A THEORY FOR CONFORMATIONS IN ISOTACTIC POLYMERS; A MARKOV PROCESS

Thesis for the Degree of Ph. D.
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Victor E. Meyer
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A THEORY FOR CONFORMATIONS IN ISOTACTIC POLYMERS;
A MARKOV PROCESS

by

VICTOR E. MEYER

AN ABSTRACT

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

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Approved ____

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Body of Abstract

An equation has been derived which relates the mean square end-to-end length of an isotactic vinylic hydrocarbon-type chain to the detailed geometry of the chain. The equation is restricted to long linear chains with regular head-to-tail structure which can be represented by a diamond lattice model. The chain bonds are all considered to have constant and equal length, and are connected at the tetrahedral valence angle. The rotational angle, as defined by any three consecutive bonds, is restricted to the *trans* and two *gauche* conformations. Furthermore, the bonds are considered to be statistically independent, which allows the problem to be solved by Markov chain statistics. The mean square length is expressed as a function of the probabilities of finding the bonds in their respective *trans* and *gauche* conformations.

The mean square end-to-end length of a polymethylene-type chain has also been calculated by the methods indicated above. The equations obtained are discussed relative to pertinent experimental data. It is concluded that "crystalline" polymers tend to retain their crystalline state "conformations" in their "unperturbed" states.

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VITA

The author was graduated from St. Louis High School, St. Louis, Michigan in June, 1950. He entered Michigan State College in September, 1950 and studied history until June, 1952. At that time he enlisted in in the United States Army and spent the next three years as a member of the Army Security Agency. After receiving an honorable discharge in May, 1955, he re-entered Michigan State College as a chemistry major. He received the Bachelor of Science degree in June, 1957.

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I. INTRODUCTION

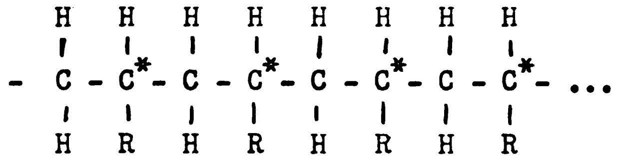
A. General

The Nobel prizewinner (1953) H. Staudinger was the first to recognize the dependence of physical properties of macromolecules on their structural detail. Staudinger proposed that amorphous (glassy) polymers could not be crystallized because of non-symmetrical arrangement along the polymer chain. Staudinger[1] suggested that the lack of crystallinity in polymers such as polystyrene might result from the formation of a great number of stereoisomers during polymerization. He advanced the hypothesis that polymers which crystallize require repetitious and symmetrical order to achieve the rigorous demands of chain packing for the crystalline state.

Later M. L. Huggins[2] suggested that the observed changes in the solution properties of poly-α-olefins (viz., polystyrene) polymerized at different temperatures, resulted from the change in stereosequence of the polymers. Specifically, he suggested that as the temperature of polymerization of polystyrene is increased, the distribution of (d) and (l) configurations becomes more random. That is, at lower temperatures of polymerization it is probable that a certain arrangement of asymmetric centers along the backbone of the chain would be more favored. For example, in polystyrene the alternate (d) and (l) configurations are most probable, since this results in the maximum distance of separation of the bulky pendant phenyl groups. As the temperature of polymerization increases, the distribution of asymmetric centers may be expected to become more random relative to this "favored" arrangement of asymmetric centers. This interpretation was proposed for the experimental results of T. Alfrey, A. Bartovics, and H. Mark[3]. The recent nuclear magnetic resonance studies of F. A. Bovey et. al.[4,5] on poly(methyl methacrylate) gives some very direct evidence in support of Huggins' suggestion. J. W. L. Fordham et al.[6] also show a relationship between polymerization temperature and the degree of crystallinity in poly(vinyl chloride). The degree of crystallinity increased with decreasing temperature, indicating an increase in configurational order as the temperature of polymerization is decreased.

The successful search for catalytic processes which would produce vinyl polymers with extremely regular configurational order was first reported by C. E. Schildknecht[7,8] et al., who in 1947 prepared isotactic poly(vinyl isobutyl ether), using a boron fluoride etherate catalyst. However, it was not until 1955 that the significance of stereospecific polymerization caught the imagination and attention of the polymer chemists when G. Natta[9], reported the successful preparation of *crystalline*, *isotactic* polypropylene and polystyrene of high molecular weight using a Ziegler-type catalyst (usually a mixture of triethyl aluminum and titanium tetrachloride in an inert solvent). The discovery of stereoregular polymerization has been actively explored and at the present time poly-α-olefins and vinyl polymers with the following configurations have been reported and classified.

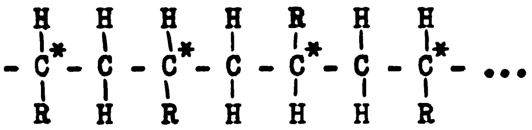
1. Isotactic macromolecules. The asymmetric carbon atoms of any given molecule have either all (d) or all(l) configurations.



$$\begin{array}{cccccccccccccccccc}
 & H & & H & & H & & H & & H & & H & & H & & H & & \\
 & | & & | & & | & & | & & | & & | & & | & & | & & \\
- & C & - & C^* & - & C & - & C^* & - & C & - & C^* & - & C & - & C^* & - & \ldots \\
 & | & & | & & | & & | & & | & & | & & | & & | & & \\
 & H & & R & & H & & R & & H & & R & & H & & R & &
\end{array}$$

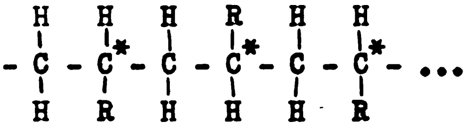
The asterisk indicates the pseudo-asymmetric centers.

2. Atactic macromolecules. The asymmetric carbon atoms of any given molecule have random (d) or (l) configurations.



$$\begin{array}{ccccccccccccccc} & H & & H & & H & & H & & R & & H & & H & \\ & | & & | & & | & & | & & | & & | & & | & \\ - & C^* & - & C & - & C^* & - & C & - & C^* & - & C & - & C^* & - \cdots \\ & | & & | & & | & & | & & | & & | & & | & \\ & R & & H & & R & & H & & H & & H & & R & \end{array}$$

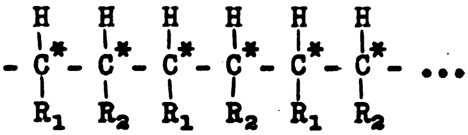
3. Syndiotactic macromolecules.[10,11] The asymmetric carbon atoms of any given molecule have alternate (d) and (l) configuartions.



$$\begin{array}{ccccccccccccc} & H & & H & & H & & R & & H & & H & \\ & | & & | & & | & & | & & | & & | & \\ - & C & - & C^* & - & C & - & C^* & - & C & - & C^* & - \cdots \\ & | & & | & & | & & | & & | & & | & \\ & H & & R & & H & & H & & H & & R & \end{array}$$

Chains of the type $(\text{CHR}_1\text{-CHR}_2)_x$ have recently been polymerized stereospecifically[10] to yield stereoregular polymers of the form:

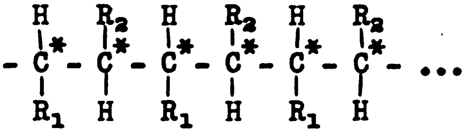
4. Diisotactic macromolecules. The asymmetric carbon atoms of any given molecule have either all (d) or all (l) configurations.



$$\begin{array}{ccccccccccccc} & H & & H & & H & & H & & H & & H & \\ & | & & | & & | & & | & & | & & | & \\ - & C^* & - & C^* & - & C^* & - & C^* & - & C^* & - & C^* & - \cdots \\ & | & & | & & | & & | & & | & & | & \\ & R_1 & & R_2 & & R_1 & & R_2 & & R_1 & & R_2 & \end{array}$$

, and

5. Disyndiotactic macromolecules. The asymmetric carbon atoms have alternate (d) and (l) configurations.



$$\begin{array}{ccccccccccccc} & H & & R_2 & & H & & R_2 & & H & & R_2 & \\ & | & & | & & | & & | & & | & & | & \\ - & C^* & - & C^* & - & C^* & - & C^* & - & C^* & - & C^* & - \cdots \\ & | & & | & & | & & | & & | & & | & \\ & R_1 & & H & & R_1 & & H & & R_1 & & H & \end{array}$$

B. Introduction to Theory

The mathematical analysis of the properties and structure of high polymer molecules has developed through a statistical approach. To begin, the chain must be denoted by various symbols which represent important characteristics of the chemical structure.[12] Referring to Figure 1, the covalent chemical bonds joining the atoms of the "backbone" are regarded as jointed vectors (vector-bonds) $\underset{\sim}{l}_0$, $\underset{\sim}{l}_1$, $\underset{\sim}{l}_2$, ..., $\underset{\sim}{l}_{n-1}$, numbered according to their position along the chain from the first to the last atom. The angle formed by the two bonds connecting any three consecutive atoms is called the valence bond angle (θ). The rotational angle (ϕ) is defined as the angle made by bond $\underset{\sim}{l}_{i+2}$ from the plane formed through bonds $\underset{\sim}{l}_{i+1}$ and $\underset{\sim}{l}_i$.

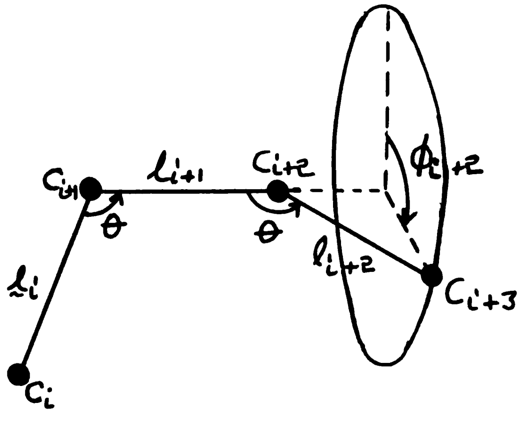


Figure 1. Segment of a schematic chain showing bond length (l), valence angle (θ), and the rotational angle (ϕ).

Because high molecular weight polymers consist of a large number of chain bonds or monomer units, the theoretical treatment, considering now the entire chain, is limited to a statistical approach. One of the important descriptive parameters is the mean square end-to-end length, a quantity which is by definition, statistical. The magnitude of this parameter is found to be dependent on the number of links in the chain, the state of the system, the temperature, and the internal structure of the polymer chain. Another related quantity, the mean square radius of gyration, is defined as the average of the squares of the distances from the center of gravity to each segment of the chain. Many physical properties of polymer molecules depend on the mean square radius of gyration and, for linear polymer chains whose mean square lengths have a Gaussian-type distribution, the mean square radius of gyration is equal to one-sixth the mean square end-to-end length. Because of this simple relationship between the two parameters the mean square end-to-end length has become the parameter most frequently used in conjunction with physical properties.

Phenomena which follow Gaussian-type distribution curves normally have certain random properties. W. Kuhn[13] showed that the mean square end-to-end lengths of real linear polymer chains obey Gaussian-type distributions despite the fact that the directions of the connected links(bonds) are severely limited by the valence angle(θ), and the restricted angle of rotation (ϕ). Kuhn has demonstrated that a long linear chain of n bonds may be considered as composed of (n/m) segments , where m is selected such that because of the more or less free rotations about the bonds, the (n/m) segments are directed randomly relative to one another. Thus, unless real linear polymer chains are small or unusually rigid, their mean square end-to-end lengths can be expected to have Gaussian-type distributions, and the simple relationship between the mean square length and the mean square radius of gyration will be valid. In addition, experimental evidence[14] exists which demonstrates that within experimental error the mean square end-to-end length is proportional to the molecular weight as should be true for an "ideal" Gaussian-type linear macromolecule.

C. Root Mean Square End-to-End Length.

The first theoretical treatment of the mean square end-to-end length was the "freely jointed" chain, where each bond is considered statistically independent and all angles of (θ) occur with equal probability. The model was obviously a vast oversimplification for real macromolecules, however, with appropriate corrections real polymer molecules do conform to certain distribution functions (viz., Gaussian-type distributions) derived from this model.

Subsequent authors introduced a more realistic model with fixed bond angles[15], but with free rotations. This model can be treated by Markovian statistical methods and has been termed the "freely rotating chain".

In recent years considerable attention has been focused on the problem of taking into account the effects of hindered rotations on the mean square end-to-end dimensions. One approach to this problem is to treat the chain with restricted rotations through averages of the rotational angle (ϕ). However, more refined analysis shows that the chain bonds are most likely to fix themselves at specific rotational angles depending on the nature of the near neighbor interactions. That is, because of the near neighbor interactions along the backbone of the chain, not all conformations are energetically equivalent, and indeed some conformations are practically excluded.

The stereoregular polymers possess structural regularity; therefore the problem of relating the mean square end-to-end lengths to the detailed geometry of the chain is much simpler than the older problem of atactic (random) structures.

Two different mathematical techniques have been developed to relate the detailed geometry of the chain to the mean square end-to-end length. The first of these, which is presently receiving much attention, was originated by H. Eyring.[15]

In 1932, Eyring proposed a method of solving for the mean square end-to-end length of linear macromolecules. The principal features of the method are as follows:

1. Assign to each bond a suitably defined coordinate system.

2. By means of rotational matrices relate all vector-bonds to a single coordinate system, usually the one associated with the first bond of the chain.

3. Take the dot product of the end-to-end length, and consider the averages of the rotational matrices as they occur in the dot product.

The method of rotational matrices is presently the subject of investigation of a large number of workers.[16-22] Several of these workers have extended the method to consider the case of isotactic and/or syndiotactic macromolecules. The results obtained by these workers are frequently cumbersome, occasionally not obtainable in closed form and are difficult to compare.

Tobolsky[23] has suggested an alternative approach to this problem. The principal features of his method are:

1. Describe the chain in terms of a diamond lattice[24] and a matrix of transition probabilities which relates to a "walk" on a diamond lattice. (This applies to all chains which take predominantly staggered conformations).

2. Mathematically relate the mean square end-to-end length to the "walk" as described by the matrix of transition probabilities.

Specifically, Tobolsky considered the case of a polymethylene chain with hindered rotations. The two gauche positions are considered to be energetically equivalent, and different from the trans positions. The mean square end-to-end length is then expressed as a function of the tendency for any three bonds to be found in the trans position.

Recently R. P. Smith[25] demonstrated the equivalency of the rotational matrix and the diamond lattice approach for the polymethylene chain. However, his method relies heavily on the rotational matrix technique and it is therefore not immediately obvious whether the method may be extended to treat structurally more complicated chains.

In the calculation presented in this thesis, the diamond lattice model has been utilized. However, it is not possible to deal with the matrix of transition probabilities in the manner suggested in the treatment of the polymethylene chain by Tobolsky. It was therefore necessary to develop a different mathematical technique in evaluating the mean square end-to-end dimensions from the matrix of transition probabilities.

II. CALCULATION OF THE MEAN SQUARE END-TO-END LENGTH OF A POLYMETHYLENE CHAIN.

A. Introduction.

Because the polymethylene chain contains only a single type of chain bond, it is both conceptually and mathematically much simpler than the isotactic chain. For this reason the polymethylene chain calculation is presented first in its entirety, although it may be treated alternatively as a special case of the isotactic chain. Because the polymethylene chain is simpler, this approach allows a more orderly and clearer presentation of the salient mathematical and conceptual aspects of the calculation, and then, when the isotactic case is considered, particular attention and emphasis may be given to those aspects of the calculation which are peculiar to the isotactic chain. In keeping with this objective, the detailed mathematical evaluations have been placed in appendixes which are collected at the end of this thesis.

B. The Diamond Lattice Model.

It is desired to compute the mean square length of a polymethylene-type chain of n+1 carbon atoms connected by n vector-bonds of constant length (l_o), with constant tetrahedral valence angle (θ). Recently, W. J. Taylor[26] showed that the error involved in neglecting the variation in bond lengths and bond angles due to vibrations, in the calculation of the mean square end-to-end length, is of the order of magnitude of a few tenths of one percent at normal temperatures, and thus need not be considered here.

The bonds are numbered consecutively as indicated in Figure 1. Each bond has vector components $(X^{(i)}, Y^{(i)}, Z^{(i)})$, $i = 0,1,2,\ldots, n-1$. For simplicity of calculation, the magnitude of each component is taken to be unity. If (l_o) is the actual bond length, then the calculated mean square length must, in the last step of the calculation, be scaled by the factor $l_o^2/3$.

Each vector-bond is thus represented by one of the eight combinations $(\pm 1, \pm 1, \pm 1)$ and successive bonds differ only in the change of exactly one algebraic sign. This representation of hydrocarbon molecules is commonly referred to as the diamond lattice model.

First, it is desired to demonstrate how the components of each bond may be represented by ±1. Since each vector-bond may have components only as given by one of the eight combinations $(\pm 1, \pm 1, \pm 1)$; each vector-bond is thereby restricted to lie along one of the principal diagonals of the eight quadrants of the cartesian coordinate system. Thus, regardless of the quadrant in which a vector-bond lies, one obtains for the dot product of the vector-bond into itself

$$\underset{\sim}{l}_i \cdot \underset{\sim}{l}_i = l_o^2 = (X^{(i)} + Y^{(i)} + Z^{(i)}) \cdot (X^{(i)} + Y^{(i)} + Z^{(i)}) \quad (1)$$

$$= (X^{(i)})^2 + (Y^{(i)})^2 + (Z^{(i)})^2. \quad (2)$$

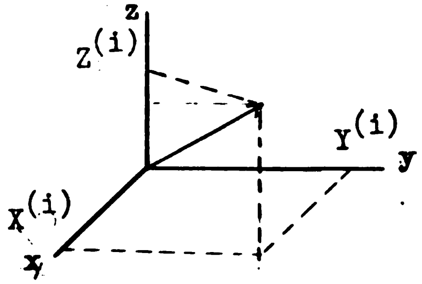


Figure 2. Vector-bond $\underset{\sim}{l}_i$ in the first quadrant of a cartesian coordinate system.

From Figure 2 it may be shown by simple trigonometry that for the case of a vector lying along the principal diagonal of a cartesian coordinate system, all of the components along the coordinate axes are equal, i.e.,

$$\left|X^{(i)}\right| = \left|Y^{(i)}\right| = \left|Z^{(i)}\right| \tag{3}$$

Equation (2) may therefore be written as,

$$l_0^2 = 3(X^{(i)})^2 = 3(Y^{(i)})^2 = 3(Z^{(i)})^2 \tag{4}$$

or

$$(X^{(i)})^2 = (Y^{(i)})^2 = (Z^{(i)})^2 = l_0^2/3 \tag{5}$$

From which

$$\frac{(X^{(i)})}{(l_0^2/3)^{1/2}} = \pm 1 \tag{6}$$

For vectors which are restricted to lie along the principal diagonals of a cartesian coordinate system it is permissible to replace the components of the vectors by ± 1. Since in the final equation for a polymethylene chain only the squares of the components occur, the final equation must be multiplied by $l_0^2/3$.

Next it is desired to demonstrate how the change in exactly one algebraic sign is consistent with a hydrocarbon chain of constant tetrahedral valence angle θ. From Figure 1 it is seen that the cosine of the angle between two consecutive vector-bonds e.g., $\underset{\sim}{l}_i$, $\underset{\sim}{l}_{i+1}$ is given by

$$\cos(\pi - \theta) = 1/3 \tag{7}$$

Now, if according to the diamond lattice model $\underset{\sim}{l}_i$ is represented by the set (-1,1,1) then $\underset{\sim}{l}_{i+1}$ according to the change of any one algebraic sign, is represented by the set (-1,1,-1). Then since the dot product of two vectors is defined as the product of the magnitudes of the two vectors multiplied by the cosine of the angle between them,

$$\underset{\sim}{l}_i \cdot \underset{\sim}{l}_{i+1} = |\underset{\sim}{l}_i|\,|\underset{\sim}{l}_{i+1}|\cos(\underset{\sim}{l}_i,\ \underset{\sim}{l}_{i+1}) \qquad (8)$$

From which

$$\cos(\underset{\sim}{l}_i \cdot \underset{\sim}{l}_{i+1}) = \frac{\underset{\sim}{l}_i \cdot \underset{\sim}{l}_{i+1}}{|\underset{\sim}{l}_i|\,|\underset{\sim}{l}_{i+1}|} = \frac{(-1,1,1)\cdot(-1,1,-1)}{3^{1/2}\ 3^{1/2}} = 1/3 \qquad (9)$$

The result (1/3) is obtained for any of the possible combinations of (±1, ±1, ±1) which may be considered, with the requirement that the two successive bonds differ only in the change of exactly <u>one</u> algebraic sign. Thus, the diamond lattice model preserves the property of hydrocarbon chains that the bonds be connected at the tetrahedral valence angle (θ).

The diamond lattice model imposes another restriction on the hydrocarbon chain. That is, due to the requirement that successive bonds may have only one sign change, the rotational angle (ϕ) is therefore restricted to the trans ($\phi = 0°$) and two gauche ($\phi = \pm 120°$) conformations[‡].

[‡] "Conformation" has two different meanings as used in this thesis. It will sometimes be used in reference to "trans" or "gauche" conformation, and alternatively to indicate the orientation of the total chain. The meaning will be clear from the context.

C. Mean Square End-to-End Length.

The end-to-end dimension of a polymethylene chain is the sum of the bond vectors

$$\underset{\sim}{h} = \underset{\sim}{l}_o + \underset{\sim}{l}_1 + \underset{\sim}{l}_2 + \dots + \underset{\sim}{l}_{n-1} = \sum_{i=0}^{n-1} \underset{\sim}{l}_i \qquad (10)$$

where

$$\underset{\sim}{l}_i = (X^{(i)}, Y^{(i)}, Z^{(i)}). \qquad (11)$$

The expected square length is given by

$$\overline{h^2} = \sum_{i=0}^{n-1} \sum_{j=0}^{n-1} \overline{\underset{\sim}{l}_i \cdot \underset{\sim}{l}_j} = \sum_{i=0}^{n-1} \sum_{j=0}^{n-1} E\left\{X^{(i)}X^{(j)} + Y^{(i)}Y^{(j)} + Z^{(i)}Z^{(j)}\right\} \qquad (12)$$

where $E\left\{X^{(i)}X^{(j)} + Y^{(i)}Y^{(j)} + Z^{(i)}Z^{(j)}\right\}$ is the expected value of the quantity enclosed in the curly brackets. Written in the convenient form of an array, the double sum (12) becomes:

$$\overline{h^2} = \left| \begin{array}{l} \overline{\underset{\sim}{l}_o \cdot \underset{\sim}{l}_o} + \overline{\underset{\sim}{l}_o \cdot \underset{\sim}{l}_1} + \overline{\underset{\sim}{l}_o \cdot \underset{\sim}{l}_2} + \dots + \overline{\underset{\sim}{l}_o \cdot \underset{\sim}{l}_{n-1}} \\ \overline{\underset{\sim}{l}_1 \cdot \underset{\sim}{l}_o} + \overline{\underset{\sim}{l}_1 \cdot \underset{\sim}{l}_1} + \overline{\underset{\sim}{l}_1 \cdot \underset{\sim}{l}_2} + \dots + \overline{\underset{\sim}{l}_1 \cdot \underset{\sim}{l}_{n-1}} \\ \cdot \\ \cdot \\ \cdot \\ \overline{\underset{\sim}{l}_{n-1} \cdot \underset{\sim}{l}_o} + \overline{\underset{\sim}{l}_{n-1} \cdot \underset{\sim}{l}_1} + \overline{\underset{\sim}{l}_{n-1} \cdot \underset{\sim}{l}_2} + \dots + \overline{\underset{\sim}{l}_{n-1} \cdot \underset{\sim}{l}_{n-1}} \end{array} \right| \qquad (13)$$

If end effects are neglected i.e., $\overline{\underset{\sim}{l}_o \cdot \underset{\sim}{l}_o} = \overline{\underset{\sim}{l}_1 \cdot \underset{\sim}{l}_1} = \dots$, and $\overline{\underset{\sim}{l}_o \cdot \underset{\sim}{l}_1} = \overline{\underset{\sim}{l}_1 \cdot \underset{\sim}{l}_2} = \dots$, and $\overline{\underset{\sim}{l}_o \cdot \underset{\sim}{l}_2} = \overline{\underset{\sim}{l}_1 \cdot \underset{\sim}{l}_3} = \dots$, etc.; and also since the dot product commutes i.e., $\overline{\underset{\sim}{l}_o \cdot \underset{\sim}{l}_1} = \overline{\underset{\sim}{l}_1 \cdot \underset{\sim}{l}_o}$; then because of the symmetry about the principal diagonal of the array (13) may be simplified to:

$$\overline{h^2} = nl_o^2 + 2 \times \left. \begin{array}{rrrr} \overline{\underset{\sim}{l}_o \cdot \underset{\sim}{l}_1} & + \overline{\underset{\sim}{l}_o \cdot \underset{\sim}{l}_2} & + \cdots & + \overline{\underset{\sim}{l}_o \cdot \underset{\sim}{l}_{n-1}} \\ & + \overline{\underset{\sim}{l}_1 \cdot \underset{\sim}{l}_2} & + \cdots & + \overline{\underset{\sim}{l}_1 \cdot \underset{\sim}{l}_{n-1}} \\ & & + \cdots & \\ & & & + \overline{\underset{\sim}{l}_{n-2} \cdot \underset{\sim}{l}_{n-1}} \end{array} \right| \qquad (14)$$

$$= nl_o^2 + 2(n-1)\,\overline{\underset{\sim}{l}_o \cdot \underset{\sim}{l}_1} + 2(n-2)\,\overline{\underset{\sim}{l}_o \cdot \underset{\sim}{l}_2} + \cdots + 2\,\overline{\underset{\sim}{l}_o \cdot \underset{\sim}{l}_{n-1}} \qquad (15)$$

When (14) is written in terms of its rectangular coordinates it becomes

$$\overline{h^2} = 3n + 2 \sum_{i=0}^{n-2} \sum_{k=1}^{n-1-i} E\left\{X^{(o)}X^{(k)} + Y^{(o)}Y^{(k)} + Z^{(o)}Z^{(k)}\right\} \qquad (16)$$

Put

$$L_k = E\left\{X^{(o)}X^{(k)} + Y^{(o)}Y^{(k)} + Z^{(o)}Z^{(k)}\right\} \qquad (17)$$

then (16) becomes

$$\overline{h^2} = 3n + 2 \sum_{i=0}^{n-2} \sum_{k=1}^{n-1-i} L_k \,, \qquad (18)$$

and analogous to (15), this may be further simplified to give

$$\overline{h^2} = 3n + 2 \sum_{k=1}^{n-1} (n-k)\, L_k \qquad (19)$$

D. Probability Matrix.

The sequence of pairs $(\underset{\sim}{l}_o \underset{\sim}{l}_1)$, $(\underset{\sim}{l}_1 \underset{\sim}{l}_2)$, ... , $(\underset{\sim}{l}_{n-1} \underset{\sim}{l}_n)$ is now considered. Each pair is a state in the Markov sense with the matrix of transition probabilities given in Figure 4. The coordinates may be chosen such that $l_o = (1,1,1)$, and $l_1 = (1,1,-1)$. Now $\underset{\sim}{l}_2$ may have the possible sets (1,-1,-1), (-1,1,-1), and (1,1,1) with probabilities b, b, and a,

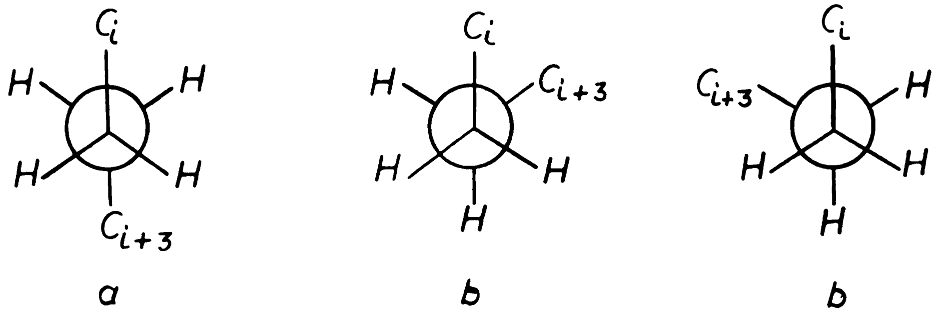


Figure 3. Newman projections of the trans (a) conformation ($\phi = 0$), and the two equivalent gauche (b) conformations ($\phi = \pm 120°$).

respectively, corresponding to their respective conformations, with $b + b + a = 1$. In Figure 4 it is seen that these sets correspond to transitions from state (<u>row</u>) 1 to states (<u>columns</u>) 4, 5, and 6, respectively. Each of these events is treated as though it has occurred, and the subsequent possibilities are considered. For example, if $\underset{\sim}{l}_2 = (1,-1,-1)$ has occurred, corresponding to the transition from state (<u>row</u>) 1 to state (<u>column</u>) 4, with probability (b) (Figure 4), as just discussed, then, the next transition originates from state (<u>row</u>) 4, and may proceed to states (<u>columns</u>) 13, 14, and 15, with probabilities (conformations) b, a, and b, respectively. The next transitions then originate from states (<u>rows</u>) 13, 14, and 15, depending on the outcomes of the preceeding trials. Now, $\underset{\sim}{l}_1$ may also have the sets (1,-1,1), and (-1,1,1) as well as the set (1,1,-1), given above. Therefore, these possibilities and all possible subsequent events must also be considered. This procedure is then continued until the matrix of transition probabilities, Figure 4 has been obtained. It is then discovered that all subsequent bond pairs return to some previously considered state of Figure 4.

Since the coordinate system has been chosen such that $\underset{\sim}{l}_o$ has unity for its components, it is seen that L_k (17) simplifies to

$$L_k = E\left\{X^{(k)} + Y^{(k)} + Z^{(k)}\right\} . \tag{20}$$

The definition is now made

$$U_k = X^{(k)} + Y^{(k)} + Z^{(k)} . \tag{21}$$

Next, it is desired to consider the sequence of pairs (U_oU_1), (U_1U_2), $\ldots$, $(U_{n-1}U_n)$.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
1				b	b	a																		
2							b	b	a															
3										b	b	a												
4													b	a	b									
5																b	a	b						
6	a	b	b																					
7																			a	b	b			
8													a	b	b									
9	b	a	b																					
10																			b	a	b			
11																a	b	b						
12	b	b	a																					
13							b	a	b															
14				a	b	b																		
15																						b	b	a
16										b	a	b												
17				b	a	b																		
18																						a	b	b
19										a	b	b												
20							a	b	b															
21																						b	a	b
22																b	b	a						
23																			b	b	a			
24													b	b	a									

Figure 4. The complete matrix of transition probabilities (P_{24x24}) for a polymethylene chain. The meaning of the column and row headings are explained in Table I.

Table I

The twenty four states of the polymethylene chain.

State	Magnitude of U_j U_{j+1}	Components* of U_j U_{j+1}	State	Magnitude of U_j U_{j+1}	Components of U_j U_{j+1}
1	3 1	$3 \quad 1_3$	13	-1 1	$-1_1 \quad 1_2$
2	3 1	$3 \quad 1_2$	14	-1 1	$-1_1 \quad 1_3$
3	3 1	$3 \quad 1_1$	15	-1 -3	$-1_1 \quad -3$
4	1 -1	$1_3 \quad -1_1$	16	-1 1	$-1_2 \quad 1_1$
5	1 -1	$1_3 \quad -1_2$	17	-1 1	$-1_2 \quad 1_3$
6	1 3	$1_3 \quad 3$	18	-1 -3	$-1_2 \quad -3$
7	1 -1	$1_2 \quad -1_3$	19	-1 1	$-1_3 \quad 1_2$
8	1 -1	$1_2 \quad -1_1$	20	-1 1	$-1_3 \quad 1_1$
9	1 3	$1_2 \quad 3$	21	-1 -3	$-1_3 \quad -3$
10	1 -1	$1_1 \quad -1_3$	22	-3 -1	$-3 \quad -1_2$
11	1 -1	$1_1 \quad -1_2$	23	-3 -1	$-3 \quad -1_3$
12	1 3	$1_1 \quad 3$	24	-3 -1	$-3 \quad -1_1$

* $(1,1,1) = 3$; $(1,1,-1) = 1_3$; $(1,-1,1) = 1_2$; $(-1,1,1) = 1_1$; $(-1,-1,-1) = -3$; $(-1,-1,1) = -1_3$; $(-1,1,-1) = -1_2$; $(1,-1,-1) = -1_1$.

Since only the magnitude of U_j is needed for the calculation, the 24 x 24 matrix of transition probabilities (Figure 4) is more elaborate than need be, and the twenty-four states can be combined to give only eight states of the desired Markovian character. This "collapsing" process involves combining states of the same value of U_j, and of the same transition probability, with the exception of those states of the 8 x 8 matrix of transition probabilities (22) which have unity as their transition probability. The unities result from the fact that a bond may differ by only <u>one</u> algebraic sign from the components of an adjacent bond. Thus, if $U_j = 3$, then $U_{j-1} = 1$, and $U_{j+1} = 1$, of necessity, and a (1,3)-state has probability of unity of going to a (3,1)-state, and the states with unity as transition probability result from combining $a + b + b = 1$. By this "collapsing" technique Figure 4. reduces to the matrix P of transition probabilities (22).

$$P = \begin{array}{cc|cccc|cccc|} & & 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 \\ & & 3\,1 & -1\,1 & -1\,1 & -1\,-3 & -3\,-1 & 1\,-1 & 1\,-1 & 1\,3 \\ \hline 1 & 3\,1 & & & & & 0 & b & b & a \\ 2 & -1\,1 & & & & & 0 & b & a & b \\ 3 & -1\,1 & & & & & 0 & a & b & b \\ 4 & -1\,-3 & & & & & 1 & 0 & 0 & 0 \\ \hline 5 & -3\,-1 & 0 & b & b & a & & & & \\ 6 & 1\,-1 & 0 & b & a & b & & & & \\ 7 & 1\,-1 & 0 & a & b & b & & & & \\ 8 & 1\,3 & 1 & 0 & 0 & 0 & & & & \\ \hline \end{array} = \begin{bmatrix} 0 & S \\ S & 0 \end{bmatrix} \qquad (22)$$

The relation of the relabeled states to the original states are given in Table II. The matrices of transitions probabilities $P_{24 \times 24}$ and (22) both have the property that the sum of the elements of any row or column add to unity. This property is preserved in the higher powers of $P_{24 \times 24}$ and (22) and in probability theory the matrices are referred to as "doubly stochastic" (see reference 27, p. 358). This property has a very simple physical interpretation. If one proceeds down a hydrocarbon chain in a diamond lattice, then after each "step", the appropriate bond has a total probability of unity of being found in one of its possible positions (conformations). This condition results in a simple stochastic matrix (only the rows add to unity). However, if the probability of proceeding in a forward direction is the same as proceeding in a reverse direction, then, this condition results in a doubly stochastic matrix of transition probabilities. In the example just discussed, if the transition $U_oU_1 \rightarrow U_1U_2$ corresponding to (1,1,1), (1,1,-1), (1,1,1) has probability (a), and if the probability is also (a) for the transition $U_2U_1 \rightarrow U_1U_o$ corresponding to (1,1,1), (1,1,-1), (1,1,1), (this being true in general for all transitions), then, the resultant matrix of transition probabilities will be doubly stochastic.

Table II

Relation of the relabeled states to the original states for the polymethylene chain.

Relabeled State Number	Original State Number	Value Relabeled State
1	1, 2, 3,	3 1
2	13, 17, 20	-1 1
3	14, 16, 19	-1 1
4	15, 18, 21	-1-3
5	22, 23, 24	-3-1
6	4, 7, 11	1-1
7	5, 8, 10	1-1
8	6, 9, 12	1 3

The power and utility of the matrix of transition probabilities approach to statistical problems may be demonstrated by the following considerations. Let the problem be posed, "What is the probability of ending up in state two (-1 1) after two steps, if the starting point is state one (3 1) of Equation (22). Otherwise worded, "If four consecutive bonds are considered with the first two bonds in state one (3 1), what is the probability that the last two bonds will be in state two (-1 1)?" From (22), it is seen that there are two possible paths by which state two may be reached; path one: state one → state six → state two, with probability of b^2; and path two: state one → state seven → state two, with probability ba. The transition from state one to state six, and from state six to state two are independent events [28] and therefore the probability is b^2, and by the same reason the probability of path two is ba. Now, "the probability that some one or other of the set of mutually exclusive events will happen in a single trial is the sum of their separate probabilities of happening," therefore the total probability of going from state one to state two in two steps is $b^2 + ab$.

Now, if the $p_{12}^{(2)}$ element of P^2 is calculated, the result, $p_{12}^{(2)} = b^2 + ba$ is obtained, and indeed, it is found that the elements $p_{ij}^{(k)}$ of P^k automatically give the desired probability of transition from state (i) to state (j) in (k) steps. For example, it would be an almost impossible task to calculate the probability of going from state one to state two in twenty steps by the method of considering all different paths. However, to find $p_{12}^{(20)}$ of P^{20} by matrix methods can be done in a relatively short period of time and, indeed, the method gives <u>all</u> of the transition probabilities from any state one through eight to any other state one through eight. Thus by the use of a matrix of transition probabilities, a great deal of information is expressed in a very simple and useful manner. Naturally, some of the "information" has been lost by collapsing from the twenty-four by twenty-four matrix of transition probabilities, however, the above approach does demonstrate some of the useful features of this formulation of the problem.

From the above discussion it is seen that all states are assumed to be statistically independent. If strong near neighbor interactions are present, then the assumption of statistical independence represents an approximation to the actual physical situation, since the state of any given bond depends on the states of its near neighbor bonds[22].

E. Calculation of the Mean Square Length from the Probability Matrix.

The coordinate system has been chosen such that $U_{(o)} = (1+1+1) = 3$ therefore, L_0 becomes simply

$$L_0 = 3 \tag{20a}$$

and (19) may be written as

$$\overline{h^2} = -3n + 2 \sum_{k=0}^{n-1} (n-k)\, L_K \tag{19a}$$

Let the matrix of transition probabilities (22) appropriate for $0 \rightarrow k$ transition in the sequence $(U_0\, U_1), (U_1\, U_2), \ldots, (U_{k-1}\, U_k)$, be denoted by P^k. If the first row of P^k has elements $p_{11}^{(k)}, p_{12}^{(k)}, \ldots, p_{18}^{(k)}$, the probability that $U_{(k)} = 3, -3, 1, -1$ equals, respectively $p_{11}^{(k)}, p_{15}^{(k)}, p_{16}^{(k)} + p_{17}^{(k)} + p_{18}^{(k)}, p_{12}^{(k)} + p_{13}^{(k)} + p_{14}^{(k)}$, and hence

$$L_k = 3(p_{11}^{(k)} - p_{15}^{(k)}) + (p_{16}^{(k)} + p_{17}^{(k)} + p_{18}^{(k)} - p_{12}^{(k)} - p_{13}^{(k)} - p_{14}^{(k)}) \tag{23}$$

$$= -3\, p_{15}^{(k)} + (p_{16}^{(k)} + p_{17}^{(k)} + p_{18}^{(k)}) \quad \text{for k odd, and} \tag{24}$$

$$= 3\, p_{11}^{(k)} - (p_{12}^{(k)} + p_{13}^{(k)} + p_{14}^{(k)}) \quad \text{for k even.} \tag{25}$$

From the stochastic property,

$$p_{12}^{(k)} + p_{13}^{(k)} + p_{14}^{(k)} = 1 - p_{11}^{(k)} \quad \text{for k even, and} \tag{26}$$

$$p_{16}^{(k)} + p_{17}^{(k)} + p_{18}^{(k)} = 1 - p_{15}^{(k)} \quad \text{for k odd.} \tag{27}$$

it follows that (23) becomes simply:

$$L_k = (4\, s_{11}^{(k)} - 1)(-1)^k \tag{28}$$

where $s_{11}^{(k)}$ stands for the 1,1-element of the S -submatrix.

Therefore Equation (19a) becomes:

$$\overline{h^2} = -3n + 2 \sum_{k=0}^{n-1} (n-k)(-1)^k(4s_{11}^{(k)} - 1) \tag{29}$$

$$\overline{h^2} = -3n - 2n \sum_{k=0}^{n-1} (-1)^k + 2 \sum_{k=0}^{n-1} (-1)^k k + 8 \sum_{k=0}^{n-1} (-1)^k (n-k) s_{11}^{(k)} \; . \tag{30}$$

Evaluation of the first two summations of (30) yields

$$\overline{h^2} = \begin{Bmatrix} -4n \\ -4n-1 \end{Bmatrix} + 8 \sum_{k=0}^{n-1} (-1)^k (n-k) s_{11}^{(k)} \tag{31}$$

where the upper term in the curly brackets is for n even and the lower term is for n odd. The summation term of (31) is, exclusive of the factor 8

$$\delta = \sum_{k=0}^{n-1} (-1)^k (n-k)\, S_{11}^{k} \tag{32}$$

where S_{11}^k stands for the 1,1-element of the matrix S^k.

The expansion of (32) gives

$$= n \sum_{k=0}^{n-1} (-1)^k S_{11}^k - \sum_{k=0}^{n-1} (-1)^k k \, S_{11}^k \tag{33}$$

$$= n(1 - S + S^2 - S^3 + \ldots) + (1 - 2S + 3S^2 - 4S^3 + \ldots) \, S$$

$$\pm (1 - 2S + 3S^2 - 4S^3 + \ldots) \, S^{n+1} \tag{34}$$

where again the upper sign is for n even and the lower sign is for n odd, and the series of (34) are infinite series. Now $(1 + S) \times (1 - S + S^2 - S^3 + \ldots) \equiv 1$, and if $(1+S)^{-1}$ exists, then

$$1 - S + S^2 - S^3 + \ldots = (1 + S)^{-1} \tag{35}$$

Similarly $(1+S)^2(1-2S + 3S^2 - 4S^3 + \ldots) \equiv 1$, and if $[(1 + S)^2]^{-1}$ exists, then

$$(1 - 2S + 3S^2 - 4S^3 + \ldots) = [(1 + S)^2]^{-1} \tag{36}$$

With these assumptions (31) becomes:

$$\overline{h^2} = \left\{ \begin{matrix} -4n \\ -4n-1 \end{matrix} \right\} + 8n(1+S)^{-1} + 8[(1+S)^2]^{-1} \, S \mp 8S^{n+1}[(1+S)^2]^{-1} \tag{37}$$

and the 1,1-elements of the above matrix expressions are desired. The detailed calculation of the above matrix expressions is given in APPENDIX A, B, C, respectively. The results of these calculations are

$$8n(1 + S)^{-1} = 2n \frac{(3 + a)}{(1 - a)}$$

$$8[(1 + S)^2]^{-1} S = 1 - \frac{(3 + a)(5a - 1)}{(1 - a)^2}$$

and

$$8 \, S^{n+1} [(1 + S)^2]^{-1} = 1/2 \quad \text{for large n.}$$

Substitution of these quantities into (37) and rearranging, yields

$$\overline{h^2} = \frac{2n\,(1 + 3a)}{(1 - a)} - \frac{(3 + a)(5a - 1)}{(1 - a)^2} + 1/2 \qquad (38)$$

This result must be multiplied by $l_0^2/3$ to give the "desired" mean square length

$$\overline{h^2} = \frac{l_0^2}{3} \quad \frac{2n\,(1 + 3a)}{(1 - a)} - \frac{(3 + a)(5a - 1)}{(1 - a)^2} + 1/2 \qquad (39)$$

III. CALCULATION OF THE MEAN SQUARE END-TO-END LENGTH OF A VINYLIC ISOTACTIC CHAIN.

A. Introduction

The vinylic isotactic chain (Figure 5) is more complicated than the polymethylene chain in two respects:

1. The asymmetric carbon atoms of a given chain may be either of all (d)- or of all (l)-configuration. However, since both types of molecule can be expected to have the same mean square end-to-end lengths (if they have the same degree of polymerization), this consideration is of no further concern in this particular calculation.

2. The second difficulty encountered is that a given chain possesses two different types of bond. In the manner of S. Lifson[18], the distinction is made between the clockwise sequence of bonds (attached groups) about the asymmetric carbon atoms.

If the asymmetric carbon atom C_i is viewed from the direction of $\underset{\sim}{M}_{i-1}$, the clockwise sequence of attached groups is: H, C_{i+1}, R. Now, if the same asymmetric carbon atom is viewed from the direction of $\underset{\sim}{R}_i$, the clockwise sequence of attached atoms is : H, R, C_{i-1}, or the <u>counterclockwise</u> sequence is: H, C_{i-1}, R. Thus, although each bond is between a methylene carbon atom and an asymmetric carbon atom, because of the differences in the relative orientations of the bonds to their asymmetric carbon atom, the isotactic chain is composed of two alternating types of bond as is indicated in Figure 5.

It is desired to consider a vinylic isotactic chain containing

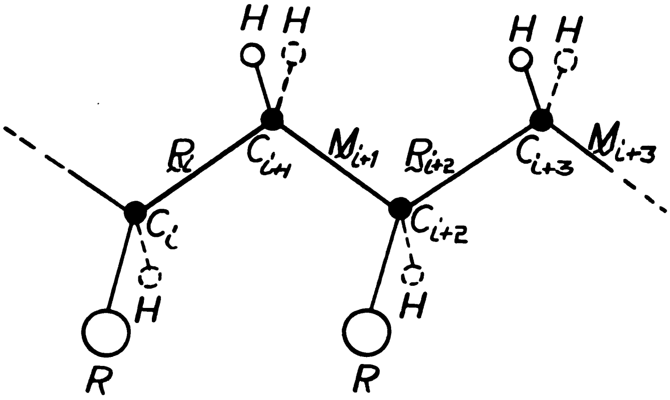


Figure 5. Planar zigzag illustration of a segment of an isotactic macromolecule.

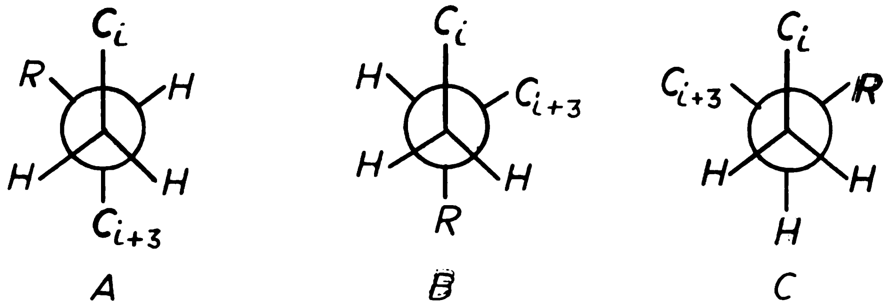


Figure 6. Newman projections of $\underset{\sim}{R}_i$ -$\underset{\sim}{M}_{i+1}$ -$\underset{\sim}{R}_{i+2}$ bond sequences in the _trans_ and two _gauche_ conformations.

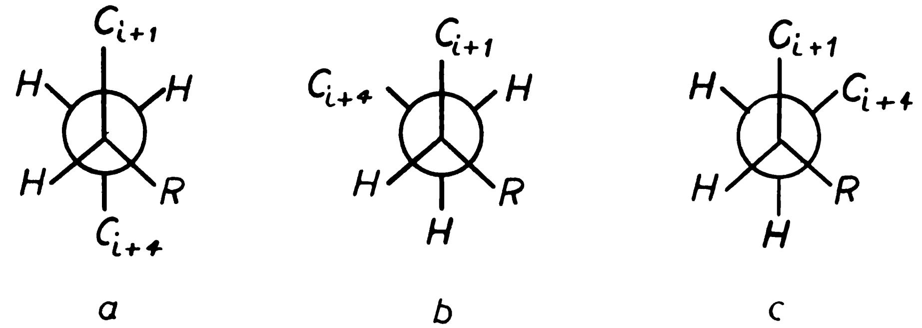


Figure 7. Newman projections of $\underset{\sim}{M}_{i+1}$ -$\underset{\sim}{R}_{i+2}$ -$\underset{\sim}{M}_{i+3}$ bond sequences in the _trans_ and two _gauche_ conformations.

n+1 backbone carbon atoms connected by n vector-bonds of constant length (l_o), at the constant tetrahedral valence angle (θ). Each vector-bond has rectangular vector components ($X^{(i)}$, $Y^{(i)}$, $Z^{(i)}$), $i = 0, 1, 2, \ldots, n-1$. As in the polymethylene chain, for simplicity of calculation, the magnitude of each component is taken to be unity. If (l_o), is the actual bond length, the calculated mean square length must therefore, as the last step of the calculation, be scaled by the factor $l_o^2/3$. Each vector-bond is again represented by one of the eight combinations (±1, ±1, ±1) and successive bonds differ only in the change of *one* algebraic sign.

If an $\underset{\sim}{R}_i$-bond is in position (1,1,1) and the succeeding $\underset{\sim}{M}_{i+1}$ bond is in position (1,1-1), then the probability of occurrence of the following $\underset{\sim}{R}_{i+2}$-bond in the (1,1,1) position is taken to be A; in the (-1,1,-1) position is taken to be B; and in the (1,-1,-1) position is taken to be C. These correspond to the *trans* and two *gauche* conformations (Figure 6) respectively, with, A + B + C = 1. The conformations and positions of B and C will be reversed depending on whether one is dealing with a macromolecule of (d)- or (l)-configuration. Therefore care must be taken to consider the molecule as depicted in Figure 5, and in particular the number sequence of the subscripts on the backbone carbon atoms must be rigorously observed. To be definite, the molecule is selected such that when the above mentioned three bonds are in the *trans* conformation, the pendant R group of carbon atom C_{i+2} lies in the (1,-1,-1) position. If the above three bonds are in the *trans* conformation, then the

$\mathbf{M}_{i+3}$-bond has probabilities a, b, and c of being found in positions (1,1,-1), (-1,1,1) and (1,-1,1) respectively. The probabilities a, b, and c correspond to the <u>trans</u> and the two <u>gauche</u> conformations (Figure 7) in that order; and $a + b + c = 1$. It should be carefully noted that these conformations are uniquely determined by the last three bonds which have been added to the chain. From this it is seen that A, B, and C refer to $\mathbf{R} - \mathbf{M} - \mathbf{R}$ three-bond-combinations; and a, b, and c refer to $\mathbf{M} - \mathbf{R} - \mathbf{M}$ three-bond-combinations.

B. Mean Square End-to-End Length.

If a chain commences with an $\mathbf{R}$-bond the end-to-end length is the magnitude of

$$\mathbf{h}_R = \mathbf{R}_0 + \mathbf{M}_1 + \mathbf{R}_2 + \mathbf{M}_3 + \cdots + \mathbf{M}_{n-1} \tag{40}$$

and if the chain commences with an $\mathbf{M}$-bond the end-to-end length is the magnitude of

$$\mathbf{h}_M = \mathbf{M}_0 + \mathbf{R}_1 + \mathbf{M}_2 + \mathbf{R}_3 + \cdots + \mathbf{R}_{n-1} \tag{41}$$

The <u>a priori</u> probabilities of occurence of these two situations is assumed to be one-half for each of the two cases, since polymers are formed by pairs of chain atoms. Alternatively, one may only consider a molecule such as is given by (40). The mean square distance is then given by the array,

$$\overline{h_R^2} = \left| \begin{array}{l} \overline{\underset{\sim}{R}_0 \cdot \underset{\sim}{R}_0} + \overline{\underset{\sim}{R}_0 \cdot \underset{\sim}{M}_1} + \overline{\underset{\sim}{R}_0 \cdot \underset{\sim}{R}_2} + \cdots + \overline{\underset{\sim}{R}_0 \cdot \underset{\sim}{M}_{n-1}} + \\ \overline{\underset{\sim}{R}_1 \cdot \underset{\sim}{R}_0} + \overline{\underset{\sim}{M}_1 \cdot \underset{\sim}{M}_1} + \overline{\underset{\sim}{M}_1 \cdot \underset{\sim}{R}_2} + \cdots + \overline{\underset{\sim}{M}_1 \cdot \underset{\sim}{M}_{n-1}} + \\ \quad \cdot \\ \quad \cdot \\ \quad \cdot \\ \overline{\underset{\sim}{M}_{n-1} \underset{\sim}{R}_0} + \overline{\underset{\sim}{M}_{n-1} \underset{\sim}{M}_1} + \overline{\underset{\sim}{M}_{n-1} \underset{\sim}{R}_2} + \cdots + \overline{\underset{\sim}{M}_{n-1} \underset{\sim}{M}_{n-1}} \end{array} \right| \qquad (42)$$

Or, if a molecule represented by (41) is selected, the mean square distance is then given by

$$\overline{h_M^2} = \left| \begin{array}{l} \overline{\underset{\sim}{M}_0 \cdot \underset{\sim}{M}_0} + \overline{\underset{\sim}{M}_0 \cdot \underset{\sim}{R}_1} + \overline{\underset{\sim}{M}_0 \cdot \underset{\sim}{M}_2} + \cdots + \overline{\underset{\sim}{M}_0 \cdot \underset{\sim}{R}_{n-1}} + \\ \overline{\underset{\sim}{R}_1 \cdot \underset{\sim}{M}_0} + \overline{\underset{\sim}{R}_1 \cdot \underset{\sim}{R}_1} + \overline{\underset{\sim}{R}_1 \cdot \underset{\sim}{M}_2} + \cdots + \overline{\underset{\sim}{R}_1 \cdot \underset{\sim}{R}_{n-1}} + \\ \quad \cdot \\ \quad \cdot \\ \quad \cdot \\ \overline{\underset{\sim}{R}_{n-1} \cdot \underset{\sim}{M}_0} + \overline{\underset{\sim}{R}_{n-1} \cdot \underset{\sim}{R}_1} + \overline{\underset{\sim}{R}_{n-1} \cdot \underset{\sim}{M}_2} + \cdots + \overline{\underset{\sim}{R}_{n-1} \cdot \underset{\sim}{R}_{n-1}} \end{array} \right| \qquad (43)$$

From either (42) or (43) the leading term corresponding to the leading term of (37), i.e. $[(1+S)^{-1}]$ is obtained. However, if either (42) or (43) is expanded separately, it will be discovered that the non-leading terms are extremely irregular, and can not be easily expressed as simple series as obtained in the polymethylene case. However, (42) and (43) may be rearranged to give

$$\overline{\underset{\sim}{b}_R\cdot\underset{\sim}{b}_R} + \overline{\underset{\sim}{b}_M\cdot\underset{\sim}{b}_M} = \begin{array}{r} (42) \\ (43) \\ (42) \\ \\ \\ \\ (43) \end{array} \left| \begin{array}{l} \overline{\underset{\sim}{R}_0\cdot\underset{\sim}{R}_0} + \overline{\underset{\sim}{R}_0\cdot\underset{\sim}{M}_1} + \overline{\underset{\sim}{R}_0\cdot\underset{\sim}{R}_2} + \cdots + \overline{\underset{\sim}{R}_0\cdot\underset{\sim}{M}_{n-1}} + \\ \overline{\underset{\sim}{R}_1\cdot M_0} + \overline{\underset{\sim}{R}_1\cdot\underset{\sim}{R}_1} + \overline{\underset{\sim}{R}_1\cdot\underset{\sim}{M}_2} + \cdots + \overline{\underset{\sim}{R}_1\cdot\underset{\sim}{R}_{n-1}} \\ \overline{\underset{\sim}{R}_2\cdot\underset{\sim}{R}_0} + \overline{\underset{\sim}{R}_2\cdot\underset{\sim}{M}_1} + \overline{\underset{\sim}{R}_2\cdot\underset{\sim}{R}_2} + \cdots + \overline{\underset{\sim}{R}_2\cdot\underset{\sim}{M}_{n-1}} \\ \cdot \\ \cdot \\ \cdot \\ \overline{\underset{\sim}{R}_{n-1}\cdot\underset{\sim}{M}_0} + \overline{\underset{\sim}{R}_{n-1}\cdot\underset{\sim}{R}_1} + \overline{\underset{\sim}{R}_{n-1}\cdot\underset{\sim}{M}_2} + \cdots + \overline{\underset{\sim}{R}_{n-1}\cdot\underset{\sim}{R}_{n-1}} \end{array} \right| (44)$$

$$+ \begin{array}{r} (43) \\ (42) \\ \\ \\ \\ (42) \end{array} \left| \begin{array}{l} \overline{\underset{\sim}{M}_0\cdot\underset{\sim}{M}_0} + \overline{\underset{\sim}{M}_0\cdot R_1} + \overline{\underset{\sim}{M}_0\cdot\underset{\sim}{M}_2} + \cdots + \overline{\underset{\sim}{M}_0\cdot\underset{\sim}{R}_{n-1}} \\ \overline{\underset{\sim}{M}_1\cdot\underset{\sim}{R}_0} + \overline{\underset{\sim}{M}_1\cdot\underset{\sim}{M}_1} + \overline{\underset{\sim}{M}_1\cdot\underset{\sim}{R}_2} + \cdots + \overline{\underset{\sim}{M}_1\cdot\underset{\sim}{M}_{n-1}} \\ \cdot \\ \cdot \\ \cdot \\ \overline{\underset{\sim}{M}_{n-1}\cdot\underset{\sim}{R}_0} + \overline{\underset{\sim}{M}_{n-1}\cdot\underset{\sim}{M}_1} + \overline{\underset{\sim}{M}_{n-1}\cdot\underset{\sim}{R}_2} + \cdots + \overline{\underset{\sim}{M}_{n-1}\cdot\underset{\sim}{M}_1} \end{array} \right| (45)$$

where the origins of each row are indicated by the numbers in parentheses along the left-hand side of the arrays. As a consequence of "mixing" (42) and (43) in this manner it is now possible to write general expressions for the resulting series which are obtained. The use of two molecules i.e., (40) and (41) may be further justified on the basis that one may, when selecting a molecule "grab" one end one-half of the time or the other end one-half of the time. However, both approaches lead to the same approximate expression and the advantage of similtaneously considering (40) and (41) is that considerable symmetry is introduced into the intermediate steps. Returning to (40) and (41) the over-all mean square length for both situations will be $\overline{h^2}$ (where the bar indicates average quantities), and

$$\overline{h^2} = 1/2\ \overline{\mathbf{b}_R\cdot\mathbf{b}_R} + 1/2\ \overline{\mathbf{h}_M\cdot\mathbf{b}_M} \tag{46}$$

If end effects are neglected, $\overline{\mathbf{M}_i\cdot\mathbf{R}_{i+j}} = \overline{\mathbf{M}_{i+k}\cdot\mathbf{R}_{i+j+k}}$, $\overline{\mathbf{R}_i\cdot\mathbf{M}_{i+j}} = \overline{\mathbf{R}_{i+k}\cdot\mathbf{M}_{i+j+k}}$; then (46) can be arranged in the form corresponding to (44) and (45)

$$\overline{h^2} = 1/2[3n + 2\sum_{j=1}^{n-1}(n-j)\overline{\mathbf{R}_o\cdot\mathbf{N}_j}] + 1/2[3n + \sum_{k=1}^{n-1}(n-k)\overline{\mathbf{M}_o\cdot\mathbf{N}_j}] \tag{47}$$

where $\mathbf{N}_j = \mathbf{R}_j$ for j even, $\mathbf{N}_j = \mathbf{M}_j$ for j odd; $\mathbf{N}_k = \mathbf{R}_k$ for k odd and $\mathbf{N}_k = \mathbf{M}_k$ for k even.

Let L_j be defined as the expected value of the scalar product term occurring in (47), i.e.,

$$L_j = E\left\{X^{(o)}X^{(j)} + Y^{(o)}Y^{(j)} + Z^{(o)}Z^{(j)}\right\}, \tag{48}$$

then,

$$\overline{h^2} = 1/2\ [3n + 2\sum_{j=1}^{n-1}(n-j)\ L_j]_R + 1/2\ [3n + 2\sum_{k=1}^{n-1}(n-k)\ L_k]_M \tag{49}$$

where in this expression L_j pertains to terms for which $(X^{(o)}, Y^{(o)}, Z^{(o)})$ is an $\mathbf{R}$-bond, and L_k pertains to terms for which $(X^{(o)}, Y^{(o)}, Z^{(o)})$ is an $\mathbf{M}$-bond. The coordinate system is now chosen such that $(X^{(o)}, Y^{(o)}, Z^{(o)}) = (1,1,1)$, in which case

$$L_j = E\left\{X^{(j)} + Y^{(j)} + Z^{(j)}\right\} \tag{50}$$

and clearly $L_o = 3$. However, $(X^{(o)}, Y^{(o)}, Z^{(o)}) = (1,1,1)$ may still be an $\mathbf{M}$-bond or an $\mathbf{R}$-bond.

C. Probability matrix.

Again as in the polymethylene chain, the sequence of bond-pairs

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
1				C	B	A																		
2							C	B	A															
3										B	C	A												
4													b	a	c									
5																c	a	b						
6	a	c	b																					
7																			a	b	c			
8													a	c	b									
9	b	a	c																					
10																			c	a	b			
11																a	b	c						
12	c	b	a																					
13							B	A	C															
14				A	C	B																		
15																						B	C	A
16										C	A	B												
17				B	A	C																		
18																						A	B	C
19							A	C	B															
20										A	B	C												
21																						C	A	B
22																b	c	a						
23																			b	c	a			
24													c	b	a									

Figure 8. The submatrix of transition probabilities P_R. The column and row headings (state) are explained in Table III.

	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48
25				b	c	a																		
26							b	c	a															
27										c	b	a												
28													C	A	B									
29																B	A	C						
30	A	B	C																					
31																			A	C	B			
32													A	B	C									
33	C	A	B																					
34																			B	A	C			
35																A	C	B						
36	B	C	A																					
37							c	a	b															
38				a	b	c																		
39																						c	b	a
40										b	a	c												
41				c	a	b																		
42																						a	c	b
43							a	b	c															
44										a	c	b												
45																						b	a	c
46																C	B	A						
47																			C	B	A			
48													B	C	A									

Figure 9. The submatrix of transition probabilities P_M. The column and row headings are explained in Table III.

$(\underset{\sim}{R}_0\underset{\sim}{M}_1)$, $(\underset{\sim}{M}_1\underset{\sim}{R}_2)$, ... , $(\underset{\sim}{R}_{n-1}\underset{\sim}{M}_n)$ is considered. (Stick and ball models will be found helpful in the following considerations.) The coordinates may be chosen such that $\underset{\sim}{R}_0 = (1,1,1)$, $\underset{\sim}{M}_1 = (1,1,-1)$. $\underset{\sim}{R}_2$ may then have the sets of components (1,-1,-1), (-1,1,-1), and (1,1,1), with probabilities C, B, and A, corresponding to their respective conformations. In Figure 8 it is seen that these sets correspond to transitions from state(<u>row</u>) 1 to states (<u>columns</u>) 4, 5, and 6, respectively. Now, each of these events is treated as though it had occurred, and the subsequent possibilities are considered. For example, if $\underset{\sim}{R}_2 = (1,-1,-1)$ has occurred, corresponding to the transition state (<u>row</u>) 1 to state (column) 4 with probability C (Figure 8), as just discussed, then, the next transition originates from state (<u>row</u>) 4, and may proceed to states (<u>columns</u>) 13, 14, and 15, with probabilities (conformations) b, a, and c, respectively. The next transitions then originate from states (<u>rows</u>) 13, 14, and 15, depending on the outcomes of preceeding trials. Now, $\underset{\sim}{M}_1$ may also have the sets (1,-1,1), (-1,1,1) as well as the set (1,1,-1), given above. Therefore, these possibilities and all possible subsequent events must also be considered. This procedure is then continued until the submatrix of transition probabilities P_R, Figure 8, has been obtained. It is then discovered that all subsequent bond pairs return to some previously considered state of Figure 8.

Now, the bond with coordinates (1,1,1) may also be an $\underset{\sim}{M}$-bond. By methods analogous to those given above, the case where $\underset{\sim}{M}_0 = (1,1,1)$ leads to the submatrix P_M given in Figure 9. The two submatrices are then combined to give (51), which describes all possible transitions.

$$P_{48 \times 48} = \begin{bmatrix} P_R & 0 \\ 0 & P_M \end{bmatrix} \tag{51}$$

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1					0	C	B	A								
2					0	B	A	C								
3					0	A	C	B								
4					1	0	0	0								
5	0	c	b	a												
6	0	b	a	c												
7	0	a	c	b												
8	1	0	0	0												
9													0	b	c	a
10													0	c	a	b
11													0	a	b	c
12													1	0	0	0
13									0	B	C	A				
14									0	C	A	B				
15									0	A	B	C				
16									1	0	0	0				

Figure 10. The matrix of transition probabilities P.

The submatrices P_R and P_M are given in Figures 8, and 9, respectively.

Table III. The forty-eight states of the isotactic vinylic chain

State	U_j	U_{j+1}	State	U_j	U_{j+1}
1	$\underset{\sim}{R}\ 3$	$\underset{\sim}{M}\ 1_3$	13	$\underset{\sim}{R}\ -1_1$	$\underset{\sim}{M}\ 1_2$
2	$\underset{\sim}{R}\ 3$	$\underset{\sim}{M}\ 1_2$	14	$\underset{\sim}{R}\ -1_1$	$\underset{\sim}{M}\ 1_3$
3	$\underset{\sim}{R}\ 3$	$\underset{\sim}{M}\ 1_1$	15	$\underset{\sim}{R}\ -1_1$	$\underset{\sim}{M}\ -3$
4	$\underset{\sim}{M}\ 1_3$	$\underset{\sim}{R}\ -1_1$	16	$\underset{\sim}{R}\ -1_2$	$\underset{\sim}{M}\ 1_1$
5	$\underset{\sim}{M}\ 1_3$	$\underset{\sim}{R}\ -1_2$	17	$\underset{\sim}{R}\ -1_2$	$\underset{\sim}{M}\ 1_3$
6	$\underset{\sim}{M}\ 1_3$	$\underset{\sim}{R}\ 3$	18	$\underset{\sim}{R}\ -1_2$	$\underset{\sim}{M}\ -3$
7	$\underset{\sim}{M}\ 1_2$	$\underset{\sim}{R}\ -1_3$	19	$\underset{\sim}{R}\ -1_3$	$\underset{\sim}{M}\ 1_2$
8	$\underset{\sim}{M}\ 1_2$	$\underset{\sim}{R}\ -1_1$	20	$\underset{\sim}{R}\ -1_3$	$\underset{\sim}{M}\ 1_1$
9	$\underset{\sim}{M}\ 1_2$	$\underset{\sim}{R}\ 3$	21	$\underset{\sim}{R}\ -1_3$	$\underset{\sim}{M}\ -3$
10	$\underset{\sim}{M}\ 1_1$	$\underset{\sim}{R}\ -1_3$	22	$\underset{\sim}{M}\ -3$	$\underset{\sim}{R}\ -1_2$
11	$\underset{\sim}{M}\ 1_1$	$\underset{\sim}{R}\ -1_2$	23	$\underset{\sim}{M}\ -3$	$\underset{\sim}{R}\ -1_3$
12	$\underset{\sim}{M}\ 1_1$	$\underset{\sim}{R}\ 3$	24	$\underset{\sim}{M}\ -3$	$\underset{\sim}{R}\ -1_1$

The remaining twenty-four states are numbered from twenty-five to forty-eight in the order above and with $\underset{\sim}{M}$ and $\underset{\sim}{R}$ interchanged.

However, for the purpose of calculating the mean square length, the bond components are <u>not</u> needed. Since $U_{(j)} = X^{(j)} + Y^{(j)} + Z^{(j)}$, only the sum of the components is needed. Therefore, the 48 x 48 matrix of transition probabilities (51), is more elaborate than need be, and by a collapsing process similar to that used in the polymethylene chain, (51) may be collapsed to Figure 10, corresponding to the sequence of pairs (U_0U_1), (U_1U_2), (U_2U_3), ... , $(U_{n-1}U_n)$. Again each member of this sequence is a state in the sense of the Markov formalism and

and the sequence of pairs forms a Markov chain with matrix of transition probabilities given in Figure 10. The states are relabeled from one to sixteen, and the relationship of the original to the relabeled states is given in Table IV.

Table IV. Relation of the relabeled states to the original states for the isotactic vinylic chain.

Relabeled State Numbers		Original State Number
Number	Relabeled State	
1	3 1	1, 2, 3
2	-1 1	13, 17, 20
3	-1 1	14, 16, 19
4	-1 -3	15, 18, 21
5	-3 -1	22, 23, 24
6	1 -1	4, 7, 11
7	1 -1	5, 8, 10
8	1 3	6, 9, 12

The remaining eight states (states nine through sixteen) are obtained from the original states twenty five through forty-eight by a similar scheme in analogous order.

The matrix of transition probabilities P in terms of the relabeled sixteen states is given in Figure 10. The states one through eight and nine through sixteen constitute "closed sets"[27]. That is, from any of the states one through eight it is not possible, regardless of the number of "steps" taken, to end up in any of the states nine through sixteen and vice versa.

D. Calculation of Mean Square End-to-End Length from the Probability Matrix.

From the selection of $U_{(o)}$ as (1+1+1) viz., 3, and from (50) it follows that if the k-th power of P is denoted by P^k and its matrix elements by $p_{ij}^{(k)}$, then

$$L_k = 3p_{9,9}^{(k)} - (p_{9,10}^{(k)} + p_{9,11}^{(k)} + p_{9,12}^{(k)}) - 3p_{9,13}^{(k)} + (p_{9,14}^{(k)} + p_{9,15}^{(k)} + p_{9,16}^{(k)}) \tag{52}$$

and

$$L_j = 3p_{11}^{(j)} - (p_{12}^{(j)} + p_{13}^{(j)} + p_{14}^{(j)}) - 3p_{15}^{(j)} + (p_{16}^{(j)} + p_{17}^{(j)} + p_{18}^{(j)}) \tag{53}$$

For convenience, the complete matrix of transition probabilities may be denoted by

$$P = \begin{bmatrix} 0 & S & 0 & 0 \\ T & 0 & 0 & 0 \\ 0 & 0 & 0 & V \\ 0 & 0 & U & 0 \end{bmatrix} \tag{54}$$

$$= \begin{bmatrix} P_R & 0 \\ 0 & P_M \end{bmatrix} \tag{55}$$

Since P_R and P_M constitute closed sets, they may be considered separately (see reference 27, p. 349). Only the leading term will be calculated for the isotactic case (this is an excellent approximation for large n). A straightforward application of the method of calculation used in the polymethylene case generates matrix inverses of the form $(1-ST)^{-1}$. These inverses, however, do not exist, since $\det(1-ST) \equiv 0$, and the calculation gives a leading element of the form 0/0.

To avoid this difficulty it is necessary to set

$$P_R = \begin{bmatrix} 0 & K \\ K & 0 \end{bmatrix} + \begin{bmatrix} 0 & S' \\ T' & 0 \end{bmatrix} \tag{56}$$

where K is the four by four matrix all of whose elements are 1/4 (see Appendix C), and $S' = S - K$, and $T' = T - K$. Observing that $K^n = K$ for all n; that the sum of the elements of any row or column of S' or T' is equal to zero; and that this null property is preserved for any product matrix from T' and S'; it is found that

$$P_R^2 = P_R P_R = \begin{bmatrix} K & 0 \\ 0 & K \end{bmatrix} + \begin{bmatrix} S'T' & 0 \\ 0 & T'S' \end{bmatrix} \tag{57}$$

$$P_R^3 = P_R P_R^2 = \begin{bmatrix} 0 & K \\ K & 0 \end{bmatrix} + \begin{bmatrix} 0 & S'T'S' \\ T'S'T' & 0 \end{bmatrix} \tag{58}$$

and so on. P_R^0 is, of course, the unit matrix of order eight

As before, L_j is given by (53). The K matrix gives <u>no</u> contribution to L_j. Therefore, for purposes of computing E_R one may write

$$P_R^0 = 1,\ P_R^1 = \begin{bmatrix} 0 & S' \\ T' & 0 \end{bmatrix},\ P_R^2 = \begin{bmatrix} S'T' & 0 \\ 0 & S'T' \end{bmatrix},\ \ldots \tag{59}$$

and, in general

$$P_R^j = \begin{bmatrix} 0 & Q^{(j)} \\ Q'^{(j)} & 0 \end{bmatrix} \quad \text{for j odd,} \tag{60}$$

and

$$P_R^j = \begin{bmatrix} Q^{(j)} & 0 \\ 0 & Q'^{(j)} \end{bmatrix} \quad \text{for } j \text{ even,} \tag{61}$$

and the meaning of $Q^{(j)}$, and $Q'^{(j)}$ is clear from the context. For all positive j, $Q^{(j)}$ (and $Q'^{(j)}$) has the property that each of its rows and columns sums to zero. Denoting the elements of $Q^{(j)}$ by $q_{ij}^{(j)}$, (53) becomes

$$L_j = (-1)^j \, [3q_{11}^{(j)} - (q_{12}^{(j)} + q_{13}^{(j)} + q_{14}^{(j)})] \tag{62}$$

Since

$$q_{12}^{(j)} + q_{13}^{(j)} + q_{14}^{(j)} = -q_{11}^{(j)} \tag{63}$$

it follows that

$$L_j = (-1)^j \, 4 \, q_{11}^{(j)} \quad , \quad j \neq 0 \quad , \text{ and } \quad L_o = 3 \tag{64}$$

Therefore

$$E_R = - 3n + 2 \sum_{j=0}^{n-1} (n-j) \, L_j \tag{65}$$

$$= 3n + \sum_{j=1}^{n-1} (-1)^j (n-j) \, q_{11}^{(j)} \tag{66}$$

The leading term of the summation in (66) is

$$m' = \sum_{j=1}^{n-1} (-1)^j n q_{11}^{(j)} \tag{67}$$

which is the element in row one and column one of the matrix sum

$$M' = n \sum_{j=1}^{n-1} (-1)^j \, Q^{(j)} \tag{68}$$

or

$$M' = n(-S' + S'T' - S'T'S' + \ldots) \qquad (69)$$

where the convergent finite series (68) has been replaced by an infinite series (69). Now,

$$\frac{1}{n} M' = -S' + S'T' - S'T'S' + \ldots \qquad (70)$$

and upon solving for M', one secures

$$M' = n(1-S'T')^{-1}(S'T'-S') \qquad (72)$$

The needed inverse now does exist. The construction of m'_{11} is a straightforward but laborious task (APPENDIX D). After m'_{11} is found E_R follows readily.‡ One obtains

$$E = (n/D) \; [8(AB+AC+BC)(ab+ac+bc) + 4(Ab+Ac+Bc)(Ab+Ac+Cb) + \Delta] \qquad (73)$$

where

$$D = (ab+ac+bc)(B^2+BC+C^2) + (Ab+Ac+Bc)(b^2+bc+c^2) \qquad (74)$$

‡ A better approximation to E_R can be found in principle by adding to the E_R given by (47) the element of row one and column one of $16\, S'T'[(1-S'T')^2]^{-1} (S'-1) + 8(1-S'T')^{-1}S'$ (this corresponds to the second term of Equation 27, because of the null property of $(S')^{\infty}$ there is no third term). The resulting E_R in that case would be of the order of approximation that corresponds to the one for the special case of polymethylene.

and

$$
\begin{aligned}
\Delta = {} & 2\,(A^2+B^2+C^2)(a^2+b^2+c^2) - 2(Aa+Bb+Cc)^2 \\
& + (Ab-Ba)(Bb+Cb-3Bc) \\
& + (Ac-Ca)(Bc+Cc-3Cb) \\
& + (Bc-Cb)(Bb-Cc+2Bc-2Cb) \\
& + 2(BC\,a^2 - A^2bc)
\end{aligned}
\tag{75}
$$

If $A=a$, $B=C=b=c=1/2(1-a)$, then $\Delta=0$, and the remaining terms of (75) reduce readily to the leading term of (38).

Comparison of P_M with P_R shows that E_M can be obtained from E_R by making the following interchanges in E_R; A with a, B with c, and C with b. With E_M and E_R known, $\overline{h^2}$ follows from (49), and one obtains

$$
\overline{h^2} = \left\{ 4n\,\frac{(1-\sigma^2)(1-\Sigma^2) + 2\,\sigma^2\Sigma^2 - 2(\,\alpha^4 + \beta^4 + \gamma^4)}{(1-\sigma^2)(B^2 + BC + C^2) + (1-\Sigma^2)(b^2 + bc + c^2)} \right\} \frac{l_o^2}{3}
\tag{76}
$$

where

$$
\begin{aligned}
\sigma^2 &= a^2 + b^2 + c^2 \\
\Sigma^2 &= A^2 + B^2 + C^2 \\
\alpha^4 &= (A^2-BC)(a^2-bc) \\
\beta^4 &= (B^2-AC)(b^2-ac) \\
\gamma^4 &= (C^2-AB)(c^2-ab)
\end{aligned}
$$

and within the curly brackets, the mean square length is scaled by the factor $l_o^2/3$.

IV. CONCLUSIONS AND DISCUSSIONS

A. General.

Applications of equations (39) and (76) are restricted to polymer molecules whose conformations are undisturbed by interactions with solvent molecules. Thus the equations are useful for polymers only in the "unperturbed" state or in bulk(no solvent). Solvent interactions with the polymer molecules cause conformational changes which result in expansion of the polymer coil. In addition, excluded volume of a polymer becomes appreciable with resulting changes in the mean square dimensions.

However, in analogy with the Boyle point of a gas, real polymer molecules can be investigated in an "ideal solution" where the solvent-polymer interactions, which cause expansion, are precisely counterbalanced by the intramolecular interactions which favor contraction of the chain. Under these conditions, called the "unperturbed" state, the polymer coils in a "random flight" manner, the excluded volume is zero, and the chain dimensions are minimal. The exact temperature at which the unperturbed state obtains is designated as the Flory (θ)-temperature. According to Flory this condition also obtains in the "melt" state of polymer molecules.

The crystallization of polymer molecules involves the minimization of the potential energy due to rotational barriers in the chain backbone. Calculations by P. J. Flory[34] indicate that near neighbor intramolecular forces are of paramount importance in determining crystal structure. If this is true, then the preferred conformation for a polymer molecule in its unperturbed state should also tend towards the crystalline state conformation. The recent infrared spectral studies of M. Takeda and coworkers[35] on isotactic polystyrene indicates that the helical crystalline state structure of isotactic polystyrene is partially retained in solution.

Polymer molecules, however, are unable to crystallize in the continuous and orderly manner of small molecules. Since the molecules are so large it becomes extremely difficult for long segments of <u>different</u> polymer molecules to become extensively ordered (within experimentally feasible time limits) such that perfect crystals are obtained. Crystalline polymers, as normally obtained, contain extensive amorphous regions of imperfect order intermixed with crystallites of high order. This "picture" of polymer crystallization has recently come under attack, and the alternate "picture" of considering the amorphous character as resulting from exaggerated lattice defects is favored by some authors[36]. However, at the Θ-temperature the polymer molecules are in the liquid state and the difficulty of aligning many macromolecules disappears. Thus, all bonds of a particular macromolecule are free to tend towards their equilibrium positions as are indicated by their crystalline state conformations.

The following restrictions apply to the equations derived in (II) and (III);

1. The polymer chains must be long (large n), linear macromolecules of regular head-to-tail structure.

2. The valence angle has been restricted to the tetrahedral valence angle.

3. The "excluded volume" effect has not been taken into account

(see reference 12, chap. 12). That is, the chain is allowed to return to positions in space which it has already occupied, and more seriously, also to positions which are excluded because of intramolecular repulsions. However, this difficulty essentially disappears at the Flory θ-temperature.

4. The bonds are assumed to be statistically independent. This means that the conformation of any given bond is <u>not</u> influenced by the conformations of neighboring bonds.

5. Any three successive bonds are restricted to the <u>trans</u> or one of the two <u>gauche</u> conformations.

B. Polymethylene

It is desired to investigate the behavior of Equation (39) when only the leading term is considered. To be specific, the calculation will be performed for the case corresponding to free rotation, $a = 1/3$. Equation (39) becomes

$$\overline{h^2} = (2n - 3/2)\, l_0^2 \qquad (77)$$

In Table V, the magnitude of the error involved in considering only the leading term of (77) is indicated in column three. It is seen that the error becomes very small with increasing n. Since even low molecular weight polymers normally have n many times greater than one hundred, it is seen that the leading term expression is an excellent approximation.

TABLE V. Magnitude of error in the leading term approximation.

n	$\overline{h^2}/l_o^2$	$\frac{2n - (\overline{h^2}/l_o^2)}{\overline{h^2}/l_o^2} \times 100$
5	8.5	17.5
10	18.5	8.1
20	38.5	3.9
50	98.5	1.5
100	198.5	.7

In Figure 11, the leading term (large n) of (76) is plotted against increasing values of (a). For the case of free rotation a = 1/3 and $(\overline{h^2}/nl_o^2) = 2.00$. At a = .8, $(\overline{h_u^2}/nl_o^2) = 10.6$, which is the experimentally determined value of $(\overline{h^2}/nl_o^2)$ for polymethylene chains in their "unperturbed" states. The value $(\overline{h_u^2}/nl_o^2) = 10.6$ was calculated from second virial coefficient data by W. R. Krigbaum[29] from the experimental results of Q. A. Trementozzi[42].

For linear macromolecules the conformational potential energy is given by:

$$V(\phi_o, \phi_1, \ldots, \phi_{n-1}). \tag{78}$$

That is, the conformational potential energy is a simultaneous function of <u>all</u> the rotational angles. If the bonds are statistically independent, the potential energy may be expressed as the sum of the <u>individual</u> potential energies:

$$V(\phi_o, \phi_1, \ldots, \phi_{n-1}) = \sum_{i=0}^{n-1} V(\phi_i). \tag{79}$$

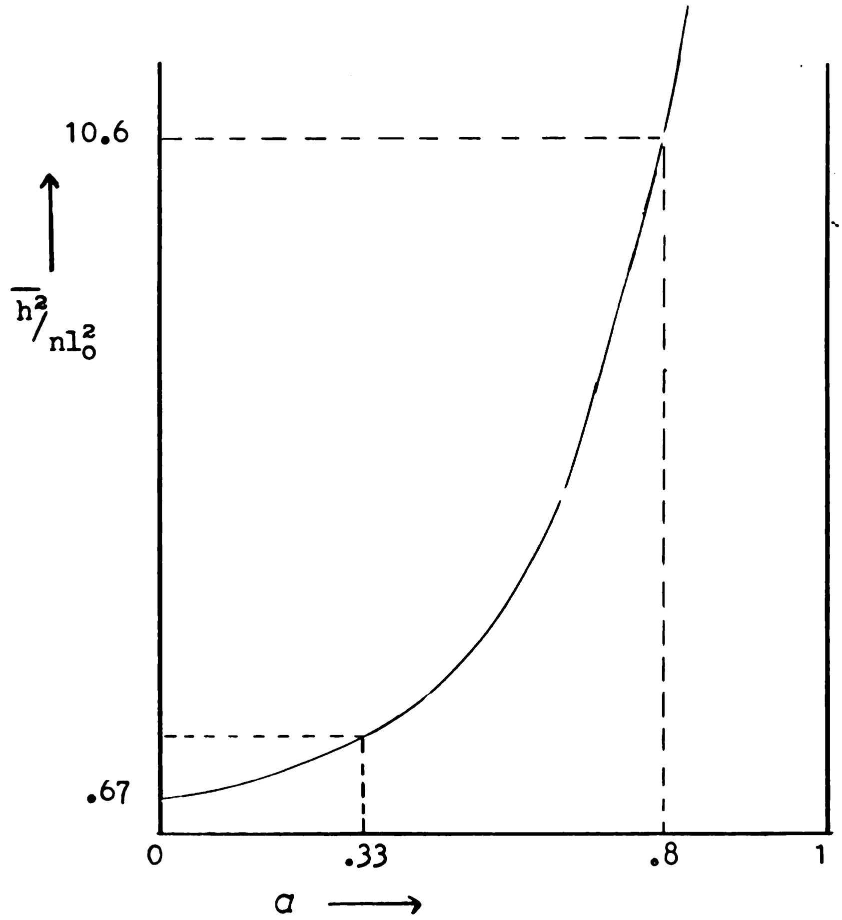


Figure 11. Plot of $\overline{h^2}/nl_o^2$ versus (a).

With this simplification, the probability (a) of occurrence of the trans position is given by:[23, 30]

$$a = [1 + 2e^{-\Delta E/RT}]^{-1} \qquad (80)$$

where ΔE is the energy difference between the *trans* and *gauche* conformations. For a = .8, R = 2 cal. $\text{mole}^{-1}\text{deg.}^{-1}$, and T = 363°K, the θ-temperature for polymethylene, the energy difference between the *trans* and *gauche* conformation is calculated to be: $\Delta E = 1.51$ kcal. mole^{-1}. This value is of the correct order of magnitude since from small molecules, ΔE has been estimated [30] to be approximately .8 kcal. mole^{-1}. Since the value of $(\overline{h_u^2}/nl_o^2) = 10.6$ reported by Krigbaum[29] was calculated from measurements made in a good solvent, the results obtained are only approximate. However, the result a = .8 does indicate considerable retention of crystalline state structure in the unperturbed state for the case of polymethylene. For statistically independent bonds this implies that eight out of every ten bonds are in the trans conformation corresponding to the planar zigzag crystalline structure.

Equation (39) may also be expressed in terms of average rotational angles by the following considerations. The average of the cosine of the rotational angle (ϕ), where (ϕ) is measured from the *trans* position (see Figure 3), is

$$\overline{\cos\phi} = a\cos(0°) + b\cos(120°) + b\cos(240°), \text{ and} \qquad (81)$$

$$\overline{\sin\phi} = a\sin(0°) + b\sin(120°) + b\sin(240°) = 0. \qquad (82)$$

Since b = (1/2)(1-a), Equation (81) becomes

$$\overline{\cos\phi} = \frac{3a-1}{2}, \text{ or} \qquad (83)$$

$$a = \frac{2\ \overline{\cos \phi} + 1}{3} \tag{84}$$

Substitute (84) into (39). The leading term expression then becomes:

$$\overline{h^2} = 2\ nl^2\ \frac{1 + \overline{\cos \phi}}{1 + \overline{\cos \phi}} \tag{85}$$

Utilizing a rotational matrix approach, H. Benoit;[31] and O.B. Ptitsyn and M. V. Volkenstein[32] obtained the expression

$$\overline{h^2} = nl_o^2\ \frac{1 + \cos(\pi - \theta)}{1 - \cos(\pi - \theta)}\ \frac{1 + \overline{\cos \phi}}{1 - \overline{\cos \phi}} \tag{86}$$

When $\theta = 109.3°$, i.e., the tetrahedral valence angle, (86) becomes the same as (85). Comparison of (86), (85), and the leading term of (39), shows that the expression for $\overline{h^2}$ corrected for any angle of (θ), and expressed as a function of the probability (a) becomes:

$$\overline{h^2} = \frac{nl_o^2}{3}\ \frac{1 + \cos\ (\pi - \theta)}{1 - \cos\ (\pi - \theta)}\ \frac{1 + 3a}{1 - a} \tag{87}$$

Since polymethylene in the crystalline state has a valence angle (θ) of 111°, a better approximation of (a) and ΔE can be obtained by (87). In this case $a = .77$, and $\Delta E = 1.38$ kcal. mole^{-1}. (The number of "significant" figures retained do not imply degree of accuracy, but are only useful for comparative purposes.)

In a recent publication (published after the completion of this calculation) R. P. Smith[25] has shown the rotational matrix method and the method of transition probabilities leads to identical equations for the simple polymethylene-type chain. By expressing $\overline{\cos \phi}$ and $\overline{\sin \phi}$ in a manner analogous to (81) and (82) he obtained by a rotational matrix approach, the expression

$$\overline{h^2} = \frac{nl_o^2\ (2 + 6a)}{3\ (1 - a)} - \left[3/2 + \frac{8\ (3a - 1)}{3\ (1 - a)^2}\right] l_o^2 \qquad (88)$$

which by appropriate rearrangement is found to be exactly the same as (39).

C. Isotactic Macromolecules.

As previously state , isotactic polymers are more complex in that two types of bond constitute the repeating mer of the chain. This type of molecule has periodicity two and requires four independent parameters to describe the chain.

Both isotactic polystyrene and isotactic polypropylene crystallize in a 3_1 helical structure[37]; a chain where trans (a) and gauche (B) conformations alternate. If there is a strong tendency to retain this structure in the unperturbed state, then the assumption may be made $B = a$, and $A = C = b = c$. The calculated values of $(\overline{h^2}/ nl_o^2)$ using Equation (76) for various assumed values of the probabilities are given in column four of Table VI. This case will be discussed later relative to pertinent experimental data.

An additional regular conformational chain of interest is one consisting of rotations of each bond in the same direction into alternate gauche positions. In this case, the assumption is made $C = b$, and all other probabilities are assumed equal. This type of conformation generates a 4_1 helix and results in a tightly packed polymer chain. Polyoxymethylene has been shown to possess a structure of this type. Although the unperturbed dimensions of this polymer have not been measured it is possible that its dimensions could be less than that calculated for the free rotation case, i.e., less than $2nl_0^2$. The values calculated according to Equation (76) for a chain of this nature is given in column five of Table VI. It may be noted that the chain dimensions expand as more trans conformations are introduced or if high retention of the gauche conformations obtains the chain dimensions pass through a minimum which is less than $2nl_0^2$.

Column six of Table VI summarizes increasing values of $(\overline{h^2}/nl_0^2)$ for increasing values $B = b$. The extreme case $B = b = 1$, corresponds to a chain which follows a path as described by the "chair" form of cyclohexane. Since real polymer chains can not occupy any position more than once, this situation is obviously unrealistic in terms of any physical model. However, it does serve as a useful check on the behavior of the derived equation. Since, the equation, if properly derived (does not contain computational errors), must predict $(\overline{h^2}/nl_0^2) \to 0$, as $B = b \to 1$.

For macromolecules which tend to crystallize in a planar zigzag conformation (2_1 helix[37]), the perfect crystalline state may be characterized by $A = a = 1$, corresponding to an all trans sequence of bonds. If there is a strong tendency to retain this structure in the unperturbed state, then the assumption may be made $A = a$, and $B = C = b = c$. The calculated values of $(\overline{h^2}/nl_0^2)$ using Equation (76) for various assumed values of the probabilities are given in column three of Table VI. The polymethylene chain is an example of a polymer chain which rigorously corresponds to the above mentioned assumptions. This chain was discussed in the preceding section.

Ball and stick models of the structures corresponding to $A = a = 1$, all trans; $B = a = 1$, gauche-trans, and, $C = b = 1$, gauche-gauche, clearly demonstrate that the mean square end-to-end length should, for the same number of bonds, and for the same value of the respective parameters, decrease in the same order as is indicated in Table VI. Comparison of columns three, four, and five shows that the mean square lengths as calculated by the derived equation, i.e., (76), does predict this relative behavior.

Table VI. Variation of mean square length with change in magnitude of probabilities.

		$(\overline{h^2}/nl_0^2)$			
↓		A=a	B=a	C=b	B=b
	↓	B=C=b=c	A=C=b=c	A=B=a=c	A=C=a=c
0.0	0.5	.67[+]	1.99[‡]	4.33[ǂ]	4.67
0.2	0.4	1.34	1.96	2.73	2.29
1/3[*]	1/3	2.00	2.00	2.00	2.00
0.4	0.3	2.45	2.12	1.84	1.78
0.6	0.2	7.14	2.96	1.81	1.08
0.8	0.1	11.8	5.96	3.10	0.47
0.84	.08	14.4	7.55	4.61	0.34
0.9	.05	24.7	12.48	6.19	0.23

[*] Corresponds to a tetrahedral macromolecule with free rotations.

[+] Indicative of macromolecules which tend to form 2_1 helices[37].

[‡] Indicative of macromolecules which tend to form 3_1 helices[37].

[ǂ] Indicative of macromolecules which tend to form 4_1 helices[37].

There are only a few measured unperturbed dimensions reported for isotactic polymers. since most of the data in the literature is for the atactic configuration. In Table VII the experimental data of J. B. Kinsinger and R. A. Wessling are summarized for atactic and isotactic polypropylene.

Table VII. Polypropylene at the Flory theta(Θ)temperatures.[39,40,43]

Configuration	Θ-solvent	Θ(°C)	‡Kx10^4	‡a	$(\overline{h_F^2}/M)^{1/2}$ x 10^{11}	$(\overline{h_u^2}/M)^{1/2}$ x 10^{11}	$(\overline{h_u^2}/\overline{h_F^2})^{1/2}$	$\overline{h_u^2}/nl_o^2$
atactic	1-chloronaphthalene	74	18.2	0.50	475	868	2.02	8.15
atactic	cyclohexanone	92	17.2	0.50	475	820	1.96	7.67
atactic	phenylether	153.4	12.0	0.50	475	571	1.75	6.12
isotactic	phenylether	145.2	16.2	0.50	475	774	1.93	7.44

ϕ is taken as 2.1 x 10^{21}

‡ $[\eta] = KM^a$

As a measure of "stiffness" of the polymer chain the unperturbed polymer dimensions ($\overline{h_u^2}$) are frequently compared with the free rotation dimensions ($\overline{h_F^2}$). The square root of the ratio of unperturbed to freely rotating dimensions are given in column eight; in column nine in order of increasing temperature. It is seen that the unperturbed dimensions of the atactic polymer <u>decrease</u> with <u>increasing</u> temperature. This is consistent with an exponential dependence of the probabilities as is indicated in the discussion of the polymethylene chain.

The retention of crystalline state structure for isotactic polypropylene may be estimated from the experimentally determined unperturbed dimensions given in Table VII. Since isotactic polypropylene has a 3_1 helical structure corresponding to a trans (a)-gauche (B) sequence of bond conformations, from column four of Table VI, one has

$$B = a = .84, \text{ and}$$
$$A = C = b = c = .08$$

This implies approximately 80% retention of crystalline state conformation in the unperturbed state. From the data of W. R. Krigbaum[41] et al. for isotactic polystyrene, the quantities

$$B = a = .91$$
$$A = C = b = c = .045$$

are obtained, indicating an even greater degree of retention of crystalline state structure in the unperturbed state.

It is desired to investigate the error involved in assuming $A = C = b = c$. For this purpose, $(\overline{h^2}/nl_0^2)$ is calculated for $B = a = .84$ but for $C = c = 0$, and $A = b = .16$. This represents a maximum in deviation from the equality $A = C = b = c$. For these values of the parameters the result is obtained $(\overline{h^2}/nl_0^2) = 7.07$, in contrast to the value $(\overline{h^2}/nl_0^2) = 7.44$ for the case where $A = C = b = c$.

Another source of error is the assumption of the tetrahedral valence angle. Actually the valence angle for isotactic polypropylene[33] is $(\theta = 114°)$, and for isotactic polystyrene $(\theta = 116°)$ as measured by X-ray diffraction in the crystalline state. An indication of how these deviations from the tetrahedral valence angle effect the calculation can be obtained by observing the behavior of the polymethylene chain as θ increases. This may be accomplished by utilizing Equation (87) which applies to polymethylene chains with constant bond length, but arbitrary bond angle. For $\theta = 114°$, Equation (87) becomes

$$(\overline{h^2}/nl_0^2) = \frac{2.37\ (1 + 3a)}{3\ (1 - a)} \tag{89}$$

Comparison of (89) with the equation for the tetrahedral valence angle viz.,

$$(\overline{h^2}/nl_0^2) = \frac{2\ (1 + 3a)}{3(1 - a)} \quad , \tag{90}$$

indicates that the "retention of crystallinity" as calculated with the assumption of tetrahedral valence angle, is probably too large. From these considerations it is seen that the calculation of "retention of crystallinity" is approximate in nature.

If the rotational angle (ϕ) is defined such that $\phi = 0$, for the trans conformations, and (ϕ) is measured counterclockwise (see figures 6 and 7), then the mean square length may be expressed in terms of average angles as follows

$$\overline{\cos \phi}_{MRM} = a \cos (0°) + b \cos (240°) + c \cos (120°) = a - 1/2\ (b + c) \tag{91}$$

$$\overline{\sin \phi}_{MRM} = a \sin 0° + b \sin (240°) + c \sin (120°) = \frac{\sqrt{3}}{2}\ (c - b), \tag{92}$$

and further

$$\overline{\cos \phi}_{RMR} = A - 1/2\ (B + C)\ , \tag{93}$$

and

$$\overline{\sin \phi}_{RMR} = \frac{\sqrt{3}}{2}\ (B - C) \tag{94}$$

By means of (91), (92), (93), and (94), and the stochastic relationships $A + B + C = a + b + c = 1$, the mean square length (74), may also be expressed as a function of average angles. With this modification, the mean square length, equation (76), then applies to isotactic vinylic chains with constant tetrahedral valence angle (θ) and statistically independent bonds, but with arbitrary (ϕ). That is, the chain is no longer restricted to staggered conformations.

D. Additional Structural Problems.

The other important configurational chain of regular asymmetric order is the syndiotactic-type vinyl polymer chain. As previously stated, this chain is composed of two mer units (four chain bonds) with the two pseudo asymmetric centers in alternate d and l configuration. With these structural restrictions this type chain has periodicity four and thus requires a separate solution.

The matrix of transition probabilities has been derived for this type chain but the solution has not been completed. The process of solution should be identical to that for the isotactic chain, but more laborious to perform.

In the case of syndiotactic macromolecules the four different types of bond may be denoted by R_d, M_d, R_l, M_l. The "collapsed" matrix of transition probabilities for a Markov chain composed of the above indicated sequence units is:

$$P = \left[\begin{array}{cccc|cccc} & & & A_d & & & & \\ & & C_1 & & & & & \\ D_1 & & & & & & & \\ & B_d & & & & & & \\ \hline & & & & & & & D_1 \\ & & & & & & B_d & \\ & & & & C_1 & & & \\ & & & & & A_d & & \end{array}\right] \tag{95}$$

where

$$A_d = \begin{bmatrix} 0 & C & B & A \\ 0 & B & A & C \\ 0 & A & C & B \\ 1 & 0 & 0 & 0 \end{bmatrix}, \quad B_d = \begin{bmatrix} 0 & c & b & a \\ 0 & b & a & c \\ 0 & a & c & b \\ 1 & 0 & 0 & 0 \end{bmatrix},$$

$$C_1 = \begin{bmatrix} 0 & B & C & A \\ 0 & C & A & B \\ 0 & A & B & C \\ 1 & 0 & 0 & 0 \end{bmatrix} \quad D_1 = \begin{bmatrix} 0 & b & c & a \\ 0 & c & a & b \\ 0 & a & b & c \\ 1 & 0 & 0 & 0 \end{bmatrix} \tag{96}$$

The states of (95) are numbered 1 through 32, and are classified in Table VIII.

Table VIII. Classification of states of the "collapsed" matrix of transition probabilities for a syndiotactic chain.

State	$U_j\ U_{j+1}$		State	$U_j\ U_{j+1}$	
1	R_dM_d	3 1	17	M_lR_d	3 1
2	R_dM_l	-1 1	18	M_lR_d	-1 1
3	R_dM_d	-1 1	19	M_lR_d	-1 1
4	R_dM_d	-1-3	20	M_lR_d	-1-3
5	M_dR_l	-3-1	21	R_dM_d	-3-1
6	M_dR_l	1-1	22	R_dM_d	1-1
7	M_dR_l	1-1	23	R_dM_d	1-1
8	M_dR_l	1 3	24	R_dM_d	1 3
9	R_lM_l	3 1	25	M_dR_l	3 1
10	R_lM_l	-1 1	26	M_dR_l	-1 1
11	R_lM_l	-1 1	27	M_dR_l	-1 1
12	R_lM_l	-1-3	28	M_dR_l	-1-3
13	M_lR_d	-3-1	29	R_lM_l	-3-1
14	M_lR_d	1-1	30	R_lM_l	1-1
15	M_lR_d	1-1	31	R_lM_l	1-1
16	M_lR_d	1 3	32	R_lM_l	1 3

Again, the limiting value matrix K must be subtracted from each of the four by four matrices in order to avoid obtaining inverses of an indeterminate form. The solution then follows in a manner analogous to that given for isotactic macromolecules.

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APPENDIX A

EVALUATION OF THE 1,1-ELEMENT OF $(1+S)^{-1}$

. Determinant of (1+S)

One has that

$$\det(1+S) = \begin{vmatrix} 1 & b & b & a \\ 0 & 1+b & a & b \\ 0 & a & 1+b & b \\ 1 & 0 & 0 & 1 \end{vmatrix} \qquad \text{(i)}$$

Adding rows two, three and four to row one,

$$\det(1+S) = \begin{vmatrix} 2 & 2 & 2 & 2 \\ 0 & 1+b & a & b \\ 0 & a & 1+b & b \\ 1 & 0 & 0 & 1 \end{vmatrix} \qquad \text{(ii)}$$

Adding column two and three to column four,

$$\det(1+S) = \begin{vmatrix} 2 & 2 & 2 & 6 \\ 0 & 1+b & a & 2 \\ 0 & a & 1+b & 2 \\ 1 & 0 & 0 & 1 \end{vmatrix} \qquad \text{(iii)}$$

Multiplying the fourth row by 2 and subtracting from row one, and expanding by the method of pivotal elements yields

$$\det(1+S) = \begin{vmatrix} 0 & 2 & 2 & 4 \\ 0 & 1+b & a & 2 \\ 0 & a & 1+b & 2 \\ 1 & 0 & 0 & 1 \end{vmatrix} = -4 \begin{vmatrix} 1 & 1 & 1 \\ 1+b & a & 1 \\ a & 1+b & 1 \end{vmatrix} \qquad \text{(iv)}$$

$$\det(1+S) = 3(1-a)^2 \qquad \text{(v)}$$

Adjoint of $(1+S)_{1,1}$

One has that

$$\operatorname{adj}\,(1+S) = \operatorname{adj}\begin{bmatrix} 1 & b & b & a \\ 0 & 1+b & a & b \\ 0 & a & 1+b & b \\ 1 & 0 & 0 & 1 \end{bmatrix} \qquad \text{(vi)}$$

The 1,1-element of the above adjoint matrix is

$$\operatorname{adj}\,(1+S)_{1,1} = (-1)^2 \begin{vmatrix} 1+b & a & b \\ a & 1+b & b \\ 0 & 0 & 1 \end{vmatrix} = (1+b)^2-a^2 \qquad \text{(vii)}$$

$$= (3/4)(3+a)(1-a) \qquad \text{(viii)}$$

Combining (v) and (viii), one obtains

$$(1+S)^{-1}_{1,1} = \frac{\operatorname{adj}\,(1+S)_{1,1}}{\det\,(1+S)} \qquad \text{(ix)}$$

$$= 1/4\,\frac{(3+a)}{(1-a)} \quad \text{and} \qquad \text{(x)}$$

$$8n\,(1+S)^{-1}_{11} = \frac{2n\,(3+a)}{(1-a)} \qquad \text{(xi)}$$

APPENDIX B

EVALUATION OF THE 1,1-ELEMENT OF $[(1+S)^2]^{-1}S$

Let $[(1+S)^2]^{-1}S = V = TS$, where

$$T = [(1+S)^2]^{-1}. \qquad \text{(i)}$$

Since the 1,1-element is desired, then by matrix multiplication:

$$\begin{aligned} v_{11} &= t_{11}\, s_{11} + t_{12}\, s_{21} + t_{13}\, s_{31} + t_{14}\, s_{41} \\ &= 0 + 0 + 0 + t_{14} \end{aligned} \qquad \text{(ii)}$$

Thus one needs to obtain only the (1,4)-element of $[(1+S)^2]^{-1}$.

Now, $\det(1+S)^2 = \det(1+S)\det(1+S) = [\det(1+S)]^2$. But $\det(1+S)$ has already been evaluated, hence

$$\det(1+S)^2 = [3(1-a)^2]^2. \qquad \text{(iii)}$$

Also,

$$\operatorname{adj}(1+S) = \begin{bmatrix} (1+b)^2-a^2 & ab-b(1+b) & ab-b(1+b) & 2+5a^2-7a-5b^2 \\ b(1+b)-ab & (1+b)+b^2-a(1+b) & a^2-a-b^2 & ab-b(1+6) \\ b(1+b)-ab & -a-b^2+a^2 & (1+b)+b^2-a(1+b) & ab-b(1+6) \\ -(1+b)^2+a^2 & b(1+b)-ab & -ab+b(1+b) & (1+b)^2-a^2 \end{bmatrix}$$

The 1,4-element of $[\operatorname{adj}(1+S)]^2$ is

$$t_{14} = [(1+b)^2-a^2]^2 + [ab-b(1+b)]^2 + [ab-b(1+b)]^2 + [(1+b)^2-a^2][1+5a^2-7a-5b^2]$$

$$= [(1+b)^2-a^2][(1+b)^2-a^2+2+5a^2-7a-5b^2] + 2[ab-b(1+b)]^2 \qquad \text{(iv)}$$

$$= 2(3/4)^2[(1-a)^4-(3+a)(5a-1)]. \qquad \text{(v)}$$

From (iii) and (v) one obtains

$$8[(1+S)^2]^{-1}S = \frac{\mathrm{adj}(1+S)^2}{\det(1+S)^2} = 1 - \frac{(3+a)(5a-1)}{(1-a)^2}. \qquad \text{(vi)}$$

APPENDIX C

EVALUATION OF THE 1,1-ELEMENT OF S^{n+1} $[(1+S)^2]^{-1}$

Since S^{n+1} is not easily obtained for arbitrary n, the approximation

$$\lim_{n\to\infty} S^{n+1} = S^{(\infty)} = K \qquad \text{(i)}$$

is made, where K is a four by four matrix all of whose elements are equal to 1/4.

The isotactic chain has periodicity two. Markovian processes of periodicity two have as their limiting value (see reference 27, page 361)

$$\lim_{n\to\infty} p_{jk}^{(n2)} = \begin{cases} 1/4 & \text{if in S} \\ 0 & \text{otherwise.} \end{cases} \qquad \text{(ii)}$$

Thus one immediately obtains

$$P^{(\infty)} = \begin{bmatrix} 0 & 1/4 \\ 1/4 & 0 \end{bmatrix} = \begin{bmatrix} 0 & K \\ K & 0 \end{bmatrix} \quad \text{for n odd, and} \qquad \text{(iii)}$$

$$= \begin{bmatrix} 1/4 & 0 \\ 0 & 1/4 \end{bmatrix} = \begin{bmatrix} K & 0 \\ 0 & K \end{bmatrix} \quad \text{for n even.} \qquad \text{(iv)}$$

Therefore

$$\lim_{n\to\infty} S^{n+1} = K \quad \text{for all n,} \qquad \text{(v)}$$

The 1,1-element of $S^{(\infty)}$ $[(1+S)^2]^{-1} = [1/4][(1+S)^2]^{-1}$, is then 1/4 times the sum of the first column of $[(1+S)^2]^{-1}$.

Since

$$[1/4][(1+S)^2]^{-1} = [1/4]\frac{\operatorname{adj}\,(1+S)^2}{\det\,(1+S)^2}\,, \qquad \text{(vi)}$$

the problem reduces to securing the first column of adj $(1+S)^2$.

If the elements of adj $(1+S)$ are denoted by j_{ij}, then the sum of the first column of adj $(1+S)^2$ is

$$\begin{aligned} \text{adj } (1+S)^2 = \quad & j_{11} + j_{12}\, j_{21} + j_{13}\, j_{31} + j_{14}\, j_{41} + \\ & j_{21}\, j_{11} + j_{22}\, j_{21} + j_{23}\, j_{31} + j_{24}\, j_{41} + \\ & j_{31}\, j_{11} + j_{32}\, j_{21} + j_{33}\, j_{31} + j_{34}\, j_{41} + \\ & j_{41}\, j_{11} + j_{42}\, j_{21} + j_{43}\, j_{31} + j_{44}\, j_{41} \end{aligned} \qquad \text{(vii)}$$

$$\begin{aligned} = \; & j_{11}\,(j_{11} + j_{21} + j_{31} + j_{41}) + \\ & j_{21}\,(j_{12} + j_{22} + j_{32} + j_{42}) + \\ & j_{31}\,(j_{13} + j_{23} + j_{33} + j_{43}) + \\ & j_{41}\,(j_{14} + j_{24} + j_{34} + j_{44}) \end{aligned} \qquad \text{(viii)}$$

$$= j_{11}\, j_1 + j_{21}\, j_2 + j_{31}\, j_3 + j_{41}\, j_4 \qquad \text{(ix)}$$

When the indicated summations are performed, one obtains

$$j_1 = j_2 = j_3 = j_4 = 6b^2 \qquad \text{(x)}$$

Therefore (ix) becomes

$$\text{adj } (1+S)^2_1 = 6b^2\,(j_{11} + j_{21} + j_{31} + j_{41}) \qquad \text{(xi)}$$

and when this sum is evaluated, one obtains

$$\text{adj } (1+S)^2_1 = 6b^2 \cdot 6b^2 = 6^2 b^4 = 9/4\,(1-a)^4 \qquad \text{(xii)}$$

The det$(1+S)$ has already been calculated (A-v), and therefore

$$\det\,(1+S)^2 = [3(1-a)^2]^2 = 9(1-a)^4 \qquad \text{(xiii)}$$

Substitution of (xii) and (xiii) gives then

$$S^{(00)}[(1+S)^2]^{-1} = 1/16\,, \qquad \text{(xiv)}$$

and finally

$$8\ S^{n+1}\ [(1+S)^2]^{-1} \cong 1/2 \qquad \text{(xv)}$$

APPENDIX D

EVALUATION OF THE 1,1-ELEMENT OF $(1-S'T')^{-1}(S'T'-S')$

Needed are:

(a) First row of $(1-S'T')^{-1}$

(b) First column of $(S'T'-S')$

Now

$$S'T' = \begin{bmatrix} -1/4 & C' & B' & A' \\ -1/4 & B' & A' & C' \\ -1/4 & A' & C' & B' \\ 3/4 & -1/4 & -1/4 & -1/4 \end{bmatrix} X \begin{bmatrix} -1/4 & c' & b' & a' \\ -1/4 & b' & a' & c' \\ -1/4 & a' & c' & b' \\ 3/4 & -1/4 & -1/4 & -1/4 \end{bmatrix} \qquad \text{(i)}$$

where $A' = A - 1/4$, etc. Matrix multiplication yields:

$$S'T' = \begin{bmatrix} A - 1/4 & Cb + Ba - 1/4 & Ca + Bc - 1/4 & Cc + Bb - 1/4 \\ C - 1/4 & Bb + Aa - 1/4 & Ba + Ac - 1/4 & Bc + Ab - 1/4 \\ B - 1/4 & Ab + Ca - 1/4 & Aa + Cc - 1/4 & Ac + Cb - 1/4 \\ -1/4 & c - 1/4 & b - 1/4 & a - 1/4 \end{bmatrix} \qquad \text{(ii)}$$

The first column of $S'T'-S'$ is therefore:

$$\begin{aligned} A - 1/4 + 1/4 &= A \\ C - 1/4 + 1/4 &= C \\ B - 1/4 + 1/4 &= B \\ -1/4 - 3/4 &= -1 \end{aligned} \qquad \text{(iii)}$$

Further,

$$(1-S'T') = \begin{bmatrix} 1-(A-1/4) & -(Cb + Ba - 1/4) & -(Ca + Bc - 1/4) & -(Cc + Bb - 1/4) \\ -(C-1/4) & 1-(Bb + Aa - 1/4) & -(Ba + Ac - 1/4) & -(Bc + Ab - 1/4) \\ -(B-1/4) & -(Ab + Ca - 1/4) & 1-(Aa + Cc - 1/4) & -(Ac + Cb - 1/4) \\ +1/4 & -(c - 1/4) & -(b - 1/4) & 1-(a - 1/4) \end{bmatrix} \qquad \text{(iv)}$$

To obtain the determinant of $(1-S'T')$, in order, one may:

1. Add columns one, two and three to column four.
2. Add rows two, three, and four to row one.
3. Subtract row one from row four.

In this manner one obtains

$$\det(1-S'T') = 1/16 \begin{vmatrix} -4 & -1 & -1 & -4 \\ 4C-1 & (Bb + Aa - 1)-1/4 & Ba + Ac - 1/4 & +1 \\ 4B-1 & Ab + Ca - 1/4 & (Aa + Cc - 1)-1/4 & -1 \\ -4 & 4c - 1 & 4b - 1 & -4 \end{vmatrix} \qquad \text{(v)}$$

4. Subtract column four from column one, and multiply row four by 1/4 and column one by 1/4 and obtain

$$\det(1-S'T') = \begin{vmatrix} 0 & -1 & -1 & -4 \\ C & (Bb + Aa - 1)-1/4 & Ba + Ac - 1/4 & -1 \\ B & Ab + Ca - 1/4 & (Aa + Cc - 1)-1/4 & -1 \\ 0 & c & b & 0 \end{vmatrix} \qquad \text{(vi)}$$

5. Expand (vi) by minors of the first row
6. Let $1 = (A + B + C)(a + b + c)$ in the expression obtained from (vi)
7. Rearrange and obtain

$$\det(1-S'T') = 2[(1-\sigma^2)(B^2 + BC + C^2) + (1-\Sigma^2)(b^2 + bc + c^2)] \qquad \text{(vii)}$$

where:

$$\sigma^2 = a^2 + b^2 + c^2$$

$$\Sigma^2 = A^2 + B^2 + C^2$$

The adjoint numerators standing in the first row of Adj (1-S'T') are:

$$[1,1] = (-1)\begin{vmatrix} (Bb + Aa - 1) - 1/4 & Ba + Ac - 1/4 & Bc + Ab - 1/4 \\ Ab + Ba - 1/4 & (Aa + Cc - 1) - 1/4 & Ac + Cb - 1/4 \\ c - 1/4 & b - 1/4 & (a-1) - 1/4 \end{vmatrix} \tag{viii}$$

$$[1,2] = (+1)\begin{vmatrix} Cb + Ba - 1/4 & Ca + Bc - 1/4 & Cc + Bb - 1/4 \\ Ab + Ca - 1/4 & (Aa + Ca - 1) - 1/4 & Ac + Cb - 1/4 \\ c - 1/4 & b = 1/4 & (a-1) - 1/4 \end{vmatrix} \tag{ix}$$

$$[1,3] = (-1)\begin{vmatrix} Cb + Ba - 1/4 & Ca + Bc - 1/4 & Cc + Bb - 1/4 \\ (Bb + Aa - 1) - 1/4 & Ba + Ac - 1/4 & Bc + Ab - 1/4 \\ c - 1/4 & b - 1/4 & (a-1) - 1/4 \end{vmatrix} \tag{x}$$

$$[1,4] = (+1)\begin{vmatrix} Cb + Ba - 1/4 & Ca + Bc - 1/4 & Cc + Bb - 1/4 \\ (Bb + Aa - 1) - 1/4 & Ba + Ac - 1/4 & Bc + Ab - 1/4 \\ Ab + Ca - 1/4 & (Aa + Cc - 1) - 1/4 & Ac + Cb - 1/4 \end{vmatrix} \tag{xi}$$

Adding columns one and two to columns three in each of the above, one obtains:

$$[1,1] = (-1)\begin{vmatrix} (Bb + Aa - 1) - 1/4 & Ba + Ac - 1/4 & -C - 3/4 \\ Ab + Ba - 1/4 & (Aa + Cc - 1) - 1/4 & -B - 3/4 \\ c - 1/4 & b - 1/4 & -3/4 \end{vmatrix} \tag{xii}$$

$$[1,2] = (+1)\begin{vmatrix} Cb + Ba - 1/4 & Ca + Bc - 1/4 & 1 - A - 3/4 \\ Ab + Ca - 1/4 & (Aa + Cc - 1) - 1/4 & -B - 3/4 \\ c - 1/4 & b - 1/4 & -3/4 \end{vmatrix} \tag{xiii}$$

$$[1,3] = (-1)\begin{vmatrix} Cb + Ba - 1/4 & Ca + Bc - 1/4 & 1 - A - 3/4 \\ (Bb + Aa - 1) - 1/4 & Ba + Ac - 1/4 & - C - 3/4 \\ c - 1/4 & b - 1/4 & -3/4 \end{vmatrix} \tag{xiv}$$

$$[1,4] = (+1)\begin{vmatrix} Cb + Ba - 1/4 & Ca + Bc - 1/4 & 1 - A - 3/4 \\ (Bb + Aa - 1) - 1/4 & Ba + Ac - 1/4 & - C - 3/4 \\ Ab + Ca - 1/4 & (Aa + Cc - 1) - 1/4 & - B - 3/4 \end{vmatrix} \tag{xv}$$

Now, multiplication of the first row of adj (1-S'T') into the first column of (S'T'-S') gives:

$$A[1,1] + C[1,2] + B[1,3] - [1,4] = (A[1,1] - [1,4]) + (C[1,2] + B[1,3]).$$

In detail:

$$A[1,1] = (-1)\begin{vmatrix} (Bb + Aa - 1) - 1/4 & Ba + Ac - 1/4 & -C - 3/4 \\ Ab + Ca - 1/4 & (Aa + Cc - 1) - 1/4 & -B - 3/4 \\ Ac - (1/4)A & Ab - (1/4)A & -(3/4)A \end{vmatrix} \tag{xvi}$$

$$-[1,4] = (-1)\begin{vmatrix} Cb + Ba - 1/4 & Ca + Bc - 1/4 & 1 - A - 3/4 \\ (Bb + Aa - 1) - 1/4 & Ba + Ac - 1/4 & - C - 3/4 \\ Ab + Ca - 1/4 & (Aa + Cc - 1) - 1/4 & - B - 3/4 \end{vmatrix} \tag{xvii}$$

$$C[1,2] = (+1) \begin{vmatrix} Cb + Ba - 1/4 & Ca + Bc - 1/4 & 1 - A - 3/4 \\ C(Ab + Ca - 1/4) & [(Aa + Cc - 1) - 1/4]C & C(-B - 3/4) \\ c - 1/4 & b - 1/4 & -3/4 \end{vmatrix} \quad \text{(xviii)}$$

$$B[1,3] = (-1) \begin{vmatrix} Cb + Ba - 1/4 & Ca + Bc - 1/4 & 1 - A - 3/4 \\ B[(Bb + Aa - 1) - 1/4] & B(Ba + Ac - 1/4) & B(-C - 3/4) \\ c - 1/4 & b - 1/4 & -3/4 \end{vmatrix} \quad \text{(xix)}$$

Combining (xvi) + (xvii) and (xviii) + (xix) one obtains

$$(-1) \begin{vmatrix} (Bb + Aa - 1) - 1/4 & Ba + Ac - 1/4 & -C - 3/4 \\ Ab + Ca - 1/4 & (Aa + Cc - 1) - 1/4 & -B - 3/4 \\ Ac + Cb + Ba - (1/4)A - 1/4 & Ab + Ca + Bc - (1/4)A - 1/4 & 1 - (7/4)A - 3/4 \end{vmatrix} + \quad \text{(xx)}$$

$$(+1) \begin{vmatrix} Cb + Ba - 1/4 & Ca + Bc - 1/4 & 1 - A - 3/4 \\ C(Ab+Ca) - B(Bb+Aa) + B + (1/4)(B - C) & C(Aa+Cc) - B(Ba+Ac) - C - (1/4)(B-C) & (3/4)(B-C) \\ c - 1/4 & b - 1/4 & -3/4 \end{vmatrix} \quad \text{(xxi)}$$

Expression (xx) will be evaluated first. The procedure is as follows:

1. Multiply column three by (-1).
2. Add rows one and two to row three.
3. Multiply column one and column two by 3.
4. Add column three to column one, and add column three to column two. This gives:

$$(xx) = 1/9 \begin{vmatrix} 3(Bb + Aa - 1) + C & 3(Ba + Ac) + C & C + 3/4 \\ 3(Ab + Ca) + B & 3(Aa + CC - 1) + B & B + 3/4 \\ -3c\,(B + C) & -3b(B + C) & (3/4)A + 9/4 \end{vmatrix} \tag{xxii}$$

$$= 1/12 \begin{vmatrix} 3(Bb + Aa - 1) + C & 3(Ba + Ac) + C & 4C + 3 \\ 3(Ab + Ca) + B & 3(Aa + Cc - 1) + B & 4B + 3 \\ -c\,(B + C) & -b\,(B + C) & A + 3 \end{vmatrix} \tag{xxiii}$$

Equation (xxiii) man be split into:

$$1/12 \begin{vmatrix} 3(Bb + Aa - 1) + C & 3(Ba + Ac) + C & 4C \\ 3(Ab + Ca) + B & 3(Aa + Cc - 1) + B & 4B \\ -c(B + C) & -b(B + C) & A \end{vmatrix} + \tag{xxiv}$$

$$+ 1/12 \begin{vmatrix} 3(Bb + Aa - 1) + C & 3(Ba + Ac) + C & 3 \\ 3(Ab + Ca) + B & 3(Aa + Cc - 1) + B & 3 \\ -c(B + C) & -b(B + C) & 3 \end{vmatrix} \tag{xxv}$$

$$= 1/12 \begin{vmatrix} 3(Bb + Aa - 1) + C & 3(Ba + Ac) + C & C \\ 3(Ab + Ca) + B & 3(Aa + Cc - 1) + B & B \\ -4(B + B)c & -4(B + C)b & A \end{vmatrix} \tag{xxvi}$$

$$+ 1/12 \begin{vmatrix} 3(Bb + Aa - 1) + C + c(B + C) & 3(Ba + Ac) + C + b(B + C) & 0 \\ 3(Ab + Ca) + B + c(B + C) & 3(Aa + Cc - 1) + B + b(B + C) & 0 \\ -c(B + C) & -b(B + C) & 3 \end{vmatrix} \tag{xxvii}$$

Equation (xxvi) is obtained by factoring out a 4 from column three of (xxiv) and multiplying row three by 4. Equation (xxvii) is obtained from (xxv) by subtracting row three from row one and from row two. The two determinants (xxvi) and (xxvii) are now evaluated in a straightforward manner. As a consequence of the modifications performed on them it is found that a number of terms will cancel when (xxi) is treated in a similar manner. The evaluation of (xxi) proceeds as follows:

1. Multiply column one and column two by 3.
2. Subtract column three from columns one and two, and substitute $(1-A) = (B + C)$ to obtain:

$$(xxi) = 1/9 \begin{vmatrix} 3(Cb + Ba) - (B + C) & 3(Ca + Bc) - (B + C) & (B + C) - 3/4 \\ 3C(Ab+Ca) - 3B(Bb+Aa) + 3B & 3C(Aa+Cc) - 3B(Ba+Ac) - 3C & (3/4)(B-C) \\ 3c & 3b & -3/4 \end{vmatrix} \tag{xxix}$$

Factor out a 3 from the third row, 1/4 from the third column:

$$1/12 \begin{vmatrix} 3(Cb+Ba)-(B+C) & 3(Ca+Bc)-(B+C) & 4(B+C)-3 \\ 3C(Ab+Ca)-3B(Bb+Aa)+3B & 3C(Aa+Cc)-3B(Ba+Ac)-3C & 3(B-C) \\ c & b & -1 \end{vmatrix} \tag{xxx}$$

Split (xxx) into two determinants as follows:

$$(1/12)C \begin{vmatrix} 3(Cb + Ba) - (B + C) & 3(Ca + Bc) - (B + C) & 4(B + C) - 3 \\ 3\ (Ab + Ca) & 3\ (Aa + Cc - 1) & -3 \\ c & b & -1 \end{vmatrix} \tag{xxxi}$$

$$+(1/12)B \left| \begin{matrix} 3(Cb + Ba) -(B + C) & 3(Ca + Bc) - (B + C) & 4(B + C) -3 \\ -3(Bb + Aa -1) & -3(Ba + Ac) & 3 \\ c & b & -1 \end{matrix} \right| \tag{xxxii}$$

From row two of (xxxi) subtract 3 times row three, and to row two of (xxxii) add 3 times row three to obtain

$$(1/12)C \left| \begin{matrix} 3(Cb + Ba) - (B + C) & 3(Ca + Bc) - (B + C) & 4(B + C) -3 \\ 3(Ab + Ca) -3c & 3(aa + Cc -1) -3b & 0 \\ c & b & -1 \end{matrix} \right| \tag{xxxiii}$$

$$+(1/12)B \left| \begin{matrix} 3(Cb + Ba) - (B + C) & 3(Ca + Bc) - (B + C) & 4(B + C) -3 \\ 3(Bb + Aa -1)) + 3c & -3(Ba + Ac) + 3b & 0 \\ c & b & -1 \end{matrix} \right| \tag{xxxiv}$$

Determinants (xxxiii) and (xxxiv) are now evaluated in a straightforward manner. When determinants (xxvi),(xxvii), (xxxiii) and (xxxiv) are evaluated and combined, one obtains for their sum

$$1/4 \begin{aligned} &3(a^2 - bc)(A^2 + B^2 + C^2 - AB - AC - BC) \\ &+3\ C\ (Cb + Ba) + 3\ B\ (Ca + Bc) - 3\ A\ (Cc + Bb + 2Aa) + 3\ A \\ &+ 9\ [(A^2 - Bc)(a^2 - bc) - (Cc + Bb + 2Aa) + 1] \\ &+ 9\ [B^2(b^2 - ac) - AB\ (c^2 -ab) -Bb] \\ &+ 9\ [C^2(c^2 -ab) - AC(b^2 -ac) - Cc] \\ &+ 4\ [-AC(b -a) + C^2(c - a) + B^2(b - a) - AB(C - a) - (B + C)] \end{aligned} \tag{xxxv}$$

In order to obtain (xxxv) it is necessary to use the relationship.

$$A^3 + B^3 + C^3 - 3ABC = A^2 + B^2 + C^2 - AB - AC - BC \qquad \text{(xxxvi)}$$

By the use of (xxxvi) it is possible to obtain an expression whose highest power terms are of the fourth power in the parameters. Further simplifications are possible by writing <u>all</u> terms of this expression as fourth power terms. This can be done by multiplying third power terms by $a + b + c = A + B + C = 1$, second power terms by $(a + b + c)^2 = (A + B + C)(a + b + c) = 1$, or $(A + B + C)^2 = 1$, etc. The advantage of this form is that the expression is then algebraically unique, whereas if lower power terms occur, there are many different possible ways to write the same expression.

When all terms are raised to the fourth power as explained above, one obtains for the sum of (xxvi), (xxvii), (xxxiii), and (xxxiv):

$$3\,A^2(b^2 + c^2 + bc) + c^2(a^2 + 2b^2 - 2ac - bc) + B^2(a^2 + 2c^2 - 2ab - bc)$$
$$+ AC(-c^2 + b^2 + 2ab + 4ac + 3bc) + AB(c^2 - b^2 + 4ac + 2ab + 4bc)$$
$$+ BC(a^2 - 2b^2 - 2c^2 + 2ab + 2ac - bc).$$