ble bonds would be valuable. Finally, one wonders whether the transformation from the diamagnetic state to the paramagnetic defect state may not play a role in the polymerization of all linear PPA and might not, in fact, be responsible for the rather low molecular weight of all polymers of acetylene derivatives.[4] Research to resolve these problems is in progress.

Acknowledgement. We are grateful to the National Science Foundation for support of this research through Grants HO-34415 and DMR 720397A01. One of the authors (E.C.M.) wishes to thank Carborundum Company for support through a C.C. Furnas Graduate Fellowship. We also wish to thank Professor J. D. Kosman, Department of Biochemistry, for loan of the Varian E-9 Spectrometer.

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The Configuration Partition Function, a priori Probabilities, and Conditional Probabilities for Branched Macromolecules Subject to the Rotational Isomeric State Approximation[1]

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Received May 28, 1975

ABSTRACT: Procedures are presented for computing the configuration partition function for branched macromolecules which are subject to the rotational isomeric state approximation. The assumptions required are (1) the short-range interactions can be adequately represented by three- and four-bond interactions, (2) bond lengths and bond angles are constant, and (3) there are a minimum of two bonds between each branching point. A molecule with any number of branches can be treated. Procedures are also presented for the computation of a priori and conditional bond probabilities. Illustrative calculations are carried out for a low-density polyethylene containing n-butyl groups.

Many configurational properties of linear chain macromolecules have been successfully treated by application of the rotational isomeric state approximation.[2,3] Branched chain molecules have not previously been treated with similar precision, although this class of polymer molecules is of considerable interest. Naturally occurring examples of such macromolecules include proteins in which disulfide bonds serve to cross-link different polypeptide chains. Many polysaccharides also exist as branched chain molecules. The objective here is to extend the methods developed[3] for linear chain molecules subject to the rotational isomeric state approximation so that they can also be applied to branched chain molecules. The terms treated are the configuration partition function, a priori probabilities, and conditional probabilities. The symbolism and procedures used by Flory[3] will be adopted, and extensions and modifications will be introduced where necessary.

Definition of the Polymer Chain

A macromolecule consisting of a main chain plus one branch is shown diagrammatically in Figure 1. Side chains are not included in this figure and will not be treated here. The macromolecule in Figure 1 can also be viewed as consisting of three branches which emanate from the atom at which branching occurs, and this viewpoint will be adopted henceforth. The branch selected as "branch 1" will be chosen arbitrarily. Branches 2 and 3 will then be assigned by requiring that $n_2 \geq n_3$, where n_j is the number of bonds in branch j. All n_j will be assumed to be greater than unity. The bonds in branch 1 are numbered sequentially, starting with the bond which is most remote from the branching point. Bonds in branches 2 and 3 will also be numbered sequentially, but in these cases numbering will commence at the branching point and proceed to the remote termini of these branches. The symbol ${}_j\mathbf{l}_i$ represents the vector for bond i in branch j and ${}_j\phi_i$ represents the rotation about bond i in branch j. Bond angles and bond lengths will be considered to be constant. The atom designated ${}_jA_i$ is located at the terminus of bond vector ${}_j\mathbf{l}_i$. The first atom in branch 1 is ${}_1A_0$.

Statistical Weight Matrices

A particular chain conformation is specified by assigning values to all ${}_j\phi_i$ except ${}_1\phi_1$, ${}_2\phi_{n_2}$ and ${}_3\phi_{n_3}$. The reference state will have a trans conformation for all of the bonds about which rotation must be specified. Special attention must be given to the meaning to be attached to "trans" for bonds involving ${}_1A_{n_1}$. Those atoms specifying the conformation at the last bond in branch 1 will be ${}_1A_{n_1-2}$, ${}_1A_{n_1-1}$, ${}_1A_{n_1}$, and ${}_2A_1$. The state at the first bonds in branches j (j = 2 or 3) will be specified by atoms ${}_1A_{n-1}$, ${}_1A_{n_1}$ ${}_jA_1$, and ${}_jA_2$. Bond n_1 in branch 1 and the first bonds in branches 2 and 3 are in the trans conformation as shown in Figure 1.

The statistical weight matrix for bond i in branch j is

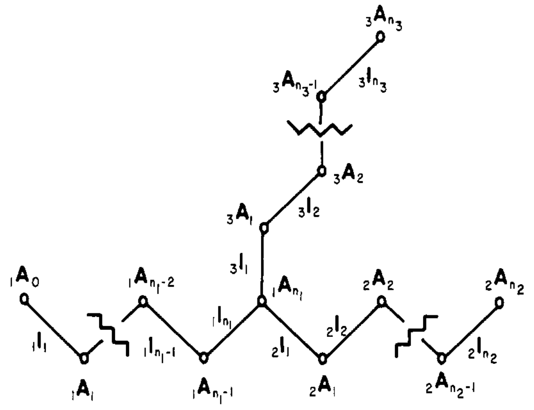

Figure 1. Diagrammatic representation of a macromolecule containing one branching point.

${}_j\mathbf{U}_i$. The elements in the statistical weight matrices (${}_1\mathbf{U}_2$ and ${}_3\mathbf{U}_1$ excepted, see below) are ${}_ju_{\xi\eta;i} = \exp(-{}_jE_{\xi\eta;i}/RT)$.[4] The energies are specified by sequentially rotating the bonds from their reference state to the desired state, η, starting with bond 2 in branch 1. The change in energy for this process at bond 2 in branch 1 is ${}_1E_{\eta;2}$ (the state, ξ, of the preceding bond cannot be specified in this case). Consequently ${}_1u_{1\eta;2} = \exp(-{}_1E_{\eta;2}/RT)$. The elements in the remaining rows of ${}_1\mathbf{U}_2$ are undefined and are not used. For succeeding bonds in branch 1 the change in energy will be ${}_1E_{\xi\eta;i}$, where bond $i - 1$ of branch 1 is in state ξ, while bond i is rotated from the reference state to state η. Since ${}_1\phi_{n_1}$ will specify the position of ${}_2A_1$ and ${}_3A_1$, the energy ${}_1E_{\xi\eta;n_1}$ must include the interactions of ${}_2A_1$ and ${}_3A_1$ with ${}_1A_{n_1-3}$ and ${}_1A_{n_1-2}$. The appropriate energy for ${}_ju_{\xi\eta;i}$ is similarly ${}_jE_{\xi\eta;i}$, where now $j = 2$ or 3 and $1 < i < n_j$. The energy ${}_jE_{\xi\eta;2}$ must account for interactions due to the sequential rotations ${}_j\phi_1$ and ${}_j\phi_2$ ($j = 2$ or 3). Consequently it must reflect the interaction of ${}_jA_3$ with ${}_1A_{n_1-1}$, ${}_1A_{n_1}$ and ${}_kA_1$ ($k = 2$ if $j = 3$, and $k = 3$ if $j = 2$).

Special attention must be given to the elements of ${}_2\mathbf{U}_1$ and ${}_3\mathbf{U}_1$. They must be formulated to properly represent the interactions arising from the sequential rotations ${}_1\phi_{n_1}$ and ${}_2\phi_1$, the sequential rotations ${}_1\phi_{n_1}$ and ${}_3\phi_1$, and the sequential rotations ${}_2\phi_1$ and ${}_3\phi_1$. In assembling ${}_2\mathbf{U}_1$, the "preceding" bond will be considered to be the last bond in branch 1. Thus ${}_2u_{\xi\eta;1} = \exp(-{}_2E_{\xi\eta;1}/RT)$, where the energy is that arising from rotation about bond 1 in branch 2 from the reference state to state η, given that the final bond in branch 1 is in state ξ and that the first bond in branch 3 is still in the reference conformation. This energy will include the interaction of ${}_2A_2$ with ${}_3A_1$ because the position of the latter has already been specified by ${}_1\phi_{n_1}$.

The elements in ${}_3\mathbf{U}_1$ must take account of all remaining interactions due to the sequential rotations ${}_1\phi_{n_1}$ and ${}_3\phi_1$, as well as ${}_2\phi_1$ and ${}_3\phi_1$. If the state at bond n_1 in branch 1 is ξ, the state at bond 1 in branch 3 is η, and the state at bond 1 in branch 2 is ζ, the appropriate expression for an element in ${}_3\mathbf{U}_1$ is ${}_3u_{\xi\eta\zeta;1} = \exp((-{}_3E_{\xi\eta;1} - {}_3E_{\zeta\eta;1})/RT)$. The term ${}_3E_{\xi\eta;1}$ represents the interactions of ${}_3A_2$ with ${}_1A_{n_1-2}$ and ${}_1A_{n_1-1}$, arising as a consequence of taking bond 1 in branch 3 to state η, given that bond n_1 in branch 1 is already in state ξ. Similarly, the term ${}_3E_{\zeta\eta;1}$ represents the interaction of ${}_3A_2$ with atoms ${}_2A_1$ and ${}_2A_2$ arising as a consequence of taking bond 1 in branch 3 to state η, given that bond 1 in branch 2 is in state ζ. It is clear from the definition of ${}_3u_{\xi\eta\zeta;1}$ that ${}_3\mathbf{U}_1$ will be an array consisting of ${}_1\nu_{n_1}$ rows, ${}_3\nu_1$ columns, and ${}_2\nu_1$ layers, where ${}_j\nu_i$ is the number of rotational states accessible to bond i in branch j. Rules will be formulated in order to ensure that the elements of ${}_3\mathbf{U}_1$ are called upon in the appropriate manner.

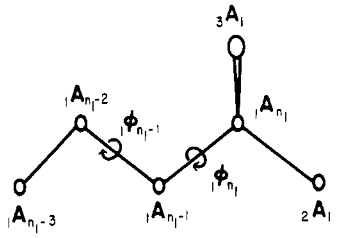

Figure 2. Interactions for ${}_1\mathbf{U}_{n_1}$.

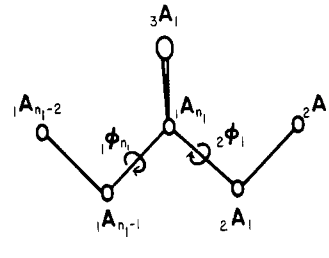

Figure 3. Interactions for ${}_2\mathbf{U}_1$.

Illustrative Example

The formulation of the statistical weight matrices described in the preceding section will be illustrated for the case where there exists a symmetric threefold rotational potential function, with states t, g^+, and g^-. The appropriate statistical weight matrix for those bonds sufficiently remote from the branching point is:[5]

$$\begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma\psi & \sigma\omega \\ 1 & \sigma\omega & \sigma\psi \end{bmatrix} \tag{1}$$

The statistical weight for a gauche three-bond interaction is σ, and ψ and ω are the statistical weights for the four-bond interactions arising from successive gauche placements of the same and opposite signs, respectively.

The atoms involved in the interactions represented by ${}_1\mathbf{U}_{n_1}$ are shown in Figure 2. It will be assumed that the branches have been numbered so that ${}_3A_1$ is above the plane of the paper. The three-bond interactions arising from ${}_1\phi_{n_1}$ are shown in (2) and the four-bond interactions arising from ${}_1\phi_{n_1-1}$ and ${}_1\phi_{n_1}$ are shown in (3), yielding the expression for ${}_1\mathbf{U}_{n_1}$ shown in (4).

$$\mathbf{D} = \mathrm{diag}\,(\sigma, \sigma, \sigma^2) \tag{2}$$

$$\mathbf{V} = \begin{bmatrix} 1 & 1 & 1 \\ \omega & \psi & \psi\omega \\ \psi & \omega & \psi\omega \end{bmatrix} \tag{3}$$

$${}_1\mathbf{U}_{n_1} = \mathbf{VD} = \sigma \begin{bmatrix} 1 & 1 & \sigma \\ \omega & \psi & \sigma\psi\omega \\ \psi & \omega & \sigma\psi\omega \end{bmatrix} \tag{4}$$

The atoms involved in the interactions incorporated in ${}_2\mathbf{U}_1$ are shown in Figure 3. The appropriate matrices are:

$$\mathbf{D} = \mathrm{diag}\,(\sigma, \sigma^2, \sigma) \tag{5}$$

$$\mathbf{V} = \begin{bmatrix} 1 & 1 & 1 \\ 1 & \psi & \omega \\ 1 & \omega & \psi \end{bmatrix} \tag{6}$$

$${}_2\mathbf{U}_1 = \sigma \begin{bmatrix} 1 & \sigma & 1 \\ 1 & \sigma\psi & \omega \\ 1 & \sigma\omega & \psi \end{bmatrix} \tag{7}$$

The array ${}_3\mathbf{U}_1$ must take account of three- and four-bond interactions generated by ${}_3\phi_1$, and the appropriate atoms

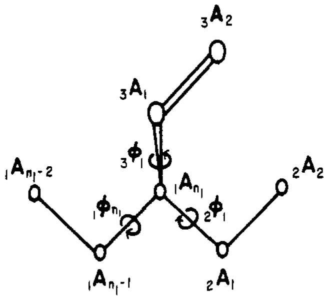

Figure 4. Interactions for $_3U_1$.

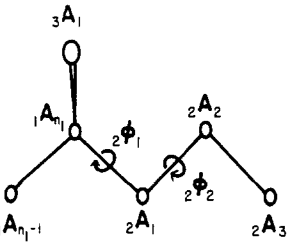

Figure 5. Interactions for $_2U_2$.

are shown in Figure 4. The three-bond interactions resulting from $_3\phi_1$ are:

$$\mathbf{D} = \mathrm{diag}\,(\sigma, \sigma, \sigma^2) \tag{8}$$

The four-bond interactions which must be accounted for occur between $_3A_2$ and $_1A_{n_1-2}$, and between $_3A_2$ and $_2A_2$. For this reason the four-bond interactions depend upon three angles: $_3\phi_1$, $_1\phi_{n_1}$, and $_2\phi_1$. The appropriate **V** matrices for the cases where $_2\phi_1$ corresponds to the t, g^+ and g^- states, respectively, are:

$$\mathbf{V} = \begin{bmatrix} \omega & \omega & \psi^2 \\ \omega & 1 & \psi \\ \omega & \psi & \psi\omega \end{bmatrix} \qquad {}_2\Phi_1 \text{ is } t \tag{9}$$

$$\mathbf{V} = \begin{bmatrix} \psi & \omega & \psi\omega \\ \psi & 1 & \omega \\ \psi & \psi & \omega^2 \end{bmatrix} \qquad {}_2\Phi_1 \text{ is } g^+ \tag{10}$$

$$\mathbf{V} = \begin{bmatrix} 1 & \omega & \psi \\ 1 & 1 & 1 \\ 1 & \psi & \omega \end{bmatrix} \qquad {}_2\Phi_1 \text{ is } g^- \tag{11}$$

Consequently the layers of $_3\mathbf{U}_1$ are:

$$_3\mathbf{U}_1 = \sigma \begin{bmatrix} \omega & \omega & \sigma\psi^2 \\ \omega & 1 & \sigma\psi \\ \omega & \psi & \sigma\psi\omega \end{bmatrix} \qquad \text{1st layer} \tag{12}$$

$$\sigma \begin{bmatrix} \psi & \omega & \sigma\psi\omega \\ \psi & 1 & \sigma\omega \\ \psi & \psi & \sigma\omega^2 \end{bmatrix} \qquad \text{2nd layer} \tag{13}$$

$$\sigma \begin{bmatrix} 1 & \omega & \sigma\psi \\ 1 & 1 & \sigma \\ 1 & \psi & \sigma\omega \end{bmatrix} \qquad \text{3rd layer} \tag{14}$$

The matrix $_2\mathbf{U}_2$ (see Figure 5) is formulated as follows:

$$\mathbf{D} = \mathrm{diag}\,(1, \sigma, \sigma) \tag{15}$$

$$\mathbf{V} = \begin{bmatrix} 1 & \psi & \omega \\ 1 & \psi\omega & \psi\omega \\ 1 & \omega & \psi \end{bmatrix} \tag{16}$$

$$_2\mathbf{U}_2 = \begin{bmatrix} 1 & \sigma\psi & \sigma\omega \\ 1 & \sigma\psi\omega & \sigma\psi\omega \\ 1 & \sigma\omega & \sigma\psi \end{bmatrix} \tag{17}$$

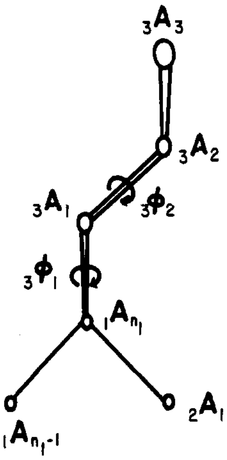

Figure 6. Interactions for $_3U_2$.

Similarly, $_3U_2$ (see Figure 6) is

$$\mathbf{D} = \mathrm{diag}\,(1, \sigma, \sigma) \tag{18}$$

$$\mathbf{V} = \begin{bmatrix} 1 & \omega & \psi \\ 1 & \psi & \omega \\ 1 & \psi\omega & \psi\omega \end{bmatrix} \tag{19}$$

$$_3\mathbf{U}_2 = \begin{bmatrix} 1 & \sigma\omega & \sigma\psi \\ 1 & \sigma\psi & \sigma\omega \\ 1 & \sigma\psi\omega & \sigma\psi\omega \end{bmatrix} \tag{20}$$

If the branches had originally been numbered so that $_3A_1$ in Figure 2 were behind the plane of the paper, the following substitutions would be required:

$$_1\mathbf{U}_{n_1} = \sigma \begin{bmatrix} 1 & \sigma & 1 \\ \psi & \sigma\psi\omega & \omega \\ \omega & \sigma\psi\omega & \psi \end{bmatrix} \tag{21}$$

$$_2\mathbf{U}_1 = \sigma \begin{bmatrix} 1 & 1 & \sigma \\ 1 & \psi & \sigma\omega \\ 1 & \omega & \sigma\psi \end{bmatrix} \tag{22}$$

$$_2\mathbf{U}_2 = \begin{bmatrix} 1 & \sigma\omega & \sigma\psi \\ 1 & \sigma\psi & \sigma\omega \\ 1 & \sigma\psi\omega & \sigma\psi\omega \end{bmatrix} \tag{23}$$

$$_3\mathbf{U}_2 = \begin{bmatrix} 1 & \sigma\psi & \sigma\omega \\ 1 & \sigma\psi\omega & \sigma\psi\omega \\ 1 & \sigma\omega & \sigma\psi \end{bmatrix} \tag{24}$$

$$_3\mathbf{U}_1 = \sigma \begin{bmatrix} \omega & \sigma\psi^2 & \omega \\ \omega & \sigma\psi\omega & \psi \\ \omega & \sigma\psi & 1 \end{bmatrix} \qquad \text{1st layer} \tag{25}$$

$$\sigma \begin{bmatrix} 1 & \sigma\psi & \omega \\ 1 & \sigma\omega & \psi \\ 1 & \sigma & 1 \end{bmatrix} \qquad \text{2nd layer} \tag{26}$$

$$\sigma \begin{bmatrix} \psi & \sigma\psi\omega & \omega \\ \psi & \sigma\omega^2 & \psi \\ \psi & \sigma\omega & 1 \end{bmatrix} \qquad \text{3rd layer} \tag{27}$$

The Configuration Partition Function

The key to the development of the configuration partition function for the branched molecules under consideration lies in the successful treatment of events which occur near the point at which branching occurs. In order to focus attention on this region, we shall consider a chain for which

$n_1 = 2$, $n_2 = 4$, and $n_3 = 3$ (Figure 7). Furthermore, it shall be assumed that only two rotational states (t and c) exist about each bond, with t being the reference state. The top row of ${}_1\mathbf{U}_2 = {}_1\mathbf{U}_{n_1}$ will be:[6]

$$\left[{}_1u_{11;2}\ {}_1u_{12;2}\right] \tag{28}$$

The columns in (28) refer to bond 2 in branch 1 being in states t and c, respectively. The matrix in (28) is $\mathbf{J}^*{}_1\mathbf{U}_2$, where $\mathbf{J}^*$ is the row defined[6] as consisting of ${}_1\nu_2$ elements, the first element being unity and all succeeding elements being zero. $\mathbf{J}^*{}_1\mathbf{U}_2$ must be postmultiplied by a matrix which contains the statistical weights appropriate for the states assigned to the first bonds in branches 2 and 3. Since each of these bonds may be in either of two states, there will be four possibilities to be combined with each possible state for bond 2 in branch 1. The possible combinations are shown in matrix form in (29). The columns in this matrix refer to bond 1 in branch 2 being in states t, t, c, and c, respectively, while bond 1 in branch 3 is in states t, c, t, and c, respectively. The rows refer to bond 2 (=bond n_1) in branch 1 being in states t and c, respectively. The elements in (29) are arranged so that postmultiplication of (28) by (29) will generate al relevant products of statistical weights for the last bond in branch 1 and the first bond in branches 2 and 3.

$$\begin{bmatrix} ({}_2u_{11;1})({}_3u_{111;1}) & ({}_2u_{11;1})({}_3u_{121;1}) & ({}_2u_{12;1})({}_3u_{112;1}) & ({}_2u_{12;1})({}_3u_{122;1}) \\ ({}_2u_{21;1})({}_3u_{211;1}) & ({}_2u_{21;1})({}_3u_{221;1}) & ({}_2u_{22;1})({}_3u_{212;1}) & ({}_2u_{22;1})({}_3u_{222;1}) \end{bmatrix} \tag{29}$$

$$\begin{bmatrix} ({}_2u_{11;2})({}_3u_{11;2}) & ({}_2u_{11;2})({}_3u_{12;2}) & ({}_2u_{12;2})({}_3u_{11;2}) & ({}_2u_{12;2})({}_3u_{12;2}) \\ ({}_2u_{11;2})({}_3u_{21;2}) & ({}_2u_{11;2})({}_3u_{22;2}) & ({}_2u_{12;2})({}_3u_{21;2}) & ({}_2u_{12;2})({}_3u_{22;2}) \\ ({}_2u_{21;2})({}_3u_{11;2}) & ({}_2u_{21;2})({}_3u_{12;2}) & ({}_2u_{22;2})({}_3u_{11;2}) & ({}_2u_{22;2})({}_3u_{12;2}) \\ ({}_2u_{21;2})({}_3u_{21;2}) & ({}_2u_{21;2})({}_3u_{22;2}) & ({}_2u_{22;2})({}_3u_{21;2}) & ({}_2u_{22;2})({}_3u_{22;2}) \end{bmatrix} \tag{30}$$

The statistical weights for the second bonds in branches 2 and 3 will be brought into consideration by postmultiplication of the matrix in (29) by a matrix which incorporates all possible combinations of states for the second bonds in branches 2 and 3 and allows for all possible combinations of states at the first bonds in branches 2 and 3. A matrix (30) which contains all of the desired elements, and no additional elements, is ${}_2\mathbf{U}_2 \otimes {}_3\mathbf{U}_2$, where $\otimes$ represents the direct product.[7] The result of multiplying the matrix in (29) onto the matrix in (30) will be a 2 × 4 matrix whose elements contain all relevant products of the statistical weights for the first two bonds in branches 2 and 3. The statistical weight for the third bond in branch 2 can be included through postmultiplication by the direct product of ${}_2\mathbf{U}_3$ and $\mathbf{E}_2$, where $\mathbf{E}_i$ is the $i \times i$ identity matrix. Premultiplication by the row in (28) will yield a row consisting of four elements which contain the statistical weights for all possible conformations of the molecule in Figure 2. They can be summed through postmultiplication by $\mathbf{J} \otimes \mathbf{J}$, where $\mathbf{J}$ is a column consisting of ${}_2\nu_3$ (or ${}_3\nu_2$) elements of unity.

The matrix in (29) will be designated ${}_2\mathbf{U}_1 \ominus {}_3\mathbf{U}_1$. The general rules for its assembly are as follows: Let ${}_2\mathbf{U}_1$ be a ${}_1\nu_{n_1} \times {}_2\nu_1$ matrix, with elements written as $u_{\alpha\beta}$. Let ${}_3\mathbf{U}_1$ be a ${}_1\nu_{n_1} \times {}_3\nu_1 \times {}_2\nu_1$ array, with elements written as $u_{\gamma\epsilon\iota}$. The matrix ${}_2\mathbf{U}_1 \ominus {}_3\mathbf{U}_1$ is a ${}_1\nu_{n_1} \times ({}_2\nu_1)({}_3\nu_1)$ matrix. Its dimensions are identical with those obtained in ${}_2\mathbf{U}_1 \otimes \mathbf{B}$, where $\mathbf{B}$ is a row containing ${}_3\nu_1$ elements. Furthermore, the elements of ${}_2\mathbf{U}_1$ occur precisely as they would in ${}_2\mathbf{U}_1 \otimes \mathbf{B}$. The proper representation for $\mathbf{B}$, however, is dependent on the element selected from ${}_2\mathbf{U}_1$. When element $u_{\alpha\beta}$ has been selected from ${}_2\mathbf{U}_1$, the appropriate representation for $\mathbf{B}$ is row α, layer β, in ${}_3\mathbf{U}_1$. The definition of ${}_3\mathbf{U}_1$ as an array consisting of rows, columns, and layers is simply a useful intermediate step in the assembly of the rectangular matrix represented by ${}_2\mathbf{U}_1 \ominus {}_3\mathbf{U}_1$.

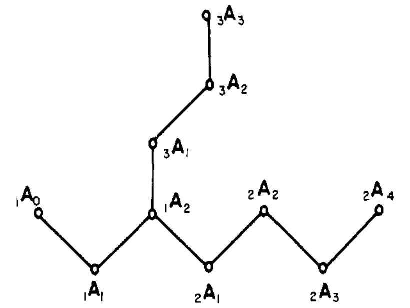

Figure 7. Molecule with $n_1 = 2$, $n_2 = 4$, and $n_3 = 3$.

Using this symbolism, the configuration partition function for the molecule in Figure 7 can be written as follows. The matrices on the right-hand side of equations requiring multiple lines of type are to be multiplied in the order indicated.

$$Z = \mathbf{J}^*{}_1\mathbf{U}_2({}_2\mathbf{U}_1 \ominus {}_3\mathbf{U}_1) \times ({}_2\mathbf{U}_2 \otimes {}_3\mathbf{U}_2)({}_2\mathbf{U}_3 \otimes \mathbf{E}_2)(\mathbf{J} \otimes \mathbf{J}) \tag{31}$$

In general, for a chain with any n_1, n_2, and n_3 (subject only to the restriction that all $n_j > 1$ and $n_2 \geq n_3$), and for any number of rotational states, the configuration partition function is given by (32). Symbolism of the type ${}_1\mathbf{U}_2^{(n_1-1)}$ (see Flory)[8] indicates the serial product of the type $({}_1\mathbf{U}_2)({}_1\mathbf{U}_3)\ldots({}_1\mathbf{U}_{n_1})$, i.e., a product of $n_1 - 1$ such terms. The expression for the configuration partition function in (32) can be simplified, by the application of the theorem on direct products,[9] to yield (33). It is apparent from inspection of (33) that the assumption that $n_2 \geq n_3$, used in (32), is no longer required.

$$Z = \mathbf{J}^*{}_1\mathbf{U}_2^{(n_1-1)}({}_2\mathbf{U}_1 \ominus {}_3\mathbf{U}_1) \times ({}_2\mathbf{U} \otimes {}_3\mathbf{U})_2^{(n_3-2)}({}_2\mathbf{U} \otimes \mathbf{E}_{{}_3\nu_{n_3-1}})_{n_3}^{(n_2-n_3)}(\mathbf{J} \otimes \mathbf{J}) \tag{32}$$

$$Z = \mathbf{J}^*{}_1\mathbf{U}_2^{(n_1-1)}({}_2\mathbf{U}_1 \ominus {}_3\mathbf{U}_1) \times \{{}_2\mathbf{U}_2^{(n_2-2)}\mathbf{J}) \otimes ({}_3\mathbf{U}_2^{(n_3-2)}\mathbf{J})\} \tag{33}$$

The a priori Probability that Bond *i* in Branch *j* is in State *η*

The a priori probability that bond i in branch j is in state η is symbolized as ${}_jp_{\eta;i}$. It is given by (34), in which ${}_jZ_{\eta;i}$ is calculated in the same manner as Z, but with the matrix ${}_j\mathbf{U}'_{\eta;i}$ replacing ${}_j\mathbf{U}_i$. For all statistical weight matrices except ${}_3\mathbf{U}_1$, ${}_j\mathbf{U}'_{\eta;i}$ is obtained from ${}_j\mathbf{U}_i$ by zeroing out all columns except the one which corresponds to the bond in question being in state η.[10] This definition is equivalent to requiring that a general element ${}_ju_{\alpha\beta;i}$ in ${}_j\mathbf{U}_i$ will be replaced by $(\delta_{\eta\beta})({}_ju_{\alpha\beta;i})$ in ${}_j\mathbf{U}'_{\eta;i}$ ($\delta_{\eta\beta}$ is the Kronecker δ). Similarly, a general element ${}_3u_{\alpha\beta\gamma;1}$ in the array ${}_3\mathbf{U}_1$ is replaced by $(\delta_{\eta\beta})({}_3u_{\alpha\beta\gamma;1})$ in array ${}_3\mathbf{U}'_{\eta;1}$.

$$ {}_jp_{\eta;i} = Z^{-1}({}_jZ_{\eta;i}) \tag{34} $$

The a priori Probability that Bond *i* in Branch *j* is in State η and that the preceding Bond is in State ξ

The a priori probability that bond i in branch j is in state η and that the preceeding bond is in state ξ is symbolized as ${}_jp_{\xi\eta;i}$. This quantity is not defined for the second bond in branch 1. For all other bonds about which rotation must be specified, it is given by (35), in which ${}_jZ_{\xi\eta;i}$ is calculated in the same manner as Z, but with the matrix ${}_j\mathbf{U}'_{\xi\eta;i}$ replacing ${}_j\mathbf{U}_i$. For all statistical weight matrices except ${}_3\mathbf{U}_1$, ${}_j\mathbf{U}'_{\xi\eta;i}$ is obtained from ${}_j\mathbf{U}_i$ by zeroing out all elements except the one which corresponds to bond i in branch j being in state η and the preceding bond being in state ξ.[10] This definition is equivalent to requiring that a general element ${}_ju_{\alpha\beta;i}$ in ${}_j\mathbf{U}_i$ will be replaced by $(\delta_{\alpha\xi})(\delta_{\beta\eta})({}_ju_{\alpha\beta;i})$ in ${}_j\mathbf{U}'_{\xi\eta;i}$. Similarly, a general element ${}_3u_{\alpha\beta\gamma;1}$ in the array ${}_3\mathbf{U}_1$ is replaced by $(\delta_{\alpha\xi})(\delta_{\beta\eta})({}_3u_{\alpha\beta\gamma;1})$ in array ${}_3\mathbf{U}'_{\xi\eta;1}$.

$$ {}_jp_{\xi\eta;i} = Z^{-1}({}_jZ_{\xi\eta;i}) \tag{35} $$

A related quantity of interest will be the a priori probability that bond n_1 in branch 1 is in state ξ, bond 1 in branch 2 is in state ζ, and bond 1 in branch 3 is in state η. This quantity is symbolized as ${}_3p_{\xi\eta\zeta;1}$, and is calculated as shown in (36). The quantity ${}_3Z_{\xi\eta\zeta;1}$ is calculated in the same manner as Z, but with the array ${}_3\mathbf{U}'_{\xi\eta\zeta;1}$ replacing ${}_3\mathbf{U}_1$. A general element ${}_3u_{\alpha\beta\gamma;1}$ in array ${}_3\mathbf{U}_1$ is replaced by $(\delta_{\alpha\xi}) \times (\delta_{\beta\eta})(\delta_{\gamma\zeta})({}_3u_{\alpha\beta\gamma;1})$ in ${}_3\mathbf{U}'_{\xi\eta\zeta;1}$.

$$ {}_3p_{\xi\eta\zeta;1} = Z^{-1}({}_3Z_{\xi\eta\zeta;1}) \tag{36} $$

Conditional Probabilities

The conditional probability that bond i in branch j is in state η, given that the preceeding bond is in state ξ, will be symbolized as ${}_jq_{\xi\eta;i}$. This quantity is not defined for the second bond in branch 1. For all other bonds about which rotation must be specified, it is given by (37).[11] The term ${}_jp_{\xi;i-1}$ will be ${}_1p_{\xi;n_1}$ for ${}_2q_{\xi\eta;1}$ and ${}_3q_{\xi\eta;1}$.

$$ {}_jq_{\xi\eta;i} = ({}_jp_{\xi\eta;i})/({}_jp_{\xi;i-1}) \tag{37} $$

An additional quantity of interest is the conditional probability that bond 1 in branch 3 is in state η, given that bond n_1 in branch 1 is in state ξ and bond 1 in branch 2 is in state ζ. This quantity is symbolized as ${}_3q_{\xi\eta\zeta;1}$ and is calculated as shown in (38).

$$ {}_3q_{\xi\eta\zeta;1} = ({}_3p_{\xi\eta\zeta;1})/({}_2p_{\xi\zeta;1}) \tag{38} $$

The results obtained here provide the means of calculating the a priori probabilities for bond 2 in branch 1 and the conditional probabilities for all other bonds about which rotation must be specified, including the conditional probability ${}_3q_{\xi\eta\zeta;1}$. Dimensional properties for unbranched macromolecules have been successfully treated by Monte Carlo calculations, once the a priori probability for the second bond and the conditional probabilities for all other bonds, about which rotation must be specified, are known.[12] The results obtained here will permit the Monte Carlo method to be applied to a macromolecule with one branch.

Procedures for Treating more Highly Branched Chains

Consider the molecule shown in Figure 8, where all $n_j > 1$. One of the four branches with a terminal group will be selected as branch 1. Branches 2 and 3 are then determined by the covalent structure. Branches 4 and 5 will be assigned by requiring that $n_4 \geq n_5$. The statistical weight matrices will be formulated as described previously. It is apparent that ${}_2\mathbf{U}_2$ and ${}_2\mathbf{U}_{n_2}$ will be identical if $n_2 = 2$.

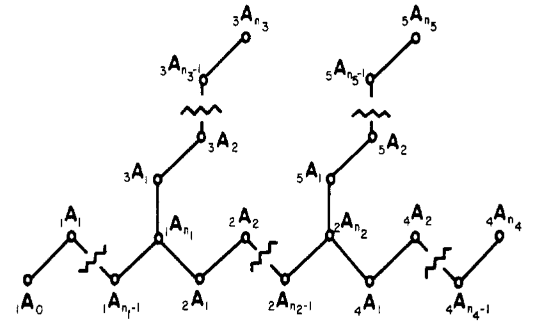

Figure 8. Diagrammatic representation of a macromolecule with two branching points.

The configuration partition function for the case where $n_2 \geq n_3 - 1$ is shown in (39). This equation can be put into the form shown in (40) by the application of the theorem on direct products and the fact that a series of direct products is associative.

$$ \begin{aligned} Z = {} & \mathbf{J}^*{}_1\mathbf{U}_2{}^{(n_1-1)}({}_2\mathbf{U}_1 \ominus {}_3\mathbf{U}_1)({}_2U \otimes {}_3\mathbf{U}_2)^{(n_3-2)} \times \\ & ({}_2\mathbf{U} \otimes \mathbf{E}_{{}_3\nu_{n_3-1}})_{n_3}{}^{(n_2-n_3+1)}\{({}_4\mathbf{U}_1 \ominus {}_5\mathbf{U}_1) \otimes \mathbf{E}_{{}_3\nu_{n_3-1}}\} \times \\ & \{{}_4\mathbf{U} \otimes {}_5\mathbf{U} \otimes \mathbf{E}_{{}_3\nu_{n_3-1}}\}_2{}^{(n_5-2)}\{{}_4\mathbf{U} \otimes \mathbf{E}_{{}_5\nu_{n_5-1}} \otimes \\ & \mathbf{E}_{{}_3\nu_{n_3-1}}\}_{n_5}{}^{(n_4-n_5)}(\mathbf{J} \otimes \mathbf{J} \otimes \mathbf{J}) \end{aligned} \tag{39} $$

$$ \begin{aligned} Z = {} & \mathbf{J}^*{}_1\mathbf{U}_2{}^{(n_1-1)}({}_2\mathbf{U}_1 \ominus {}_3\mathbf{U}_1)\{({}_2\mathbf{U}_2{}^{(n_2-1)}) \otimes ({}_3\mathbf{U}_2{}^{(n_3-2)}\mathbf{J})\} \times \\ & ({}_4\mathbf{U}_1 \ominus {}_5\mathbf{U}_1)\{({}_4\mathbf{U}_2{}^{(n_4-2)}\mathbf{J}) \otimes ({}_5\mathbf{U}_2{}^{(n_5-2)}\mathbf{J})\} \end{aligned} \tag{40} $$

Expressions analogous to (39) can be written for other cases also. Consider, for example, the case where $n_3 > n_2 + n_4$. The result for the configuration partition function is shown in (41), and this expression can be shown to be identical with (40) by the application of the theorem on direct products and the fact that a series of direct products is associative. Symbolism of the type $\{{}_4\mathbf{U}_i \otimes {}_5\mathbf{U}_i \otimes {}_3\mathbf{U}_{i+n_2}\}_{i=2}{}^{(n_5-2)}$ means the product of $n_5 - 2$ successive matrices, starting with the matrix in which $i = 2$.

$$ \begin{aligned} Z = {} & \mathbf{J}^*{}_1\mathbf{U}_2{}^{(n_1-1)}({}_2\mathbf{U}_1 \ominus {}_3\mathbf{U}_1)({}_2\mathbf{U} \otimes {}_3\mathbf{U})_2{}^{(n_2-1)} \times \\ & \{({}_4\mathbf{U}_1 \ominus {}_5\mathbf{U}_1) \otimes {}_3\mathbf{U}_{n_2+1}\}\{{}_4\mathbf{U}_i \otimes {}_5\mathbf{U}_i \otimes {}_3\mathbf{U}_{i+n_2}\}_{i=2}{}^{(n_5-2)} \times \\ & \{{}_4\mathbf{U}_{i-n_2} \otimes \mathbf{E}_{{}_5\nu_{n_5-1}} \otimes {}_3\mathbf{U}_i\}_{i=n_2+n_5}{}^{(n_4-n_5)} \times \\ & \{\mathbf{E}_{{}_4\nu_{n_4-1}} \otimes \mathbf{E}_{{}_5\nu_{n_5-1}} \otimes {}_3\mathbf{U}\}_{n_2+n_4}{}^{(n_3-n_2-n_4)}(\mathbf{J} \otimes \mathbf{J} \otimes \mathbf{J}) \end{aligned} \tag{41} $$

The procedures outlined in (39), (40), and (41) can readily be extended to treat molecules which are more highly branched than the structure shown in Figure 8, provided all $n_j > 1$ and the branching does not lead to closed loops. Consider, for example, the structure shown in Figure 9. The expression which results from the application of the procedures illustrated by (39) and (41), followed by the application of the theorem on direct products and the fact that a series of direct products is associative, is shown in (42). It is instructive to examine the kinds of terms present in (42). Each branch contributes a term of the type ${}_j\mathbf{U}_2{}^{(n_j-m)}$. All branches which connect two branching points have $m = 1$. This result is also obtained for branch 1. All other branches have $m = 2$. The term ${}_j\mathbf{U}_2{}^{(n_j-m)}$ will be followed by $\mathbf{J}$ if $m = 2$; if $m = 1$, the following term will be of the type $({}_k\mathbf{U}_1 \ominus {}_h\mathbf{U}_1)$. Each $({}_k\mathbf{U}_1 \ominus {}_h\mathbf{U}_1)$ is followed by $\{({}_k\mathbf{U}_2{}^{(n_k-m)} \ldots) \otimes ({}_h\mathbf{U}_2{}^{(n_h-m)} \ldots)\}$. This procedure continues until all branches are terminated by having $m = 2$, followed by $\mathbf{J}$.

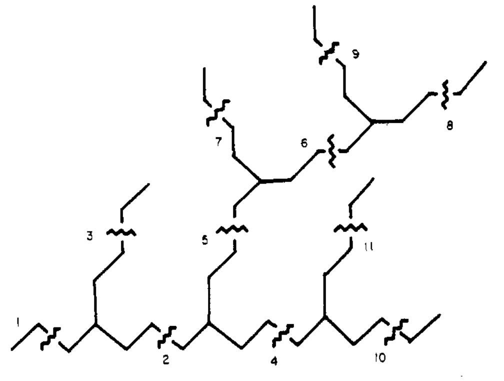

Figure 9. Example of a molecule having 11 branches. The branches are numbered as shown in the figure.

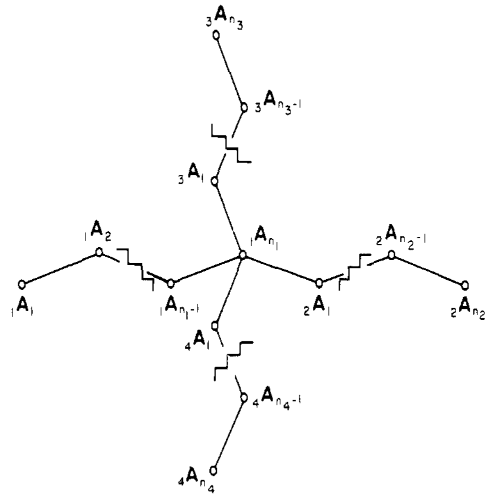

Figure 10. Diagrammatic representation of a macromolecule with four branches emanating from a common atom.

$$\begin{aligned} Z = {} & \mathbf{J}^*{}_1\mathbf{U}_2{}^{(n_1-1)}({}_2\mathbf{U}_1 \ominus {}_3\mathbf{U}_1)[{}_2\mathbf{U}_2{}^{(n_2-1)}({}_4\mathbf{U}_1 \ominus {}_5\mathbf{U}_1) \times \\ & \{[{}_4\mathbf{U}_2{}^{(n_4-1)}({}_{10}\mathbf{U}_1 \ominus {}_{11}\mathbf{U}_1)\{({}_{10}\mathbf{U}_2{}^{(n_{10}-2)}\mathbf{J}) \otimes ({}_{11}\mathbf{U}_2{}^{(n_{11}-2)}\mathbf{J})\}] \otimes \\ & \{{}_5\mathbf{U}_2{}^{(n_5-1)}({}_6\mathbf{U}_1 \ominus {}_7\mathbf{U}_1)[[{}_6\mathbf{U}_2{}^{(n_6-1)}({}_8\mathbf{U}_1 \ominus {}_9\mathbf{U}_1) \times \\ & \{({}_8\mathbf{U}_2{}^{(n_8-2)}\mathbf{J}) \otimes ({}_9\mathbf{U}_2{}^{(n_9-2)}\mathbf{J})\}] \otimes ({}_7\mathbf{U}_2{}^{(n_7-2)}\mathbf{J})]\}\} \otimes \\ & ({}_3\mathbf{U}_2{}^{(n_3-2)}\mathbf{J})] \end{aligned} \tag{42}$$

The results can also be extended to treat branch points of higher functionality. The macromolecule shown diagrammatically in Figure 10 contains four branches which emanate from the same atom. The configuration partition function in this case is obtained by an extension of the procedures used for the molecule in Figure 1. Numbering of the branches will be achieved by random selection of branch 1 and the requirement that $n_2 \geq n_3 \geq n_4$. The elements in ${}_1\mathbf{U}_{n_1}$, ${}_2\mathbf{U}_1$, ${}_3\mathbf{U}_1$, ${}_2\mathbf{U}_2$, ${}_3\mathbf{U}_2$, and ${}_4\mathbf{U}_2$ will be modified to account for the pertinent three- and four-bond interactions due to the presence of the fourth branch.

The array designated ${}_4\mathbf{U}_1$ will have four dimensions (${}_1\nu_{n_1} \times {}_4\nu_1 \times {}_3\nu_1 \times {}_2\nu_1$), and its elements will be formed in a manner analogous to those in ${}_3\mathbf{U}_1$, but including those interactions arising from the fourth branch. The matrix designated $\{({}_2\mathbf{U}_1 \ominus {}_3\mathbf{U}_1) \ominus {}_4\mathbf{U}_1\}$ is a ${}_1\nu_{n_1} \times \{({}_2\nu_1)({}_3\nu_1)({}_4\nu_1)\}$ matrix. Its dimensions are identical with those in $({}_2\mathbf{U}_1 \ominus {}_3\mathbf{U}_1) \otimes \mathbf{B}$, where $\mathbf{B}$ is a row containing ${}_4\nu_1$ elements, and the elements of $({}_2\mathbf{U}_1 \ominus {}_3\mathbf{U}_1)$ occur as they would in $({}_2\mathbf{U}_1 \ominus {}_3\mathbf{U}_1) \otimes \mathbf{B}$. When element $u_{\alpha\beta\gamma}$ has been selected from ${}_3\mathbf{U}_1$, the appropriate representation for $\mathbf{B}$ is $[u_{\alpha 1\beta\gamma}\ u_{\alpha 2\beta\gamma} \ldots u_{\alpha {}_4\nu_1 \beta\gamma}]$. The configuration partition function is shown in (43), which can be rearranged to produce (44).

$$\begin{aligned} Z = {} & \mathbf{J}^*{}_1\mathbf{U}_2{}^{(n_2-1)}\{({}_2\mathbf{U}_1 \ominus {}_3\mathbf{U}_1) \ominus {}_4\mathbf{U}_1\} \times \\ & ({}_2\mathbf{U} \otimes {}_3\mathbf{U} \otimes {}_4\mathbf{U})_2{}^{(n_4-2)}({}_2\mathbf{U} \otimes {}_3\mathbf{U} \otimes \mathbf{E}_{{}_4\nu_{n_4-1}})_{n_4}{}^{(n_3-n_4)} \times \\ & ({}_2\mathbf{U} \otimes \mathbf{E}_{{}_3\nu_{n_3-1}} \otimes \mathbf{E}_{{}_4\nu_{n_4-1}})_{n_3}{}^{(n_2-n_3)}(\mathbf{J} \otimes \mathbf{J} \otimes \mathbf{J}) \end{aligned} \tag{43}$$

$$\begin{aligned} Z = {} & \mathbf{J}^*{}_1\mathbf{U}_2{}^{(n_2-1)}\{({}_2\mathbf{U}_1 \ominus {}_3\mathbf{U}_1) \ominus {}_4\mathbf{U}_1\} \times \\ & \{({}_2\mathbf{U}_2{}^{(n_2-2)}\mathbf{J}) \otimes ({}_3\mathbf{U}_2{}^{(n_3-2)}\mathbf{J}) \otimes ({}_4\mathbf{U}_2{}^{(n_4-2)}\mathbf{J})\} \end{aligned} \tag{44}$$

Application to Low-Density Polyethylene Containing *n*-Butyl Branches

The short-chain branches in low-density polyethylene are almost exclusively *n*-butyl groups, and tetrafunctional *n*-butyl branches do not occur to any significant extent.[13] The effect of the *n*-butyl branches on the conformational properties, as reflected by the a priori probabilities for the bonds in the main chain and in the *n*-butyl groups, will be examined as a function of the number of bonds between the branching points and for neighboring branches which constitute a meso or racemic pair.

The polymer treated has the structure shown in Figure 8. Branches 3 and 5 will represent the *n*-butyl groups ($n_3 = n_5 = 4$). The remaining branches will be considered to represent the main chain, which has a total length of 60 bonds. Branch 4 will always contain 25 bonds. The number of bonds separating the atoms at the branching points will be altered by assigning n_2 according to $1 < n_2 \leq 15$ and requiring that $n_1 + n_2 = 35$. Branch 5 will always constitute an *l* placement.[14] Branch 3 will be an *l* placement for the meso pair and a *d* placement for the racemic pair.

The statistical weight matrix for bonds sufficiently remote from branching points is shown in (1). The modifications required near a branching point which constitutes an *l* placement are shown in eq 4, 7, 12, 13, 14, 17, and 20. These matrices are replaced by eq 21–27 if the branching point constitutes a *d* placement. In the cases where $n_2 = 2$, it is apparent that ${}_2\mathbf{U}_2 = {}_2\mathbf{U}_{n_2}$, and the appropriate expressions are shown in (45) and (46). In all calculations $\sigma = 0.54$, $\psi = 1.00$, and $\omega = 0.088$.[15]

$${}_2\mathbf{U}_2 = {}_2\mathbf{U}_{n_2} = \begin{bmatrix} \omega & \psi & \sigma\psi\omega \\ \psi\omega & \psi\omega & \sigma\psi^2\omega^2 \\ \psi & \omega & \sigma\psi\omega \end{bmatrix} \qquad ll \text{ pair} \tag{45}$$

$${}_2\mathbf{U}_2 = {}_2\mathbf{U}_{n_2} = \begin{bmatrix} \psi & \omega & \sigma\psi\omega \\ \omega & \psi & \sigma\psi\omega \\ \psi\omega & \psi\omega & \sigma\psi^2\omega^2 \end{bmatrix} \qquad dl \text{ pair} \tag{46}$$

Main Chain Conformation. Figure 11 shows the a priori probabilities, calculated via (34), for the main chain with $n_2 = 15$ and a racemic (*dl*) pair. The $p_{g-;i}$ (not shown) can be obtained from the $p_{g+;i}$ by switching the disturbances which occur near the two branching points. The end effects and the values for bonds sufficiently remote from the branching points are identical with those calculated for the unbranched chain.[16] Figure 11 shows that the disturbance in $p_{t;i}$ due to the *n*-butyl groups is symmetrical about the branching point and is identical for *d* and *l* branches. Bonds involving ${}_1A_{n_1}$ or ${}_2A_{n_2}$ experience a considerable reduction in $p_{t;i}$ because of unfavorable interactions with the *n*-butyl groups when both main chain bonds involving an atom at a branching point are in the trans conformation.[17] The next bonds away from the branching point have an enhanced $p_{t;i}$ because of the high probability that bonds involving ${}_1A_{n_1}$ or ${}_2A_{n_2}$ will be in one of the gauche states.

The disturbances in $p_{t;i}$ are observed to extend four bonds away from the branching point. The disturbance in

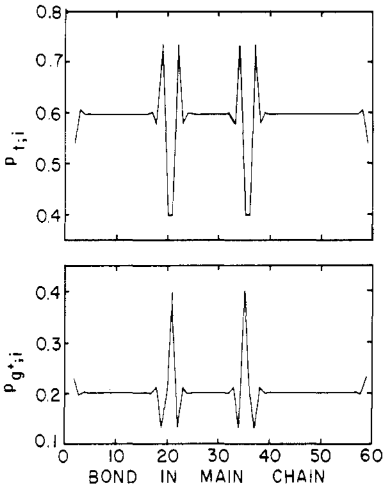

Figure 11. A priori probabilities $p_{t;i}$ and $p_{g^+;i}$ for the main chain of a polyethylene of the type shown in Figure 8 with $n_1 = 20$, $n_2 = 15$, $n_3 = 4$, $n_4 = 25$, and $n_5 = 4$. Branches 1, 2, and 4 are considered to constitute the main chain. Pairing is racemic (*dl*).

$p_{g^+;i}$ also persists four bonds away from the branching point, but it is not symmetrical about the branching point. The $p_{g^+;i}$ for bonds involving ${}_1A_{n_1}$ and ${}_2A_{n_2}$ are different and their order of occurrence is reversed for *d* and *l* branches.

The values of $p_{\xi\eta;i}$, calculated via (35), for bonds in the main chain are shown in Figures 12 and 13. In this case also the end effects and results for bonds sufficiently remote from a branching point agree with those obtained for an unbranched molecule.[16] The difficulty involved in accommodating the *n*-butyl group when both main chain bonds involving ${}_1A_{n_1}$ (or ${}_2A_{n_2}$) are in the trans conformation is apparent in the low values of the corresponding $p_{tt;i}$. The disturbance created by the presence of the *n*-butyl groups is symmetrical for $p_{tt;i}$ and $p_{g^\pm g^\mp;i}$. In addition, the results for $p_{tt;i}$ are identical for *d* and *l* branches. Results obtained for $p_{g^\pm g^\mp;i}$ for *d* and *l* branches correspond to $p_{g^\mp g^\pm;i}$ for *l* and *d* branches, respectively. The disturbances in $p_{tg^\pm;i}$, $p_{g^\pm t;i}$, and $p_{g^\pm g^\pm;i}$ are not symmetrical. Results obtained for $p_{tg^+;i}$, $p_{g^+t;i}$, and $p_{g^+g^+;i}$ near a *d* branch correspond to $p_{tg^-;i}$, $p_{g^-t;i}$, and $p_{g^-g^-;i}$, respectively, near an *l* branch.

Repetition of these calculations for smaller values of n_2 permits an estimate of the number of bonds between branching points which is required in order for the *n*-butyl groups to be independent, but the answer depends on the precise definition of independence. One possible definition would require that at least one of the bonds in branch 2 have values of $p_{\eta;i}$ which are within ±0.001 of those characteristic of a bond in the middle of a long linear chain. According to this definition, n_2 must be at least nine (for both meso and racemic pairs) in order for the *n*-butyl groups to be considered to be independent. A second definition requires that the ${}_2p_{\eta;1}$ and ${}_2p_{\eta;n_2}$ must all lie within ±0.001 of the value obtained for these bonds when the *n*-butyl groups are separated by a large number of bonds. By this definition, $n_2 = 4$ is sufficient to produce independent *n*-butyl groups for both meso and racemic pairs.

The results for $n_2 = 2$ are of special interest because they correspond to a dyad from a vinyl polymer in which the statistical weights for the conformation of an articulated side chain have been included in the configuration partition function. Matrices representing the values of ${}_2p_{\xi\eta;2}$ for $n_2 = 2$ are shown in (47) for a racemic (*dl*) pair and in (48) for a meso (*ll*) pair. The preferred conformation for vinyl chains has been obtained previously without actually including the statistical weights for the conformation of the articulated side chain in the configuration partition function. The preferred conformations for a racemic (*dl*) dyad were found to be *tt* and g^+g^+, while for a meso (*ll*) dyad the preferred conformations were g^-t and tg^+.[19] It is apparent from (47) and (48) that the present method, applied to a branched polyethylene, is in agreement on the preferred conformations, and in fact finds that their a priori probability of occurrence exceeds that of any other conformation by more than a factor of 11.

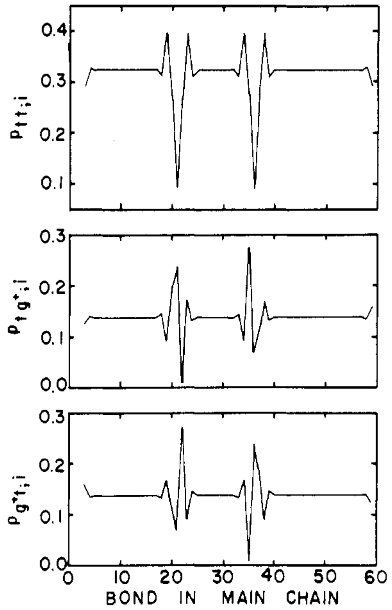

Figure 12. A priori probabilities $p_{tt;i}$, $p_{tg^+;i}$, and $p_{g^+t;i}$ for the main chain of the molecule described in Figure 11.

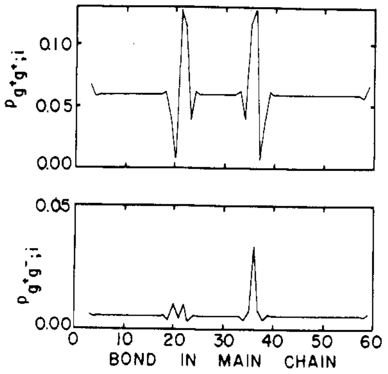

Figure 13. A priori probabilities $p_{g^+g^+;i}$ and $p_{g^+g^-;i}$ for the main chain of the molecule described in Figure 11.

$$\begin{bmatrix} 0.413 & 0.036 & 0.025 \\ 0.036 & 0.412 & 0.025 \\ 0.025 & 0.025 & 0.002 \end{bmatrix} \tag{47}$$

$$\begin{bmatrix} 0.036 & 0.412 & 0.025 \\ 0.025 & 0.025 & 0.002 \\ 0.412 & 0.036 & 0.025 \end{bmatrix} \tag{48}$$

Conformation of the *n*-Butyl Groups. The values of ${}_3p_{\xi\eta;3}$ and ${}_5p_{\xi\eta;3}$ for a molecule with $n_2 = 15$ are shown in matrix form in (49). Identical results are obtained for *d* and *l* *n*-butyl groups and for $n_2 > 3$. The corresponding values for the penultimate bond in the main chain are shown in (50) for comparison. The elements in the first row are larger in (49) than in (50), i.e., the second bond in an *n*-butyl branch is more likely to be in the trans conformation than is the bond which is third from the end of the main chain.

This effect is consistent with the observation (see Figure 11) that bonds in the main chain which are one bond away from the branch point have an enhanced a priori probability of being in the trans conformation. The value of $p_{t;i}$ is 0.733 for these bonds in the main chain, and 0.740 is obtained for the second bond in the n-butyl groups.

$$\begin{bmatrix} 0.356 & 0.192 & 0.192 \\ 0.082 & 0.044 & 0.004 \\ 0.082 & 0.004 & 0.044 \end{bmatrix} \tag{49}$$

$$\begin{bmatrix} 0.291 & 0.157 & 0.157 \\ 0.124 & 0.067 & 0.006 \\ 0.124 & 0.006 & 0.067 \end{bmatrix} \tag{50}$$

The results corresponding to (49) for the cases where $n_2 = 2$ are shown in (51) and (52). Both n-butyl branches in the racemic (dl) pair, as well as branch 5 in the meso (ll) pair, yield the $p_{\xi\eta;i}$ shown in (51), while (52) is obtained for ${}_3p_{\xi\eta;3}$ with the meso (ll) pair. Comparison with (49) reveals that the conformation of an n-butyl group is only slightly affected by another n-butyl group even when $n_2 = 2$. This result indicates that the conformations of the side chain in a vinyl polymer containing n-butyl groups would be essentially independent of one another.

$$\begin{bmatrix} 0.360 & 0.194 & 0.194 \\ 0.075 & 0.040 & 0.004 \\ 0.084 & 0.004 & 0.045 \end{bmatrix} \tag{51}$$

$$\begin{bmatrix} 0.360 & 0.194 & 0.194 \\ 0.084 & 0.045 & 0.004 \\ 0.075 & 0.004 & 0.040 \end{bmatrix} \tag{52}$$

A previous attempt[18] to treat branched polyethylene in the rotational isomeric state approximation differs significantly from the present work. A distinction of utmost importance resides in the configuration partition function used. The present work utilizes the exact configuration partition function for the entire branched molecule. In contrast, Tonelli[18] does not write a configuration partition function for the molecule, but instead writes approximate expressions for individual linear chains within the branched polyethylene. Consequently his treatment is not capable of evaluating the effect of branching on conformational properties with the rigor available in the rotational isomeric state theory. A further important distinction is that certain of the statistical weight matrices used by Tonelli[18] were formulated improperly. Specifically, his $\mathbf{U}_{i-2}$ and $\mathbf{U}_{i+2}$ (our ${}_1\mathbf{U}_{n_1-1}$ and ${}_2\mathbf{U}_3$) are in error; they should be formulated as (1), since the rotations represented by ${}_1\phi_{n_1-1}$ and ${}_2\phi_3$ bring about three- and four-bond interactions identical with those which occur in the linear molecule. Furthermore, the statistical weight matrix which he writes as $\mathbf{U}_i$ is appropriate *only* when ${}_3\phi_1$ is restricted to the reference conformation. Nevertheless, Tonelli's qualitative conclusions that bonds involving ${}_1\mathrm{A}_{n_1}$ have a reduced a priori probability of being in the trans state, and the next bond away from the branch point has an enhanced a priori probability of being in the trans state, are in agreement with the quantitative results obtained in the present work.

References and Notes

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Mean Dimension of a Polymer Chain in Athermal Solutions and in Bulk Phase

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ABSTRACT: Athermal polymer solutions are approximated by an assembly of nonintersecting self-avoiding walks on the simple cubic lattice. The mean-square end-to-end distance $\langle r_n^2 \rangle$ of walks involving n lattice sites is evaluated for n = 6, 10, 20, and 30 by means of a Monte Carlo method allowing for handling of highly concentrated systems; the fractional occupancy φ of the lattice approaches 0.95 in some cases. It is observed that $\langle r_n^2 \rangle$ diminishes steadily as φ increases. The relative decrease of $\langle r_n^2 \rangle$ with respect to the mean-square distance $\langle r_n^2 \rangle_0$ of the infinitely diluted system grows with n. Extrapolating the data to $\varphi = 1$(bulk polymer), we find that $\langle r_n^2 \rangle_1$ varies approximately like $n^{1.08}$ in the asymptotic limit (to be compared with $\langle r_n^2 \rangle_0 \sim n^{1.20}$). This result is compared with existing theories and presently available experimental data.

The configuration of polymer chains in solution is determined by both intra- and intermolecular forces. In the *athermal* case both of these forces reduce to exclusion effects and are expected to act in opposite directions if one takes the random flight chain as reference state. On the one hand, intra-exclusions eliminate self-intersecting configurations of the chain, increasing thereby its average spatial extension; on the other hand, the presence of other polymer