Unperturbed Chain Dimension of Branched Polypeptides.
I. Star-Like Polypeptides

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ABSTRACT: Theoretical calculations for the mean square of unperturbed radius of gyration $\langle S^2 \rangle_{0,av}$ and the branching factor g of star-like polypeptides in random coil form were carried out for two cases in which the degree of polymerization of the subchains distributed uniformly and randomly.   The radius of the gyration ratio $\langle S^2 \rangle_{0,av}/nl^2$ and g depended on the degree of polymerization as well as the number of branches, and increased with an increasing degree of polymerization.

KEY WORDS   Star-Like Chain / Branched Polypeptides / Unperturbed Dimension / Radius of Gyration / Branching Factor / Uniform Distribution / Random Distribution /

Some natural proteins have cross-linked structure through the S—S bond between cystine residues.   Proteins, even when they have no cross-linked structure, have complicated high-order structures owing to intramolecular interactions.   Therefore, we may consider that such proteins have similar structures to the cross-linked polymers.   Consequently, using branched polypeptide as a model of natural protein is reasonable.   By this model, we may determine step by step the complicated intramolecular interactions in proteins.

As a kind of branched polypeptides, there are star-like polypeptides, having branches stemming from one point.   These star-like polypeptides are similar to globular proteins in structures.   Thus these polypeptides may provide new information about globular proteins.

Unperturbed dimension is one of the fundamental molecular properties for investigating the form of the polymer chains in dilute solution.   Unperturbed dimensions of the branched polymer chains have been calculated using the Gaussian chain approximation by Zimm and Stockmayer,[1] and Kurata and Fukatsu.[2]   The degree of polymerization for many globular proteins is in a range of 50–200.   The method of the Gaussian

chain approximation is therefore not always adequate, as this method is useful for infinite degree of polymerization.   Flory and his co-workers[8–9] have calculated the dimension of polymer chains as a function of the degree of polymerization for linear polymer chains.   These calculations were carried out on the basis of the rotational isomeric model.   In this paper, Flory's method is applied to the star-like polypeptide chains for calculating the unperturbed dimensions.

MEAN SQUARE OF THE RADIUS OF GYRATION
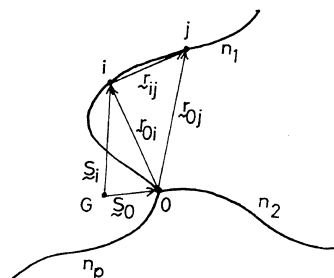
In Figure 1, a star-like chain molecule is shown.

Figure 1. A star-like chain molecule.

This chain possesses p branches (subchains) attached to one branching point 0. The degree of polymerization of the k-th subchain is assumed to be n_k. The branching point is given the symbol 0, and each atom (structural unit) in the k-th subchain is counted as $1, 2, \cdots$, and n_k toward the end of the subchain. The vector from the center of mass G of the molecule to the i-th atom of the subchain is S_i. As each atom is assumed to be equal in mass, the square radius of gyration S^2 is represented by

$$S^2 = \left(\sum_{k=1}^{p} \sum_{i=1}^{n_k} S_i^2 + S_0^2 \right)(n+1)^{-1} \qquad (1)$$

If the vector from the i-th atom to the j-th atom is r_{ij}, then

$$S^2 = \left[\sum_{1 \leq k < h \leq p}^{2} \sum_{0 \leq i < j \leq n_{kh}}^{2} r_{ij}^2 \right.$$
$$\left. - (p-2) \sum_{t=1}^{p} \sum_{0 \leq i < j \leq n_t}^{2} r_{ij}^2 \right](n+1)^{-2} \qquad (2)$$

from the theorem of Lagrange (See Appendix), where n_{nk} is represented by $n_{kh} = n_k + n_h$ and symbolism of the type $\sum^k$ indicates the serial k symbols of summation. The amide bond in polypeptide chains has a planar trans-partial double bond, so that the chain is regarded as a sequences of virtual bonds between the adjacent α-carbon atoms. Such a character of polypeptide chain makes it possible to assume that the rotation of the virtual bond is treated as if it does not depend on the rotation of its adjacent bonds. Furthermore, it may be assumed that the rotation of the virtual bonds succeeding the branching point is treated as an independent rotation. Thus one obtains

$$\langle S^2 \rangle_0 = \left[\sum_{1 \leq k < h \leq p}^{2} \sum_{0 \leq i < j \leq n_{kh}}^{2} \langle r_{ij}^2 \rangle \right.$$
$$\left. - (p-2) \sum_{t=1}^{p} \sum_{0 \leq i < j \leq n_t}^{2} \langle r_{ij}^2 \rangle \right](n+1)^{-2} \qquad (3)$$

where the suffix 0 indicates the unperturbed state. Furthermore if all subchains are statistically equal, eq 3 can be simplified as

$$\langle S^2 \rangle_0 = \left[\frac{p(p-1)}{2} \sum_{0 \leq i < j \leq n_{kh}}^{2} \langle r_{ij}^2 \rangle \right.$$
$$\left. - p(p-2) \sum_{0 \leq i < j \leq n_k}^{2} \langle r_{ij}^2 \rangle \right](n+1)^{-2} \qquad (4)$$

For a linear chain whose rotation of the bond is treated as an independent rotation, the value

$$\langle S^2 \rangle_0 = (n+1)^{-2} \sum_{0 \leq i < j \leq n}^{2} \langle r_{ij}^2 \rangle \qquad (5)$$

is represented by two methods.

One is the method (method I) to represent $\langle S^2 \rangle_0$ as a series of matrix $\langle T \rangle$ by applying the regular property of matrix $\langle T \rangle$, where $\langle T \rangle$ is the statistical average of the matrix T which transform the representation of a vector in the coordinate system of bond $i+1$ into its representation in a similar coordinate system affixed to bond i (see ref 3). In this method, $\langle S^2 \rangle_0$ is represented by eq 6,

$$\langle S^2 \rangle_0 = l^2(n+1)^{-2}$$
$$\times \{ \tfrac{1}{6} n(n+1)(n+2)[(E_3 + \langle T \rangle)(E_3 - \langle T \rangle)^{-1}]_{11}$$
$$- n(n+1)[(E_3 - \langle T \rangle)^{-2}\langle T \rangle]_{11}$$
$$+ 2n[(E_3 - \langle T \rangle)^{-3}\langle T \rangle^2]_{11}$$
$$- 2[(E_3 - \langle T \rangle)^{-4}\langle T \rangle^3(E_3 - \langle T \rangle^n)]_{11} \} \qquad (6)$$

where the subscript 11 of $[M]_{11}$ denotes the 1, 1-element of matrix M, the matrix E_k represents the unit matrix of the order k, l is the length between successive α-carbons, and n is the number of virtual bonds.

The other is Flory—Jernigan[7] matrix method (method II). In this method, $\langle S^2 \rangle_0$ is represented by eq 7.

$$\langle S^2 \rangle_0 = 2(n+1)^{-2} J_7^* D_1^{(n)} J_7 \qquad (7)$$

where

$$D_i = \begin{bmatrix} 1 & 1 & l^t\langle T \rangle & l^2/2 & l^2/2 \\ 0 & 1 & l^t\langle T \rangle & l^2/2 & l^2/2 \\ 0 & 0 & \langle T \rangle & l & l \\ 0 & 0 & 0 & 1 & 1 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}_i \qquad (8)$$

J_k^* is defined as the row vector consisting of k elements, the first element being unity and all succeeding elements being zero, and J_k is defined as the column vector consisting of k elements, the last element being unity and other element being zero. Symbolism of the type $D_1^{(n)}$ (see ref 3) indicates the serial product of the type $D_1 D_2 \cdots D_n$, i.e., a product of n such terms. 0 is rectangular null matrix of the appropriate dimension, and l is the bond vector as a column.

RADIUS OF THE GYRATION RATIO OF STAR-LIKE POLYPEPTIDES WITH UNIFORM AND RANDOM DISTRIBUTION IN LENGTH

Considering eq 5 and 6, or eq 5 and 7, the unperturbed dimension of star-like chains whose degree of polymerization are known can be calculated by using eq 3 or 4. However it seems almost impossible to determine the degree of polymerization for all subchains. So the average is carried out in two statistically interesting cases. One case is the average of the uniform distribution of subchain length. The other is the case in which the average of the random distribution of subchain length.

Uniform Distribution of Subchain Length

Let the degree of polymerization of the molecule be n, and that of the k-th subchain be n_k; then, n_k is represented by

$$n_k = n/p \quad (k = 1, 2, \cdots, p) \quad (9)$$

In the case of uniform distribution of subchain lengths, using eq 9 we obtain eq 10 from 4.

$$\langle S^2 \rangle_{0,\mathrm{av}} = (n+1)^{-2} \left[\frac{p(p-1)}{2} \sum_{0 \le i < j \le 2n_k}^{2} \langle r_{ij}^2 \rangle - p(p-2) \sum_{0 \le i < j \le n_k}^{2} \langle r_{ij}^2 \rangle \right] \quad (10)$$

The subscript av of $\langle S^2 \rangle_{0,\mathrm{av}}$ denotes the average on the distribution of the degree of polymerization of subchains. Using method I (eq 5 and 6), we obtain eq 11.

$$\langle S^2 \rangle_{0,\mathrm{av}} = nl^2 \left\{ \frac{1}{6} \frac{(n+p)[(3p-2)n+2p]}{p^2(n+1)^2} \right.$$
$$\times [(E_3 - \langle T \rangle)^{-1}(E_3 + \langle T \rangle)]_{11}$$
$$- \frac{1}{(n+1)} [(E_3 - \langle T \rangle)^{-2} \langle T \rangle]_{11}$$
$$+ \frac{2}{(n+1)^2} [(E_3 - \langle T \rangle)^{-3} \langle T \rangle^2]_{11}$$
$$+ \frac{p}{n(n+1)^2} [(E_3 - \langle T \rangle)^{-4} \langle T \rangle^3 \{(p-3)E_3$$
$$\left. - 2(p-2)\langle T \rangle^{n/p} + (p-1)\langle T \rangle^{2n/p} \}]_{11} \right\} \quad (11)$$

Using method II (eq 5 and 7), we obtain eq 12.

$$\langle S^2 \rangle_{0,\mathrm{av}} = (n+1)^{-2} [p(p-1) J_7^* D_1^{(2n/p)} J_7 - 2p(p-2) J_7^* D_1^{(n/p)} J_7] \quad (12)$$

Equations 11 and 12 are derived only by using the rotational isomeric approximation, and are applied to all star-like chains whose branches have the same degree of polymerization. Substituting 1 or 2 for p in eq 11 and 12, we obtain the equations for linear chain by simple calculation.

Random Distribution of Subchain Lengths

When the degree of polymerization of the subchains are randomly distributed, the average of the mean square of radius of gyration is obtained by the following equation.

$$\langle S^2 \rangle_{0,\mathrm{av}} = \sum_{0 < N_1 < \cdots < N_{p-1} < n}^{p-1} \langle S^2 \rangle_0 \Big/ \sum_{0 < N_1 < \cdots < N_{p-1} < n}^{p-1} 1 \quad (13)$$

where

$$N_k = \sum_{t=1}^{k} n_t \quad (14)$$

In the case of method I, according to from eq 4—6,

$$\langle S^2 \rangle_0 = l^2(n+1)^{-2} \{ \tfrac{1}{6}[n(n+1)(n+2)$$
$$- 6 \sum_{1 \le k < l < m \le p}^{3} n_k n_l n_m]$$
$$\times [(E_3 - \langle T \rangle)^{-1}(E_3 + \langle T \rangle)]_{11}$$
$$- n(n+1)[(E_3 - \langle T \rangle)^{-2} \langle T \rangle]_{11}$$
$$+ 2n[(E_3 - \langle T \rangle)^{-3} \langle T \rangle^2]_{11}$$
$$+ [\{p(p-3)E_3 + 2 \sum_{1 \le k < h \le p}^{2} \langle T \rangle^{n_k h}$$
$$- 2(p-2) \sum_{k=1}^{p} \langle T \rangle^{n_k} \} (E_3 - \langle T \rangle)^{-4} \langle T \rangle^3]_{11} \} \quad (15)$$

Using eq 13 and 15, we obtain eq 16.

$$\langle S^2 \rangle_{0,\mathrm{av}} = nl^2 \left\{ \frac{1}{6} \frac{6p}{(p+1)(p+2)} \frac{(n+2)}{(n+1)} \right.$$
$$\times [(E_3 - \langle T \rangle)^{-1}(E_3 + \langle T \rangle)]_{11}$$
$$- \frac{1}{n+1} [(E_3 - \langle T \rangle)^{-2} \langle T \rangle]_{11}$$
$$+ \frac{2}{(n+1)^2} [(E_3 - \langle T \rangle)^{-3} \langle T \rangle^2]_{11}$$
$$+ p!(p-1)(-1)^p [(E_3 - \langle T \rangle)^{-p-2} \langle T \rangle^{n+3}]_{11}$$
$$\times [\prod_{k=-1}^{p-2} (n-k)(n+1)]^{-1}$$
$$+ (p+1)!(p-2)(-1)^p$$
$$\times [(E_3 - \langle T \rangle)^{-p-3} \langle T \rangle^{n+3}]_{11}$$

$$\times[\prod_{k=-1}^{p-1}(n-k)(n+1)]^{-1}$$

$$+p!\sum_{i=0}^{p-1}\frac{(p-1)i+p-3}{(p-i-1)!}(-1)^i$$

$$\times[(E_3-\langle T\rangle)^{-i-4}\langle T\rangle^{i+3}]_{11}$$

$$\times[\prod_{k=-1}^{i}(n-k)(n+1)]^{-1}\}\qquad(16)$$

To calculate the random average of eq 15, following relations are used,

$$\sum_{0<N_1<\cdots<N_{p-1}<n}^{p-1}n_kn_ln_m=\frac{1}{(p+2)!}\prod_{i=-2}^{p-1}(n-i)$$

$$\sum_{0<N_1<\cdots<N_{p-1}<n}^{p-1}1=\frac{1}{(p-1)!}\prod_{i=1}^{p-1}(n-i)\qquad(17)$$

$$\sum_{0<N_1<\cdots<N_{p-1}<n}^{p-1}A^{n_k}$$
$$=(-1)^{p-1}(E_m-A)^{1-p}A^n+(-1)^p(E_m-A)^{1-p}A^{p-1}$$
$$+\sum_{j=2}^{p-1}\prod_{k=j}^{p-1}\frac{(n-k)}{(p-j)!}(E_m-A)^{1-j}A^{j-1}(-1)^j\quad(18)$$

$$\sum_{0<N_1<\cdots<N_{p-1}<n}^{p-1}A^{n_k+n_h}$$
$$=(n-p+1)(E_m-A)^{2-p}A^n(-1)^p$$
$$+(p-2)(E_m-A)^{1-p}A^n(-1)^p$$
$$+(E_m-A)^{1-p}\frac{\prod_{k=1}^{p-1}(n-k)}{(p-3)!}$$
$$\times\sum_{j=2}^{p-1}\frac{p-3C_{p-j-1}}{(n-j+1)(n-j)}A^j(-1)^j\qquad(19)$$

where A represents the regular matrix of the order m.

In the case of method II, we define $\langle A_{p,k}\rangle$ and $\langle B_{p,kh}\rangle$ by eq 20.

$$\langle A_{p,k}\rangle=J_7{}^*D_1{}^{(n_k)}J_7$$
$$\langle B_{p,kh}\rangle=J_7{}^*D_1{}^{(n_k+n_h)}J_7\qquad(20)$$

Using eq 4, 5, 7, and 20, we obtain

$$\langle S^2\rangle_0=(n+1)^{-2}[p(p-1)\langle B_{p,kh}\rangle-2p(p-2)\langle A_{p,k}\rangle]\qquad(21)$$

Substitution eq 21 into 13, we obtain

$$\langle S^2\rangle_{0,av}=(n+1)^{-2}[p(p-1)\langle B_p\rangle_{av}$$
$$-2p(p-2)\langle A_p\rangle_{av}]\qquad(22)$$

where $\langle A_p\rangle_{av}$ and $\langle B_p\rangle_{av}$ are defined as random average of $\langle A_{p,k}\rangle$ and $\langle B_{p,kh}\rangle$, respectively.

Calculation of $\langle A_p\rangle_{av}$ is carried out as follows. In the case of $p=3$, we let

$$a_2=\sum_{0<N_1<N_2}J_7{}^*D_1{}^{(N_1)}J_7$$

The sum in this equation is obtained by using the following matrix $\{H(2)\}_i$

$$\{H(2)\}_i=\begin{bmatrix}D&DJ_7\\0&1\end{bmatrix}_i\qquad(23)$$

As shown in eq 27, $\{H(k)\}_i$ represents a series of expanded matrices whose starting matrix is D. $\{H(2)\}_i$ in eq 23 represents the 2nd matrix of this series. Thus,

$$a_2=J_8{}^*\{H(2)\}_1{}^{(N_2-1)}J_8$$

Similarly, we let

$$a_3=\sum_{1<N_2<n}a_2\qquad(24)$$

and using the following matrix,

$$\{H(3)\}_i=\begin{bmatrix}H(2)&H(2)J_8\\0&1\end{bmatrix}_i$$

we obtain the summation in eq 24.

$$a_3=J_9{}^*\{H(3)\}_1{}^{(n-2)}J_9\qquad(25)$$

From the definition of $\langle A_3\rangle_{av}$, we obtain

$$\langle A_3\rangle_{av}=a_3/\sum_{0<N_1<N_2<n}^2 1$$

Substitution of eq 25 into this equation gives

$$\langle A_3\rangle_{av}=J_9{}^*\{H(3)\}_1{}^{(n-2)}J_9/\sum_{0<N_1<N_2<n}^2 1$$

Similarly, we obtain $\langle A_p\rangle_{av}$

$$\langle A_p\rangle_{av}=J_{p+6}^*\{H(p)\}_1{}^{(n-p+1)}J_{p+6}/\sum_{0<N_1<\cdots<N_{p-1}<n}^{p-1}1\qquad(26)$$

where

$$\{H(k)\}_i=\begin{bmatrix}H(k-1)&H(k-1)J_{k+5}\\0&1\end{bmatrix}_i\quad(k\geq2)$$
$$\{H(1)\}_i=D_i\qquad(27)$$

Calculation of $\langle B_p\rangle_{av}$ is carried out in the following way. In the case of $p=4$, we let

$$b_3=\sum_{0<N_1<N_2<N_3}^2 J_7{}^*D_1{}^{(N_1)}D_{N_1+1}^{(N_2-N_1)}J_7$$

The sum in this equation is obtained by using the following matrix

$$\{K(2)\}_i=\begin{bmatrix}D&I_0H(2)\\0&H(2)\end{bmatrix}_i\qquad(28)$$
$$\{K(2)\}_1=[D_1\quad 0]$$

where

$$I_0 = [E_7 \quad 0]$$

and orders of matrices $\{K(2)\}_1$ and I_0 are respectively, 7×15 and 7×8. Thus, we obtain

$$b_3 = J_7^* \{K(2)\}_1^{(n-1)} J_{15}$$

Similarly, we let

$$b_4 = \sum_{2 < N_3 < n} b_3$$

and using the following matrices,

$$\{K(3)\}_i = \begin{bmatrix} K(2) & K(2)J_{15} \\ 0 & 1 \end{bmatrix}_i \quad (i \geq 2)$$

$$\{K(3)\}_1 = [D_1 \quad 0]$$

we obtain b_4 as

$$b_4 = J_7^* \{K(3)\}_1^{(n-2)} J_{16} \tag{29}$$

where the order of $\{K(3)\}_1$ is 7×16. From the definition of $\langle B_4 \rangle_{av}$ and eq 29

$$\langle B_4 \rangle_{av} = J_7^* \{K(3)\}_1^{(n-2)} J_{16} / \sum_{0 < N_1 < N_2 < N_3 < n}^3 1$$

Similarly, we obtain $\langle B_p \rangle_{av}$

$$\langle B_p \rangle_{av}$$
$$= J_7^* \{K(p-1)\}_1^{(n-p+2)} J_{p+12} / \sum_{0 < N_1 < N_2 < \cdots < N_{p-1} < n}^{p-1} 1 \tag{30}$$

where

$$\{K(k)\}_i = \begin{bmatrix} K(k-1) & K(k-1)J_{k+12} \\ 0 & 1 \end{bmatrix}_i \quad (k \geq 3, \ i \geq 2)$$

$$\{K(k)\}_1 = D_1 I_{k+5} \quad (k \geq 2) \tag{31}$$

$$I_k = [E_7 \quad 0] \tag{32}$$

and the order of I_k is $7 \times (k+8)$.

Substituting eq 26 and 30 into 22, we obtain finally

$$\langle S^2 \rangle_{0,av} = [p(p-1)J_7^* \{K(p-1)\}_1^{(n-p+2)} J_{p+12} - 2p(p-2)J_{p+6}^* \{H(p)\}_1^{(n-p+1)} J_{p+6}](p-1)!$$
$$\times [(n+1)^2 \prod_{i=1}^{p-1} (n-i)]^{-1} \tag{33}$$

Substituting 1 or 2 for p in eq 16, we obtain the equation for the linear chain, for which eq 16 corresponds to eq 5. Similarly, defining $\{K(1)\}_i$ by eq 34,

$$\{K(1)\}_i = \begin{bmatrix} D & D \\ 0 & D \end{bmatrix}_i \quad (i \geq 2)$$

$$\{K(1)\}_1 = [D_1 \quad 0] \tag{34}$$

Substitution of 1 or 2 for p in eq 33 results in

the equation for the linear chain, eq 7. Equations 16 and 33 contain no mathematical approximation, and is thus useful to analyse the star-like chains having randomly distributed subchain lengths.

The branching factor g is defined as the ratio of $\langle S^2 \rangle_{0,av}$ of star-like chain to $\langle S^2 \rangle_0$ of the linear chain whose number of bond is identical with that of the branched chain. In the case of star-like chains having uniformly distributed subchain length, the branching factor g is obtained by dividing eq 11 by eq 6 or dividing eq 12 by eq 7. Then, the following equation is obtained as the g value for infinite degree of polymerization.

$$g = \frac{3p-2}{p^2} \tag{35}$$

This equation is in accord with the results obtained by Zimm and Stockmayer,[1] and Kurata and Fukatsu[2] for the Gaussian chain. Similarly, in the case of star-like chain having randomly distributed subchain lengths, the branching factor g is obtained by diving eq 16 by eq 6 or dividing eq 33 by eq 7. Then, the following equation is obtained for the infinite degree of polymerization,

$$g = \frac{6p}{(p+1)(p+2)} \tag{36}$$

This equation also agrees with Zimm's and Kurata's result.

NUMERICAL RESULTS AND DISCUSSION

The characteristic ratio $\langle R^2 \rangle_0 / nl^2$ and the radius of the gyration ratio $\langle S^2 \rangle_0 / nl^2$ of linear polypeptides were calculated by Flory, et al.,[4,5] and Tanaka and Nakajima.[10,11] It was mentioned in these papers that the value of the van der Waals radius r_{CH_2} for β-methylene group significantly affected the calculated value of the characteristic ratio and the radius of gyration ratio, and that linear side chains longer than methyl should have little influence on the characteristic ratio and the radius of gyration ratio. Thus the results calculated for poly-L-alanine may be applied to other polypeptides composed of α-L-amino acid residues. Consequently, the calculations in this study are carried out for star-like polypeptides composed of L-alanine residues.

Flory and his co-workers[5] arrived at the following matrix for poly-L-alanine.

$$\langle T \rangle = \begin{bmatrix} 0.51 & 0.20 & 0.59 \\ -0.046 & -0.61 & 0.21 \\ 0.65 & -0.23 & -0.30 \end{bmatrix} \quad (37)$$

This formula is used in our calculation.

The Radius of Gyration Ratio

Figure 2 (uniform distribution) and Figure 3 (random distribution) indicate that the radius of the gyration ratio $\langle S^2 \rangle_{0,av}/nl^2$ of star-like molecules whose branch lengths distribute uniformly and randomly, increase asymptotically with the degree of polymerization n like that of linear chain. This tendency is remarkable in the case of random distribution of subchain length. Figures 2 and 3 also show that $\langle S^2 \rangle_{0,av}/nl^2$ of star-like chains always smaller than that of linear chain of identical n. Figure 4 indicates that $\langle S^2 \rangle_{0,av}/nl^2$ decreases asymptotically with number of branches p, and $\langle S^2 \rangle_{0,av}/nl^2$ of random distribution is always larger than that of uniform
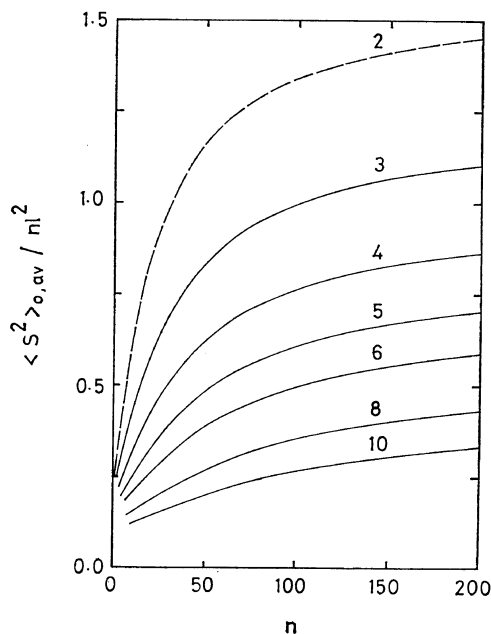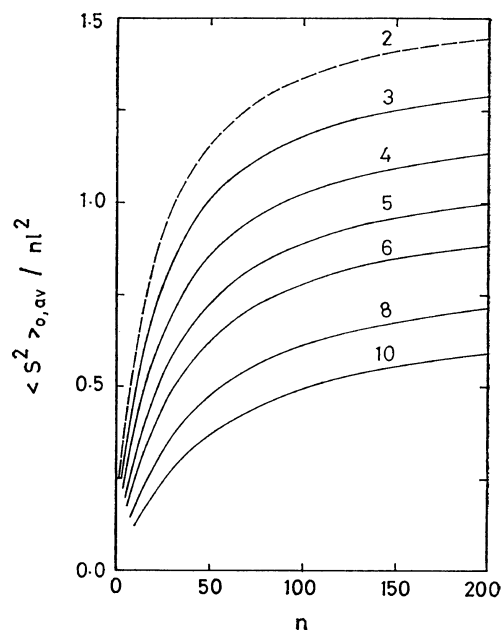

Figure 3. The radius of the gyration ratio $\langle S^2 \rangle_{0,av}/nl^2$ plotted against the degree of polymerization n for star-like polypeptides having random distribution of subchain length. The numeral on each curve indicates the number of branches.
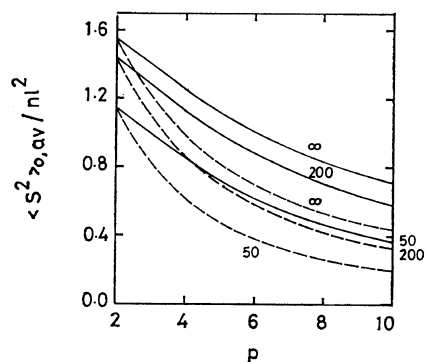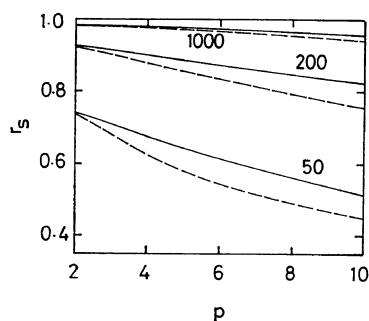

Figure 4. The radius of the gyration ratio $\langle S^2 \rangle_{0,av}/nl^2$ plotted against the number of branches p for star-like polypeptides having random distribution of subchain length (solid lines), and having uniform distribution of subchain length (broken lines). The numeral on each curve indicates the degree of polymerization.

Figure 2. The radius of the gyration ratio $\langle S^2 \rangle_{0,av}/nl^2$ plotted against the degree of polymerization n for star-like polypeptides having uniform distribution of subchain length. The numeral on each curve indicates the number of branches.

distribution of identical p. Also, Figure 5 indicates that r_s, which is the ratio $\langle S^2 \rangle_{0,av}/nl^2$ to $(\langle S^2 \rangle_{0,av}/nl^2)_\infty$ $((\langle S^2 \rangle_{0,av}/nl^2)_\infty$ is the asymptotic value of $\langle S^2 \rangle_{0,av}/nl^2$ at n), decreases asymp-

Figure 5. r_s, which is the ratio $\langle S^2 \rangle_{0,\mathrm{av}}/nl^2$ to $(\langle S^2 \rangle_{0,\mathrm{av}}/nl^2)_\infty$, plotted against the number of branches p for star-like polypeptides having random distribution of subchain length (solid lines), and having uniform distribution of subchain length (broken lines). The numeral on each curve indicates the degree of polymerization.

Table I. Summary of the number of bonds required for $(\langle S^2 \rangle_{0,\mathrm{av}}/nl^2)_\infty - \langle S^2 \rangle_{0,\mathrm{av}}/nl^2$ to be within 10 and 5% of $(\langle S^2 \rangle_{0,\mathrm{av}}/nl^2)_\infty$ for star-like polypeptides

p	Uniform		Random	
	$n(10\%)$	$n(5\%)$	$n(10\%)$	$n(5\%)$
2	157	330	157	330
3	201	414	177	370
4	248	508	205	420
5	295	605	228	470
6	342	576	255	530
8	440	896	315	640
10	540	1100	370	760

totically with the number of branches p, and r_s of random distribution is always larger than that of uniform distribution of identical p. Table I indicates that the number of bonds required for $(\langle S^2 \rangle_{0,\mathrm{av}}/nl^2)_\infty - \langle S^2 \rangle_{0,\mathrm{av}}/nl^2$ to approach to within 10 and 5% of $(\langle S^2 \rangle_{0,\mathrm{av}}/nl^2)_\infty$ is always larger for uniform distribution than for random distribution, and that the number of these increases with an increasing number of branches p. Figure 6 represents each term of eq 16 as functions of the degree of polymerization for $p=3$. The 1st term in braces of eq 16 is represented by A_1, and the 2nd and 3rd terms are by A_2. The 4 and 5th terms are, respectively, represented by B_1 and B_2. The term for $i=k$ in the 6th term are represented by C_{k+4}. The terms B_1, B_2, C_5, and C_6 have a large influence
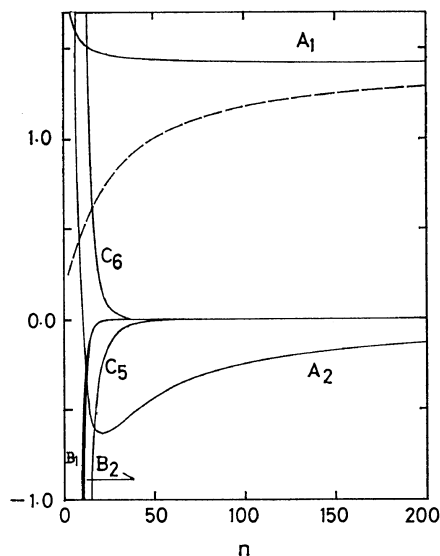
Figure 6. Each term of eq 16 calculated for $p=3$ as functions of the degree of polymerization. The 1st term within the braces of eq 16 is represented by A_1, and the 2nd and 3rd terms by A_2. The 4th and 5th terms are, respectively, represented by B_1 and B_2. The terms for $i=k$ in the 6th term are represented by C_{k+4}. The broken line indicates $\langle S^2 \rangle_{0,\mathrm{av}}/nl^2$.

on $\langle S^2 \rangle_{0,\mathrm{av}}/nl^2$ at $n<20$, but converge very rapidly to 0 with increasing n. The term A_2 converges slowly. The effect of this term cannot be neglected for a large value of n.
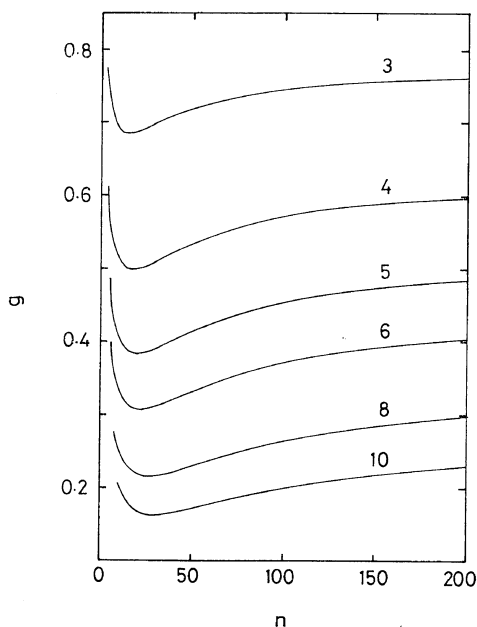
Branching Factor

Zimm and Stockmayer,[1] and Kurata and Fukatsu[2] showed that the branching factor g of star-like chains whose branch lengths distribute uniformly and randomly is dependent on the numbers of branches p. In this work Figures 7—9 show that the branching factor of star-like chain dependents not only on the number of branches p, but also the degree of polymerization n. In the case of random distribution, the value of g increases monotonously to the asymptotic limit, i.e., g_∞, while, in the case of uniform distribution, the value of g decreases with n, and passes through a minimum, i.e., $g_{\min}$, and increases with n to the value of g_∞. In the case of uniform distribution for $p=3$, the value of g reaches a minimum value $g_{\min}=0.685$ when $n=15$; the value of $g_{\min}$ decreases with p, that is, $g_{\min}=0.499$ when $n=16$ for $p=4$,
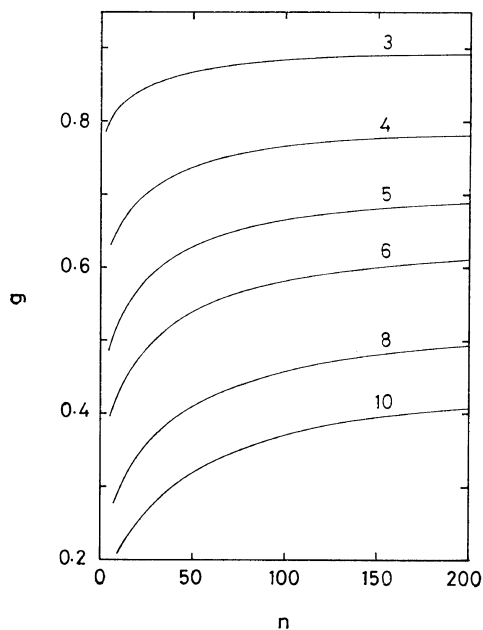
and $g_{min}=0.163$ when $n=30$ for $p=10$. The value of g converges more rapidly to g_∞ with increasing n than $\langle S^2 \rangle_{0,av}/nl^2$ in both cases of uniform and random distributions. Table II shows that the number of bonds required for $g_\infty-g$ to approach to within 10 and 5% of g_∞ is always larger for uniform distribution than for random distribution, and that the number of these increases with an increasing number of branches p.

From the results mentioned above, the radius of the gyration ratio $\langle S^2 \rangle_{0,av}/nl^2$ and the branching factor g depend not only on the number of branches p but also on the degree of polymerization n. These two parameters are important factors for the characterization of star-like polypeptides as a model of globular proteins.

Tonelli[12] has calculated the value of g for the particular star-like and comb-like polyethylenes whose subchain length is specified. In the case of a 3 branched star-like chain whose subchain lengths n_k are 25, 50, and 100, Tonelli. obtained the values of 0.737, 0.769, and 0.776 for g,

Figure 8. The branching factor g plotted against the degree of polymerization n for star-like polypeptides having random distribution of the subchain length. The numeral on each curve indicates the number of branches.

Figure 7. The branching factor g plotted against the degree of polymerization n for star-like polypeptides having uniform distribution of the subchain length. The numeral on each curve indicates the number of branches.
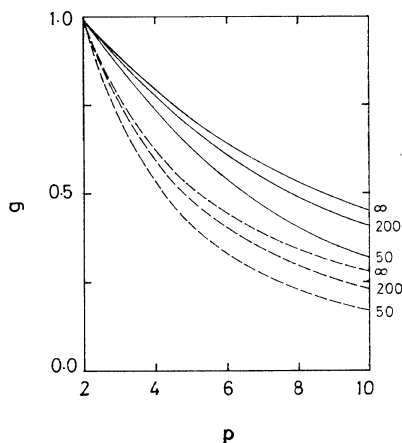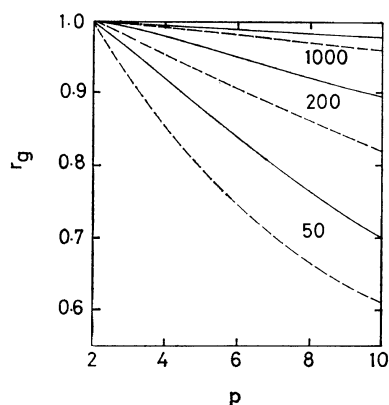

Figure 9. The branching factor g plotted against the number of branches p for star-like polypeptides having random distribution of subchain length (solid lines), and having uniform distribution of the subchain length (broken lines). The numeral on each curve indicates the degree of polymerization.

respectively. These results are slightly larger than our results 0.735, 0.756, and 0.767. In the case of a 4 branched star-like chain, his results are $g=0.568$, 0.615 and 0.608, for $n_k=25$, 50, and 100. These results are slightly smaller than our results 0.571 and 0.611 for $n_k=25$ and 100, and slightly larger than our result 0.597 for $n_k=50$. Though his configuration partition function was formulated incorrectly and the polymers used as the model were different, the difference between the two value of g is smaller than that between g_∞ and g for the corresponding n.

Recently, Mattice and his coworker[13-15] have calculated values of g for the 3 and 4 branched star-like polyethylenes whose subchain lengths are uniformly distributed. Their value for g_{min}

Figure 10. The ratio g to g_∞ plotted against the number of branches p for star-like polypeptides having random distribution of subchain length (solid lines), and having uniform distribution of the subchain length (broken lines). The numeral on each curve indicates the degree of polymerization.

Table II. Summary of the number of bonds required for $g_\infty-g$ to be within 10 and 5% of g_∞ for star-like polypeptides

p	Uniform		Random	
	$n(10\%)$	$n(5\%)$	$n(10\%)$	$n(5\%)$
3	33	84	8	34
4	84	180	37	87
5	135	280	65	142
6	186	378	93	249
8	280	576	150	315
10	380	770	208	430

Table III. Summary of the results on g for star-like chains whose subchain lengths distribute uniformly

p	$n(g_{min})$[a]	g_{min}	$n(1\%)$[b]
3	15(15)[c]	0.685(0.659)	432(650)
4	16(16)	0.499(0.480)	904(1200)
5	20	0.383	1390
6	24	0.308	1878
8	24	0.216	2500<
10	30	0.163	2500<

[a] Number of bonds at which g attains the minimum value g_{min}.
[b] Number of bonds required for $g_\infty-g$ to be within 1% of g_∞.
[c] Numerical values in parentheses are Mattice's results obtained with $\sigma=0.54$, $\phi=1$, and $\omega=0.088$ for the 3 and 4 branched star-like polyethylenes.

was slightly smaller than our results, but the number of bonds for g_{min} was identical with our results. The number of bonds required for $g_\infty-g$ within 1% of g_∞, which they have obtained, are larger than our results. That is, the convergence of the g value to the limiting value g_∞ is slower than that for star-like polyethylenes, but the difference between their results and ours is very small.

Computations were carried out by the FACOM 230–75 computer at the Kyoto University Computation Center.

APPENDIX

Modification of the Lagrange's Theorem

For the star-like chain as shown in Figure 1, if each atom is equal in mass, the square radius of gyration S^2 is represented by eq 1. Let the vector from the branching point 0 to the i-th atom be r_{0i}, and then

$$S_i=S_0+r_{0i} \qquad (A1)$$

From eq 1 and A1 we obtain the following relation

$$S^2=S_0{}^2+\frac{2}{n+1}S_0\sum_{k=1}^{p}\sum_{i=1}^{n_k}r_{0i}+\frac{1}{n+1}\sum_{k=1}^{p}\sum_{i=1}^{n_k}r_{0i}^2 \quad (A2)$$

The definition of S_i leads to

$$\sum_{k=1}^{p}\sum_{i=1}^{n_k}S_i+S_0=0 \qquad (A3)$$

By substituting eq A1 into A3, we obtain the following equation.

$$S_0 = -\frac{1}{n+1} \sum_{k=1}^{p} \sum_{i=1}^{n_k} r_{0i} \qquad (A4)$$

Combination of eq A2 with A4 results in

$$S^2 = \frac{1}{n+1} \sum_{k=1}^{p} \sum_{i=1}^{n_k} r_{0i}^2 - \frac{1}{(n+1)^2} \sum_{k=1}^{p} \sum_{i=1}^{n_k} \sum_{j=1}^{n_h} r_{0i} r_{0j}$$

$$- \frac{2}{(n+1)^2} \sum_{1 \leq k < h \leq p} \sum \sum_{i=1}^{n_k} \sum_{j=1}^{n_h} r_{0i} r_{0j} \qquad (A5)$$

Finally substituting the cosine rule

$$r_{0i} r_{0j} = \tfrac{1}{2}(r_{0i}^2 + r_{0j}^2 + r_{ij}^2)$$

into eq A5, eq 2 is obtained.

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