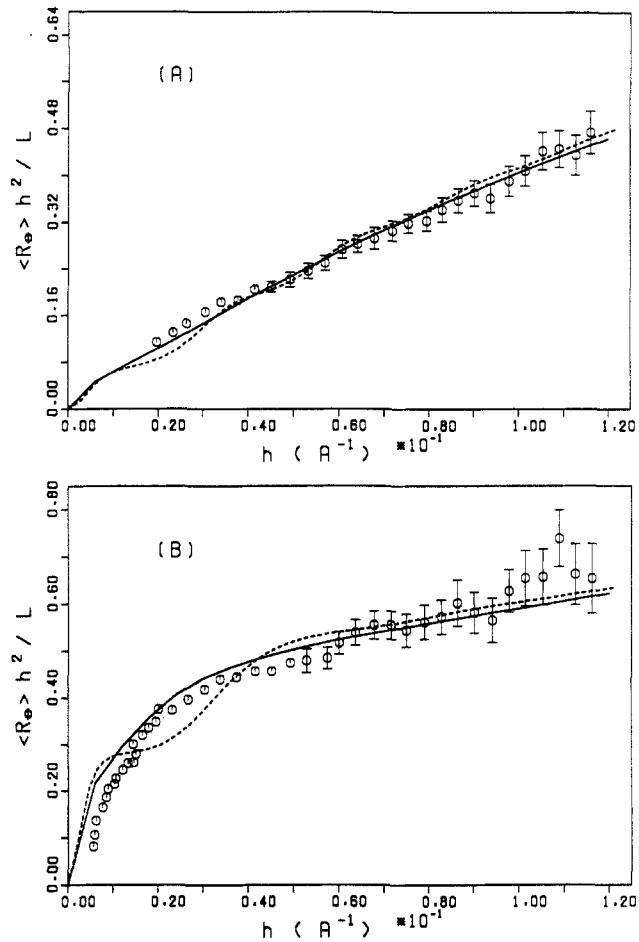

Figure 2. Comparison between the observed scattering curves of deuterated isotactic polystyrene having (A) $T = 660$ and (B) $T = 2230$ and the theoretical ones computed for the broken rodlike chain model type I (dotted curves) and type II (solid curves). The molecular parameters employed in the computations for the models are $N = 7$ and $f_T = 0.95$ in A and $N = 20$ and $f_T = 0.60$ in B. The data of $a = 20$ Å and $a_1 = 2.2$ Å are common for both samples.

In parts A and B of Figure 2 are compared the observed scattering curves for isotactic polystyrenes of samples D0.74 and D2.5 with the best fit theoretical ones (solid curves) obtained for the broken rodlike chain type II which have $T = 660$, $N = 7$, and $f_T = 0.95$ and $T = 2230$, $N = 20$, and $f_T = 0.60$, respectively. $a = 20$ Å and $a_1 = 2.2$ Å are common in both chains. The agreements between the observed and the theoretical curves are excellent and, moreover, these specified broken rodlike chains give theoretical $\langle R_g^2 \rangle^{1/2}$ of 286 and 444 Å in satisfactory agreement with the observed ones, 308 ± 25 and 448 ± 60 Å, respectively. Once the values of N and f_T are obtained, the averaged length (A) of the constituent rods can be evaluated by the relation:

$$A = a_1\langle n \rangle = a_1 \frac{Tf_T}{N-1} \quad (45)$$

The values of A are 230 and 155 Å for samples D0.74 and D2.5, respectively.

From the fact that A and f_T significantly decrease with the molecular weight of the sample, we can derive the conclusion that the higher the molecular weight, the larger the amount of disorder. Although this conclusion is in agreement with the one derived by Guenet *et al.*,[5] employing the broken rodlike chain type I, it is certain that the scattering curve in the low- and medium-angle regions as well as the radius of gyration can be more correctly analyzed by the broken rodlike chain type II. That is, the observed curves can be more satisfactory elucidated over a whole h range by the broken rodlike chain type II, rather than type I (dotted curves in Figure 2) having the same magnitude of parameters as type II.

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(10) Equation 43 is slightly different from a previous form,[9] reflecting the fact that both ends of the chain are terminated by random-coil portions in the present model. The last term in eq 32 of the previous paper[9] was incorrect, which is corrected as follows:

$$2nN^2aA\left\{\frac{(2N^2-3N+4)na^2}{2N}+\frac{(N^2-2N+2)A^2}{N}\right\}\Bigg]$$