# Mean Square Radii of Gyration for Gaussian Comblike and Cyclic Polymers†

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ABSTRACT: We present a method of calculating the mean square radii of gyration for Gaussian polymers consisting of essentially linear chains. The chains are composed of identical structural elements that can be branched or contain cycles. The method exploits regularities in inverses of Kirchhoff matrices describing connectivity within the molecules represented as graphs and the relation between an inverse and the mean square radius of gyration. It is shown that the submatrices of the Kirchhoff matrix corresponding to the structural elements in a molecule provide all sufficient information necessary to calculate its mean square radius of gyration. Known relations for linear, branched, and ring molecules are rederived. Asymptotic values of the Zimm–Stockmayer value $g$ are given for chains with many long branches and for cyclic polymers with large numbers of structural elements. The value of $g$ for a molecule with large cycles connected into a long chain by single links tends to $^1/_2$.

The Gaussian, or random-flight, molecule provides a model for studying configurational behavior of a polymer. The main approximations involved in this model are as follows:[1] (i) the length of bonds is the only restriction for otherwise free movement of units relative to each other and (ii) no volume is ascribed to the units.

The Gaussian model is believed to provide a good description for the behavior of linear polymers in Θ conditions or in bulk.[2] For other, more complicated, polymer structures the Gaussian model should be considered as a means for comparing the configurational properties of a given molecular structure with those of some simpler, usually linear, one.

Zimm and Stockmayer[3] introduced the ratio $g$ to compare average dimensions of branched polymers and rings with those of their linear analogues having the same number of units. Their treatment of randomly branched structures was rationalized and extended to copolymers by Gordon et al.[4]

Introduction of the matrix representation of polymer molecules[5-8] gave a new impact in the development of mathematical tools for treating various model molecules. The basic idea of considering a molecule with $t$ units as one spanning $(3 \times t)$-dimensional space[9] reached a high level of development as reflected in the series of papers by Eichinger,[8-12] including his excellent review.[9] Mostly, due to the matrix methods, the average dimensions of regular Gaussian molecules, i.e., molecules in which certain blocks of units have identical structure or in which other symmetry exists, can be expressed explicitly. So far, such explicit formulas have been published for linear,[5,13] ring,[7,9,14] comblike,[6,7,13] and star[7,9] molecules.

The intention of this work is to extend the set of those formulas to molecules of essentially linear structures composed of sequences of identical blocks of units that may have either branched or cyclic structure. The reference made in the title to comblike and cyclic polymers should be loosely interpreted as in the previous works dealing with the random-flight molecules.[5,13] The assumptions of Gaussian character are generally not met[2] for real comblike polymers and cyclic polymers.

In the following paragraphs the terminology of polymer science is used. When necessary, however, terms from graph theory are preferred. Definitions of the latter are taken from Essam and Fisher.[15]

## Polymer Structures

Any consideration of branched or cyclic polymers requires an unambiguous system of codifying the structures. Here, we consider a system of $m$ identical structural elements, say, superunits, arranged into a regular linear assembly (Figure 1a). Each of the elements is constructed from $n$ units (vertices). We restrict ourselves only to the elements with at most one cycle and with functionalities (vertex degrees) of units not exceeding three. For branched structures, $n - k + 1$ units belong to the linear backbone of the polymer, and $k - 1$ units extend outward as a linear branch. This type of structure will be referred to as $b(n,k)$ (cf. Figure 1b).

Three parameters are necessary to avoid ambiguity when cyclic structures are considered. We choose the total number of units in a structural element, $n$, the number of units in a cycle, $k$, and the difference, $l$, between $n$ and the number of units in the longest path through an element. The path through an element is defined as a progression of units and links between two terminal units that are adjacent to the links connecting a given structural element with the preceding and succeeding ones. Detailed analysis, including a formula for the mean square radius of gyration, is given only for those cyclic structures in which the longest path is at the same time the spanning path, i.e., the one that visits all units in a structure (cf. Figure 1c). Then $l = 0$, and the cyclic structures can be referred to as $c(n,k) \equiv c(n,k,0)$.

## Kirchhoff Matrices and Their Inverses

The Kirchhoff matrix (graph matrix[15]) of a graph is the symmetric matrix in which the diagonal entries are vertex degrees of the graph (functionalities of units) and the off-diagonal entries are zeros or negative integers. The $(i,j)$th entry $(i \neq j)$ is the negative of the number of links between the unit labeled $i$ and the unit labeled $j$.[8,15] The Kirchhoff matrix of the linear assembly shown in Figure 1a can be defined in $(mn + 1 = t)!$ ways. Therefore, the method of labeling units becomes crucial, as it may greatly reduce computational effort.

Let the units of the polymer in Figure 1a be numbered starting from the single first unit. Then let the units in the $i$th structural element be labeled with the integers $in + 1$ through $(i + 1)n$ starting from the unit connected to the preceding element and ending on the unit connected to the succeeding element. The generality is not affected if the polymer is divided into structural elements in such a way that a branch is connected to the $(in + 1)$th unit or,

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† Affectionately dedicated to Professor Manfred Gordon on his 65th birthday.

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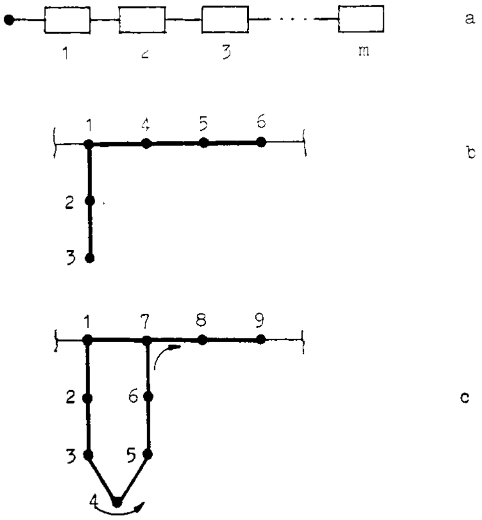

**Figure 1.** Structures for which the mean square radii of gyration are calculated explicitly. Structure a is the linear progression of *m* structural elements preceded by the single unit that is to be canceled out from the Kirchhoff matrix, thus providing nonsingularity of the remaining part of it. Examples of the structural elements represented in (a) as rectangles are also shown; (b) is branched structure *b*(6,3) of 6 units with 2 of them (=3 − 1) extending from the linear backbone, and (c) is cyclic structure *c*(9,7) with the cycle of 7 units. Cyclic structure c is not a unique one among structures of 9 units with seven-membered rings, but it represents the structure for which the longest path, shown by arrows, is at the same time the spanning path, i.e., the one that visits every vertex of the graph.

for cyclic structures, that the leading unit belongs to a cycle (Figure 1b,c). The units belonging to the branch or to the cycle should then be labeled before the units in the remaining linear part of the structural element. The pattern of labeling should be the same in all elements.

The Kirchhoff matrix takes then the form

$$\mathrm{K} = \begin{bmatrix} 1 & -\mathbf{e}^{\mathrm{T}} \\ -\mathbf{e} & \mathrm{K}_{t-1} \end{bmatrix} \tag{1}$$

where $\mathbf{e}^{\mathrm{T}} = [1,0,0,...,0]$ (superscript "T" denotes hereafter a transpose of a matrix including that of a vector, one-column matrix) and

$$\mathbf{K}_{t-1} = \begin{bmatrix} \mathrm{A} & -\mathrm{C}^{\mathrm{T}} & 0 & \dots & 0 & 0 \\ -\mathrm{C} & \mathrm{A} & -\mathrm{C}^{\mathrm{T}} & \dots & 0 & 0 \\ 0 & -\mathrm{C} & \mathrm{A} & \dots & 0 & 0 \\ & \cdot & & \dots & & \\ 0 & 0 & 0 & \dots & \mathrm{A} & -\mathrm{C}^{\mathrm{T}} \\ 0 & 0 & 0 & \dots & -\mathrm{C} & \mathrm{B} \end{bmatrix} \tag{2}$$

The matrices appearing in the tridiagonal form (2) each have dimensions $n \times n$. **A** and **B** are related to the Kirchhoff matrices of subgraphs corresponding to the structural elements,[16] and

$$\mathbf{C} = \delta_{1,n} \tag{3}$$

where

$$\begin{aligned} \delta_{i,j} &= 1; \quad i = j \\ &= 0; \quad i \neq j \end{aligned}$$

is the Kronecker delta function. The difference between **A** and **B** follows from the position of corresponding structural elements in the polymer chain

$$\mathbf{B} = \mathbf{A} - \delta_{n,n} \tag{4}$$

The trace of the Moore–Penrose general inverse,[9] $\mathbf{K}^{+}$, of a Kirchhoff matrix is directly related to the mean square radius of gyration, $\langle s^2 \rangle_0$, of the molecule in which connectivity is described by **K**

$$\langle s^2 \rangle_0 / \langle l^2 \rangle = t^{-1}\,\mathrm{Tr}\,(\mathbf{K}^{+}) \tag{5}$$

where $t$ is the number of units and $\langle l^2 \rangle$ is the mean square length of the bonds. In terms of the nonsingular matrix, $\mathbf{K}_{t-1}$, and for the bond length taken as unity

$$\langle s^2 \rangle_0 = t^{-1}\,\mathrm{Tr}\,(\mathbf{K}_{t-1}^{-1}) - t^{-2}\sum_i \sum_j \{\mathbf{K}_{t-1}^{-1}\}_{i,j} \tag{6}$$

where summation runs over all elements $\{\mathbf{K}_{t-1}^{-1}\}_{i,j}$ of $\mathbf{K}_{t-1}^{-1}$.

The values of determinants $|\mathbf{A}|$ and $|\mathbf{B}|$ and the form of $\mathbf{B}^{-1}$ have the key significance in calculating the inverse of $\mathbf{K}_{t-1}$. It is known[9,17] that $|\mathbf{B}|$ is equal to the number of spanning trees rooted on a unit to which the subgraph described by **B** is adjacent. In our case it is simply the number of bonds (or units) in the cycle of that subgraph. For linear or branched structures $|\mathbf{B}| = 1$. One can easily verify that for branched structures $|\mathbf{A}|$ does not depend on branch size and it is equal to the number of units in the linear backbone plus one. The relation between $|\mathbf{A}|$ and a cyclic structure is less obvious for the author. In the case of cyclic structures with the spanning path $c(n,k)$, one can calculate $|\mathbf{A}|$ from the relation

$$|\mathbf{A}| = k(n - k + 3) - 1 \tag{7}$$

Similar relations exist for other types of cyclic structures (see eq 44).

A very important property of **B** is that $\mathbf{B}^{-1}$ has one row (and column) composed of ones. Due to the method of labeling it is always the first row (and the first column), as can be proved by noting that one valency is used for linking the first unit of the subgraph, described by **B**, with the rest of a molecule. Thus, the sum of all elements in each row of **B** is zero (as follows from the definition of Kirchhoff matrices[15]) except in the first row, where it equals one. Therefore, only the vector $\mathbf{j}^{\mathrm{T}} = [1,1,...,1]$ satisfies the conditions

$$\mathbf{j}^{\mathrm{T}}\mathbf{B} = \mathbf{e}^{\mathrm{T}}; \qquad \mathbf{B}\mathbf{j} = \mathbf{e} \tag{8}$$

Making use of that property of $\mathbf{B}^{-1}$, we note that eq 4 can be rewritten as

$$\mathbf{A} - \mathbf{C}^{\mathrm{T}}\mathbf{B}^{-1}\mathbf{C} = \mathbf{B} \tag{4a}$$

and then the inverse of $\mathbf{K}_{t-1}$ takes the form

$$\mathbf{K}_{t-1}^{-1} = \begin{bmatrix} \mathbf{B}^{-1} & \mathbf{B}^{-1}\mathbf{C}^{\mathrm{T}}\mathbf{B}^{-1} & \dots & \mathbf{B}^{-1}\mathbf{C}^{\mathrm{T}}\mathbf{B}^{-1} \\ \mathbf{B}^{-1}\mathbf{C}\mathbf{B}^{-1} & (\mathbf{B} - \mathbf{C}\mathbf{A}_2^{-1}\mathbf{C}^{\mathrm{T}})^{-1} & \dots & (\mathbf{B} - \mathbf{C}\mathbf{A}_2^{-1}\mathbf{C}^{\mathrm{T}})^{-1}\mathbf{C}^{\mathrm{T}}\mathbf{B}^{-1} \\ \cdot & \cdot \quad \cdot & \dots & \\ \mathbf{B}^{-1}\mathbf{C}\mathbf{B}^{-1} & \mathbf{B}^{-1}\mathbf{C}(\mathbf{B} - \mathbf{C}\mathbf{A}_2^{-1}\mathbf{C}^{\mathrm{T}})^{-1} & \dots & (\mathbf{B} - \mathbf{C}\mathbf{A}_m^{-1}\mathbf{C}^{\mathrm{T}})^{-1} \end{bmatrix} \tag{9}$$

where

$$\mathbf{A}_{i+1} \equiv \mathbf{A} - \mathbf{C}\mathbf{A}_i^{-1}\mathbf{C}^{\mathrm{T}}; \qquad \mathbf{A}_2 \equiv \mathbf{A} \tag{10}$$

As the terms $\mathbf{C}\mathbf{A}_i^{-1}\mathbf{C}^{\mathrm{T}}$ appearing in eq 9 are matrices with only one nonzero element in their upper left corners, we may take advantage of having ones in the first row and column of $\mathbf{B}^{-1}$ and produce the remarkable relation

$$(\mathbf{B} - \mathbf{C}\mathbf{A}_i^{-1}\mathbf{C}^{\mathrm{T}})^{-1} = \mathbf{B}^{-1} + \alpha_i\mathbf{U} \tag{11}$$

where **U** is the matrix of ones. Now the inverse of $\mathbf{K}_{t-1}$ may be split into

$$\mathbf{K}_{t-1}^{-1} = \mathbf{R} + \mathbf{P} \tag{12}$$

where

$$\mathbf{R} = \begin{bmatrix} \alpha_1\mathbf{U} & \alpha_1\mathbf{U} & \alpha_1\mathbf{U} & \ldots & \alpha_1\mathbf{U} \\ \alpha_1\mathbf{U} & \alpha_2\mathbf{U} & \alpha_2\mathbf{U} & \ldots & \alpha_2\mathbf{U} \\ \alpha_1\mathbf{U} & \alpha_2\mathbf{U} & \alpha_3\mathbf{U} & \ldots & \alpha_3\mathbf{U} \\ \cdot & \cdot & & \ldots & \cdot \\ \alpha_1\mathbf{U} & \alpha_2\mathbf{U} & \alpha_3\mathbf{U} & \ldots & \alpha_m\mathbf{U} \end{bmatrix} \qquad (13)$$

and

$$\mathbf{P} = \begin{bmatrix} \mathbf{B}^{-1} & \mathbf{S}^{\mathrm{T}} & \mathbf{S}^{\mathrm{T}} & \ldots & \mathbf{S}^{\mathrm{T}} \\ \mathbf{S} & \mathbf{B}^{-1} & \mathbf{S}^{\mathrm{T}} & \ldots & \mathbf{S}^{\mathrm{T}} \\ \mathbf{S} & \mathbf{S} & \mathbf{B}^{-1} & \ldots & \mathbf{S}^{\mathrm{T}} \\ \cdot & \cdot & & \ldots & \cdot \\ \mathbf{S} & \mathbf{S} & \mathbf{S} & \ldots & \mathbf{B}^{-1} \end{bmatrix} \qquad (14)$$

with

$$\mathbf{S} \equiv \mathbf{B}^{-1}\mathbf{C}\mathbf{B}^{-1} \qquad (15)$$

Now, it is necessary to find values in the series $\alpha_1$, $\alpha_2$, ..., $\alpha_m$. The first element of that series is zero, as it was introduced merely to preserve the form of eq 13. Verifying eq 11, we find

$$\alpha_i = \{\mathbf{A}_i^{-1}\}_{n,n}/(1 - \{\mathbf{A}_i^{-1}\}_{n,n}) \qquad (16)$$

where $\{\mathbf{A}_i^{-1}\}_{n,n}$ is the lower right element of $\mathbf{A}_i^{-1}$. From the definition

$$\{\mathbf{A}_i^{-1}\}_{n,n} = \mathrm{cof}_{n,n}\,(|\mathbf{A}_i|)/|\mathbf{A}_i| \qquad (17)$$

where $\mathrm{cof}_{i,j}\,(|\mathbf{M}|)$ is the cofactor of element $i,j$ of the determinant $|\mathbf{M}|$, one may expand $|\mathbf{A}_i|$ by the $n$th row to find

$$\mathrm{cof}_{n,n}\,(|\mathbf{A}_i|) = |\mathbf{A}_i| - |\mathbf{B}_i| \qquad (18)$$

with the same relation between $\mathbf{A}_i$ and $\mathbf{B}_i$ as given by eq 4. Then using eq 10 one gets

$$|\mathbf{A}_i| = |\mathbf{A}| - \{\mathbf{A}_{i-1}^{-1}\}_{n,n}\,\mathrm{cof}_{1,1}\,(|\mathbf{A}|) \qquad (19)$$

and

$$|\mathbf{B}_i| = |\mathbf{A}| - \{\mathbf{A}_{i-1}^{-1}\}_{n,n}\,\mathrm{cof}_{1,1}\,(|\mathbf{B}|) \qquad (20)$$

The value of $\mathrm{cof}_{1,1}\,(|\mathbf{B}|)$ is easy to calculate. Addition of all the remaining rows to the first row of $|\mathbf{B}|$ transforms that row into $\mathbf{e}^{\mathrm{T}}$. Expansion yields

$$\mathrm{cof}_{1,1}\,(|\mathbf{B}|) = |\mathbf{B}| \qquad (21)$$

In order to calculate $\mathrm{cof}_{1,1}\,(|\mathbf{A}|)$ one can define a matrix $\mathbf{A}^*$ differing from $\mathbf{A}$ only by having $\{\mathbf{A}^*\}_{1,1} = \{\mathbf{A}\}_{1,1} - 1$. We note that $\mathbf{A}^*$ is the submatrix of a graph in which the link adjacent to the first vertex is deleted. $|\mathbf{A}^*|$ is just the number of spanning trees rooted on the unit adjacent to the $n$th vertex of the graph described by $\mathbf{A}^*$.[17] Clearly, $|\mathbf{A}^*| = |\mathbf{B}|$. Expanding $|\mathbf{A}^*|$, we extract

$$\mathrm{cof}_{1,1}\,(|\mathbf{A}|) = |\mathbf{A}| - |\mathbf{B}| \qquad (22)$$

Making use of eq 16 and expressing both $\alpha_{i+1}$ and $\alpha_i$ in terms of $\{\mathbf{A}_i^{-1}\}_{n,n}$, one finally finds

$$a \equiv \alpha_{i+1} - \alpha_i = (|\mathbf{A}| - |\mathbf{B}|)/|\mathbf{B}| \qquad (23)$$

It remains to substitute the results of summation of the elements in eq 13 and 14 into eq 6 to obtain, using eq 23,

$$\langle s^2 \rangle_0 = (mn + 1)^{-1}[X - (mn + 1)^{-1}Y] \qquad (24)$$

where

$$X \equiv (1/2)m(m - 1)na + m\,\mathrm{Tr}\,(\mathbf{B}^{-1}) \qquad (25)$$

and

$$Y \equiv (1/6)m(m - 1)(2m - 1)n^2a + m(m - 1)n\sum_i^n\{\mathbf{B}^{-1}\}_{n,i} + m\sum_i^n\sum_j^n\{\mathbf{B}^{-1}\}_{i,j} \qquad (26)$$

## Branched Polymers

The Kirchhoff submatrix, $\mathbf{B}$, of a linear structural element, $b(n,1)$, a degenerate case with no branch, is a tridiagonal matrix. In the main diagonal it has twos except that the $n,n$th element is one.[18] The other two diagonals consist of $-1$'s. The inverse of $\mathbf{B}$ has the form

$$\mathbf{B}^{-1} = \begin{bmatrix} 1 & 1 & 1 & \ldots & 1 \\ 1 & 2 & 2 & \ldots & 2 \\ 1 & 2 & 3 & \ldots & 3 \\ & & \cdot & \cdot\;\ldots & \\ 1 & 2 & 3 & \ldots & n \end{bmatrix} \qquad (27)$$

Elementary summations give terms appearing in eq 25 and 26

$$\mathrm{Tr}\,(\mathbf{B}^{-1}) = \sum_i^n\{\mathbf{B}^{-1}\}_{n,i} = (1/2)n(n + 1) \qquad (28a)$$

$$\sum_i^n\sum_j^n\{\mathbf{B}^{-1}\}_{i,j} = (1/6)n(n + 1)(2n + 1) \qquad (28b)$$

and, as $|\mathbf{A}| = n + 1$ and $|\mathbf{B}| = 1$, $a = n$. Substitution in eq 24 gives for any $m$ the familiar result[9]

$$\langle s^2 \rangle_0 = (1/6)t(1 - 1/t^2) \qquad (29)$$

where $t = mn + 1$. In terms of the number of bonds[19] $(=mn)$

$$\langle s^2 \rangle_0 = (1/6)mn\frac{mn + 2}{mn + 1} \qquad (29a)$$

The submatrix $\mathbf{B}^{-1}$ for the branched structures with the element $b(n,k)$ has the form

$$\mathbf{B}^{-1} = \begin{bmatrix} 1 & 1 & \ldots & 1 & 1 & 1 & \ldots & 1 \\ 1 & 2 & \ldots & 2 & 2 & 1 & \ldots & 1 \\ & \cdot & \ldots & & \cdot & & \cdot\;\ldots & \\ 1 & 2 & \ldots & k-1 & k-1 & 1 & \ldots & 1 \\ 1 & 2 & \ldots & k-1 & k & 1 & \ldots & 1 \\ 1 & 1 & \ldots & 1 & 1 & 2 & \ldots & 2 \\ & \cdot & \ldots & & \cdot & \cdot & & \\ 1 & 1 & \ldots & 1 & 1 & 2 & \ldots & n-k+1 \end{bmatrix} \qquad (30)$$

which instantly gives

$$\mathrm{Tr}\,(\mathbf{B}^{-1}) = (1/2)k(k + 1) + (n - k)(n - k + 3) \qquad (31a)$$

$$\sum\{\mathbf{B}^{-1}\}_{n,i} = k + (1/2)(n - k)(n - k + 3) \qquad (31b)$$

$$\sum\sum\{\mathbf{B}^{-1}\}_{i,j} = (1/6)k(k + 1)(2k + 1) + (n - k + 1) \times (n - k + 2)(2n - 2k + 3) + 2(k - 1)(n - k) - 1 \qquad (31c)$$

and $a = n - k + 1$ since for acyclic structures the quantity $a$ is simply equal to the number of units in the linear backbone of an element.

Substitution of eq 31 into eq 24–26 makes it possible to consider some special cases. Putting $m = 1$ and $n = k$, we rederive eq 29, this time for a "vertical" chain, as we have only two units in the backbone and a branch extending from one of them.

Considering chains composed of many structural elements, i.e., with $m \gg 1$, we can truncate the terms $X$ and $Y$ defined by eq 25 and 26 and leave only the highest powers of $m$. Then

$$X = (1/2)m^2n(n - k + 1) \qquad (32)$$

$$Y = (1/6)m^3n^2(n - k + 1) \qquad (33)$$

and

$$\langle s^2 \rangle_0 = (1/6)m(n - k + 1) \qquad (34)$$

Denoting the fraction of units in the linear backbone by $\lambda \equiv (n - k + 1)/n$, we rediscover the result of Forsman[6]

$$\lim_{m\to\infty} \frac{6\langle s^2\rangle_0}{mn} = \lim_{m\to\infty} g = \lambda \tag{35}$$

which reminds us that despite the presence of branches in an essentially linear Gaussian molecule, it can always be considered as exactly linear if it is sufficiently long.

A "long-hair-comb" molecule is one with branches extending from every unit in the main chain and having a length comparable with that of the backbone. Let the ratio of the lengths be $\rho = k/m$. Substituting $k = n = m$ into eq 31 and taking $m \gg 1$ and $m\rho \gg 1$, we obtain

$$6\langle s^2\rangle_0/m = 3\rho + 1 \tag{36}$$

Equation 36 shows that branches in a long-hair-comb molecule contribute substantially to its dimensions, particularly when $\rho$ is sufficiently large, i.e., when branches are long and the number of units in the main chain is not too large.

### Cyclic Molecules

The advantage of the present method over previous ones[3,20] can be fully exploited when dimensions of chains with cyclic elements are to be calculated. Although we give explicit formulas for just one type of structure, the method is more general and covers all cases of regular linear forms in which segments with disjoint cycles can be distinguished.

We consider a particular case of an element $c(n,n)$ having all its units belonging to a cycle, with the longest path through the element being the spanning one. The inverse of the matrix **B** describing connectivity in the element can be written as

$$\mathbf{B}^{-1} = \mathbf{U} + |\mathbf{B}|^{-1}\mathbf{Z} \tag{37}$$

where **Z** is the symmetric matrix with elements defined as

$$\begin{aligned} \{\mathbf{Z}\}_{i,j} &\equiv (n - i + 1)(j - 1); \qquad i \geq j \\ &\equiv (n - j + 1)(i - 1); \qquad j \geq i \end{aligned} \tag{38}$$

The form of **Z** is characteristic for the spanning-path cyclic structures.

As $|\mathbf{B}| = n$, the number of units in the cycle, the entries to be substituted into eq 25 and 26, take remarkably simple forms

$$\mathrm{Tr}\ (\mathbf{B}^{-1}) = n + (1/6)(n^2 - 1) \tag{39a}$$

$$\sum\{\mathbf{B}^{-1}\}_{n,i} = n + (1/2)(n - 1) \tag{39b}$$

and

$$\sum\sum\{\mathbf{B}^{-1}\}_{i,j} = n^2 + (1/12)n(n^2 - 1) \tag{39c}$$

Substituting $a = (2n - 1)/n$, as follows from eq 7 and 23, and neglecting the auxiliary first unit (i.e., putting $t = mn$), we obtain for $m = 1$

$$\langle s^2\rangle_0 = (1/12)n(1 - 1/n^2) \tag{40}$$

the result known previously[9,14] to describe a ring molecule.

The structural elements with a cyclic and a linear part, $c(n,k)$, have the inverse of **B** of the form

$$\mathbf{B}^{-1} = \begin{bmatrix} \mathbf{B}_\mathrm{c}^{-1} & \mathbf{S}^{*\mathrm{T}} \\ \mathbf{S}^* & a_\mathrm{c}\mathbf{U} + \mathbf{B}_{n-k}^{-1} \end{bmatrix} \tag{41}$$

where $\mathbf{B}_\mathrm{c}$ is the submatrix of the cyclic part of a structural element, i.e., is identical with **B** for $c(k,k)$ (cf. eq 37 and 38); $\mathbf{S}^*$ is the $(n - k) \times k$ matrix that has all rows identical with the last row of $\mathbf{B}_\mathrm{c}^{-1}$. $\mathbf{B}_{n-k}^{-1}$ is the inverse of the Kirchhoff matrix for linear chains of length $n - k$ (cf. eq 27). The multiplier, $a_\mathrm{c}$, in front of the $(n - k) \times (n - k)$ matrix of ones, **U**, can be calculated by using eq 23 provided that the determinants in that equation are taken for matrices describing the cyclic part of the structural element, here the element $c(k,k)$.

Equation 41, as well as eq 30, which can be partitioned in a similar way, shows that the part of the inverse of matrix **B** corresponding to the linear part of the structural element can be easily factored out and considered independently of the other part. This is again a consequence of eq 11 that can be further exploited for simplification of calculations. Thus, for any branched or cyclic structure it remains necessary to calculate the inverse matrix for a branch or cycle alone while addition of the linear part becomes just a routine matter.

From eq 41 we get for $c(n,k)$

$$\begin{aligned} \mathrm{Tr}\ (\mathbf{B}^{-1}) = k + (1/6)(k^2 - 1) &+ \\ (1/2)(n - k)(n - k + 1) &+ (2k - 1)(n - k)/k \end{aligned} \tag{42a}$$

$$\begin{aligned} \sum\{\mathbf{B}^{-1}\}_{n,i} = k + (1/2)(k - 1) &+ \\ (1/2)(n - k)(n - k + 1) &+ (2k - 1)(n - k)/k \end{aligned} \tag{42b}$$

$$\begin{aligned} \sum\sum\{\mathbf{B}^{-1}\}_{i,j} &= \\ k^2 + (1/12)k(k^2 - 1) &+ (1/6)(n - k)(n - k + 1) \times \\ (2n - 2k + 1) + (n - k)(3k - 1) &+ (2k - 1)(n - k)^2/k \end{aligned} \tag{42c}$$

The equations given so far enable one to calculate average dimensions for specific regular molecules. In order to deduce the effect of cyclization on the dimensions of molecules with cycles in a more general way, one should refer to the asymptotic behavior of $\langle s^2\rangle_0$ for cyclic polymers. Again, truncating the terms $X$ and $Y$ of eq 25 and 26, we obtain the expression

$$g_\infty \equiv \lim_{m\to\infty} \frac{6\langle s^2\rangle_0}{mn} = \frac{a}{n} = \frac{|\mathbf{A}| - |\mathbf{B}|}{n|\mathbf{B}|} \tag{43}$$

revealing the direct relation between the asymptotic $g$ and the determinants of the Kirchhoff matrices for structural elements.

It remains a matter of algebra to show that the Forsman[6] relation (eq 35) does not hold for cyclic polymers. In the case of three-parameter cyclic structures, $c(n,k,l)$, with $l$ being simply the number of units missed by the longest path through the structure, it is conjectured (verified up to $l = 3$) that

$$|\mathbf{A}| = k(n - k + l + 3) - (l + 1)^2 \tag{44}$$

giving

$$g_\infty = \lambda\left[1 - \frac{(l + 1)^2}{k(n - k + l + 2)}\right] \tag{45}$$

Here, the fraction of units in the main chain is redefined to be the fraction of units in the shortest path through the molecule, $\lambda \equiv (n - k + l + 2)/n$.

The value of $g_\infty$ assumes its lowest value when alternative paths through a structural element have equal lengths ($l = k/2 - 1$) and the molecule consists just of cycles linked by single bonds ($n = k$)

$$g_\infty(\mathrm{min}) = \lambda\left[1 - \frac{k}{2(k + 2)}\right] \tag{46}$$

For sufficiently large cycles in such molecules $g_\infty \to {}^1/_2$, as for a unicyclic (ring) molecule.

### Conclusions

The need for a method of estimating dimensions of polymers with branched or cyclic structures follows from the simple fact that there are many processes involving polymers in which cyclization or competition between branching and cyclization occurs. Here, we refer to the pregel stage of vinyl–divinyl copolymerization as an example.[21] If we choose a cyclopolymerization process as one extreme and random cyclization of linear or branched chains as the other, the vinyl–divinyl polymerization could be placed somewhere between these two extremes.[22] A short distance between a reaction center and a reactive site in the process favors[23] formation of separated cycles along a linear primary chain. On the other hand, conformational behavior of most commonly used divinyl cross-linking agents and the presence of previously formed large cycles randomize cycle sizes. Obviously, the reaction sites, i.e., side chains with unreacted vinyls, may remain unchanged as well.

For the randomly cyclized linear chains, very simple reasoning[24] leads to the relation first given by Allen et al.[25]

$$g_\infty(\min) = 1/(r + 1) \qquad (47)$$

where $r$ is the number of cross-links (contacts[24]) existing in the cyclized volumeless chain. Equation 45 provides a similar relation for the other extreme, while eq 36 describes, as a kind of reference, a case when long side chains belonging to a cross-linking agent are not involved in any cyclization but provide extensive branching instead. The relations above offer a new method for calculating the configurational behavior of idealized Gaussian molecules. Furthermore, the method has wider applicability and in particular suggests some general trends for dimensions of vinyl–divinyl primary molecules.[21]

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### References and Notes

(1) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, NY, 1953.

(2) For references, see, e.g.: Ross-Murphy, S. B. In "Macromolecular Chemistry"; Jenkins, A. D.; Kennedy, J. F., Editors; Royal Society: London, 1980.

(3) Zimm, B. H.; Stockmayer, W. H. *J. Chem. Phys.* **1949**, *17*, 1301.

(4) Dobson, G. R.; Gordon, M. *J. Chem. Phys.* **1964**, *41*, 2389. Gordon, M.; Malcolm, G. N.; Butler, D. S. *Proc. R. Soc. London, Ser. A* **1966**, *295*, 29.

(5) Fixman, M. *J. Chem. Phys.* **1962**, *36*, 306.

(6) Forsman, W. C. *Macromolecules* **1968**, *1*, 343.

(7) Šolc, K. *Macromolecules* **1973**, *6*, 378.

(8) Eichinger, B. E. *J. Polym. Sci., Polym. Symp.* **1976**, *No. 54*, 127.

(9) Eichinger, B. E. *Macromolecules* **1980**, *13*, 1.

(10) Eichinger, B. E. *Macromolecules* **1972**, *5*, 496.

(11) Eichinger, B. E. *Macromolecules* **1977**, *10*, 671.

(12) Martin, J. E.; Eichinger, B. E. *J. Chem. Phys.* **1978**, *69*, 4588. Eichinger, B. E.; Martin, J. E. *Ibid.* **1978**, *69*, 4595.

(13) Gupta, S. K.; Forsman, W. C. *Macromolecules* **1973**, *6*, 285. Gupta, S. K.; Forsman, W. C. *Ibid.* **1974**, *7*, 853. Gupta, S. K.; Forsman, W. C. *Ibid.* **1972**, *5*, 779.

(14) Šolc, K. *Macromolecules* **1972**, *5*, 705.

(15) Essam, J. W.; Fisher, M. E. *Rev. Mod. Phys.* **1970**, *42*, 272.

(16) Kirchhoff matrices describe graphs uniquely although not conversely. The matrix **A** (**B**) describes a graph having all units and links of the structural element, but vertex degrees of two (one) terminal units are increased by one.

(17) Bryant, P. R. In "Graph Theory and Theoretical Physics"; Harary, F., Editor; Academic Press: New York, 1967.

(18) Matrices essentially identical with the Kirchhoff matrices of linear chain graphs often arise in solving problems involving certain differential equations. They were first applied for studying polymers by Rouse (Rouse, P. E. *J. Chem. Phys.* **1953**, *21*, 1272), and his matrix was identical, in terms of symbols used here, with the matrix **A**. The matrix used by Zimm (Zimm, B. H. *J. Chem. Phys.* **1956**, *24*, 269) was exactly the Kirchhoff matrix of a linear chain. By deleting the first row and the first column in the Zimm matrix, one can obtain the matrix here called **B**.

(19) Flory, P. J. "Statistical Mechanics of Chain Molecules"; Interscience: New York, 1969.

(20) Berry, G. C.; Orofino, T. A. *J. Chem. Phys.* **1964**, *40*, 1614.

(21) Dušek, K.; Galina, H.; Mikeš, J. *Polym. Bull.* **1980**, *3*, 19.

(22) Dušek, K.; Prins, W. *Adv. Polym. Sci.* **1969**, *6*, 1.

(23) *Jackobson*, H.; Stockmayer, W. H. *J. Chem. Phys.* **1950**, *18*, 1600.

(24) Gordon, M.; Torkington, J. A.; Ross-Murphy, S. B. *Macromolecules* **1977**, *10*, 1090. Torkington, J. A. Thesis, Essex University, 1979.

(25) Allen, G.; Burgess, J.; Edwards, S. F.; Walsh, D. J. *Proc. R. Soc. London, Ser. A* **1973**, *334*, 453, 465, 477.

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# New Method for Estimating the Parameters of the Wormlike Chain Model from the Intrinsic Viscosity of Stiff-Chain Polymers

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ABSTRACT: It has been found that the term $\Phi_0$ in the Yamakawa–Fujii equation for the intrinsic viscosity of the wormlike continuous cylinder model, $[\eta]_0 = \Phi_0(\lambda^{-1})^{3/2}L^{1/2}/M_L$, can be given a simple form valid over a broad range of the chain contour length $L$: $\Phi_0 = \Phi_{0,\infty}[B_0 + A_0(\lambda^{-1}/L)^{1/2}]^{-3}$. The parameter $A_0$ is a function of the ratio $d/\lambda^{-1}$ while $B_0$ is nearly constant. On the basis of these results, new methods are proposed for evaluating the model parameters (Kuhn segment length $\lambda^{-1}$, relative molecular mass per unit contour length $M_L$, and chain diameter $d$) from the intrinsic viscosity data for stiff-chain polymers. Accordingly, the plot of $(M^2/[\eta])^{1/3}$ vs. $M^{1/2}$ is linear, and the random-coil value of $\langle R_0^2\rangle/M$, i.e., $(\langle R_0^2\rangle/M)_\infty$, is simply evaluated from the slope of the plot. The possibilities of estimating $M_L$ and $d$, either from the intrinsic viscosity data alone or, preferably, from their combination with the partial specific volume of the polymer, are discussed. The procedures are applied to nine typical stiff-chain polymers (polyisocyanate, cellulose trinitrate, polypeptides in helical conformation, aromatic polyamides, etc.). The results agree well with those obtained by more involved procedures. The effect of the excluded volume on the shape of the plot is also qualitatively discussed.

## Introduction

The category of stiff-chain polymers includes important natural and synthetic macromolecular substances, the number of which steadily increases. Since the determination of molecular dimensions by means of the light-scattering method is frequently difficult with these substances, their conformational characteristics are derived from the hydrodynamic quantities, mainly from the in-